Comparing asphaltenes: Deposit versus crude oil

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HIGHLIGHTS

- Deposit solubility fractionation reveals solubility distribution of deposit.
- Heptane extracted asphaltenes do not represent asphaltenes deposited during production.
- Deposit asphaltenes are less soluble and more aromatic than heptane extracted asphaltenes.

ARTICLE INFO

ABSTRACT

Changes in operating conditions such as pressure, temperature and composition of the oil can trigger asphaltene deposition during oil recovery operations. In the present work, an asphaltene deposit obtained during cleaning of a submersible pump was analyzed. The oilfield was under CO_2 flooding as secondary EOR process. The deposit was separated into solubility fractions that were characterized in terms of composition and solubility properties. A comparison with heptane asphaltenes extracted from the crude oil that produced the deposit was carried out and the results indicated that these extracted asphaltenes do not represent the type of asphaltenes present in the solid. Asphaltenes present in the deposit are less soluble and more aromatic than those found in the heptane extracted asphaltenes coming from the original crude oil. Plausible explanations for this observation are discussed based on current knowledge.

1. Introduction

Changes in operating conditions such as pressure, temperature and composition of the oil can trigger asphaltene deposition during oil production operations. It is well known that asphaltene deposition increases operation costs due to cleanup treatments and deferred production [1].

The precipitation of asphaltenes occurs when asphaltene and/or maltene characteristics change as a consequence of pressure, temperature variations, and/or chemical modifications, etc. In general, these changes and their effects are relatively well understood based on experimental evidence as well as thermodynamic modeling. However, the reason why some crude oils produce deposits while others do not, even under similar conditions, is still a matter of intense research. In particular, it has been difficult to link asphaltene chemical characteristics with their solubility/deposition behavior. Earlier work in this area showed that high aromaticity and low hydrogen to carbon molar ratios are observed for asphaltenes from crude oils with precipitation problems during upstream operations [2,3].

Enhanced oil recovery methods can produce changes in operating conditions and therefore, induce the formation of asphaltene deposits. In a previous work [4], it was shown how enhanced oil recovery methods and well treatments can induce changes that affect asphaltene solubility as measured using two recently developed techniques [5,6].

In enhanced oil recovery applications using CO_2 flooding, the ability of carbon dioxide to become miscible with reservoir oil is of paramount importance to the oil displacement mechanism. However, in laboratory tests, it has been shown that the use of supercritical CO_2 can induce asphaltene precipitation causing rock permeability reductions [7–13]. In real conditions, it has been observed that CO_2 flooding induces asphaltene deposition in areas closer to the wellbore. In several different injection projects [14–17], problems caused by asphaltene precipitation have been reported: electrical submersible pump failures, tubing plugging, wellhead freezing and injectivity losses. However, it is important to mention that asphaltene deposition during CO_2 flooding is not a widespread condition in all the oilfields produced by CO_2

flooding. In fact, in the same oilfield, problems can be observed just in a few wells with variable severity.

In the present work, an asphaltene deposit obtained during the cleaning of a submersible pump in an oilfield under CO_2 flooding was analyzed and its characteristics were compared with the heptane asphaltenes extracted from the crude oil. In order to carry out the analysis, the deposit was fractionated based on solubility.

One of the main difficulties in the characterization of organic deposits is their high complexity. A common strategy to characterize heavy non-volatile fractions has been to fractionate them in solubility fractions. This strategy reduces the complexity of the material to study and provides a distribution of properties for the asphaltenes instead of just averages. In fact, fractionation studies [6,18–20] using different separation schemes have shown regular variations in terms of H/C, aromaticity, and heteroatom content for the different fractions. In general, the less soluble fractions have shown decreased H/C molar ratios and increased heteroatom content. One downside is that these separation methodologies produce fractions with significant overlaps [6,21]. Despise this disadvantage, fractionation and subsequent characterization can provide significant insight about the distribution of properties on deposits and heavy fractions. Extensive characterization together with the practical knowledge of deposition can provide significant clues about this phenomenon. In particular, the main interest of this work is to shed some light on how the composition of the deposit is related to the heptane asphaltenes present in the crude oil.

2. Experimental

2.1. Materials

A deposit sample and the corresponding crude oil were obtained from an oilfield produced by CO_2 flooding. Methylene chloride, toluene, chloroform, methanol, and n-heptane HPLC grade solvents were purchased from Fisher Scientific and used without further purification.

2.2. Asphaltene extraction

Asphaltenes were extracted from the crude oil using a modification of the ASTM D6560 test [22]. In this modified version, A 1/20 sample/n-heptane ratio is used, and the blend is filtered at 80 °C. The precipitated material is washed using hot heptane prior to drying and weighing.

2.3. Deposit fractionation

The fractionation of the deposit was performed using an Accelerated Solvent Extractor Dionex 300. A sample of the material is weighed (mass around 5.0 g) and dissolved in 50 mL of Methylene Chloride. 50 g of PTFE are added to the solution and stirred during 1 h at room temperature. The solvent was removed by heating at 60 °C under nitrogen. The PTFE supported sample is placed into a 100 mL stainless steel cell and extracted with heptane at room temperature with 60 min of soaking time. This produces the first extracted fraction, the maltenes (heptane solubles). The cell is then extracted with $15/85CH_2Cl_2$/n-heptane (Fraction #1), $30/70CH_2Cl_2$/n-heptane (Fraction #2), 100% CH_2Cl_2 (Fraction #3) and $90/10$ CH_2Cl_2/Methanol(Fraction #4), respectively, for 60 min at room temperature each step. Finally, the cell is "washed" three times with $90/10CH_2Cl_2$/MeOH (Fraction #5) at 120 °C for 15 min.

2.4. Elemental analysis

Carbon, hydrogen, and nitrogen (CHN) analysis was carried out with a Carlo Erba model 1108 analyzer. Metal and sulfur were determined using a Thermo Intrepid ICP.

2.5. Solubility profile

Solubility profile analyses were carried out in all the fractions using the following procedure: solutions of the samples in methylene chloride (0.1 wt%) were prepared and injected in a column packed with an inert material using n-heptane as the mobile phase. This solvent induces the precipitation of asphaltenes and, as a consequence, their retention in the column. The first eluted fraction from the column is the maltenes which is soluble in n-heptane. After all this fraction has eluted, the mobile phase is changed gradually from pure n-heptane to 90/10 methylene chloride/methanol and then to 100% methanol. Asphaltenes are quantified using an Evaporative Light Scattering Detector (ELSD). The HPLC system consisted of a HP Series 1100 chromatograph and an Alltech ELSD 2000 detector. The flow rates used were kept constant during all the experiments. The volumetric flow of the mobile phase was 4.0 mL/min and 3.5 L/min of nitrogen was used for the nebulizing gas of the ELSD. The analysis took 35 min to be completed. Duplicates are run for each sample to assure good quality results. The injected volume is 80 μL in all the experiments. A detailed account of the technique is presented elsewhere [5]. Based on the ELSD detector, a curve is generated that is related to the solubility properties of the asphaltenes and can be quantified to reflect the tendency of the sample toward asphaltene precipitation. Two main variables are calculated using this procedure: T_{av} the average time of elution of the asphaltenes in the sample and ΔPS that reflects the tendency of asphaltenes toward precipitation and is measured as the difference in time between the maximum of the first peak and 75% of the distribution. The larger the ΔPS, the more prone toward precipitation are the asphaltenes.

2.6. IR measurements and fluorescence measurements

Infrared spectra were obtained in a Varian 7000e FT-IR infrared spectrophotometer. Transmission measurements were carried out on a Diamond Anvil Cell (DAC), which is used to compress the sample for transmission analysis. Spectra were measured from 4000 cm^{-1} to approximately 400 cm^{-1} using a Deuterated Triglycine Sulfate (DTGS) detector as the average of 32 scans acquired at 4 cm^{-1}. Since aromatic C=C, C—H and COOH carbonyl bonds showed strong absorbance, they were used to evaluate their presence in each fraction.

Solutions in toluene with concentrations ranging around 5 ppm were used in the experiments. Fluorescence spectra were recorded on a Fluorescence Spectrometer Hitachi Model F-4500 with a 150 W Xenon Lamp as the excitation source. In this instrument, the fluorescence is measured at a 90° angle relative to the excitation light. Emission and excitation slits were set at 5 nm. The scanning speed was set constant (1200 nm/min). An excitation wavelength of 310 nm was used for the solutions and the emission spectra were recorded for wavelengths 200–900 nm. The measurements were carried out at room temperature in a quartz cell of 2 mm path length.

2.7. Density

Density measurements were performed using a high precision density meter Paar DSA 5000 M. Four solutions of the sample in toluene are prepared in concentrations ranging from 0.20% to 0.50% w/w. The sample solutions are injected into the digital