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Yield stress measurement of gelled waxy crude oil: Gap size requirement

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ABSTRACT

The strength of gelled waxy crude oil is an important parameter required to determine the restart pressure of pipelines filled with the gelled waxy crude oil. Several measurement methods have been proposed in the literature to quantify the yield strength utilizing a rheometer. Minimal discussions, are however, provided on the effects of rheometer geometry gap on the yield stress measurements. This study is intended to propose a systematic protocol to determine the geometry gap settings for better repeatability of the yield stress measurements of gelled waxy crude oils. The reliability of the yield stress data measured has been shown to be highly dependent on the gap selection in the rheometer. The ten-to-one gap ratio has been proven to be inapplicable for the case of gelled waxy crude oils which consists of wax crystal networks entrapping the oil phase. Presence and strong interactions of large wax crystals presents wall effects and subsequently reduces the repeatability of the measurements. The method proposed in this study has been proven to work on a mild waxy crude oil as well as on a more "severe" waxy crude oil. It can be utilized prior to any transient rheological measurements as gap setting is crucial to ensure accurate and reliable measurements.

1. Introduction

Waxy crude oils are aliphatic hydrocarbon having high molecular weight paraffin with carbon number ranging from C_{18} to C_{65} [18]. The paraffin waxes can be classified as either macro-crystalline or micro-crystalline. Macro-crystalline waxes are mainly linear paraffin (n-alkanes) with chain lengths between C_{18}–C_{30}. They have needle-like and plate-like morphology with crystal size up to 100 μm. Their presence within the crude oil promotes strong gel formation. Micro-crystalline waxes on the other hand contain greater percentage of iso-paraffin (branched alkanes) and naphtenes (cyclic alkanes) with carbon number found to be greater than 30. The crystal size is much smaller (up to 10 μm) with spherical morphology. It is amorphous in nature as the crystal growth is hindered by the side and cyclic groups present in the molecules. Misra et al. [13] reported that if the micro-crystalline waxes are present, it will be the main constituent of the sludge at the bottom of crude oil storage tanks.

The solubility of paraffin waxes is dependent on the temperature, it decreases with decreasing temperature. At reservoir conditions where the temperature ranges between 70 and 150 °C with pressure ranges between 50 and 100 MPa, the solubility of the paraffin in the crude oil is adequately high. The wax molecules are fully dissolved in the crude oil mixture resulting in a single-phase crude oil and in the absence of other components and contaminants the crude oil behaves predominantly Newtonian with low viscosity. Once the crude oil leaves the reservoir and flows through cold pipelines placed on the seabed with temperature as low as 5 °C, the crude oil temperature begins to drop dramatically due to the heat loss to the surroundings. The crude oil will then be subjected to phase transformation from liquid state, showing Newtonian behavior, to a gel-like structure exhibiting non-Newtonian characteristics. The three main stages of the phase transformation process are wax precipitation, wax deposition and wax gelation. Wax gelation will be induced when the temperature of the crude oil drops below the pour point temperature of the crude beyond which, the crude oil flow ceases completely.

Wax gelation is not a new phenomenon in the petroleum industry and this issue has already captured the interest as early as in the 1920s [14]. Various classical descriptions of gel have been documented in the literature. Flory [8] regards a gel as a homogeneous system within which the liquid is not distinguishable from the solids suspended in the liquid. The liquid tend to disappear

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and the solid mass is formed, which may display either a fluid-dominant characteristics or a more solid-dominant structure. A gel also exhibits greater elastic to viscous properties [4].

Kané et al. [11] and Singh et al. [17] proposed that the gelation of waxy crude oil involves three stages; formation of lamellar sub-crystals which grows in two dimensions as sheet like crystals, aggregation of sub-crystals to form a large space filling network and finally overlapping and interlocking of the aggregation due to strong interactions and attractions between wax crystals. Subsequently, a 3-D volume spanning network of crystals that traps liquid oils and exhibits both the elastic properties and the viscous properties is formed. The amount of trapped oil, or "wax porosity" within the wax crystals network would influence the strength of the waxy crude gels. For "soft" wax a porosity of up to 90% has been reported while for "hard" wax, the porosity is within the range of 50–70%. Ageing, internal diffusion and large temperature differential within the pipeline, amongst others, could result in "harder" wax and subsequently higher gel strength [5].

The wax gelation has great impact especially during production shutdowns where the crude oil temperature drops below the pour point temperature allowing the formation of a "candle"-like structure or solid wax column. This phenomenon can completely block the pipeline and during restart operation, a large pressure may then be required to initiate the crude oil flow again. In order to determine the breakdown pressure required to restart the flow, it is important to estimate the gel strength, measured in terms of the yield stress. The yield strength of waxy crude oil gel has been characterized by many within the literature [1,6,7,16,15,9,19,10], amongst others. As documented, the yield stress can be measured via various experimental protocols; the creep-recovery test, the oscillatory test, the stress ramp test and many more. Several geometries can be utilized to determine the yield stress of gelled crude oil; the cone and plate, the parallel plate and the vane geometry, with the surface of these geometries is maintained smooth, sandblasted or cross hatched. Throughout the study on the yield stress of waxy crude oil documented within the literature, least discussions have been extended on the effects of the geometry gap to the measurements. The rheometer gap size is critical to minimize wall effects and at the same time allowing freedom for the sample to move under shearing action and subsequently behave as a continuum. As highlighted by Marchesini et al. [12], equilibrium flow properties of gelled waxy oils are less influenced by experimental conditions. However, transient measurements including oscillatory measurements are highly dependent on the gap selection in the rheometer which is supported by the work of Wardhaugh and Boger [20].

Barnes [2] proposed a rule of thumb to decide for a geometry gap where a minimum ratio of gap to particle size of 10:1 is recommended. For large particle systems, the requirement is often impossible to be met in small angle cone and plate geometry as it is limited by the truncation height or the gap of the cone and plate. Later in 2000, Barnes discovered that the "ten-to-one" ratio is only applicable for samples with phase volume of up to 25%. Greater gap size is then required in higher phase volume samples, which, may, at times, be unrealistic for a medium containing large particles such as waxy crude oil gel. Cautious treatment of data collected is then required especially on melts and gels obtained using the cone and plate rheometer. The presence of the wax crystals whose characteristic dimension is of the same order of magnitude of the gap within the cone and plate may then introduce measurement errors.

The works presented in this paper are intended to propose a systematic assessment on gap determination (for 3 waxy crude oils) and to compare between the thermal cycle tests by Marchesini et al. [12] and the proposed strain sweep test method. Morphology of wax crystal was also investigated for further understanding on its effects to the rheological behavior. An image processing technique was performed to quantitatively determine wax fraction and maximum aggregated wax crystal length. The values were utilized to theoretically estimate gap size required from Barnes [2,3] and compared with the results from the thermal cycle test and the proposed strain sweep test methods.

2. Characterizations and measurements

2.1. Working fluid and pre-conditioning process

The crude oils utilized throughout the study are waxy crude oils produced within the South East Asia. The WAT, as measured using CPM, pour point temperature (ASTM 5985-96) and API gravity (ASTM D1250) of the waxy crude oils are tabulated in Table 1. Conditioning of the crude oil upon received from the operator involves heating at ~20 °C above the WAT for 8 h within a large water bath. The crude oil was then poured into smaller containers (~20 mL) to ensure minimal sample variations due to light and heavy components, and allowed to cool at room temperature.

As thermal history or heat treatment to which the crude oil samples are subjected to influences the flow behavior of the sample, it is important to standardize the pre-conditioning treatment to ensure repeatability of the yield stress measurements. Prior to measurements the crude oil in the smaller container was soaked again in a water bath at ~20 °C above the WAT for 2 h to dissolve any wax crystals present ensuring homogeneity and promote a stable composition during testing.

2.2. Equipments

A TA instrument controlled stress rheometer, AR-G2, was utilized for all rheological measurements. The geometry (parallel plate) is either a 20 mm or a 40 mm (depending on the strength of the gel) cross hatched plate with the groove to be greater than 10 μm [2] to minimize wall slip phenomena where complete adhesion is violated. A cross hatched surface is suitable as it possesses sufficient rugosity greater than the crystal size aggregates assuming that the crude oil samples contains mainly of macro-crystalline waxes. Assumptions that no flow occurs between the protrusions and shear occurs between the surfaces consisting of the protruding tips were made. It is the same assumption for vane rheometry measurement. Visual observations were performed to verify any presence of slip on smooth surface geometries. When both smooth upper and lower geometries were utilized, the smooth upper surface was practically clean after what is thought to be an apparent yielding of the sample while the sample remained intact on the smooth lower surface. However, yielded sample using the roughened upper surface showed that the gelled crude failed within the sample indicating no slip on the upper roughened surface as well as on the smooth lower surface. Hence, the authors believed that an upper roughened surface is sufficient to minimize the slip effect. The waveforms produced at the same % strain for different gap settings have also been analyzed. The similar waveforms produced at different gaps settings confirmed minimal slip effects as proposed by Yoshimura and Prud'homme [22]. A solvent trap was used to minimize evaporation of the light end components from the sample for all the rheological measurements and subsequently the stability

Table 1
Properties of waxy crude oil sample.

Properties	Crude A (Se)	Crude B (An)	Crude C (Pe)
WAT (°C)	41.2	41.1	68.2
Pour point	39	33	60
API gravity (at 15 °C)	33.76	36.86	25.15