



Chemical–physical analysis of rheologically different samples of a heavy crude oil



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ABSTRACT

Heavy crude oil samples extracted from the same well showed some rheological differences mainly in terms of viscosity and response to the addition of a small amount of dodecyl benzen sulfonate. Also slight differences in the activation energy and in the viscosity dependence on a solvent concentration were observed. The crude oil samples, also separated in maltenic and asphaltenic fractions, were fully characterized by elemental and proximate analysis, solvent extraction, thermogravimetry, mass spectrometric and spectroscopic analyses. No significant differences were found showing that the samples have the same composition and molecular structure and demonstrating that the different rheological behavior has to be related only to a different microstructural organization that is not sensed by the chemical–physical tests. This result helps to complete the picture of the complex correlation between rheological and chemical–physical properties of heavy crude oils. While it is accepted that chemical–physically different samples may, or may not, have a different rheology, we show for the first time that unperturbed samples with the same chemical–physical properties may exhibit differences in the rheological behavior.

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1. Introduction

Nowadays unconventional oils represent the vast majority of the world oil reserves and thus both the scientific and technical interests on their exploitation are significantly increasing. Unconventional oils are principally formed by bitumen (30 wt.%), extra-heavy crudes (25 wt.%) and heavy crudes (15 wt.%) [1]. According to UNITAR (United Nations Institute for Trading and Research), heavy crudes have API gravity between 20° and 10°, extra-heavy crudes have API < 10° and viscosity, at 15.6 °C, smaller than 10⁴ cP (10 Pa s) and bitumen have API < 10° and viscosity larger than 10⁴ cP [2].

The elemental composition of unconventional oils varies with the crude source, it mainly consists of hydrogen (8–12 wt.%) and carbon (80–88 wt.%) [3]. “Heteroatoms” like sulphur (0–9 wt.%), nitrogen (0–2 wt.%) and oxygen (0–2 wt.%) are generally present. Traces of metals, naturally occurring or added during the refinery process, are also typically found; the most abundant being vanadium and nickel [4].

Unconventional oils have an extremely complex chemical composition, with more than 100,000 components [5], whose precise

determination is still debated in the literature [3] and indeed, currently, several studies are focused on the components characterization [6,7]. A traditional analysis of the petroleum products composition is known as SARA fractionation that consists in dividing the oil in four fractions (Saturates, Aromatics, Resins, and Asphaltenes) with different solubility in solvents of different polarity. Usually, saturates amount to 5–20% of a heavy oil [8], and are in form of a colorless or lightly colored liquid. Saturates are mainly aliphatic molecules with some branching structures. Their molecular weight is about 470–880 g mol⁻¹ and their H/C ratio is close to 2 [3]. Aromatics amount to 15–35% of a heavy oil [8] and are in form of a yellow to red colored liquid. They are constituted of few condensed aromatic rings substituted with aliphatic chains and have a molecular weight equal to about 570–980 g mol⁻¹ [3]. Resins amount to 20–45% of a heavy oil [8]. They form a black solid at room temperature. Their composition is close to that of asphaltenes even though they exhibit a lower molecular weight, varying from 780 to 1400 g mol⁻¹, a somewhat higher H/C ratio between 1.38 and 1.69 and a less complex aromatic structure with 2–4 fused rings [3]. Asphaltenes amount to 5–20% of a heavy oil, in few cases they reach values up to 43% [8]. They form a black powder at room temperature when eluted by *n*-heptane and they are largely responsible for the black color of the crudes.

Unfortunately, there are numerous issues that render the use of SARA fractionation problematic for unconventional oils such as the variation of procedures among different laboratories leading to different

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results [9] and an error of 10% in the content of resins and asphaltenes has been often observed [8]. The difficulty in fractionating a crude oil lies in the fact that it is a “chemical continuum”, with a gradual increase of molar mass, aromatic content and polarity from saturates to asphaltenes. It is often more convenient to perform pentane or heptane extraction for separating the three fractions (saturates, aromatics, resins) soluble in pentane/heptane as a unique class, called maltenes, from the other pentane/heptane insoluble fraction named asphaltenes. Similarly to the historical definition given in 1837 by Boussingault [10], asphaltenes are operationally defined as the crude oil components soluble in toluene and insoluble in *n*-heptane. Lesueur [3] emphasizes that solubility must be understood here as “not generating a precipitate” and not as molecular solubility, since asphaltenes are known to form aggregates in toluene [11].

Asphaltenes are the most studied fraction of the oils for their viscosity-building role and for clogging the tubes as a consequence of their precipitation. So, they are the principal cause of the current scarce exploitation of unconventional oils. Kokal and Sayegh [12] pictorially defined them as “the cholesterol of petroleum”. In the last two decades, the properties of asphaltenes and, in particular, their molecular weight have been studied with several methodologies. The molecular weight has been estimated at values spanning six orders of magnitude, from less than 10^3 g mol^{-1} to 10^9 g mol^{-1} [13]. The principal issues of asphaltene microstructure resolved in the last years led to the structural Yen-Mullins model [7]: The predominant asphaltene molecular architecture contains a single polycyclic aromatic hydrocarbon (PAH), formed by 4–10 fused rings, with peripheral alkanes and few heteroatoms (about 1–3 per molecule) [3], the average molecular weight is $400\text{--}1000 \text{ g mol}^{-1}$; the almost planar asphaltene molecules can associate, through principally $\pi\text{--}\pi$ interactions (Van der Waals forces), to form a nanoaggregate that is a stack of approximately six PAH layers; the nanoaggregates can further associate to form a cluster containing approximately eight nanoaggregates. This complex microstructural organization explains why it is so difficult to set the asphaltene role in the physical behavior of oils.

Nowadays, there is general agreement on the difficulty to relate directly the oil viscosity to the asphaltene content and the intuitive conclusion that the higher the asphaltene content, the higher the oil viscosity, is not necessarily true. It holds for oils with the same origin [14], but it is not self-consistent for oils with different origins [8,15]. In the latter case, the physical properties, like the viscosity, of the oil are also related to the chemical structure and composition of the asphaltenes and to the composition of the rest of the oil.

In the last two decades, new studies combining chemical–physical and rheological analyses have been performed. Michalica et al. [16] considered two asphalts of different origin having very different elemental composition, fractional composition and molecular weight. The authors found that the molecular weight and the polarity (principally related to content of heteroatoms) of the asphalts compounds affect the rheological behavior of the samples. The asphalt with less heteroatoms showed a larger viscosity and a stronger shear–thinning behavior. Loeber et al. [17] tried to correlate the chemical, structural and rheological properties of more than 25 colloidal bitumen extracted from five different world areas. Asphaltenes can form either isolated domains or interconnected structures that were observed with SEM (scanning electron microscopy) and AFM (atomic force microscopy). For bitumen coming from the same world area, a larger viscosity corresponded to a more interconnected microstructure, but this did not hold for samples coming from different sites. Mouazen et al. [18] tried to associate the bitumen rheological behavior, characterized both in simple shear and in oscillatory mode, to its chemical–physical properties that were modified with γ -irradiation. They used a single bitumen and the effect of γ -irradiation was amply characterized by means of: differential scanning calorimetry, SARA fractionation, size exclusion chromatography (SEC), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and X-ray diffraction. The γ -irradiation induced a

modification of both the relative amounts and the mean molecular weights of the SARA fractions. The authors demonstrated that a larger viscosity and an enhanced elastic behavior were associated to the increase of asphaltene molecular weight and, in general, to an increase of the bitumen aromaticity to the detriment to its aliphaticity. To summarize, the just discussed works start from oils with measurable chemical–physical differences and try to associate them to the different rheological behaviors, and more specifically to the different viscosities.

Sanière et al. [19], while discussing a possible strategy to reduce the heavy oil viscosity, showed that a heavy crude oil with its native colloidal microstructure (i.e. with well dispersed asphaltenes) exhibits a viscosity three times larger than that of the corresponding “reconstituted” crude oil obtained by re-mixing, after the fractionation, the asphaltenic and the maltenic phase. The latter showed a slurry morphology, with precipitate asphaltenes forming aggregates suspended in the maltenes. This proves that two samples sharing the same composition and molecular structure may have a different rheology for the sole effect of a different microstructural organization. However, the reconstituted slurry gradually evolved toward the original colloidal microstructure and the viscosity also increased reaching that of the original oil when the colloidal microstructure was not entirely reformed. This shows that a univocal correspondence between microstructural organization and viscosity cannot be easily drawn.

Ultimately, the chemical–physical analysis of crude oils must be detailed as much as possible to be sure whether a different rheological behavior is due to even small differences in the chemical composition and molecular structure or is, consequently, ascribable only to a different microstructural organization.

In this framework, we studied in deep detail the chemical–physical characteristics of three samples of a heavy crude oil that, though extracted from a single well, showed a measurable different rheological behavior, namely a different viscosity, a different dependence on the temperature and on the solvent concentration when diluted with naphtha, and a different interaction with an acid and a base. Specifically, the contents of C, H and N and of metals (V, Ni, Fe, Mo and Cu) were quantified by elemental analysis and by inductively coupled plasma–mass spectrometry (ICP–MS), respectively. Proximate analysis, fractionation in maltenes and asphaltenes, gas chromatography–mass spectrometry (GC–MS) of the heavy oils and maltenic fractions have been carried out to analyze the composition of the crudes. The molecular weight distributions of the three crude oils and the related solvent-separated fractions were determined by size exclusion chromatography (SEC), and by atmospheric pressure photoionization ion–trap–mass spectrometry (APPI–MS). The thermal behavior of the samples was studied by thermogravimetric analysis (TGA). Further details on the structure of heavy oils and in particular of asphaltenes not amenable to traditional chemical analysis have been obtained by means of UV–Visible (UV–vis) spectroscopy, FTIR and fluorescence spectroscopy.

2. Materials and sample preparation

We considered three heavy crude oil samples (here labeled as A, B and C), coming from the same well. Sample C was collected from the same barrel of sample B, but few months later, while sample A comes from a different barrel. The three samples had the same density equal to 988 kg m^{-3} at $20 \text{ }^\circ\text{C}$, corresponding to 11.6°API.

The chemical–physical analyses were run on the raw crude oils and their maltenic and asphaltenic fractions. Heptane and toluene (ACS grade, Sigma Aldrich) were used for the raw crude oils fractionation. Dichloromethane, DCM (ACS grade, Sigma Aldrich), was used as solvent for most of the spectroscopic analyses.

Rheological tests were run on different typologies of samples: i) raw crude oils, ii) mixtures of raw crude oil and solvent, whose weight fractions varied from 5 to 30 wt.%, iii) mixture of raw crude oil, solvent and other chemicals, henceforth referred to as additives, with a fixed composition equal to 90 wt.% of raw crude oil, 7 wt.% of solvent and 3 wt.%

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