Determining rheology for settling suspensions

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Abstract

Within the oil refinery industry, there are several flow processes which involve settling suspensions. Velocity profile models for multiphase flow with partially settling particles require correlations relating viscosity as a function of particle concentration. The parameters of such correlations can only be determined experimentally. However, under partial settling conditions, a particle distribution forms within the rheometer established by a balance between gravitational particle settling and shear induced migration of the particles. Considering the large particle sizes and the low interparticle forces, viscosity data from the rheometer will show anomalous behavior since the homogenous assumption is not met when making viscosity measurements. If the rheological parameters are interpreted through a model that accounts for the particle settling dependence upon shear rate, particle size and other physical properties, a more realistic viscosity description may be obtained.

1 INTRODUCTION

An important technique for hydrocarbon production from subsea wells has, for some time, been the direct transfer of untreated well fluids through flow lines. Water, sand, hydrates and reservoir solids thus follow the oil and gas streams in a pipeline flowing from the wellhead to a processing plant at some distance away. With the presence of water and the possible formation of hydrates, solids transport represent serious flow assurance problems caused by agglomerate formation, deposition onto walls or blockage of production lines or wellhead at low temperature and high pressure conditions. One way of mitigating the flow assurance problem is to use anti-agglomerates as an additive chemical which allow the formation of hydrates in the form of small non-associating particles. Together with the oil, these particles form a transportable slurry.

Direct well flow transfer has recently been complemented by subsea separation, where the water is separated off as practically possible near the wellhead in order to reduce the burden of water carried by the flow stream. This reduces the gravitational pressure drop and thus increasing the productivity. However, in both cases of transporting slurries, sand, hydrate and wax particles will remain in the flow stream thus affecting the pressure drop through the density and viscosity of the dispersion.

Due to their size and density, solid particles have a tendency to settle out in hydrocarbon liquids. A concentration distribution of the particles will form across the pipe cross section depending on both the particle concentration and pipeline velocity in pipeline [1,2].

To describe the settling and flow processes and how they affect the pressure drop and production capacity, a cross sectional model has been developed by Peysson [1], Nuland [2]. A crucial facet of this model is the rheology model which is used to calculate the dispersion viscosity at every local concentration within the cross section. Therefore, correct determination of dispersion viscosity is paramount for practical application of the model.

As for the experimental determination of dispersion viscosity, settling particles has to be addressed. There are devices for rheological determination that include mixing elements intended to create a homogeneous dispersion [3]. Dealing with low viscosity oil dispersions with rapidly settling particles for viscosity measurement is an important issue in the oil industry as well as our studies. Accordingly, the dispersion homogeneity may be questioned. Another issue to be addressed is that in low viscosity samples the torque created is often near the lowest measurable limit of the rheometer. Furthermore, the use of mixing
devices in a rheometer generates non-viscometric flow with these low viscosity samples, as well as turbulence being promoted at very low shear rates. These factors will all induce inaccuracies in the viscosity measurement. In this study, we intend to use the conventional Couette cup and bob geometry for the viscosity measurement whilst accounting for settling effects via modeling.

Directly interpreting viscosity measurement with settling dispersions provides unphysical results that are useless if directly applied in a transport model.

2 THEORY

2.1 Basic method – minimizing difference between the viscosity from model and from experiment

The goal is to develop a model with adjustable parameters which give an estimate of the viscosity as measured by the rheometer, and then to determine the parameters by minimizing the difference between the estimated and the measured viscosities. This model will consist of two physical sub-models: (1) a model for particle distribution and (2) a viscosity correlation to be used at every level in the gap between cup and bob. In addition, the resulting viscosity distribution is averaged for comparison with that obtained experimentally. The viscosity correlation contains the adjustable parameters while the model for particle distribution is considered to be fixed.

2.2 Modeling of particle dispersion in the rheometer

We utilize a model for particle distribution in laminar flow. We will essentially assume that under conditions where Taylor vortices arise, the measurements are not valid. Existence of the Taylor vortices during the measurement is usually observed by a sudden rise in apparent viscosity with increasing shear rate. This is of course, a problem when working with low viscosity solvents. In this situation the particle distribution mechanism is shear induced migration. We will use the model of Leighton and Acrivos [4] and Acrivos [5] which describes a dynamic equilibrium between gravitational settling and shear induced migration. This relation is given by:

$$
\phi_{\text{term}} = \left[ -\frac{1}{3} \gamma^2 \left( \bar{\phi} \right) \left( 0.5 \exp(8.8\phi) \right) \right] \frac{\partial \phi}{\partial y} \tag{1}
$$

In this relation $\phi$ is the particle concentration, $\gamma$ is the shear rate, $V_{\text{term}}$ is the terminal settling velocity which includes a hindered settling term, and $r_p$ is the particle radius. Equation 1 is applicable to medium to high concentrated dispersions. This concentration range can be regarded to be from a concentration of about 0.5 x the maximum packing fraction to a concentration close to the maximum packing fraction.

We assume that a certain average dispersion concentration is prepared and tested in the rheometer. A certain bottom concentration is selected, and equation 1 is integrated numerically from the bottom to the top. The particle distribution is then averaged and compared to the experimental average concentration. Subsequently, the bottom concentration is iterated based on such comparisons upon using the so called Brent’s method, [6]. Iterations continue until the calculated and actual average concentration values converge.

2.1.1 The terminal velocity

The terminal velocity of a suspension is modelled as the terminal velocity of an isolated particle in a Newtonian liquid, $u_{\text{term}}$, undisturbed by walls or other particles, modified by a hindered settling function:

$$
V_{\text{term}} = u_{\text{term}} f_h \tag{2}
$$

For the terminal velocity of an isolated particle we used correlations by Wallis [7]. These relationships have been chosen for their simplicity. First a dimensionless radius is defined:

$$
r^* = r_p \left[ \frac{\rho_i g \Delta \rho}{\mu_f} \right]^{1/3} \tag{3}
$$

where $\rho_i$ and $\mu_i$ are the density and viscosity of the continuous phase, and $\Delta \rho$ is the density difference between the particle and the fluid. The dimensionless velocity is then calculated as:

$$
v^* = u_{\text{term}} \left[ \frac{\rho_i^2}{\mu_i g \Delta \rho} \right]^{1/3} \tag{4}
$$
For \( r^* < 1.5 \):

\[
v^* = \frac{2}{9}(r^*)^{\frac{1}{3}}
\]

Equation 5

For \( 1.5 \leq r^* < 10 \):

\[
v^* = 0.307(r^*)^{1.21}
\]

Equation 6

For \( 10 \leq r^* < 36 \):

\[
v^* = 0.693(r^*)^{0.888}
\]

Equation 7

For \( 36 \leq r^* \):

\[
v^* = 2.5(r^*)^{0.5}
\]

Equation 8

The hindered settling function is a modification of the Richardson and Zaki correlation given by Yin and Koch [8]:

\[
f_k = \frac{V_{term}}{u_{term}} = k(1 - \varphi)^n,
\]

Equation 9

with \( k \) in the range 0.86 to 0.92, and the exponent \( n \) being dependent on particle Reynolds number given by:

\[
n = 4.23 - 0.0536 \text{Re} + 0.011 \text{Re}^2.
\]

Equation 10

where the particle Reynolds number is defined as:

\[
\text{Re}_p = \frac{2r_p u_{term} \rho_p}{\mu_f}
\]

Equation 11

2.3 Simulation results for particle distribution

Figure 1 shows how the particle distribution changes with shear rate for an average particle concentration of 40 %. The result is shown for the water phase. According to the model, the particles are just lifted up to half the gap height at low shear rates. Here, the concentration at the bottom is higher in order to accommodate all the particles over a shorter height. As the shear rate increases, the particles elevate to higher heights thus reducing concentration at the bottom.

Figure 2 compares the horizontal particle distribution between two average concentrations at different shear rates. We observe the effect of a strong increase in the diffusion coefficient in equation 1 in that the higher the average concentration is, the higher the particles are lifted.
Figure 1 Vertical concentration distribution in the rheometer at various shear rates. The average concentration of particles is 40%.

Figure 2 Comparison of particle concentration profiles at low and high shear rates.

Open symbols: 20 s\(^{-1}\)  Half-filled symbols: 500 s\(^{-1}\)
2.4 Dispersion viscosity and local viscosities

We use the Krieger Dougherty [9] correlation to model the relative viscosity of the dispersion at a position above the rheometer bottom:

\[
\mu_r(h) = \frac{1}{(1 - \frac{\phi(h)}{\phi_m})^{[\eta]}_m} = \frac{1}{(1 - \frac{\phi(h)}{\phi_m})^m}
\]

Equation 12

where \(\phi(h)\) represents actual volume fraction of particles at each elevated height (h), \([\eta]\) is the intrinsic viscosity of the suspension, and \(\phi_m\) the maximum packing fraction. Both \(\phi_m\) and m are adjustable constants used in fitting the model to measured viscosities. \(\phi_m\) is typically denoted as the maximum settled fraction, and is usually close to maximum fraction that can be settled from stagnant fluids. This correlation is used for each calculated concentration in the rheometer gap. A typical result is shown in Figure 3 for the water phase.

Equation 12 assumes that slurry viscosity is consistent with Newtonian flow pattern. However, the dispersion viscosity may be dependent on the shear rate in a non-Newtonian flow manner. To evaluate this possibility a power law dependency has been assumed which correlates the viscosity with both the shear rate and particle concentration according to:

\[
\mu_r(h) = \frac{\gamma^{n-1}}{(1 - \frac{\phi(h)}{\phi_m})^m}
\]

Equation 13

This equation collapses back to equation 12 when \(n=1\).

Figure 3 Local viscosity distributions at 500s\(^{-1}\)
2.5 Optimization method
An optimization procedure was used to obtain the parameters in equations 12 and 13. The object function to be minimized was:

\[ I = \sum_{i} \left( \frac{\mu_{\text{meas}} - \mu_{\text{model}}}{\mu_{\text{model}}} \right)^2 \]  

Equation 14

We used an unconstrained nonlinear MATLAB optimization method which applied the simplex search method [10]. This is a direct search method that does not use numerical or analytic gradients. The search method uses the Nelder-Mead simplex algorithm as described by Lagarias et al. [10]. The algorithm first makes a simplex around the initial guess and modifies the simplex repeatedly according to a minimization finding procedure. Iteration based on constructing several small simplexes is repeated and terminated when the diameter of the simplex is less than a specified tolerance.

3 EXPERIMENTAL

3.1 Materials and sample preparation
Well behaved particles of fairly large diameter (230 micron) were used in this study. Due to the particle size and the surface properties of these particles, we have assumed that the hydraulic interaction between the liquid and the particle will dominate over the interparticle forces. The particles were polystyrene of high purity produced by Microbeads AS (Norway). These particles were silver coated by Nanotechnology (Netherlands) in order to increase the density of the particles to be similar to that for sand or hydrate particles in oil / water mixtures. The adjusted density was 1150 kg m\(^{-3}\). Particle size measurements obtained with a Master sizer (Malvern instruments) indicate a fairly narrow size distribution as shown in Figure 4. This plot shows a number average size of 220.1 \(\mu\)m, and a weighted average of 235 \(\mu\)m. Because of this narrow size distribution, the particles are considered to be monodisperse with an average size of 230 micron.

Ultra pure water (Millipore milli-Q system = 18.2M\(\Omega\) cm) and a low viscosity/density synthetic oil (Exxsol D80) were used as the continuous phases. Their respective viscosities were 0.87 and 2.2 mPa.s, with their respective densities being 996 and 790 kgm\(^{-3}\) at 25°C.

![Particle Size Distribution](image)

Figure 4. Size distribution of silver coated polystyrene particles

Prior to the rheological measurements, slurries were prepared by gradually adding water to the measured particle amounts. Four different particle concentrations were prepared for each water and oil phase. The particle concentrations ranged from 30 to 60 \%wt. Since the silver coated polystyrene particles were considered to be partially hydrophobic, it was important for them to be wetted with water before being agitated. Agitation was carried out in 10 minutes at 1000 rpm using a 4-bladed propeller to form completely homogenous slurries. Higher speeds were avoided in order to prevent air entrainment in the sample and foam formation. Residual bubbles were eliminated by placing the samples under vacuum or in an ultrasonic bath for 10 minutes.

3.2 Shear flow testing
The shear flow rheology experiments were conducted using a Physica MCR 301 rheometer (Anton Paar). The experiments were performed using the Couette bob and cup geometry. The height of the rotating bob is 4 cm.

Samples were directly prepared inside the rheometer sample holder and were agitated using the propeller. The experiment immediately started right after cessation of mixing. This was performed in order to prohibit any particle sedimentation or loss of
sample outside the rheometer. However partial losses of the sample did occur during the mixing process when preparing the sample thus affecting the concentration. Hence, the actual concentration was checked by solvent evaporation (when using water as a suspending medium) after the tests were completed in the rheometer. For the slurries prepared in oil, verification was performed by measuring densities of available samples in the rheometer by knowing their weight and the volume. The concentrations were theoretically prepared to 35, 40, 45 and 50 wt% in the water phase, and 40, 50, 55 and 60 wt% in the oil phase (Exxsol D80). However, the actual volume fraction of particles was determined to be 0.31, 0.37, 0.42 and 0.47 for the aqueous based suspensions, and 0.31, 0.42, 0.46 and 0.50 for the oil based suspensions. These actual volume fractions were used in the viscosity model inversion process.

Measurements were taken at a constant temperature of 25°C. The shear rate range covered was from 1000 to 20 s⁻¹. Each sample was subjected to several decreasing and increasing shear ramps at each test. Starting with the highest shear rate, the change in torque values were recorded at each shear rate until an equilibrium value was reached. The viscosity corresponding to equilibrium torque was saved and the shear rate was changed to the lower value. This approach was applied for all shear rates covered. For most shear rates, equilibrium was reached in a short time. However, at low shear rate and low particle concentration, the torque-time curve oscillated and therefore discarded. At these shear rates, the rheometer was operating at its lower torque limit.

The protocol was programmed to run shear cycles with no time delay between each shear rate step. This prevented any unwanted settling from occurring. Subsequently, the sample was ramped up and down several times to check for the presence of any possible thixotropic or time dependent effects in the sample. This was found to be negligible.

3.3 Maximum packing fraction
The principle method for measuring maximum packing fractions of concentrated suspensions is sedimentation by gravity or centrifugation. The maximum packing fraction is defined as [11]:

\[ \phi_m = \frac{\text{Bulk density of particles}}{\text{Density of particle}} \]

Bulk density was measured by the sedimentation of particles in a low viscosity solvent. Direct settling measurements were performed in three solvents, pure water, saline water and Exxsol D-80. The suspensions were prepared according to the procedure described in Section 3.1, and the resulting dispersions were left to settle for 24 hours prior to measurement. Measurements of maximum packing parameter were performed at least three times in order to ensure statistical accuracy. Standard deviations were found to be less than 2%. An analysis of the systematic errors in the experimental technique revealed that the uncertainty in \( \phi_m \) measurement to be less than approximately 2%.

4 RESULTS
Viscosity-shear rate plots of all the slurries showed an absence of any thixotropic, or any other time dependent effects based on several up and down shear rates ramps. However, we have not shown this observation in any of the plots here. Viscosity results for all particle concentrations are illustrated as a function of shear rate for the whole range of shear rate. This is shown in Figure 5 for the experiment done in aqueous phase with particle concentrations of 35, 40, 45 and 50 wt%. This plot showed the viscosity-shear rate curves increases with increasing particle concentration. The variation of viscosity with concentration was more pronounced at the smaller shear rates. At each concentration the apparent viscosity decreases with increasing shear rate. As this was confirmed to be attributed to the onset of Taylor vortices, this data was excluded from the subsequent analysis. Similar trends to those in Figure 5 were also observed for suspensions prepared with Exxsol D-80. However this plot is not shown here.

Looking at data in Figure 5, shear-thinning behaviour could be interpreted if no consideration is paid to the settling behaviour of the suspensions. However, this degree of shear thinning is so high compared with that reported for the particulate systems with dominating attractive interparticle forces. These occur in colloidal systems with nano-sized particles or lower than some few microns. With our particle size of being 230 micron, the degree of the shear thinning is higher than can be expected, considering very low effect of interparticles forces. Our hypothesis is that particles are lifted at higher shear as shown in Figure 2 causing a reduction in concentration in the lower part of the rheometer cup. Since there is a direct relationship between the particle concentration and the viscosity, increase in the rate of shear would decrease the overall viscosity.
The observations made from Figure 5 were explained by our model where the rheological model parameters were determined by an optimization process involving our particle settling model. The model parameters $\phi_m$ and $m$ in Equation 13, were found to be 0.71 and 2.21 respectively for water based suspensions and 0.69 and 2.03 respectively for the oil-based suspensions. These values were found to be in agreement with those reported for non aggregating hard spheres [11, 12]. A comparison of the viscosities calculated from our model with the measured viscosities is depicted in Figures 6 and 7 for the water-based and the oil-based suspensions respectively. These plots show a good agreement between the measured and predicted viscosities. The average relative error corresponding to each point was found to be 10.5% and 9.8% for water based and oil-based suspensions respectively.
Figure 7 Comparison between measured and model viscosities after optimization for oil-based suspensions, all shear rates

A major discrepancy between model and experiment is observed in Figures 6 and 7 at the higher viscosities obtained at the lowest shear rates during the viscosity measurements, where the torque did not reach equilibrium even after long time due to the large fluctuations.

Figure 8 Comparison of measured and modeled viscosities in water phase after optimization with the lowest unstable shear rates eliminated
Since the accuracy of rheology parameters is dependent on the reliability of experimental data, the viscosity points corresponding to low shear rates were removed. The optimization process was then repeated using the reduced dataset. Figures 8 and 9 show Figures 6 and 7 but with the corrected dataset where good agreement between the model and measured viscosities was obtained. The model parameters $\phi_m$ and $m$ in Equation 13 were found to be 0.68 and 1.93, with a corresponding error of 6.5% between the measured and predicted viscosity in the water phase, and 0.68 and 1.97 with a corresponding error of 4.7% for the oil phase. The optimisation results for both water based and oil based suspensions, considering/not considering all shear rates are summarised in Table 1.

Up to now, Newtonian flow behaviour was assumed for the model viscosity. An improved model incorporating a shear dependency according to the power law relation is now considered. Hence, the use of Equation 13 led to a three parameter optimisation problem. The power law exponent was found to be $1 \pm 0.05$ for the water based system and $1 \pm 0.025$ for oil based system, indicating Newtonian flow behaviour. However when using three variables, optimisation could not be reached. This is due to the optimisation function having a high degree of nonlinearity some of the parameters having similar effect on the object function. No unique point was found but the object function did form a valley with a function value being the same for several combinations of parameters. In this situation, the end point is dependant on the starting condition. From this non-linear optimisation process, the values of the maximum packing fraction was still between 0.64 and 0.7 for the water based system whereas a smaller range lying between 0.67 and 0.69 was found for the oil based system.

<table>
<thead>
<tr>
<th>Suspending medium</th>
<th>All shear rates</th>
<th>Without small shear rates</th>
<th>All shear rates</th>
</tr>
</thead>
<tbody>
<tr>
<td>From rheology experiments and model inversion</td>
<td>$\phi_m$</td>
<td>m</td>
<td>Error%</td>
</tr>
<tr>
<td>Exxsol D-80</td>
<td>0.69</td>
<td>2.03</td>
<td>9.8</td>
</tr>
<tr>
<td>Water</td>
<td>0.71</td>
<td>2.21</td>
<td>10.5</td>
</tr>
</tbody>
</table>

Maximum packing fractions, obtained from direct settling experiments were found to be 0.64, 0.65 and 0.67 for pure water, saline water and Exxsol D-80, respectively. Several different values have been previously reported for $\phi_m$. These range from...
0.52 for a simple cubic packing to 0.74 for a rhombohedral packing [12]. Because packing type is usually not known in most applications, an average value of 0.68 is often suggested for monodisperse spherical particles whose aspect ratio is close to one [11, 12]. Our values were found to be in good agreement with those reported for non-aggregating particles. However, the difference between the maximum packing value obtained by optimisation and that by the sedimentation method was more pronounced for the water-based suspensions.

We propose that the difference in maximum packing fraction observed for different solvents arises from the degree of interparticles/particle-solvent interaction. Electrostatic stability (stabilisation by existence of charges) is much stronger in polar solvents. These forces decrease by the addition of electrolyte thus neutralizing the surface charge of the particles. This can be totally removed in non-polar solvents as in the oil. It has been also stated that the state of the particle wettability in any solvent would affect the interparticle attractive forces. The more the particles become wetted, the smaller the attractive forces become. By this, it can be concluded that the magnitude of maximum packing fraction for the hydrophobic particles for example, will decrease with increasing solvent polarity. However, the effect of these particle-particle and solvent-particle interactions has dominating effect as the particle size decreases. Since the effect of any particle-particle and particle/solvent interactions have been neglected in our model, a larger consistency between the maximum packing fraction from the model and the experimental data is obtained for Exxsol oil.

5 CONCLUSIONS

Using a balance between gravitational particle settling and shear induced migration; a model describing the particle distribution in the vertical direction was developed. Combining the particle distribution model with a well-defined dispersion viscosity model such as Krieger Dougherty, a model with unknown rheological parameters was obtained. These rheological parameters can be obtained from an optimisation process which minimizes the difference between measured and calculated viscosity.

The obtained viscosity description serves to simplify the raw viscosity data. The apparent shear thinning was difficult to reconcile with what is known about particle and fluid properties. The trend of viscosities was explained by the shear rate dependent characteristic of the settling process. The two model parameters within the rheology correlation are estimated to be physically quite realistic, and the values are in good agreement with values reported for non-aggregating hard spheres.

One of the rheological parameters within the viscosity model is the maximum packing fraction of the suspension. The maximum packing fraction in various suspending solvents was measured by observing particle settling in a stagnant fluid. Comparison of the maximum packing fraction results obtained by model inversion in the optimisation process showed a good agreement with those obtained from settling experiments. The agreement was found to be much better when the suspending medium was oil. This was related to the better particle wetting in the oil compared to that in the water. Therefore, the interparticle attractive forces are smaller in the oil phase and the possibility of aggregate formation being smaller as well. This led to a larger packing fraction.

These conclusions play an important role in general applications in the oil industry, including sediment transport in inclined settlers, pipelines and other flow applications.

6 REFERENCES


