Fluid Phase Equilibria 291 (2010) 103–110

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Characterization of asphaltenes precipitated with three light alkanes under different experimental conditions

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ARTICLE INFO

Article history:
Received 17 August 2009
Received in revised form 4 December 2009
Accepted 10 December 2009
Available online 16 December 2009

Keywords:
Asphaltenes
Asphaltene precipitation
In situ deasphalting
Solvent-based heavy oil recovery

ABSTRACT

Asphaltene precipitation plays an important role in both oil production and refining processes. In this paper, asphaltenes are precipitated from a heavy oil sample under different experimental conditions by using three different light alkanes, i.e., propane, *n*-pentane, and *n*-heptane. A variety of analytical techniques are applied to characterize the precipitated asphaltenes and deasphalted heavy oil (i.e., maltenes), such as the density and viscosity measurements, vapour-pressure osmometry, freezing-point osmometry, scanning electron microscope (SEM) imaging, nuclear magnetic resonance (NMR) measurement, and simulated distillation for compositional analysis. It is found that the yields and properties of the precipitated asphaltenes and remaining maltenes strongly depend on the specific precipitant tested and the liquid precipitant-to-oil volume ratio used. The asphaltene yield decreases as the carbon number of an alkane increases, while it increases monotonically and finally reaches a plateau if the liquid precipitant-to-oil volume ratio increases up to 20–40 for *n*-pentane and *n*-heptane, respectively. As a result, *n*-heptane-precipitated asphaltenes (C_7-asphaltenes) have the highest molecular weight and aromaticity among the three kinds of precipitated asphaltenes. C_7-asphaltenes are bright and black particles, whereas *n*-pentane-precipitated asphaltenes (C_5-asphaltenes) are dull and brown powders. Propane-precipitated asphaltenes (C_3-asphaltenes) together with some amount of co-precipitated resins are found to be highly viscous and semi-solid like immediately after the flashed-off process but become more and more liquid-like afterward. Compositional analysis results of the original heavy crude oil and three different maltenes indicate that the carbon numbers of most precipitated asphaltenes are higher than C_{50}.

1. Introduction

With the depletion of the conventional crude oil resources, the oil industry has begun to explore and exploit abundant unconventional heavy oil reserves. In recent years, solvent-based heavy oil recovery processes have gained increasing attention because of their cost-effectiveness and environmental friendliness [1,2]. In a typical solvent-based heavy oil recovery process, such as vapour extraction (VAPEX) process, a light hydrocarbon solvent [3] or carbon dioxide [4] is injected into reservoir formations to extract heavy oil. A heavy oil usually contains more than 10 wt.% of asphaltene content [5], which has a dramatic effect on the heavy oil physicochemical properties. It is well known that asphaltene precipitation from the heavy oil due to compositional, pressure, and temperature changes can be beneficial and/or problematic in heavy oil production, transportation, and ultimate refining processes [6–8].

Asphaltenes are the heaviest and most complex fraction in a crude oil sample, which appear as brown or black solid particles precipitated from a crude oil by using a low boiling-point alkane, e.g., *n*-pentane or *n*-heptane [9]. They consist of condensed polynuclear aromatics, small amounts of heteroatoms (S, N, and O), and some traces of nickel, vanadium, and other metal elements. Because asphaltenes are defined in terms of their insolubility rather than their chemical structures, this definition gives a broad distribution of molecular structures of asphaltenes that are precipitated from different crude oil samples. Even for a given crude oil sample, the yield and properties of the precipitated asphaltenes strongly depend on the specific precipitation method [10] and precipitant used [11].

It has been found that the yield and properties of asphaltenes precipitated from a crude oil depend on various factors, such as the precipitant, liquid precipitant-to-oil volume ratio, contact time, pressure, and temperature [12–14]. Some standard precipitation methods have been developed in laboratory to obtain an accurate and consistent asphaltene content. A number of studies have been published to characterize *n*-pentane- or *n*-heptane-precipitated

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doi:10.1016/j.fluid.2009.12.010

asphaltenes by using different analytical techniques. However, it should be noted that the yield and properties of precipitated asphaltenes with a lighter alkane (e.g., propane) can be rather different from those precipitated with *n*-pentane or *n*-heptane in the laboratory test. For example, propane is often used as the most effective solvent and injected into a heavy oil reservoir during a VAPEX process to in situ dilute and extract the heavy oil [15]. Also dissolution of a light hydrocarbon solvent into a viscous crude oil is found to be an effective method to significantly reduce its viscosity and thus greatly facilitate its long-distance transportation through pipelines. In the literature, there are few data available for characterizing the asphaltenes precipitated with a lighter hydrocarbon solvent, such as propane [16–18]. Hence, a better understanding of the differences between the asphaltenes precipitated with *n*-pentane or *n*-heptane in the laboratory test and those precipitated with propane being used as a light hydrocarbon solvent in the VAPEX heavy oil recovery and daily crude oil transportation processes will help to promote or control asphaltene precipitation in practice.

In this study, a heavy oil sample is tested to precipitate its asphaltenes by using three light alkane precipitants, i.e., propane, *n*-pentane, and *n*-heptane. The precipitated asphaltenes and remaining maltenes are characterized by applying various analytical techniques, which include the density and viscosity measurements, vapour-pressure osmometry, freezing-point osmometry, scanning electron microscope (SEM) observation, nuclear magnetic resonance (NMR) spectroscopy, and simulated distillation. The precipitated asphaltenes in terms of insoluble removal from the heavy oil and the remaining maltenes under different experimental conditions are characterized and their yields and physicochemical properties are analyzed in detail.

2. Experimental

2.1. Materials

A heavy oil sample was collected from the Lloydminster area, Canada. The density and viscosity of the field-cleaned sales heavy oil were measured to be $\rho_{\text{oil}} = 975\,\text{kg/m}^3$ and $\mu_{\text{oil}} = 9440\,\text{mPa s}$ at the atmospheric pressure and a constant room temperature of $T = 24.0\,^\circ\text{C}$ (reservoir temperature), respectively. The asphaltene content of the original heavy crude oil was measured to be $w_{\text{asp}} = 13.9$ wt.% (*n*-pentane insoluble) by using the standard ASTM D2007-03 method [19] and filter papers (Whatman No. 2, England) with a pore size of 2 μm. The compositional analysis result of this heavy oil was obtained by using the standard ASTM D86 [20] simulated distillation method and is given in Table 1. It can be seen from this table that there are no hydrocarbon components under C_9 and that heavy hydrocarbon components of C_{50+} are 24.09 wt.%. Given the measured asphaltene content of $w_{\text{asp}} = 13.9$ wt.% (*n*-pentane insoluble), it is obvious that the carbon numbers of most asphaltenes in this heavy oil are higher than C_{50}. The purity of propane (Praxair, USA) used as a precipitant in this study is equal to 99.5%. And the purities of both *n*-pentane and *n*-heptane (Fisher Scientific, USA) used as respective precipitants are equal to 99.9%.

2.2. Asphaltene content measurements

The experimental procedure for the standard ASTM D2007-03 method [19] is briefly described as follows. First, one volume of the heavy oil was mixed with 40 volumes of liquid precipitant (either *n*-pentane or *n*-heptane). It is worthwhile to note that different liquid precipitant-to-oil volume ratios were tested to study the volume-ratio effect on the asphaltene yield. The heavy oil–*n*-pentane or *n*-heptane mixture was agitated by using a magnetic stirrer (SP46925, Barnstead/Thermolyne Corporation, USA) for 12 h and then filtered through 2 μm pore size filter papers (Whatman No. 2, England). The filter cake, which was mainly composed of precipitated asphaltenes, was kept rinsing with the liquid precipitant until the precipitant after passing through the filter papers remained colourless. The precipitated asphaltenes were slowly dried at $T = 100\,^\circ\text{C}$ on the heated magnetic stirrer until their weight did not change from the reading of an electric balance (PM 4600, Mettler Toledo, Canada). On the other hand, the filtrate was distilled at the boiling-point temperature of either *n*-pentane or *n*-heptane under the atmospheric pressure for at least 2 h. The remainder was the deasphalted heavy oil (i.e., maltenes) after the precipitant was completely evaporized.

Table 1
Compositional analysis result for the original heavy crude oil with the asphaltene content of $w_{\text{asp}} = 13.9$ wt.% (*n*-pentane insoluble).

Carbon number	wt.%	Carbon number	wt.%	Carbon number	wt.%
C_1	0.00	C_{18}	3.00	C_{35}	1.98
C_2	0.00	C_{19}	3.00	C_{36}	1.85
C_3	0.00	C_{20}	2.60	C_{37}	1.25
C_4	0.00	C_{21}	3.10	C_{38}	1.22
C_5	0.00	C_{22}	1.86	C_{39}	1.68
C_6	0.00	C_{23}	2.79	C_{40}	1.60
C_7	0.00	C_{24}	2.25	C_{41}	1.13
C_8	0.00	C_{25}	2.50	C_{42}	1.05
C_9	0.05	C_{26}	2.54	C_{43}	1.38
C_{10}	1.12	C_{27}	2.24	C_{44}	1.38
C_{11}	0.97	C_{28}	2.52	C_{45}	0.84
C_{12}	1.50	C_{29}	2.45	C_{46}	0.84
C_{13}	1.92	C_{30}	2.03	C_{47}	1.16
C_{14}	2.30	C_{31}	2.06	C_{48}	1.05
C_{15}	2.98	C_{32}	2.06	C_{49}	1.08
C_{16}	2.83	C_{33}	1.50	C_{50+}	24.09
C_{17}	2.73	C_{34}	1.52	Total	100.00

To precipitate asphaltenes by using propane as a precipitant under a high pressure, a saturation cell with a total net volume of $310\,\text{cm}^3$ was used to saturate the heavy oil sample with propane at two respective equilibrium pressures of $P_{\text{e}} = 908$ and $P_{\text{e}} = P_{\text{v}} = 928$ kPa (vapour pressure) and $T = 24.0\,^\circ\text{C}$ (reservoir temperature). A precision digital pressure gauge (2086, Ashcroft, USA) with an accuracy of 0.1% at its full scale of 3.5 MPa was connected to the saturation cell. The saturation test was conducted inside a house-made air bath, whose constant temperature $T = 24.0\,^\circ\text{C}$ was maintained by using a temperature controller (Standard-89000-00, Cole-Parmer, Canada). After the heavy oil–propane system reached an equilibrium state, as indicated by a constant pressure and a constant gas-cap volume for three days, the propane-saturated heavy oil was gradually flashed off through an inline stainless steel filter (Swagelok, USA) with pore size of 2 μm. The total weight of C_3-asphaltenes retained inside the filter and at the bottom of the saturation cell was determined by measuring the weight of the flashed oil and applying the material balance equation. It is worthwhile to note that the propane and heavy oil sample were at the vapour–liquid equilibrium (VLE) at $P_{\text{e}} = 908$ kPa. In another saturation test, the liquid propane–heavy oil volume ratio was chosen to be four at the initial pressure of $P_{\text{i}} = 2000$ kPa. After the heavy oil–propane system was kept for one week, a small gas cap was formed and the final equilibrium pressure was equal to the propane vapour pressure of $P_{\text{e}} = P_{\text{v}} = 928$ kPa at the tested temperature of $T = 24.0\,^\circ\text{C}$.

For brevity, in this paper, the asphaltenes precipitated by using propane at 928 and 908 kPa, *n*-pentane, and *n*-heptane are called C_3-asphaltenes (928 kPa), C_3-asphaltenes (908 kPa), C_5-asphaltenes, and C_7-asphaltenes, respectively. The corresponding maltenes are referred to as C_3-maltenes (928 kPa), C_3-maltenes (908 kPa), C_5-maltenes, and C_7-maltenes, respectively.