Rheology of Petroleum Fluids

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ABSTRACT

Among the areas where rheology plays an important role in the oil and gas industry, the focus of this paper is on crude oil rheology related to production. The paper gives an overview of the broad variety of rheological behaviour, and corresponding techniques for investigation, encountered among petroleum fluids.

INTRODUCTION

Rheology plays a very important role in the petroleum industry, in drilling as well as production. The focus of this paper is on crude oil rheology related to production. Drilling and completion fluids are not covered.

Petroleum fluids are immensely complex mixtures of hydrocarbon compounds, ranging from the simplest gases, like methane, to large asphaltenic molecules with molecular weights of thousands. This chemical variation is reflected in a large variation in viscosities, ranging from fractions of a centipoise to millions of centipoise, and rheological behaviour, from perfectly Newtonian to highly non-Newtonian, visco-elastic and nearly solid-like. Description and rheological characterization of petroleum fluids thus requires a broad variety of experimental techniques and modelling approaches.

NEWTONIAN FLUIDS

In gas reservoirs, the flow properties of the simplest petroleum fluids, i.e. hydrocarbons with less than five carbon atoms, play an essential role in production. It directly impacts the productivity. The viscosity of single compounds are well defined and mixture viscosity can relatively easily be calculated. Most often reservoir gas viscosity is though measured at reservoir conditions as part of reservoir fluid studies. The behaviour is always Newtonian. The main challenge in terms of measurement and modelling, is related to very high pressures (>1000 bar) and/or high temperatures (170-200°C) which is encountered both in the North Sea and Gulf of Mexico.

Hydrocarbon gases also exist dissolved in liquid reservoir oils and thereby impact the fluid viscosity and productivity of these reservoirs. Reservoir oils are also normally Newtonian fluids, but the variation in viscosity can be extremely large, both as a result of chemical variation, ranging from light, low-viscous gas condensates to highly viscous heavy oils, and temperature variation, which always has a large, and fairly predictable impact on the Newtonian viscosity. Fig. 1 shows an example of a rather heavy North Sea oil with nearly perfectly Newtonian behaviour, even at a low temperature. This is quite typical also of much heavier oils. The mentioned temperature variation of the viscosity of

these Newtonian fluids, is most often very well described by a so-called Arrhenius relation, i.e. a linear relationship between the logarithm of the viscosity µ and the inverse temperature[1]:

$$\mu = A\, e^{\frac{E_a}{RT}} \qquad (1)$$
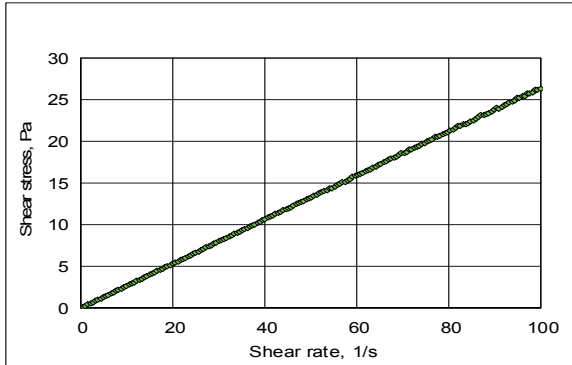
where E_a is the flow activation energy.

Figure 1. Example of perfectly Newtonian behaviour of a 21 °API North Sea crude oil at 5 °C.

At a given temperature, there is also normally a simple relationship between the viscosity and the average molecular weight[2] or density of the fluid[18]. The graph in Fig. 2 shows a useful correlation between density and Newtonian viscosity of North Sea crude oils, valid above the wax appearance temperature of the oils. It has been found to provide viscosity estimates typically within 10-15%, which may be acceptable as a first estimate in many cases.

Although they are typically Newtonian and rheologically fairly simple, viscosity measurements with heavy oils are not trivial. There is no strict definition of 'heavy oil', but here is meant an oil with a density higher than about 950 kg/m³. The sample preparation and pretreatment w.r.t. gas saturation and stabilization prior to measurements with such oils, has to be carried out very carefully in order to obtain measured viscosities which are

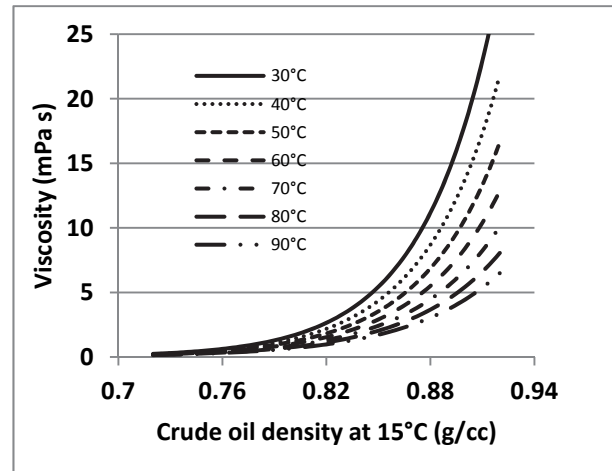representative of the fluid at real field conditions.

Figure 2. Correlation between density and viscosity of North Sea crude oils[18].

NON-NEWTONIAN FLUIDS

The more 'interesting' rheological behaviour of petroleum fluids is found among fluids containing either solid paraffin waxes or dispersed water. Depending on the volume fraction of dispersed, solid wax particles or water droplets, such fluids exhibit all degrees of non-Newtonian behaviour, which is described in some detail below.

As soon as paraffin (wax) crystals start to precipitate in a crude oil, the behaviour starts to deviate from the Newtonian behaviour described above. In fact, the onset of deviation from simple Arrhenius temperature dependency is one method to detect the onset of wax crystallization, or the wax appearance temperature. The first wax crystals have though a limited impact on viscosity and rheology. But as soon as the volume fraction of particles has reached a few tenths of a per cent, significant shear rate dependency can be observed, characteristic of non-Newtonian behaviour. Fig. 3 shows a typical example of pronounced shear-thinning behaviour of a waxy North Sea crude oil at different temperatures below the wax appearance
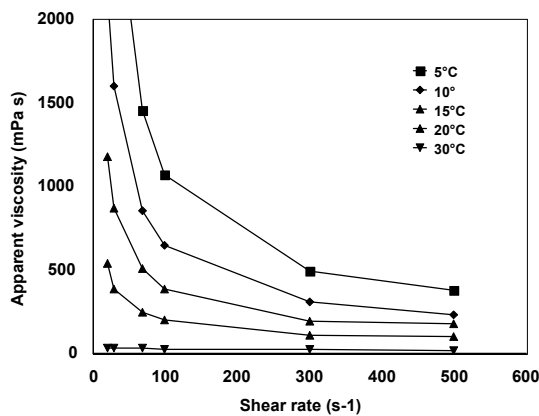
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temperature.

Figure 3. Shear-thinning behaviour of waxy North Sea crude oil.

Modelling and predicting non-Newtonian viscosities is much harder than Newtonian, and few non-Newtonian viscosity models exist. However, using a similar approach as modelling of the viscosity effect of dispersed water in crude oil, a semi-empirical non-Newtonian viscosity model based on experimental data for a large number of North Sea crude oils, has been developed[3]. The viscosity model is directly linked to a thermodynamic model for calculating the fraction of solid wax as function of temperature and pressure[4].

CRUDE OIL GELS AND TIME-DEPENDENT RHEOLOGY

Several subsea North Sea oil fields produce highly paraffinic, high pour point oils. In addition to the wax deposition challenges with these fluids, there are additional challenges related to transient operations such as shut-downs, cool-down and pipeline restart, due to their gelling tendency. The origin of this tendency is the interaction between wax crystals in the crude oil upon cooling. When the volume fraction of solid wax particles exceeds about four per cent[5], these interactions cause a three-dimensional network to form under quiescent conditions. The properties and behaviour of such gelling oils has been studied for decades. One milestone work is that of Davenport and Somper[6] more than forty years ago, where they studied gelled oil behaviour in both lab-scale rheometers and a large-scale pipeline. Various aspects of gelling and restart behaviour of waxy North Sea oils have since been studied extensively[7-9].

In addition to developing a yield stress, i.e. a certain threshold shear stress that has to be imposed in order to start breaking the gel structure and make it flow, the crude oil gels exhibit a complex time-dependent rheology. Due to lack of reversibility, the term thixotropy, though often used, is not actually the right word to describe this behaviour, rather time-dependent shear degradation.

When subjected to a given shear stress, the rheological response is characterized by an initial, transient elastic deformation, followed by a creep flow period at very low shear rate, the length of which depends on the shear stress, then a fairly rapid collapse of the gel towards an equilibrium shear rate, characteristic for a given temperature. This is illustrated in Fig. 4.
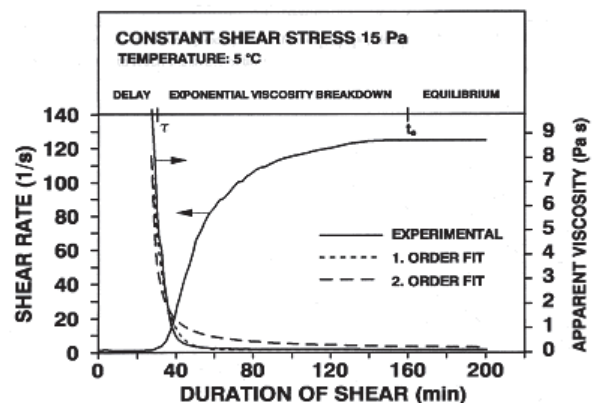

Figure 4. Time development of shear rate when a gelled oil is subjected to a constant shear stress[7].

As shown by Rønningsen[7], and recently confirmed by Schüller et al.[9], this overall behaviour can be expressed mathematically by a time-dependent Bingham plastic

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rheological equation of state:

$$\sigma = \sigma_y(t) + \mu_B(t)\,\dot{\gamma} \qquad (2)$$

where σ is the shear stress. The Bingham viscosity (μ_B) is essentially constant and the Bingham yield stress (σ_y) breaks down according to a second-order rate equation (Fig. 5), indicating that the progressive breakdown process, to a good approximation, can be represented by a series of linear and parallel flow curves with progressively lower yield stress[7]. Schüller et al.[9] also devised a method for using a modern rheometer to obtain the time-dependent yield parameters, incl. the time constant for yield stress breakdown.
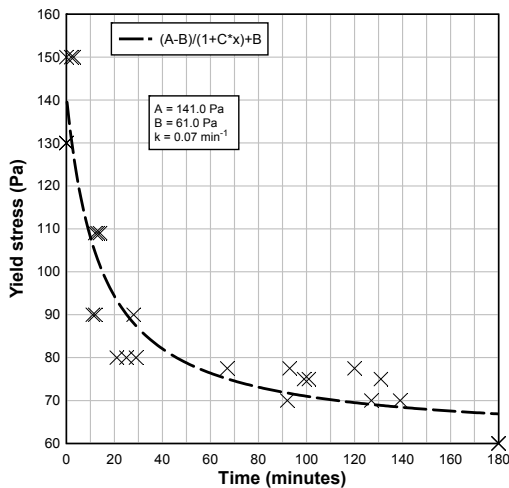

Figure 5. Breakdown of gelled oil yield stress of a North Sea crude oil[9].

A very interesting observation is that the restart behaviour observed by Davenport and Somper[6] in a large scale (78 mm) flow loop, is very similar to the behaviour observed by Rønningsen[7] in a completely different geometry, i.e. a small scale cone-and-plate rheometer, confirmed by Schüller et al.[9] and also observed by Paso et al.[10] in similar modern type rheometers. Overall, there seems to be good evidence in support of the adequacy of a time-dependent rheological equation of state of this kind for describing shear-induced breakdown of waxy crude oil gels.

One feature of waxy crude oil gels that complicates the experimental characterization, is the dependency of yield stress and gel breakdown not only on the actual temperature (and pressure), but also on the thermal and shear history prior to the measurement conditions[5,11]. This has its origin in a complex interplay of various chemical constituents in the oil which is only partly understood. The prevailing theory is that some of the polar constituents of an oil act as a kind of natural wax structure modifiers, similar to synthetic pour point depressants, and that the effect of these substances in terms of their ability to interact with wax crystals, strongly depend on their solubility state, and hence on the history of heating and cooling. The similarity to synthetic wax modifiers has been demonstrated in several studies[5,8]. In any case, the sensitivity to history may be very large. It is also often referred to as the minimum-maximum gelling point (or pour point) phenomenon, since the gelling temperature may be higher or lower depending on the thermal history as well. This puts very high requirements on the pre-conditioning methodology and skill of operators in order to produce reproducible rheological data of high quality.

In relation to real oil production systems, there are some additional factors that need to be taken into account. First, oil well streams contain dissolved gas which has a positive impact on the wax solubility[4] as well as the rheology in general and the gelling behaviour specifically. As an example, increasing the saturation pressure of an oil from 1 bar (gas-free oil) to 100 bar, typical for many multiphase pipelines, has been found to reduce the yield stress by 60-70%[8,12]. Furthermore, a free gas phase in a pipeline reduces the effective contact area between gelled oil and pipe wall in a shutdown situation, and thereby the required restart force or pressure. The pressure required to initiate movement of a gelled oil plug effectively depends on these two

parameters, i.e. the so-called 'break-away' yield stress and the contact area. The further progress of the restart depends on the more detailed time-dependent rheology, as described above. A multiple plug pipeline restart model presented by Nossen et al.[13] might form basis for a more sophisticated future multiphase gelled oil restart model. This is currently an important area of research in many oil companies. In a multiphase pipeline, a water phase may have a significant additional impact on viscosity and gelling properties, as discussed below.

Some researchers have applied oscillatory shear experiments to study the viscoelastic properties of crude oil gels. Vinogradov[14] stated that the yield stress was close in magnitude to the storage modulus measured at low frequency of oscillation. Hou and Chang[15] recently applied oscillatory measurements to study the effect of thermal and shear history on the viscoelasticity of some Chinese crude oils.

Although the general picture of the crude oil gel breakdown process seems to be reasonably well understood, and confirmed by several independent studies, there is still a way to go both to have really reliable and reproducible experimental methods for determination of the rheological parameters, and a coherent modelling framework, enabling detailed calculations of the restart of gelled oil multiphase pipelines.

WATER-IN-CRUDE OIL DISPERSIONS

Transport of unprocessed well stream, i.e. mixtures of oil, gas and produced water, is very common in oil field developments. The effective viscosity of the transported fluid mixture is an important parameter for pipeline capacity and sizing evaluations. Due to energy input from turbulence or pumps, oil-water mixtures will tend to form dispersions of droplets of one phase in the other. Depending on the fluid chemistry, specifically the content of polar, interfacially active compounds in the oil, the type and stability of such dispersions can vary a lot, but normally water-in-oil (w-i-o) dispersions are formed as long as the water volume fraction (water cut) is not too high. Stable dispersions, i.e. dispersions which are stable for a long period without continuous energy input from shear or turbulence, are often called emulsions. When the water cut exceeds a certain value, the inversion point, the dispersion changes to an oil-in-water (o-i-w) type with water as the continuous phase. In fact, rather than a specific water fraction, the transition from w-i-o to o-i-w normally occurs over a range, the inversion range. Predicting when the inversion takes place for a specific crude and a specific production system, is highly important and a major challenge in many oil production systems, especially heavy oil systems. The reason is that as the produced water cut increases, the inversion point (or range) determines the maximum viscosity of the well stream and hence the transport capacity for a given design. Experimental determination of realistic inversion behaviour is thus a highly prioritized area of research at the moment.

A recent paper by Zhilin et al.[16] describes how such realistic flow loop experiments, taking into account variables related to flow as well as pump energy input, can be carried out. Primary focus in this work was to determine the transition from oil continuous to water continuous flow and thereby the maximum viscosity to be designed for.

Although a number of factors has an impact on the actual viscosity of a water-in-oil dispersion, such as the oil viscosity, droplet size distribution etc., it turns out, that the relative viscosity of such dispersions, up to the maximum point, can be expressed by some fairly simple models with surprisingly large robustness and general validity. The simplest of these is probably the so-called Brinkman formula[17]:

$$\eta_r = (1 - \phi)^{-2.5} \qquad (3)$$

where η_r is the relative viscosity and ϕ is the volume fraction of dispersed water. Zhilin et al.[16] found that a large number of experimental flow loop data could be represented well by this simple formula, which needs no input on dispersion characteristics other than volume fraction of water.

Based on a large set of experimental rheometer viscosity data for dispersions with different North Sea crude oils, another simple, empirical correlation was established by Rønningsen[18], also taking into account the effect of temperature and shear rate. The 'high' shear rate version of this correlation (500 s^{-1}) is most often used in pipeline simulations. This is one option for dispersion viscosity in the commercial flow simulator OLGA. It has the general form:

$$\ln \eta_r = k_1 + k_2 T + k_3 \Phi + k_4 T\Phi \qquad (4)$$

where T is temperature (°C) and Φ is volume% water. The coefficients from ref. 18 are shown in Appendix A. This correlation is based on the well-known exponential relationship between relative viscosity and water cut of Richardson[19]. Fig. 6 shows the correlation graph for shear rate 500 s^{-1} and various temperatures together with the Brinkman correlation.

Johnsen and Rønningsen[20] tested this and other correlations against experimental data for 'live', pressurized water-in-crude oil dispersions in a wheel-shaped flow simulator and found reasonable agreement up to a water volume fraction of at least 60-65% in most cases. In fact, this appears to be the most interesting range of water cuts since real crude oil dispersions very often tend to invert at volume fractions not higher than this. It can be noted in Fig. 6 that the Rønningsen correlation is very similar to the Brinkman formula up to a volume fraction of about 55%. At very low water fractions (less than about 5 vol%), the Brinkman

formula is believed to give somewhat more realistic predictions than the empirical correlation, which is not based on experimental data below 10% water cut.
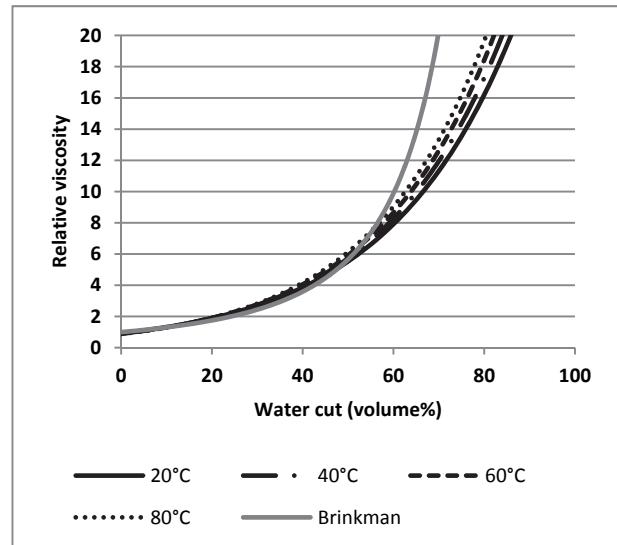

Figure 6. Correlations for relative viscosity of water-in-crude oil emulsions. Black lines show the Rønningsen correlation[18] at different temperatures and shear rate 500 s^{-1}. The grey line shows the Brinkman formula[17].

The robustness of these correlations towards variations in flow conditions, droplet sizes etc. seems to be surprisingly large. It is fairly safe to assume that the relative viscosity of a water-in-crude oil dispersion is about 5-6 at 50% water cut and about 8-9 at 60% water cut. Often, these are good enough estimates for engineering purposes. More important, and more challenging experimentally, is to predict accurately where inversion will occur, or more precisely, the water cut of maximum viscosity. An important area of research where more work is needed, is thus to be able to measure realistic phase inversion behaviour, that can be transformed into wellbore and pipeline transport conditions, using small scale laboratory equipment. This is important since very often, limited sample volumes does not allow large scale

experiments to be carried out in early phase of field design.

Finally, when waxy crude oils are co-produced with formation water, and subjected to cool-down in a transport system, two complex phenomena are combined, creating even more complexity, in form of waxy crude oil emulsion gels. The properties of such gels have been studied recently by several groups[21,22], showing that highly stable emulsions with very high viscosities and yield stresses, and strong non-Newtonian behaviour, are formed. An example of the effect of water cut on the yield stress of two waxy North Sea crude oils is shown in Fig. 7.
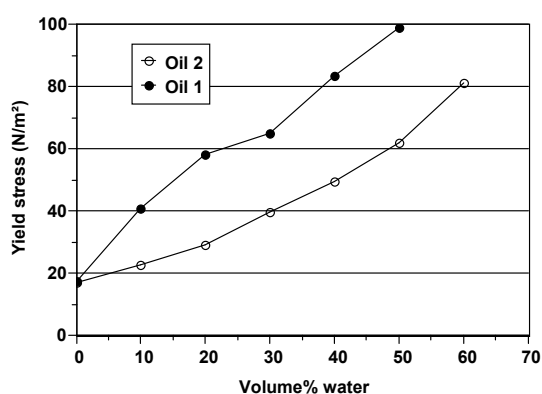

Figure 7. Effect of dispersed water on yield stress[8].

SUMMARY AND CONCLUSIONS

Petroleum fluids show a large variation of rheological behaviour and an extremely large range of viscosities. Some areas are relatively well understood, some remain less understood. Some main challenges and areas where more research is needed, has been identified in this paper:

1. The effects of gas solution kinetics in relation to heavy oil viscosity measurements.
2. Accurate and realistic measurements of the time-dependent shear degradation of crude oil gels and emulsion gels.
3. Realistic measurement and prediction of phase inversion (maximum viscosity water fraction) in water-crude oil systems using small-scale equipment.

APPENDIX

Table A1. Coefficients of the correlation for relative viscosity of water-in-oil dispersions, Eq. (4)[18].

	Shear rate		
	30 s^{-1}	100 s^{-1}	500 s^{-1}
k_1	0.01334	0.0412	-0.06671
k_2	-0.003801	-0.002605	-0.0007750
k_3	0.04338	0.03841	0.03484
k_4	0.0002628	0.0002497	0.0000500

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