Rheology of crude oil at high pressure

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Rheology is the branch of science dealing with the flow and deformation of materials. Rheological instrumentation and rheological measurements have become essential tools in the analytical laboratory for characterizing component materials and final products, monitoring process conditions, as well as predicting product performance and consumer acceptance.

Rheologically speaking, crude oil is a low-viscosity, Newtonian fluid at high temperature (*Figure 1*) but it exhibits non-Newtonian behavior due to the precipitation of waxes as the crude oil is cooled. This dramatic change in rheology is due to the fact that crude oil is a complex mixture of hydrocarbons that contain different functional groups such as paraffins, aromatics, naphthenes, resins, and asphaltenes. The high-molecular-weight fractions of these components are predominantly responsible for their flow characteristics. At reservoir temperatures, typically 70–150 °C, the solubility of these high-molecular-weight components is sufficient to keep them dissolved in the mixture. However, once the crude oil leaves the reservoir, it begins to cool and the solubility decreases drastically. Transporting complex crude oil presents technical and economic problems.

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Today, rheological instrumentation and rheometry are accepted techniques to more fully characterize, understand, and provide control for crude oil production and transportation. How a particular chemical structure is studied or analyzed, the techniques and instrumentation involved, and how these may be used or modified to solve a problem are paramount.

Importance of acceptable rheology

The oil industry faces a retrieval process that is extremely costly and difficult. Oil exploration and retrieval efforts must overcome the complex flow issues, or rheology, of the crude oil. It is known that oil is extracted from subterranean-level wells. The complexity of this process arises because crude oil exhibits a phase change at low temperatures, which is common to their subterranean environments. The waxy crude oil is known to form congregates of complex morphology at low temperatures due to the formation of crystalline wax. High pour point crude oil will present congealing problems in most ambient conditions. It may congeal on the walls of tankers, resulting in stock loss, and if it congeals in a pipeline, the required restart pressure may exceed the burst pressure of the line. In the case of high pour point crude oil, wax may precipitate out of solution and stick to pipe walls or form sludge at the bottom of a storage tank, even in warm climates. This wax deposition can block flow lines, reduce throughput, clog pumps, and inhibit the performance of metering devices that measure transferred crude oil. The pressure required to start the flow of a pipeline or the temperature at which the oil crystallizes depends greatly on its temperature history. For this reason, it is critical that the effect of cooling rate on the waxy crude crystallization be well understood and documented.

The ability to understand the crystallization process has been restricted by available technology to mimic the processing conditions in a laboratory setting. Rheological characterization of crude oil mixtures requires several unique instrument capabilities: 1) wide torque, angular displacement, and angular velocity capability; 2) wide temperature ranges with controlled heating/cooling rates to 0.1 °C/min; 3) multiple sample holding configurations; and 4) the ability to follow samples from low-viscosity liquids to hard solids. In addition, the sample must be maintained above atmospheric pressure throughout the loading and testing process. In light of this challenging application, **ATS RheoSystems** (North Hollywood, CA) and **REOLOGICA Instruments** (Bordentown, NJ) have developed an approach to studying the rheology of materials under pressure with accurate controlled heating/cooling capability.

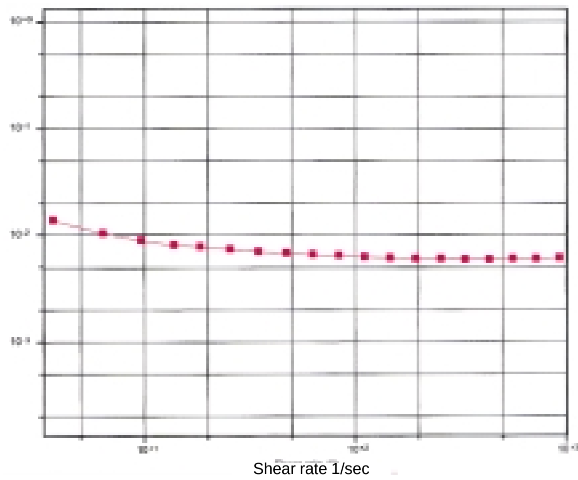

Figure 1 *Graph of oil viscosity versus shear rate.*

Figure 2 *DYNALYSER rheometer.*

Figure 3 *STRESSTECH rheometer.*

Figure 4 *High Pressure Cell.*

Rheological instrumentation

In principle, the solidification/crystallization process can easily be followed by using dynamic mechanical rheological measurements as the buildup of a three-dimensional network is reflected in the change of viscoelastic properties. Today, rheological instrumentation is considered a required analytical tool by scientists and is used on a daily basis. The research-grade instruments discussed here are **Microsoft** (Redmond, WA)Windows™ based, and measurements are made quickly and easily with the use of straightforward, user-friendly software. The operator simply loads the sample into the instrument and selects the appropriate experiment, and the instrument does the rest.

Crude oil is not homogeneous, and the properties vary throughout the sample. Traditionally, single-point viscosity tests have been performed using empirical techniques. These simple viscosity experiments compress the complex viscoelastic response of a sample into a single parameter, and are not adequate in characterizing and/or providing insight into the true flowability of the materials. Detailed knowledge and an objective, reproducible, multipoint measurement, performed under pressure, capable of decomposing the rheological behavior into individual components is necessary. The DYNALYSER, The Complete Rheological Characterization System (*Figure 2*) (both from **ATS RheoSystems/REOLOGICA Instruments**), and the STRESSTECH HR rheometer (*Figure 3*) (**ATS RheoSystems/REOLOGICA Instruments**), used in conjunction with the resistively heated High Pressure Cell (HPC) (**ATS RheoSystems/REOLOGICA Instruments**) (*Figure 4*), meet all of the measurement requirements.

The research-grade analytical instruments are capable of measuring the viscous, elastic, and viscoelastic properties of liquids, gels, and solids. Both instruments were developed for use by the serious rheologist, and provide a very broad measurement range, from low-viscosity samples such as crude oil at high temperatures to the structurally crystallized waxy crude oil at low temperatures. The instruments are well suited for characterizing materials that exhibit phase transitions that demand excellent low sensitivity and/or high torque to meet the challenge.

The rheometers incorporate the following patented features: the AC asynchronous motor drive system; universal temperature cells based on the Joule-Thomson effect; wide torque, shear stress, temperature, shear rate, and frequency range; true Windows-based operational software (**Microsoft Corp.**); patented differential pressure quantitative normal force; patented sealed cell measuring system for full-range dynamic oscillatory testing of samples above their boiling point; automatic gap setting; remote diagnostics capability via modem; and automatic inertia compensation. In addition, all **ATS RheoSystems/REOLOGICA Instruments** rheometers are designed on a modular platform, allowing easy upgradeability. A wide range of accessories are available to satisfy the most demanding applications with ease of operation.

Temperature is one of the critical controlling parameters for processing and characterizing crude oil materials.

The HPC is hermetically sealed and designed for rheological measurements under conditions of high pressure and/or temperature. The upper limit for the HPC is 5800 psig and 300 °C. The upper temperature may be limited below 300 °C depending on the sample's vapor pressure at the desired test temperature. The HPC incorporates several unique design features, including sample injection and removal ports, pressurization and release ports, an adjustable pressure relief valve, and variable concentric cylinder measuring systems. The HPC is constructed of corrosion resistant metals and is equally suited for both steady shear and dynamic oscillatory experiments. It can easily be mounted on any **ATS RheoSystems/REOLOGICA Instruments** research rheometer.

Temperature control and profiling

Temperature is one of the critical controlling parameters for processing and characterizing crude oil materials. Studying crude oil requires precise control of sample temperature and/or sample temperature profiling. Research rheometers utilize various temperature control systems in order to achieve the desired stability, range, and transient rates. **ATS RheoSystems/REOLOGICA Instruments** developed the use of resistive heating for the HPC and the Joule-Thomson effect principle for the Couette (Concentric Cylinder Elevated [CCE]) and Parallel Plate Extended Temperature Cells (ETC). These methods were selected over other typical designs such as thermoelectric (Peltier) and forced-air convection furnaces used on other commercial rheometers for several important reasons: 1) wide continuous temperature range, 2) high transient rates, 3) cooling without the use of LN_2, 4) small bench space, and 5) minimal temperature gradients in the sample.

Figure 5 shows typical open-loop heating and cooling profiles for the HPC. The maximum system transient rate is better than 20 °C/min for heating and 10 °C/min for cooling. Normally, when studying crude materials, transient rates in excess of 5 °C/min are not employed due to sample thermal inertia. However, fast transient rates are useful to precondition the sample and for faster test setup and cleanup. For crude oil studies, precise, slow cooling profiles are required. *Figure 6* shows controlled cool-

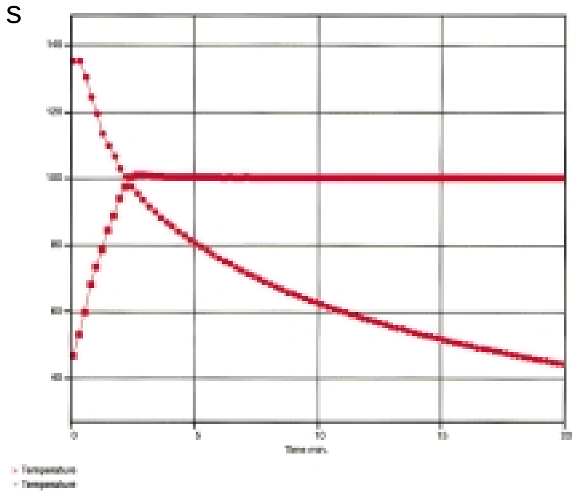

Figure 5 *Transient temperature profile HPC.*

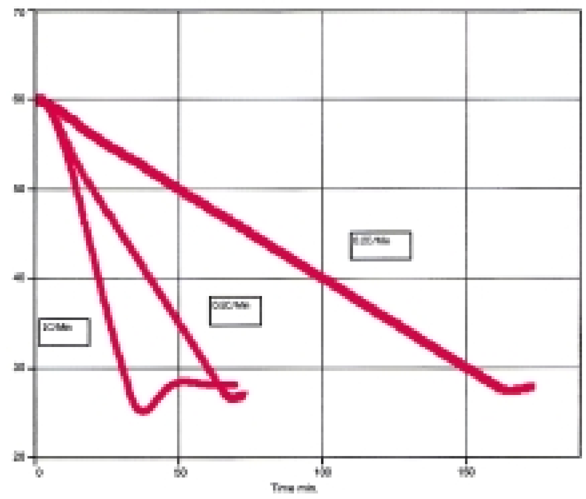

Figure 6 *Controlled cooling profile HPC.*

ing performance of the HPC system in the temperature range 60–25 °C. The control loops are critically damped, producing minimum overshoot while maintaining stability of ±0.1°C.

Crude wax-oil gels

The STRESSTECH HR rheometer, equipped with the HPC, was used to study the effect of the cooling rates on the crystallization of crude oil. The HPC was designed to measure the rheological properties of materials such as crude oil and polymer solutions under high pressure, up to 5800 psig. The novel resistively heated measuring system, used in conjunction with the STRESSTECH HR rheometer, allows measurements under pressure with full steady shear viscometric and moderate frequency dynamic oscillation capabilities.

Initially, steady shear rate and dynamic frequency sweep experiments were performed on a 1.0 Pa/sec silicone oil at 25 °C with 0 psig and 300 psig pressure to demonstrate the performance of the HPC. The results plotted in *Figures 7* and *8* show the expected pressure dependence on viscosity of approx. 10% per 1000 psig due to the normal pressure density relationship.

To characterize and understand a crude oil at processing conditions, it must be studied under pressure. This is accomplished by injecting the sample into the HPC while maintaining a controlled pressure. First, the HPC and the sample chamber are pressurized to the same level with nitrogen gas. Then the sample is injected into the HPC at overpressure, allowing the oil sample to occupy the displaced pressurized nitrogen.

Dynamic oscillatory temperature sweeps were performed at cooling rates of 1.0, 0.5, and 0.2 °C/min from 60 to 25 °C. All samples were heated to 60 °C before being injected into the HPC for analysis. The

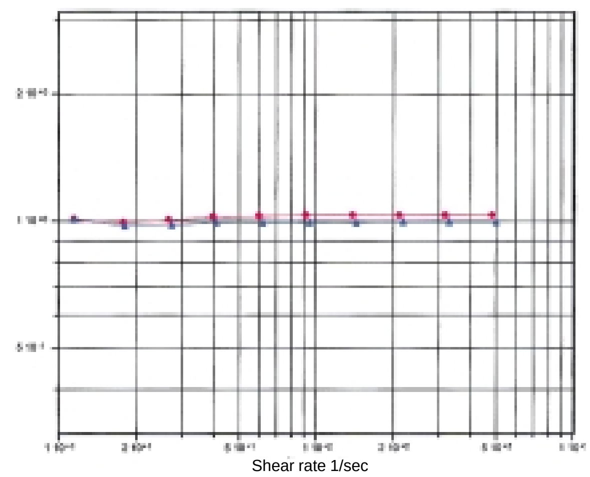

Figure 7 *Flow curve viscosity versus shear rate oil, ambient (red circles), and 300 psi pressure (blue triangles).*

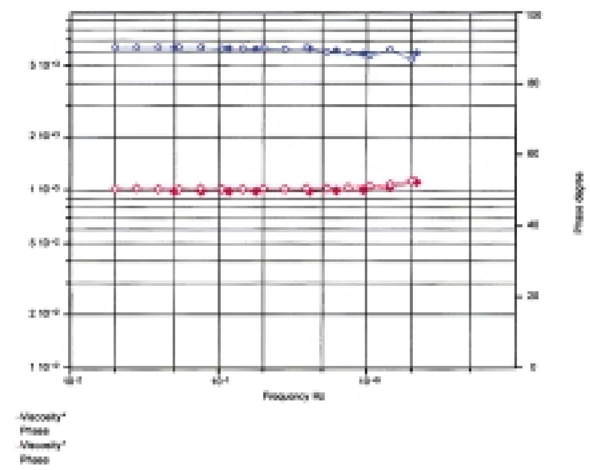

Figure 8 *Frequency sweep complex viscosity versus frequency ambient and 300 psi pressure.*

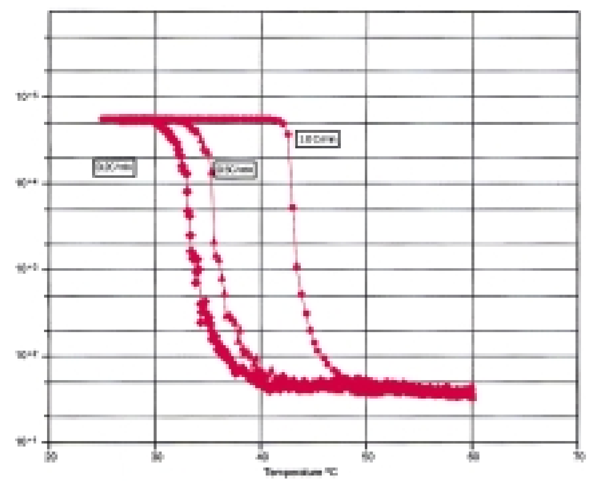

Figure 9 *Oscillation temperature sweep complex viscosity versus temperature at three different heating rates: diamonds, 0.2 °C/min; triangles, 0.5 °C/min; circles, 1.0 °C/min.*

nitrogen head pressure was maintained at 300 psig for all experiments. Samples were loaded at 60 °C and conditioned for 60 sec using a shear rate of 50 sec^{-1}. The samples were then held idle for a 60-sec equilibrium time prior to data collection. A controlled frequency of 1 rad/sec and stress of 20 Pa were used to conduct the oscillatory measurements.

The results plotted in *Figure 9* indicate that the crystallization temperature of a crude oil is a strong function of cooling rate. The viscosity data show that the slower the cooling rate, the lower the crystallization temperature, marked by a sharp increase in viscosity. This decrease in the so-called "crack point" is due to the formation of smaller, more uniform crystals at the slower cooling rate. These results agree well with the previous published work of

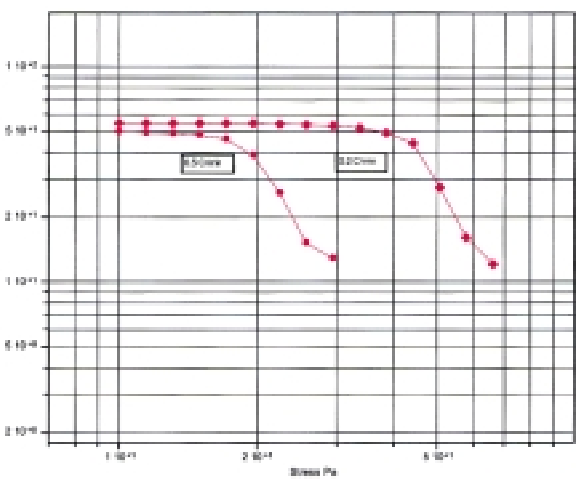

Figure 10 *Oscillation temperature sweep complex modulus versus temperature at two different heating rates: diamonds, 0.2 °C/min; triangles, 0.5 °C/min.*

Figure 11 *VISCOTECH rheometer.*

Singh et al.[1] Below the crystallization temperature, all three cooling rate data sets approach similar viscosity values of approx. 55,000 mPa/sec.

In order to confirm that the forcing function used for the dynamic cooling experiments noted above was appropriate and did not affect the crystal formation process, the authors performed a dynamic oscillatory stress sweep experiment on the controlled cooled samples to determine the linear viscoelastic region (LVE). The LVE is analogous to the linear portion of a stress/strain curve and represents the region of deformation where the sample's rheological properties are a function of time and temperature only. For the rheological determination of structured systems, it is imperative to make measurements under conditions where the rheology is not affected by the stress magnitude. The LVE was determined by measuring the shear modulus (G*, Pa) as a function of the stress at a frequency of 1 rad/sec after cooling for 60–28 °C at 0.5 and 0.2 °C/min. The results are shown in *Figure 10* as a function of stress (Pa). The results indicate that the cooling rate has a pronounced effect on the magnitude of the LVE: Slower cooling results in a wax crystal/oil structure that is more robust and, in addition, slightly stiffer. The large drop in modulus at stresses of 17 and 40 Pa for 0.5 and 0.2 °C/min, respectively, is the result of the breakdown in the wax crystal network. On breakdown, entrained oil is released, decreasing the effective volume fraction and reducing the internal friction controlling flow.

System setup

DYNALYSER and STRESSTECH HR are designed for testing any rheologically significant material. The modular research rheometers feature a wide range of measuring systems and accessories. Measuring systems are available as concentric cylinders, cone/plate, parallel plate, double concentric cylinders, sealed/pressure cells, and dynamic mechanical analysis (DMA) of rods, bars, fibers, and films. Special measuring systems for low volume, high shear rates, and high sensitivity are also available. The measuring systems can be made in stainless steel, titanium, polycarbonate, or any user-defined material. The instruments come standard with the patented Differential Pressure Quantitative Normal Force Sensor (**REOLOGICA**) for reproducible sample loading history, thermal expansion measurements, and quantitative normal stress measurements. The diffusion air bearing has a low inertia with high axial and radial mechanical stiffness.

A reliable, high-performance, research-level rheometer and a thorough understanding of rheological measurements are now a requisite for success in today's marketplace.

The rheometers operate with a separate power supply unit that should be left on continuously. This reduces start-up time and makes it possible for the instrument processor to maintain values for gap and other user-defined settings.

Universal temperature control cells are available using circulating fluid, Joule-Thomson effect, and cryogenics covering the range –180 to 500 °C. All measuring systems are supported, i.e., cone/plate/parallel plate, concentric cylinder, and solids in torsion and tension. A patented Sealed Cell for viscoelastic measurements above the sample's boiling point and several high-pressure cells with an upper range of 5800 psig are also available.

Rheometer electronic unit

The rheometer's electronic components are contained within the mechanical unit, and the instrument is built around a dedicated, high-speed 32-bit CPU. This consolidation enhances performance and versatility due to electrical connections on the motherboard bus rather than through cables to a separate electronics cabinet. In addition, valuable bench space is kept to a minimum. The AC asynchronous motor drive system's control is based on digital rather than analog technology. The unit comes with a built-in diagnostic system and quick diagnostic service port for service engineers. Also included is a modem port for remote control operation and fault diagnostics for service. The electronics power supply is designed to operate on a line voltage of 180–260 V or 90–140 V and an operating frequency of 47–63 Hz.

Software

The RheoExplorer 5.0 software package is based on the Windows operating platform and runs under Windows 2000 or XP. The standard software package is a true multitasking interface with selectable user levels, thus providing many advantages to the researcher. It is designed to provide flexibility for configuring and using the **ATS RheoSystems/REOLOGICA Instruments** rheology system. The computer is not dedicated simply to running the instrument and is available for other use when making measurements. The computer can be used for printing previous results, writing a report, or performing measurements with another instrument.

The software enables a normal PC to be used as the interface to allow the user to control the instrument, and then collect and analyze the resulting data. Viscometry, oscillation under stress or strain control, stress relaxation, creep and recovery, constant rate, yield stress, fast oscillation, process control and project (multiexperiment linking), time/temperature superposition, and spectrum visualization and transformation packages are available, allowing the sample to be analyzed via different rheological procedures. Powerful data analysis capability allows model fitting, graph and table customization, and cut/paste operation to all other Windows-based software.

RheoExplorer 5.0 includes the capability of linking user-designed methods including instrument setup and zero gapping using Project software. The dialog windows have many storable, editable functions for unique testing requirements, and can be reset using default buttons. An example is the oscillation frequency step measuring program, where stresses, delay times, integration periods, and sample sizes may be set individually for all frequencies. Another example is the zooming function that is present in both the viscometry stress step and the oscillation frequency step, allowing any number of steps and increments to be selected. The instrument comes with automatic gap adjustments and thermal expansion compensation using the patented Differential Pressure Normal Force Sensor. The system enhances measurement reproducibility since the sample loading history is reproduced identically each time.

Rheometers for any user level, application, and budget

VISCOANALYSER is an expandable, research-level rheometer system specifically designed with a clear upgrade path to a STRESSTECH HR unit as the user's needs and requirements dictate. VISCOTECH, an entry-level rheometer, provides research-level rheometer performance on a QC rheometer budget (*Figure 11*).

All **REOLOGICA Instruments** rheometers are produced according to ISO 9001 and are tested to operate according to the electromagnetic compatibility rules within the European Community. The instruments are certified with the CE mark.

Conclusion

This article reviews the important rheological characteristics of a waxy crude oil and presents results generated at several different cooling rates using the STRESSTECH HR rheometer and HPC. In addition, a detailed interpretation of data and correlation of the rheological response with the physical/chemical properties of waxy crystalline buildup due to thermal history is given. The rheological characterization of waxy crude oil under controlled pressure and temperature provides important information for engineers and scientists to improve and optimize their products and manufacturing processes. Today, most researchers and manufacturers count on rheological measurements to develop customer-driven products with a competitive edge in the marketplace. A reliable, high-performance, research-level rheometer and a thorough understanding of rheological measurements are now a requisite for success in today's marketplace.

Reference

1. Singh P, Fogler HS, Nagarajan N. J Rheol 1999; 43:6.

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