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Wax Precipitation: Compositional Study and Cloud Point Measurements

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Summary

A novel cold-finger approach has been used to fundamentally understand wax precipitation from oils of different compositions. The experimental set-up and procedure allows measurement of the amount of precipitate as both the cold-finger and bulk-oil temperatures are varied. As either temperature is decreased while the other is held constant, the amount of precipitated wax increases. The study also compares results from viscosity versus temperature measurements to demonstrate that shear rate versus shear stress data with variable temperatures provide novel insight to the phenomena of wax precipitation.

The composition of parent oils and precipitated waxes are determined by high temperature gas chromatography and mass spectrometry (HTGC and HTGC-MS). The composition of the precipitated material is shown to shift to lower carbon numbers as either the cold-finger or bulk oil temperature is decreased. Even if the parent oil has a preponderance of iso-alkanes, it is observed that the wax precipitate will predominantly consist of *n*-alkanes, but will also include a second envelope of compounds at higher molecular weight. It is clearly established that the amount of precipitate depends on the overall oil composition and that it is not correct to perform "wax" material balances on different oil fractions.

Introduction

The deposition of wax within the reservoir, surface tubulars, flowlines, and pipelines hamper petroleum operations in many regions, although it is most troublesome in offshore production/transport facilities. This is attributed to non-isothermal conditions which lead to wax deposition on the cooler surface. The result is increased operation cost due to the need for wax removal by heat, chemical, and/or mechanical methods. Fundamental questions arise as to which crude oil (or condensate) is subject to wax deposition, particularly under specific conditions of temperature and/or pressure. It is equally relevant to possess knowledge of the susceptibility of the deposit to remediation procedures.

The traditional methodology for predicting wax deposition is the cloud point, but this technique has proven to be ineffective for most crude oils due to their opacity. Alternative techniques have proven to be highly variable, subjective, and/or method dependent[1]. This is particularly relevant to crude oils that are not intuitively prone to wax deposition and/or mixtures that may be encountered in a pipeline.

As the principal concern is with the deposition of wax, a direct test of the phenomena is most appropriate; hence, a wax appearance temperature (WAT) with a cold-finger apparatus is advocated. A distinct advantage of the technique include variation of the cold-finger versus bulk oil temperature that are tested in various *what if* scenarios of reservoir and/or transport conditions. Incipient wax deposition is identified by the appearance of a "blush" on the cooled surface. The technique has additional advantages of being independent of oil opacity, allowing recognition of extremely small wax volumes, and the ability to quantify rates of

deposition. The analysis by HTGC and HTGC-MS allow these deposits to be defined on a molecular level.[2,3]

Methodology

The laboratory simulation of the precipitation event is based on a cold-finger technique (Figure 1) which involves a glass loop through which the temperature of the circulated water can be varied along with independent control of the oil phase. The magnetic stirrer provides circulation of the oil phase, a condition necessary to bring the dissolved wax in contact with the cold-finger. The current system does not restrict the evaporative loss of the low molecular weight fraction or allow for pressurized experiments.

Gas chromatography is commonly used to separate individual components in a complex mixture. The technique relies on the ability of the individual components to be separated by differential partitioning between two phases: a stationary liquid phase and a mobile gas phase. The abundance of each component is recorded with a detector and presented as a function of time. Conventional analysis by gas chromatography (Figure 2a) provides data to the range of carbon number 40, whereas high temperature methods (Figure 2b) provide data to at least carbon number 90 (if present). GC-quantification is accomplished with a perdeuterated triacontane internal standard at a concentration of 2500 ppm. The instruments used in this study are based on the Hewlett Packard 6890 series; additional details of the methodology are available.[2,3]

Viscosity of the oil is measured using a Brookfield digital cone and plate viscometer equipped with temperature control and computer-controlled real-time data acquisition. Measurements are conducted over a wide temperature range at various shear rates and shear stresses. The data is stored for post-acquisition processing.

Results and Discussion

This study provides fundamental knowledge for understanding the process of wax precipitation. As the cold-finger approach allows variation of two critical parameters, oil versus surface temperature, persistent questions related to wax precipitation can be addressed in quantitative predictive terms. Figure 3 presents the results of experiments where the oil temperature is held constant (65°, 70°, and 75°C experimental series) and the cold-finger varied between 0° and 70°C at 10°C increments. Each data point represents an independent experiment with a duration of 30 seconds; this time interval was selected to reduce complications of the insulatory effects of wax layers on the cold-finger surface. The results demonstrate that as either temperature is decreased, while holding the other constant, the amount of precipitated wax increases. The changes in slope within each temperature series may provide support for the suggestion that each crude oil has multiple cloud points.[1]

The viscosity measurements versus temperature traditionally provide indirect estimates of cloud points (Figure 4a). A clear transition in the slope of the curve is observed between 125° and 130°F (51.67° and 54.44°C), which is interpreted to represent the cloud point of this oil. However, there is always uncertainty about the correct shear rate to use in these types of viscosity measurements. The cloud point transition can also be observed by examining viscosity as a function of shear stress. The oil shows absolutely no shear thinning behavior at temperatures of 130°F (54.44°C) and above. The shear rates, shear stresses, and viscosities at three different temperatures are shown in Table 1. The shear thinning behavior

becomes more prominent at lower temperatures. Thus, the onset of shear thinning would be another possible test for cloud point.

Detailed analysis of the shear stress versus shear rate data is used by rheologists to identify transition phenomena. The shear stress versus shear rate data at all temperatures is summarized in Figure 4b. The temperature range in the plot is from 105° to 170°F (76.67° to 40.55°C). The lines are relatively parallel with unit slopes which indicate, for the most part, Newtonian behavior. A shift factor (a_T) is then calculated that would shift all of the straight lines to a reference temperature. The shift factor has been interpreted as the ratio of the molecular relaxation time at the given temperature to the relaxation time at the reference temperature.[4] The shift factor, in turn is believed to have an Arrhenius form:

$$a_T = Ae^{E/RT}$$

where A is a constant pre-exponential factor and E is is the activation energy. If this form is correct, $log(a_T)$ versus (1/T) should yield a straight line relationship; deviation from the linear relationship is expected to coincide with the cloud point. The semi-log plot of the shift factor (calculated with 150°F as the reference temperature) versus the reciprocal of absolute temperature (in Kelvin) indicates that the deviation starts at 1/T value of 0.00308 (Figure 4c), which corresponds to a temperature of 324.66°K (125°F or 51.67°C). Thus, this demonstrates a fundamental shift in the rheology of the oil at the apparent cloud point temperature, establishing a precedence for a novel cloud point measurement.

Knowledge of conditions that lead to wax precipitation in quantitative and predictive terms is important, but this study also addresses the composition of the precipitated material. HTGC analysis indicates that the composition of the precipitated waxes shift to lower carbon numbers as either the cold-finger or bulk oil temperature is decreased (Figure 5). Other indicators of the wax precipitation event includes an increase in the width of the wax envelope with greater temperature fluctuation during precipitation, the significant volume of occluded crude oil within the wax with rapid (catastrophic) deposition, and bimodal wax envelopes to represent multiple crystallization events (transported after crystallization versus on the cooled surface). These experiments also demonstrate that even if the parent oil has a preponderance of iso-alkanes, the wax precipitate will predominantly consist of *n*-alkanes (Figure 6), but will also include a second envelope of compounds at higher molecular weight. The fractionations observed between the original oil and the precipitated wax are documented to be consistent in both the laboratory simulations and field data (Figure 7). As a result, it is clearly established that the novel approaches reported here provide fundamental knowledge for understanding the process of wax precipitation.

References

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Table 1: Viscosity, shear rate and shear stress data at three different temperatures (raw data)

Temperature 130^0 F			Temperature 120^{0}F			Temperature 115^{0}F		
Viscosity (cp)	Shear Rate (1/sec)	Shear Stress (dynes/cm^2)	Viscosity (cp)	Shear Rate (1/sec)	Shear Stress (dynes/cm^2)	Viscosity (cp)	Shear Rate (1/sec)	Shear Stress (dynes/cm^2)
23.2	34.8	150	29.6	44.4	150	34	25.5	75
23.5	35.3	150	29.6	44.4	150	34	25.5	75
23.7	53.2	225	29.6	44.4	150	34.3	25.8	75
24	54	225	29.6	44.4	150	34	25.5	75
23.4	87.8	375	29.6	44.4	150	34	25.5	75
23.7	88.8	375	23.7	88.8	375	33.5	50.3	150
23.5	105.7	450	28.6	107.2	375	33.5	50.3	150
23.7	106.4	450	28.6	107.2	375	33.8	50.8	150
23.3	174.9	750	28.7	107.7	375	33.7	50.5	150
23.5	176.3	750	28.6	107.4	375	34	51	150
			28.6	107.4	375	32.6	122.4	375
			28.4	212.9	750	32.6	122.1	375
			28.4	212.9	750	32.6	122.4	375
			28.4	212.9	750	32.8	122.9	375
			28.4	213.1	750	32.8	122.9	375
						32.2	241.6	750
						32.2	241.6	750
						32.1	240.8	750
						32.5	243.5	750
						32.5	243.8	750

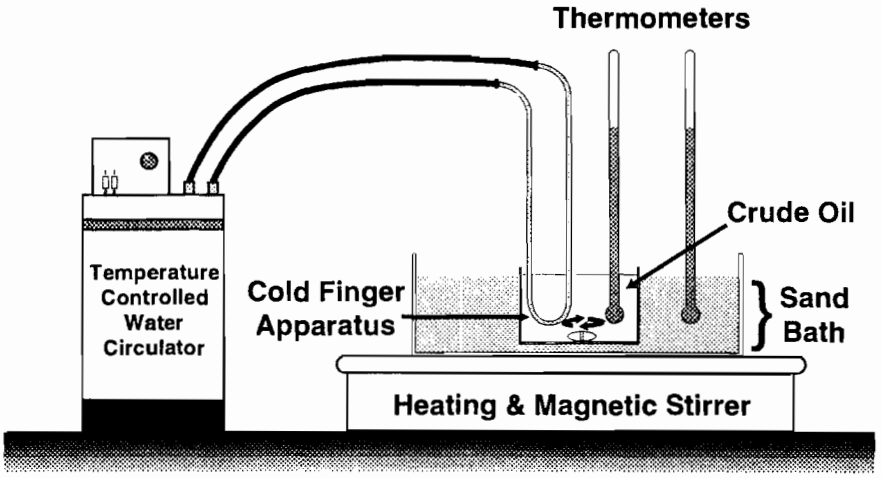

Figure 1. Schematic representation of the cold-finger apparatus

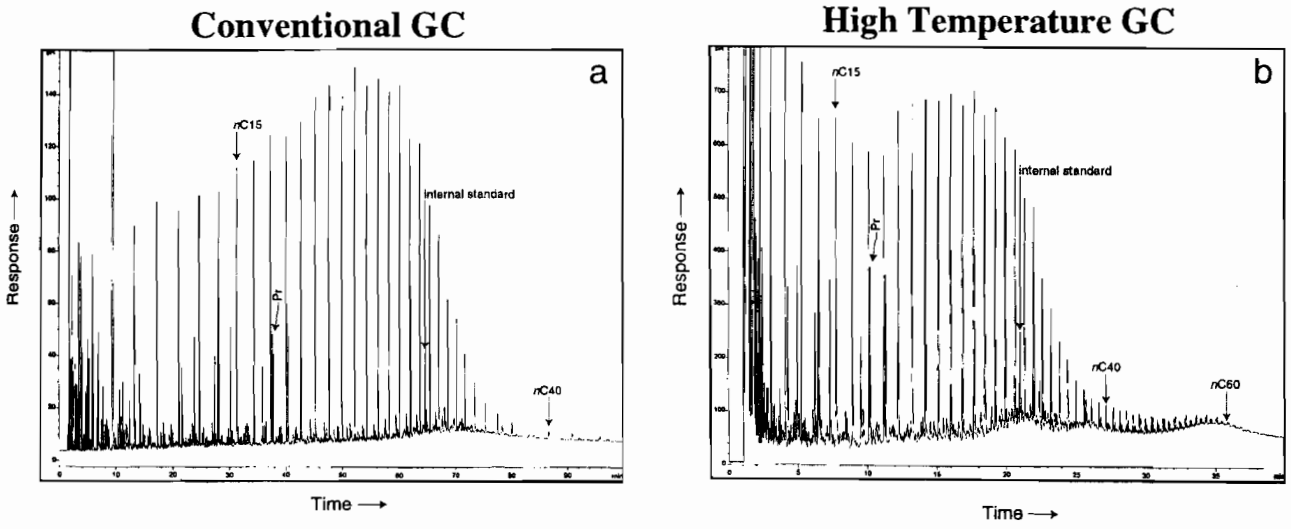

Figure 2. Conventional GC (a) and HTGC (b) analysis of the "black wax" sample from Uinta basin (Utah, USA) with key peaks indicated. Internal standard is perdeuterated triacontane at 2500 ppm

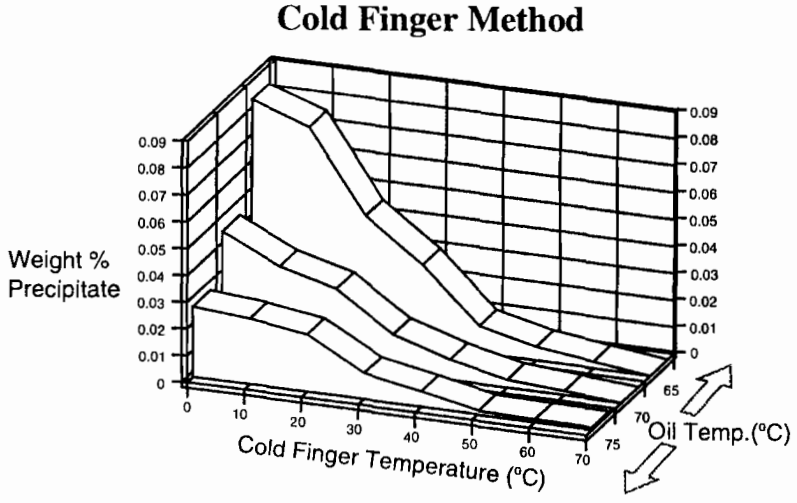

Figure 3. Results from cold-finger experiments on "black wax" samples

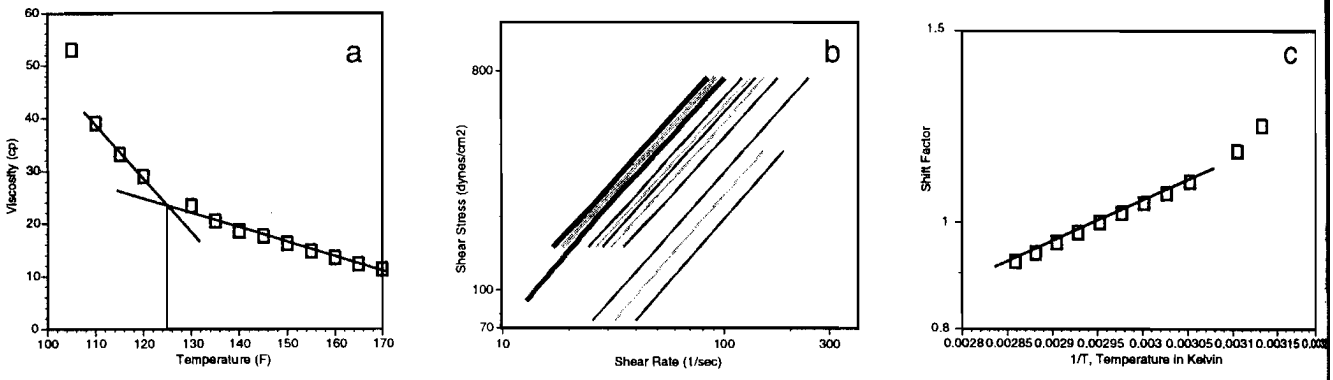

Figure 4. Representation of the rheology data collected for the "black wax" sample in terms of viscosity versus temperature (a), shear stress versus shear rate (b), and shift factor versus the reciprocal of absolute temperature (c).

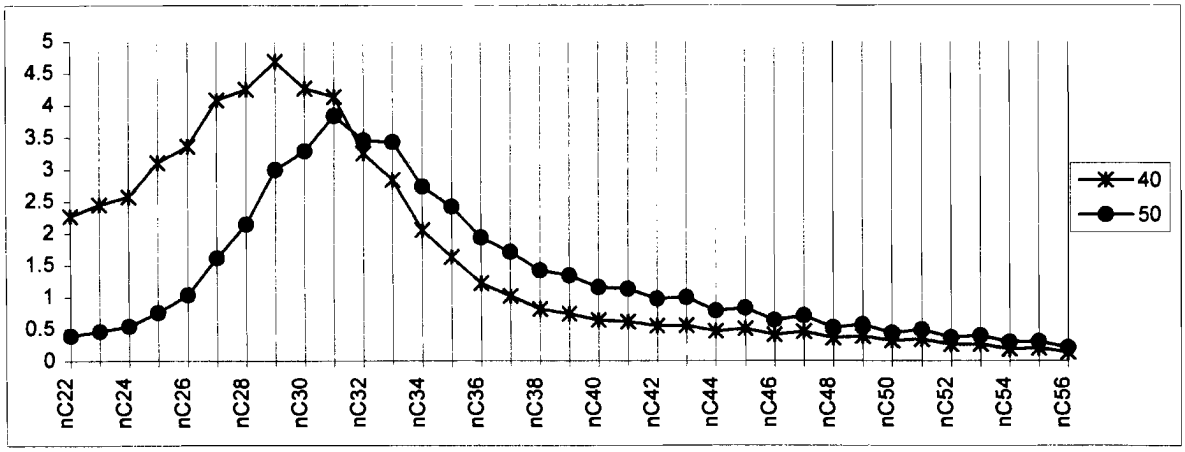

Figure 5. Effect of cold-finger temperature on deposition from "black wax" sample. Note the shift to lower carbon number and increased rate at lower cold-finger temperatures (experimental constants of 30 second duration and 75°C bulk oil temperature).

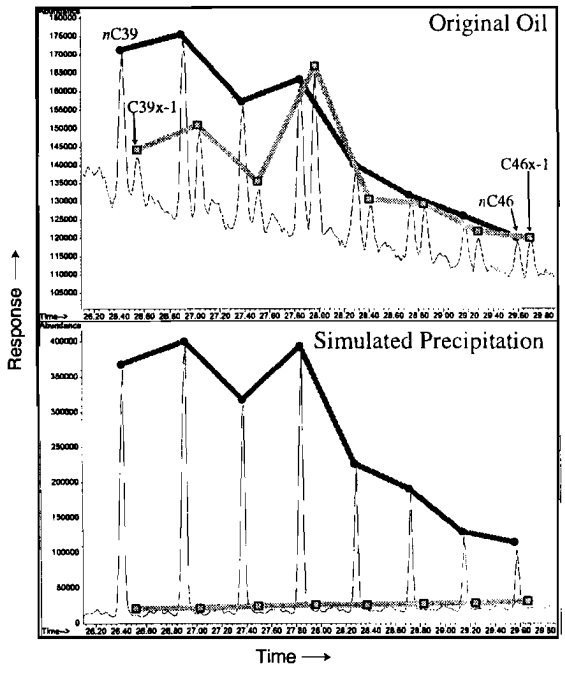

Figure 6. Molecular fractionation is documented between the original oil and the precipitated products in the laboratory, an observation that is confirmed with field studies. HTGC-MS data presented from experiment with Neuquen basin (Argentina) oil.

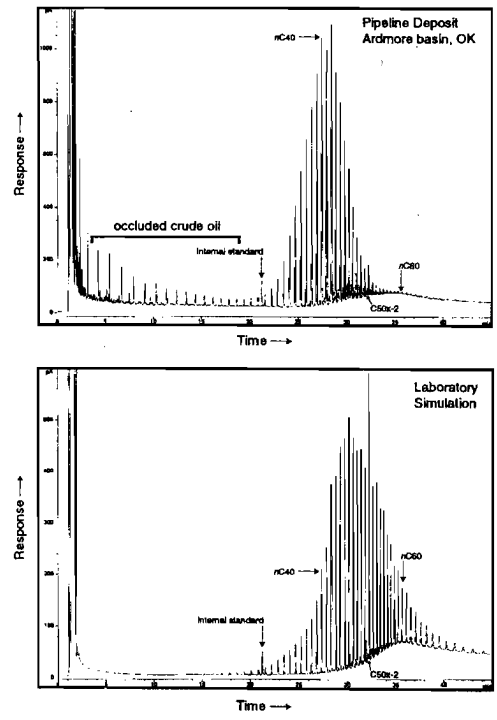

Figure 7. Comparison of HTGC analysis of pipeline deposit (a) versus the laboratory simulation (b) using same oil as flows in Ardmoree basin (Oklahoma, USA) pipeline. Note the second envelope of compounds designated "Cnx-2" at higher molecular weight.