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The influence of the heating temperature on the yield stress and pour point of waxy crude oils

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ABSTRACT

The yield stress and pour point are two important parameters related to flow assurance problems in waxy crude oil pipelines. The yield stresses at temperatures below the pour points of five waxy crude oils after heating to different temperatures have been investigated in the present paper. Both the experimental results in this work and data from the literature show that the yield stress values increase exponentially with the decreasing measurement temperature. The experimental results show that the heating temperature has an obvious influence on the yield stress and the pour point. However, it was noted that the yield stress values at the gel point temperature, defined as the highest temperature at which the movement of the sample cannot be observed during the quiescent pour point testing process, are approximately the same for a waxy crude oil after heating to different temperatures. An exponential relationship exists between the yield stress and the difference between the measurement temperature and gel point that is independent of the heating temperature. To explore this phenomenon, the relative magnitudes of the gravitational stress and the structural strength of the wax crystal network during the gel point test has been analyzed, and it was found that the yield stress value at the gel point has a favorable linear relationship with the oil density.

1. Introduction

With the increasing demand for petroleum and the declining resources of conventional oil, the production of non-conventional oils, such as waxy crudes and heavy crudes, is increasing. The flow properties of waxy crude are crucial to its production and transportation (Djemiat et al., 2015). The rheological behaviors of waxy crude oils below the wax appearance temperature (WAT) are complex due to the formation of a wax crystal structure (Chang et al., 2000; Li and Zhang, 2003; Livescu, 2012; Rønningsen, 1992; Rønningsen et al., 1991; Wardhaugh and Boger, 1991; Zhang and Liu, 2008). The pour point and yield stress are two important flow properties related to flow assurance problems in waxy crude oil pipelines. The pour point is widely used as the industrial standard to define the gel temperature of crude oils, and it is defined as "the lowest temperature at which movement of the test specimen is observed under the conditions of the test" (ASTM D5853-11, 2011). The yield stress represents the gel strength of the waxy crude oil, and it is a better measure of pumpability than the pour point (Davenport and Somper, 1971; Uhde and Kopp, 1971; Verschuur et al., 1971). To restart a horizontal pipeline of a gelled crude oil, the required pump pressure may be approximately estimated through the yield stress of the oil, the pipe length and the pipe diameter (Davenport and Somper, 1971; Uhde and Kopp, 1971), although it gives a rather conservative result. Due to the combined effects of the thixotropy and compressibility of the gelled crude oil, the flow can actually restart at a pressure below the estimated value (Wachs et al., 2009).

The yield stress of a waxy crude oil is not only dependent on the oil composition, such as wax content, wax type, and the amounts of asphaltenes and resins, but it is also influenced by the thermal and shear history (Paso, 2014; Paso et al., 2009), as well as the measurement conditions. Venkatesan et al. (2005) tested the yield stress values of model waxy oils with various wax contents, and they found a power law dependency on the overall wax content in the oil, with an exponent of 2.3. Oh and Deo (2009) reported that "the extent of increase in yield stress values with temperature was greater for model oils that had a higher percentage of wax", and "the amount of asphaltenes played a major

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part in lowering yield stress". They observed that the yield stress values were reduced with asphaltene addition. This conclusion was in accordance with the observation of Venkatesan et al. (2003), and such a trend was also reported by Zhao et al. (2012) using model waxy-oil systems. Bai and Zhang (2013) studied the effect of the carbon number distribution of the wax on the yield stress of waxy oil gels, and their results showed that "the yield stresses dramatically decrease with increase of average carbon number of wax regardless of the quiescent or shear conditions, and the changing rate of yield stress with respect to the solid wax content is smaller for the gel with higher average carbon number of wax".

The impact of the thermal history on the yield stress of waxy crude oils has been investigated by some scholars. Chang et al. (2000) and Ghannam et al. (2012) used waxy crude oils and heavy crude oil, respectively, to investigate the influence of the test temperature, cooling rate and isothermal holding time before the yield stress measurement. The authors concluded that the test temperature is the most important factor influencing the rheological properties of waxy crude oils. Their experiments showed that the slower the cooling rate, the larger the wax crystals and their consequent agglomeration and the higher their yield stress. The isothermal holding time before testing was found to have less influence than the temperature or cooling rate. The observation of Chang et al. of higher yield stresses at slower cooling rates was in agreement with Rønningsen's (1992) results obtained on a model pipeline and controlled stress rheometer for different samples of waxy North Sea crudes as well as those of Visintin et al. (2005) from oscillatory tests in a controlled stress rheometer. Venkatesan et al. (2005) investigated the yield stress values at different cooling rates under both static and shear conditions. Their experimental results showed that the yield stress increased with the decreasing cooling rate under static conditions, but it decreased with a decreasing cooling rate under high shear stress. Russell and Chapman (1971) and Cawkwell and Charles (1989) also reported that the yield stress decreased with a decreasing cooling rate.

In addition to the measurement temperature and cooling rate, the heating temperature is another crucial thermal factor affecting the flow behavior of waxy crude oils below the WAT (Li and Zhang, 2014; Rønningsen et al., 1991; Zhang and Liu, 2008). Due to their high pour point, waxy crude oils are often heated for transport, and the heating temperature usually varies with the ambient temperature and the flow rate. Therefore, the influence of the heating temperature on the flow properties should be taken into consideration for the flow assurance of waxy crude oil pipelines. Up to now, there has been no comprehensive study on the influence of heating temperature on the yield stress of waxy crude oils. In this work, experiments were conducted to investigate the influence of the heating temperature on the yield stress value and pour point. The experimental results show that the heating temperature has obvious effects on the yield stress and pour point of waxy crude oils. However, it was observed that the yield stress value at the gel point, which is defined as the highest temperature at which the movement of the specimen cannot be observed under the conditions of test, is approximately the same when a waxy crude oil is heated to different temperatures. By analyzing the relative magnitude of the gravitational stress and the structural strength of the wax crystal network during the gel point test process, it was found that the yield stress value at the gel point has a favorable linear relationship with the oil density. These results provide some useful information for the shutdown and restart operations of heated waxy crude oil pipelines.

2. Experiment

2.1. Crude oil samples and pretreatment

Five typical waxy crude oils produced from five different oil fields in China were used to investigate the influence of temperature on the flow behavior of waxy crude oils in this work.

The oils taken from pipeline pump stations were stored in 5-L plastic containers. All containers were heated while sealed to 50 °C and shaken thoroughly before the oil was transferred to sealed gas-tight 100-mL blue cap pretreatment bottles.

To erase the memory effect of the thermal and shear history that the samples experienced and to obtain better reliability and repeatability, pretreatment was performed before the measurements. The oil samples were heated to 80 °C for 2 h and then left to cool quiescently to room temperature (approximately 25 °C) and maintained for 48 h before use (Yan and Luo, 1987). The pretreated oil samples should be used within 60 h after the pretreatment.

Table 1 presents some physical properties of the oil samples. The density of the oil sample was measured according to standard ISO 3675-1998 "Crude Petroleum and Liquid Petroleum Products-Laboratory Determination of Density-Hydrometer Method". The WAT and the wax content were determined by differential scanning calorimetry (DSC) with a Q20 apparatus (TA Instruments, USA). Tests were conducted from 80 °C to −30 °C at a cooling rate of 5 °C/min. The recorded calorimetric signal during the cooling was used to determine the WAT and the wax content. The detailed information of determining the WAT and the wax content from DSC can be found in the literature (Bai and Zhang, 2013; Chen et al., 2004; Li et al., 2003).

2.2. Pour point and gel point

The pour point was determined under protocols set forth in ASTM D5853-11, "Standard Test Method for Pour Point of Crude Oils". The specimen after the pretreatment was heated from ambient temperature to a temperature higher than the sample's WAT (termed heating temperature) and kept at this temperature for 30 min. Then, it was transferred to pour point glass tubes preheated to the same heating temperature and cooled at a rate of 0.5 °C/min. According to the test method, the flowability of the tested sample was checked every 3 °C from 9 °C above the anticipated pour point until a point was reached at which the tested specimen showed no movement when the test tube was held horizontally for 5 s. The pour point is 3 °C above the temperature at which the sample remains stationary.

In this work, the highest temperature at which the movement of the sample cannot be observed when the test tube is held in a horizontal position for 5 s is defined as the gel point.

According to ASTM D5853-11 (2011), the repeatability of the pour point test is 3 °C. To obtain more accurate pour points and gel points, the tests were carried out at least five times under every condition, and the average values were recorded as the results.

Table 1
Some properties of crude oil samples.

Oil sample no.	Density at 15 °C (kg/m^3)	WAT (°C)	Wax content (wt%)
1	872.6	44.6	20.3
2	836.7	17.8	6.3
3	858.5	29.5	7.9
4	855.0	33.3	10.2
5	851.1	27.0	11.6