Thermogravimetric assessment of thermal degradation in asphaltenes

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ABSTRACT

Monitoring asphaltenes is very important with a view to optimizing visbreaking units in oil refineries. Current analyses based on selective dissolution in different solvents are slow, so new, more expeditious methods for measuring asphaltenes are required to facilitate fuel-oil production. In this work, we studied the thermal degradation of asphaltenes as the potential basis for a thermogravimetric method for their monitoring in visbreaking streams. The thermal degradation of asphaltenes occurs largely from 400 to 500 °C; the process is quite smooth in an inert environment but involves several fast mass loss events in the air. Kinetic parameters for characterizing the process were determined by using two model-free methods and the modified Prout–Tompkins kinetic equation to examine asphaltene thermolysis. Both types of methods showed the activation energy to increase during pyrolysis but to remain almost constant during cracking in the presence of oxygen or even diminish during char oxidation. Deconvoluting the thermogravimetric profiles revealed that asphaltene thermolysis in the air cannot be accurately described in terms of an nth order kinetic model because it involves some acceleratory phases. Also, thermogravimetric analyses of visbreaking streams revealed that char production in them is proportional to their asphaltene content. This relationship enables the thermogravimetric measurement of asphaltenes.

1. Introduction

Given the significance of asphaltenes to fuel-oil stability, developing an effective alternative to the sluggish methods currently available for their chemical characterization is certainly a priority. The term "n-heptane asphaltenes" designates a family of compounds of ill-defined chemical composition. In addition to being insoluble in n-heptane under standard conditions (e.g., IP 143/90 and ASTM D4055), asphaltenes are assumed to be polycyclic, polyaromatic and polar, and to have high heteroatom and metal contents.

The chemical structure of asphaltenes has so far been described by using two different types of models depending on the presence of separate or fused aromatic moieties, namely: (a) the archipelago model and (b) the island model. Recent studies favor the island model [1,2], which assumes asphaltene molecules to be about 1.5 nm in size and to consist of a polycyclic aromatic hydrocarbon core surrounded by naphthenic rings and aliphatic chains forming superstructures such as nanoaggregates and nanoaggregate clusters [3]. Accordingly, differences between asphaltene molecules must arise from the relative importance of aromatic and aliphatic

structures in them, the average number of aromatic carbons typically ranging from 14 to 22—which corresponds to an average of 3–5 aromatic rings per asphaltene molecule [4].

The asphaltene content is an important variable with a view to controlling the streams entering and leaving visbreaking units in oil refineries. Visbreaking is an effective technology for valorizing vacuum residue and other heavy residues generated in oil refineries producing fuel-oil. In fact, visbreaking facilitates soft thermal cracking in a liquid phase, thereby maximizing distillate production in parallel to fuel-oil production [5]. However, the stability of the resulting fuel is compromised by asphaltene deposition, which can lead to poor combustion and accumulation of carbonaceous residues in pipes [6,7]. Visbreaking processes are usually monitored by using standard ASTM methods [8] to measure at least density, viscosity, asphaltenes, sulfur, residual carbon and flash point in each of two major streams, namely: visbreaking feed (VF) and visbreaking residue (VR).

In order to replace currently available chemical methods for asphaltene measurement with a more effective alternative based on specific char production during pyrolysis, in this work we studied asphaltene thermolysis by using thermogravimetric analysis. Under thermogravimetric conditions, the thermal degradation of heavy oil components yields volatiles and char (coke), asphaltenes constituting the SARA component with the strongest tendency to form coke [9,10]. Coke formation involves a complex mechanism

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including the following reactions: (a) cracking of alkyl chains, (b) dehydrogenation of naphthenes to aromatics and (c) condensation of aromatic moieties to higher fused-ring aromatics [11]. This process increases the aromatic/aliphatic carbon ratio and decreases the hydrogen/carbon ratio [12]. In the presence of oxygen, however, the predominant reaction pathway for initiation involves abstraction of the benzyl proton by molecular oxygen to form a hydrocarbon radical and a hydroperoxy radical [13].

Thermogravimetric analysis can be used not only to assess char production, but also to examine the kinetics of thermolysis. By using an appropriate kinetic model to interpret mass losses, one can obtain useful information about the kinetic parameters describing the thermal degradation of asphaltenes (e.g., activation energy, reaction order). The activation energy is known to increase with increasing temperature during pyrolysis [14]. However, estimated values above 350 °C (viz., the cracking zone) differ between authors; thus, Park et al. [14] found the activation energy to be 146–246 kJ/mol, Nassar et al. [15] 153.34 kJ/mol and Mahinpey et al. [16] 93.46–117.7 kJ/mol.

In this work, we used the modified Prout–Tompkins kinetic equation instead of the traditional methods based on an nth-order kinetics in order to consider acceleratory phases during the oxidative cracking of samples [17]. Also, we simulated asphaltene thermolysis by using five pseudo-components undergoing degradation at different temperatures. Based on the results, measurements of char mass during pyrolysis in visbreaking streams afford the accurate estimation of their asphaltene contents.

2. Material and methods

2.1. Samples

The visbreaking unit of La Rábida-CEPSA Refinery in Huelva, Spain, was monitored over a period of 6 months by analyzing 32 samples of visbreaking feed (VF) and residue (VR). Also, individual asphaltenes in each sample were separated and determined.

2.2. Chemical analyses

Physicochemical analyses of the samples were performed according to the following standards: ISO 12185 and ASTM 4052 for density; ISO 3104 and ASTM D-445 for viscosity; ISO 10370 and ASTM D-4530 for carbon residue; ISO 8754 and ASTM D-4294 for sulfur; IP 143 and ASTM D-6560 for asphaltenes; and ASTM D-2887, D-3710, D-7096, D-7169 and D-7213 for simulated distillate.

2.3. FT-IR spectroscopy

The FT-IR spectra were obtained using a Perkin Elmer Spectrum 100 FT-IR spectrometer. The spectra were recorded over the range 4000–450 cm^{-1}, with a resolution of 1 cm^{-1} and 20 scans for each sample.

2.4. Thermogravimetric analyses

All thermogravimetric analyses were performed on a TGA Q5000IR balance from TA Instruments (New Castle, DE, USA), using a sample mass of ca. 5 mg under nitrogen in pyrolysis runs, and a 4:1 mixture of nitrogen and oxygen in combustion runs. The temperature was raised from 25 to 900 °C at three different rates (5, 10 or 20 °C/min).

Table 1
Mean values of selected physicochemical properties of high- and low-sulfur visbreaking feed.

Property	High-sulfur VF		Low-sulfur VF	
	Mean	S.D.	Mean	S.D.
Asphaltenes (g/100 g)	8.7	2.8	1.8	1.1
Sulfur (g/100 g)	3.7	0.6	0.8	0.1
Density at 15 °C (g/mL)	1.022	0.028	1.001	0.022
Ash (g/100 g)	0.8	0.3	0.7	0.3
Viscosity (cSt)	2155	777	1455	557

3. Results and discussion

3.1. Visbreaking feed

The studied asphaltenes were obtained from feed and residue of the visbreaking unit in an oil refinery. Despite the natural variability of vacuum residue and other heavy slots processed in the unit, process engineering ensures smooth feeding of the visbreaking unit with two types of load (heavy or light, which have high and low, respectively, sulfur and asphaltene contents, and viscosity). As can be seen in Table 1, the heavy feeds of the visbreaking contained 8.7 wt% asphaltenes and 3.7 wt% sulfur, and had 2155 cSt viscosity on average. On the other hand, the light feeds contained 1.8 wt% asphaltenes and 0.8 wt% sulfur, and had 1455 cSt viscosity. About 30% of the studied feed samples were of the heavy type and 70% of the light type.

3.2. FT-IR spectroscopy of asphaltenes. Influence of asphaltene origin

Although, based on FT-IR spectra, all asphaltenes are chemically similar and possess a structure consisting of aliphatic and aromatic units plus a variable number of heteroatoms, they differ depending on source: heavy or light visbreaking feed (or oil). To illustrate this point, Fig. 1 compares the FT-IR spectra for two asphaltene samples, namely: AHVF (asphaltenes from heavy visbreaking feed obtained from heavy Iraqi crude) and ALVF (asphaltenes from light visbreaking feed obtained from light West African crude). The most salient differences between the two are as follows:

(a) ALVF contained more aliphatic structures than AHVF. The paraffin absorption bands for the asphaltenes were very strong and overlapped with that at 3048 cm^{-1}, which was due to C—H stretching vibration in aromatics structures. However, the bands at 2852 and 2924 cm^{-1} in the C—H stretching vibration region (2800–3000 cm^{-1}), which were due to symmetric and asymmetric vibrations in methylene (—CH$_2$—) and methyl (—CH$_3$) groups, were significantly stronger for ALVF. Likewise, the bands at 1378 cm^{-1} and 1454 cm^{-1}, were due to symmetric and asymmetric bending vibrations in aliphatic groups attached to aromatic rings [18], were stronger in ALVF than in AHVF. On the other hand, although the absorption pattern in the fingerprint region (1300–700 cm^{-1}) is complex and very difficult to interpret, ALVF and AHVF exhibited bands at 747, 807 and 871 cm^{-1} possibly due to wagging vibrations of protons in substituted aromatic rings [18]. It should be noted that ALVF – but not AHVF – exhibited a band at 727 cm^{-1} due to wagging vibrations of C—H bonds in long aliphatic chains – more than four methylene groups. This result confirms the presence of long aliphatic chains in ALVF [18].

(b) AHVF contained more aromatic structures and heteroatoms than ALVF. The band at 1600 cm^{-1}, which is assigned to stretching vibrations in C=C bonds present in polycyclic aromatic compounds (coke band) [19], was stronger in AHVF than