



# Effect of temperature on the analysis of asphaltenes by the on-column filtration/redissolution method



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## HIGHLIGHTS

- A new method to study the effect of temperature on asphaltene determination.
- Asphaltene contents are reduced as temperature is raised.
- Maltene contents increased as temperature is raised.
- Mass balances for virgin and processed n-heptane asphaltenes were carried out.
- Similar behavior was found for whole virgin or hydroprocessed samples.

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## ABSTRACT

The study of the effect of temperature on the analysis of asphaltenes by the on-column filtration/redissolution method is presented. The goal of this work is the prediction and early detection of asphaltene/solid precipitation at reservoir and refining conditions using simple, fast and reliable analytical techniques. A description of the new experimental methodology is introduced followed by the results of the analysis of n-heptane asphaltenes and virgin, vacuum residue (VR), visbroken and hydroprocessed petroleum samples in the temperature range 35–195 °C. Mass balances were effectively carried out and the presence of adsorbed species on the column surface was found. Consistent with gravimetrically separated asphaltenes, the new method showed that asphaltene contents are reduced as the temperature is raised whereas the maltene contents increased. Similar behavior was found for separated asphaltenes and whole virgin, VR or whole hydroprocessed samples. In general, it was observed that the amount of adsorbed species seems to increase with the temperature.

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## 1. Introduction

The study of asphaltene phase behavior at elevated temperatures and pressures has very important applications overall the petroleum industry [1,2]. In upstream operations, the prediction of asphaltene precipitation in very deep and high temperature and pressure reservoirs, such as those found in the Gulf of Mexico, could help with the mitigation of this problem and with the design of offshore platforms. In downstream units, improved monitoring and control of asphaltene-caused fouling is highly desirable to increase the reliability and profitability of refining operations. These examples are just a few of the asphaltene precipitation issues that be found in all the steps of the petroleum value chain at different temperatures and pressures.

The effects of the temperature on the asphaltene precipitation have been studied by several authors [3–11]. In 1995, Andersen separated n-heptane-asphaltenes from Boscan and Kuwait crudes in the 0–80 °C range [3,4]. He observed a decrease in gravimetric yield of asphaltenes as the temperature increased. For Boscan crude the percentages of asphaltenes decreased from 24 wt% at 0 °C to 17 wt% at 80 °C (29% decrease). Similar behavior was observed for Kuwait C. These results are in agreement with the known behavior of ideal and regular solutions and with the reduction of intermolecular association upon heating [3,4].

The characterization by FTIR, Size Exclusion Chromatography (SEC), Vapor Pressure Osmometry (VPO) and elemental analysis indicated that the asphaltenes precipitated at higher temperatures are more aromatic (lower molar H/C) and have higher molecular weight [3]. For heteroatoms (N, S, and O) no common tendency was found [3]. Porphyrins and low molecular weight components show higher solubility as the temperature increase [5]. The presence of functional groups remains rather constant in the precipitated

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asphaltenes indicating that their solubility was not affected by the temperature.

Additionally, the characterization by  $^1\text{H}$  and  $^{13}\text{C}$  NMR and by Fluorescence Spectroscopy indicated that aromaticity increases and the alkyl chain lengths decrease with the temperature at which the precipitation was carried out [4]. The results by Fluorescence Spectroscopy indicated that content of large and complex chromophores increases with temperature [4]. Based on these results it was concluded that as the smaller molecules are solubilized at higher temperatures, the precipitated asphaltenes should have more tendency to associate [3,4].

Andersen et al. studied the asphaltene precipitation at temperatures above the boiling point of the precipitants in the 40–200 °C range [5]. Consistent with previous experiments, they found a decrease in the asphaltene amount from 2.5 wt% to 2.06 wt% as the temperature increased from 40 °C to 200 °C (18% reduction). However, little differences are observed in the functional group contents between the conventional separated asphaltenes and the elevated temperature analogs [5].

In 1994, Mehrotra and coworkers studied the effect of temperature (0–150 °C) and pressures (0–800 psi or, 0–5.6 MPa) on asphaltene particle size distributions using n-pentane as precipitant [6]. Four crude oils were evaluated from a condensate (60°API and 0.6% C<sub>5</sub>-Asphaltenes) to Cold Lake (10.5°API and 21.8% C<sub>5</sub>-Asphaltenes). The results indicated that the mean asphaltene particle sizes range between 266 and 495 μm and that the sizes increased with pressure and decreased slightly with temperature. These observations are consistent with an increase on the asphaltene solubility upon heating [6].

Guo and Hu determined the effect of temperature and molecular weight of n-alkane precipitant (from n-C<sub>5</sub> to n-C<sub>12</sub>) on asphaltene precipitation of a Chinese crude oil (Caoqiao) in the temperature range from 20 to 65 °C [7]. Consistent with previous researchers, the amounts of C<sub>7</sub>-asphaltene precipitation decrease from 5.9 wt% to 3.9 wt% as the temperature increases from 20 °C to 65 °C (34% decrease). Similar results were found with the other precipitants. No chemical characterization was carried out but the data was used to test the model proposed by Rassamdana et al. [8]. This model gave reasonable good predictions not only for the amount of asphaltene precipitated at different temperatures but also in the value of the flocculation onset [8].

Espinat and coworkers reported the effect of temperature (30–290 °C) and pressures (4–3500 psi or 4–240 MPa) on asphaltene agglomeration and disaggregation using dynamic light (DLS), small angle X-ray (SAXS) and small-angle neutron scattering techniques (SANS) [9]. At high temperatures, reversible aggregation of asphaltene leads to stable small entities confirming the increase on asphaltene disaggregation. These results are explained in terms of being the asphaltene aggregate not a rigid entity but rather an aggregate composed of several smaller molecules exhibiting van der Waals or hydrogen bonding interactions [9]. Experimental data suggested that asphaltene disaggregation is a continuous process as the temperature increases. They also found that pressure has not significant influence on the state of asphaltene aggregation. This phenomenon could be attributed to chemical nature of the asphaltene systems investigated and is not necessarily a general behavior for other asphaltenes from different origins [9].

Calles and coworkers studied the asphaltene precipitation from a residue 190 °C+ using n-pentane, n-hexane and n-heptane in the temperature range 25–100 °C [10]. As expected the amount of C<sub>7</sub>-asphaltenes decrease from 3 wt% to 2.5 wt% as the temperature increases from 25 °C to 100 °C (17% decrease). Similar results were found with the other precipitants. As reported by Andersen [3–5] the asphaltenes precipitated at higher temperatures have higher aromatic contents. No significant differences were observed in the nitrogen and sulfur distributions [10].

In 2011, Fogler and coworkers reported the effect of temperature (20–50 °C) on the precipitation kinetics of C<sub>7</sub>-asphaltenes from a Gulf of Mexico crude oil (32°API and 3.6% asphaltenes) [11]. Consistent with all previous researchers, the solubility of the asphaltenes increases (12 wt%) with temperature and, at the same time, the precipitation onset time becomes shorter. These observations were rationalized by examining three major competing effects [11]:

- (1) The higher solubility of asphaltene as the temperature increase will yield in a smaller amount of asphaltenes precipitated. Therefore, a lower number of particle collisions will occur with the concomitant slower rate of aggregation [11].
- (2) As the crude oil/precipitant mixture is heated, alkanes and other lighter fractions expand which in turn reduces the solubility parameter of the mixture making the asphaltenes less soluble. This phenomenon leads to shorter precipitation onset times [11].
- (3) Finally, as the viscosity of the crude oil/precipitant mixture decreases with temperature, the rate of diffusion of the particles increases and leads to faster aggregation rates [11].

After analyzing all these three factors, the authors concluded that the viscosity difference from the temperature change is the key parameter to control the precipitation onset times [11].

In 2012, Bjoroy and coworkers studied the asphaltene precipitation from Athabasca bitumen using trifluorotoluene, n-pentane, n-hexane and n-heptane at different temperatures (22–90 °C) [12]. At 22 °C, the authors found a linear correlation between the asphaltene yields and the surface tension of the precipitants. As the temperature increases, the onset of asphaltene precipitation moves toward higher volumes of the precipitant solvents (more stable) and, as other authors have found [3,4,8,11], lower amounts of asphaltenes were isolated. Finally, the composition of the precipitated asphaltenes did not change significantly with temperatures. Only a small increase on the sulfur content was reported [11].

In all these previous reports, asphaltene separations were carried out gravimetrically with the concomitant high expense of time and money. In this work, the application of a much faster and less expensive on-column filtration/redissolution technique [13] is presented to determine asphaltene precipitation in the temperature range 35–195 °C. For this work, asphaltenes are defined as the fraction which is insoluble in n-heptane and soluble in 10% methanol in dichloromethane. Mass balances were effectively carried out. Asphaltene samples from different origins and whole virgin, vacuum residue (VR), visbroken and hydroprocessed samples were used to evaluate the new technique.

## 2. Experimental section

### 2.1. Materials and equipment

All solvents used were HPLC grade unless otherwise noted. Gravimetric asphaltenes and maltenes preparative separation were carried out using a modified ASTM Test Method D-6560 [14]. This method consists in mixing the sample with heptane (1/20 ratio) and the blend is filtered at 80 °C. The precipitated material is washed using hot n-C<sub>7</sub> prior to drying and weighing. The last traces of precipitate are removed from the digestion beaker using chloroform and then recovered. By using this method, sufficient asphaltenes were isolated and characterized by elemental analysis and  $^1\text{H}$  and  $^{13}\text{C}$  NMR. A range of asphaltenes, virgin, VR and processed samples were tested and their properties and compositions are presented in Tables 1 and 2.

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