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Effect of precipitation time and solvent power on asphaltene characteristics

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HIGHLIGHTS

- Composition of precipitated asphaltenes changes widely as a function of time.
- Asphaltene precipitation involves reorganization of the aggregates.
- Reorganization of aggregates includes expulsion and incorporation of molecules.
- 24 h is not enough time to reach a steady composition of the asphaltenes.

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ABSTRACT

The kinetics of asphaltene precipitation is studied regarding the characterization of the precipitated material. The association of different components of the crude oil depends on the solvent power of the blend heptane/oil and produces aggregates with a variable composition that change as a function of time. It was found that the precipitate contains a significant amount of maltenes whose relative content decreases as a function of time. In agreement with this behavior, the precipitate becomes more hydrogen deficient. These changes also produced a significant increase in the apparent average molecular weight of the precipitate as measured using size exclusion chromatography. This increase correlated with the amount of asphaltenes in the precipitated material independently of time or heptane/oil ratio. Solubility profile measurements showed that the average characteristics of the asphaltenes found in the precipitate varied as a function of time. As more asphaltene molecules precipitated, the distributions of these molecules changed decreasing its average solubility parameter. Considerable differences in the amount collected at low and high heptane/oil ratios as a function of time were also found. Based on the measurements, a new model was developed that describes the complex aggregation behavior involved in asphaltene precipitation.

1. Introduction

Asphaltenes are undesirable compounds that precipitate during different stages of petroleum production and refining. As they are not defined as a compound class but as a solubility class, characterization of asphaltenes is challenging since variations in the procedure to obtain them produce not only different amounts but also distributions of compounds with different characteristics [1–3].

It is well known that asphaltene precipitation is affected by several factors, including type of solvent [1,3,4], temperature [5,6], precipitant/sample ratio [3,7], contact time [7], and washing of the filter cake [2,7]. In practical terms, this means that comparison of asphaltenes obtained using even slightly different methodologies must be made carefully: the asphaltene yields and the chemical composition are going to be different. The main reason for this behavior is the high polydispersity regarding composition and molecular weight of petroleum components. This combination of factors results that under slightly different conditions, a different set of molecules precipitate forming a distinct asphaltene. Although it is expected that the molecules more prone to precipitate are going to be those with the higher aromaticity (poor in hydrogen), higher molecular weight and/or higher polar nature, significant variations in the amount and distribution of the molecules can occur as shown by previous studies [3,5].

Particularly important is the understanding of kinetic aspects related to asphaltene precipitation as this is a variable frequently neglected in asphaltene studies [8] and can have important practical consequences during production and processing of crude oils. Recently, a series of experiments using optical microscopy

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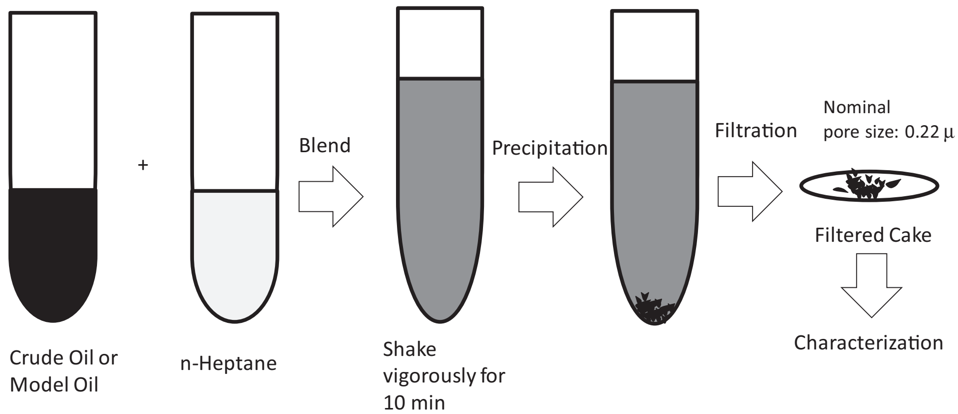

Fig. 1. Scheme of the experiments.

observations and centrifugation based separations [8,9], has shown that kinetic factors are underestimated during conventional flocculation experiments aimed to determine chances of asphaltene precipitation. In fact, it was found that these test over predict solubility as it was observed that the beginning of precipitation could take from minutes to several months depending on the precipitant concentration used [8,9]. From these experiments, we also know that the precipitated amount varies as a function of time and that those variations depend on the precipitant concentration.

When asphaltenes precipitate in the reservoir or during refinery operations, factors such as solvent power and time have also a significant influence. In particular, aging can have a definitive impact on deposit characteristics [10,11] or emulsion formation [12]. Additionally, kinetic effects and solvent power play a relevant role in understanding how recently developed solvent injection processes (i.e. Vapex or N-solv) [13,14] might affect the reservoir and crude oil production. In these processes, hydrocarbons in the range C3 to C5 are injected downhole to make the crude oil mobile. Recent physical and numerical simulations [15] of propane injection into a heavy oil reservoir indicated that the kinetics of asphaltene precipitation plays a significant role in the production as well as in the quality of the produced crude oil.

From many perspectives, the understanding of how time and solvent power affect asphaltene composition can provide useful information to design new strategies in diverse areas including analytical characterization, precipitation prevention, deposit removal, and new production methods.

In the present work, the effect that time and solvent power have on asphaltene properties is investigated using a combination of analytical techniques. We evaluate several physicochemical properties that are strongly linked to precipitation behavior such as hydrogen deficiency, solubility distribution, and molecular size. The changes in the amount and composition of the precipitated material as a function of time are also examined.

2. Experimental section

2.1. Materials

Crude oil and *n*-pentane asphaltenes were used in the precipitation experiments. Crude Oil A is a medium crude oil (30.4 API) with an asphaltene content 2.43 wt% using the standard method ASTM D-6560 [16]. *n*-Pentane asphaltenes were obtained following the standard ASTM D-4055 [17] from a heavy Crude Oil B (7.7oAPI) with an *n*-pentane asphaltene content of 18.7 wt%. Toluene, *n*-heptane, *n*-pentane, methylene chloride and methanol are HPLC grade (Fisher Chemical)

2.2. Separation of precipitated material

Studied samples included Model Oil and Crude Oil A. The Model Oil was prepared by dissolving the *n*-pentane asphaltenes in toluene (2 wt%)

n-Heptane was used to induce precipitation at room temperature of the Model Oil, and Crude Oil A. Different *n*-heptane/samples ratios from 1.5 to 100 were used. Flocculation onset experiments using *n*-heptane as precipitant agent indicated that precipitation starts at a *n*-heptane/Crude Oil ratio of 1.5. Blends prepared with a *n*-heptane/Crude Oil ratio of 1 did not show precipitation during the first 24 h.

Solutions are prepared by mixing 10 mL of sample with the corresponding volume of *n*-heptane and shaking vigorously for 10 min in a shaker. After blending, the solutions are kept in static conditions. Blends were filtered using a Teflon membrane filter with an average pore size of 0.2 μm so that particles could be recovered and analyzed. Fig. 1 shows a scheme of the procedure to obtain the filtered cakes. Since the goal is to replicate the precipitation behavior as close as possible to a real situation, the filtered cake was not washed with additional *n*-heptane after filtration. Additionally, it has been reported that precipitation procedures where asphaltenes are not washed seem to be more repeatable [2].

Once collected, the filtered cake was dried under nitrogen flow, weighed and analyzed using the characterization methods listed below. Samples were run in duplicates which on average differ by 10%.

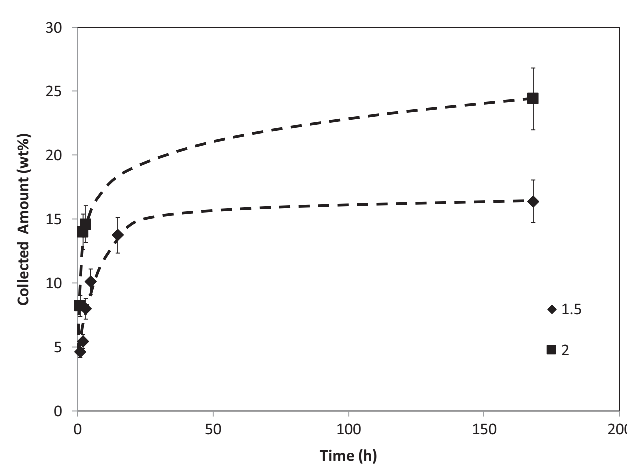

Fig. 2. Collected amount as a function of time and *n*-heptane/Model Oil ratio. Trace lines added for visualization purposes.