



OTC 19690

Asphaltene Instability Induced by Light Hydrocarbons

Jefferson L. Creek, SPE, Chevron Energy Technology Company; Jill S. Buckley, SPE, New Mexico Institute of Mining & Technology; Jianxin Wang, SPE, Chevron Energy Technology Company

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This paper was prepared for presentation at the 2008 Offshore Technology Conference held in Houston, Texas, U.S.A., 5–8 May 2008.

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Abstract

Anticipating when and where asphaltenes may flocculate during oil production is a key step in successfully preventing or mitigating asphaltene problems in the field. Since there will be no deposition without precipitation, mapping of asphaltene stability over a wide range of temperature, pressure, and composition is required. The Asphaltene Instability Trend (ASIST) allows the determination of the onset of asphaltene instability to be established with a series of liquid n-alkanes. These data are used to predict asphaltene stability of live fluids by extrapolating the onset condition from the base data to reservoir conditions using a linear extrapolation of the onset solubility parameter versus square root of the partial molar volume of the precipitant. This extrapolation has previously been demonstrated to be accurate for methane and a model oil. The present work verifies that such an extrapolation is valid for predicting the asphaltene instability for mixtures of methane, ethane, and propane with a representative stock tank oil. The stock tank oil was combined with known amounts of methane, ethane, or propane. The asphaltene onset pressure was determined by a combination of Near-IR light scattering and microscopic observation. The onset conditions at ambient pressures were examined for flocculation periods ranging from 20 minutes to 24 hours. Onset pressures calculated with the 5 hour ASIST trends compared well with measured onset pressures.

Introduction

Asphaltene are materials in a crude oil that are among the highest molecular weight and/or those with the highest degree of polarity (Long, 1981) and aromaticity (Cimino et al., 1995). These large molecules have limited solubility in saturated hydrocarbons, tend to form aggregates that are dispersed in crude oils, and form separate heavy phases in response to changes in pressure, temperature, or composition of the oil mixture. The amount of material that separates (asphaltene amount) and the solubility conditions at which separation occurs (asphaltene flocculation onset) vary not only with the composition of the asphaltene themselves, but also with the size of the paraffinic precipitants, whether these are the native crude oil light ends or added non-solvents (typically n-pentane or n-heptane).

Wang (2000) demonstrated that asphaltene onset conditions—defined in terms of the mixture refractive index, which for non-polar species can be related to the mixture solubility parameter (Buckley et al., 1998)—changed predictably with molar volume of n-alkane precipitating agents. Extrapolation of the relationship established by measurements with liquid n-alkanes to predict asphaltene instability during depressurization was proposed (Wang and Buckley, 2001a). Numerous successful applications of the Asphaltene Instability Trend (ASIST) have since been published (e.g., Wang et al., 2004) suggesting that extrapolation of the ASIST relationship is reasonable. Nevertheless, direct verification of the link between asphaltene instability upon addition of normal alkanes and the asphaltene that appear during depressurization of a crude oil is needed.

Predictions with thermodynamic models.

Hirschberg, et al. (1984) introduced the use of the Flory-Huggins approach to development of thermodynamic models of large asphaltene molecules in solution in much smaller solvent species. An improved Asphaltene Solubility Model (ASM) was proposed by Wang and Buckley (2001b). ASM calculations, shown as the solid line in Fig. 1, are compared to measured data points for Mars-P stock-tank oil. Values of solubility parameter (δ) were calculated from measured values of refractive index (RI) using Eqs. 1 and 2.

$$\delta = 52.042F_{RI} + 2.904 \quad (1)$$