PRF# 57692-ND9
Project Title: Altering wax appearance using shear and pressure
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## Overview

Investigating wax appearance temperature under different shear, temperature, and pressure offers an opportunity to provide a more complete phase diagram and understanding of flow-induced phenomena in waxy oil systems, which is an important flow assurance problem. Students are using state of the art equipment to gain hands-on laboratory experience, specifically rheometry and scattering. One graduate student and a visiting researcher are compiling research results. Dissemination will include a M.S. thesis in addition to peer reviewed journal publications. At least 1 publication is expected in 2020.

The researchers are working collaboratively to compile four types of measurements in a comprehensive analysis of waxy mineral oil flow behavior. The first two measurements are rheological measurements at ambient pressure under static (no flow) and shear flow conditions. Rheological testing includes flow sweep, peak hold, and temperature ramp tests. More difficult measurements, such as rheology under high pressure and rheo-small angle light scattering, have begun and will continue in the next year. Once new insights are quantified, the project should allow the industry to construct wax phase diagrams with shear and pressure as independent variables without a full factorial experimental design. Select findings are described below.

## Findings to date

Changes in wax appearance temperature (WAT) under flow used six different wax concentrations in light or heavy mineral oil. Rheological measurements are examining WAT at ambient pressure and at elevated pressure up to 2000 psi. Ambient pressure rheological experiments were carried out using a 60 mm parallel plate geometry at a constant gap of 0.5 mm. Changes in WAT at varying shear rates (1, 10, 100, 1000 $s^{-1}$) were quantified. Wax appearance temperature decreased about 2°C for various wax concentrations. For 25 wt% paraffin wax in light mineral oil, wax appearance temperature reduces from 45.5°C to and 43.2°C between shear rates 1 and 1000$s^{-1}$ (Figure 1). Other measurements were conducted to investigate changes in WAT, including water bath for static phase behavior, rheo-small angle light scattering to identify size of wax particles forming, and differential scanning calorimetry to measure thermal properties. Combining techniques will be better examine the effect of shear to WAT.

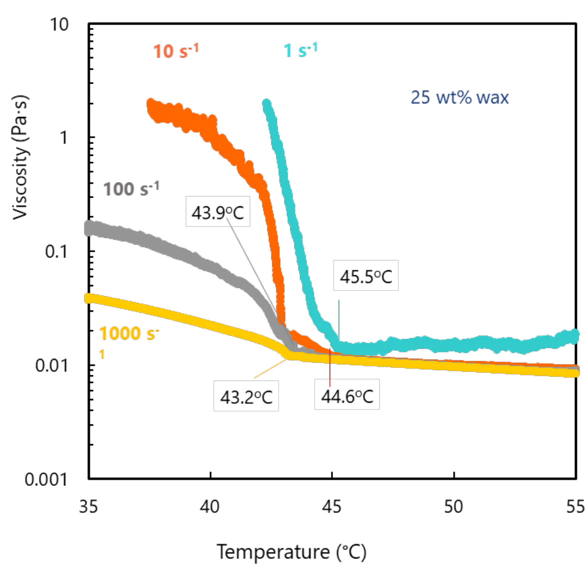

Figure 1. Effect of shear on Wax Appearance Temperature of 25 wt% wax in light mineral oil.

Experiment are carried out first by preconditioning the samples at 65°C to erase any thermal history of the sample. Temperature is lowered from 65°C at a constant rate of 0.2 °C /min to 10 °C, for shear rate 1, 10, 100, 1000 $s^{-1}$. All samples of wax/mineral oil behave as Newtonian fluid at 65°C. Next, samples are cooled from 65°C at rate of 0.2°C /min, viscosity remains relatively constant until ~45°C. When the wax begins forming, a sharp increase in viscosity is observed. The sharp change in viscosity is quantified as the wax appearance temperature under shear. In Figure 1, the wax appearance temperature at shear rates of 1, 10, 100, and 1000 $s^{-1}$ was measured at ambient pressure to be 43.2, 43.9, 44.6, and 45.5°C, respectively. Therefore, increasing shear rate lowered the WAT by >2 °C. Furthermore, viscosity after the phase change for low shear rates increase dramatically - about 3 orders of magnitude - that may be due to the wax particles agglomerating and forming larger wax particles. At high shear rate of 1000 $s^{-1}$, the viscosity before the WAT is observed is less than 1 order of magnitude when compared to the viscosity at the WAT.

High-pressure rheological measurements were conducted using a system comprised of a mixing cell, high pressure pump, and a pressure cell on a rheometer. Each experiment takes several days, so a more limited set of wax concentrations (5, 10, 15 wt.%) in heavy mineral oil were studied. The concentration limitation was due to solidification of samples with high wax concentrations (>15%) during loading of the pressure cell. WAT of methane-saturated samples at a pressure of 500, 1000, 1500, 2000 psi are being measured. To date, increasing pressure led to lower viscosity and lower WAT by about 2°C (Figure 2).

As oil samples are cooled from 65 °C at rate of 0.2 °C /min, the viscosity changes slowly until ~40°C. At shear rate 1000 $s^{-1}$, the wax appearance temperature of 10 wt% wax in mineral oil at pressures changes from 39 and 37°C at 15 and 1500 psi, respectively. Therefore, both shear and pressure have quantitative effects on wax appearance temperature.

Academic achievements

Some results were presented at the Society of Rheology meeting in October 2018 in Houston. The graduate student working on this project also participated at Wayne State/University of Toledo chemical engineering research symposium and earned the 3rd place in poster award. Good progress is being made toward a master's thesis that will be defended by the end of 2019.

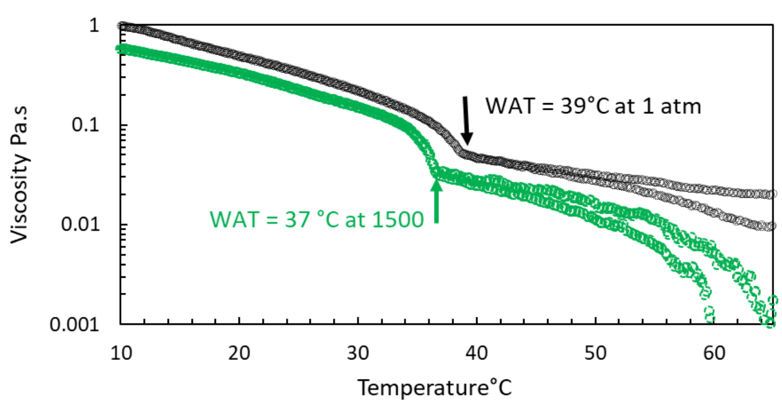


Figure 2. Effect of pressure on wax appearance temperature of 10 wt% wax in mineral oil.

Topics for next year

Future study of higher wax concentration samples using high-pressure rheology may proceed. by optimizing the equipment. In addition to studying rheological behavior of macrocrystalline structure (paraffin wax) in oil, the research will also explore behavior of microcrystalline (asphaltene wax) in oil. At least 1 journal paper on ambient rheology will address how shear alters the wax appearance temperature will be submitted. In addition, a second paper discussing the effect of pressure on wax appearance temperature will also be submitted for publication.