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Asphaltene characterization as function of time on-stream during hydroprocessing of Maya crude

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Abstract

Determining a series of physical parameters has allowed the behavior of the asphaltene constituents to be monitored during hydrotreating of Maya crude oil. In keeping with the thermal behavior of the asphaltenes constituents, the observations are the aromaticity of the asphaltene increases with time-on-stream and the number and length of the alkyl chains decreases. Sulfur and nitrogen constituents tend to accumulate in the asphaltene before giving rise to carbenes, carboids, and coke. As the reaction progresses, the nickel and vanadium concentrate in the asphaltene fraction, but only to a point (up to 700-h on-stream). After 700-h on-stream, the nickel and vanadium contents of the asphaltene fraction are reduced presumably because the nickel and vanadium concentrate on the coke that is laid down on the catalyst.

Keywords: Asphaltenes; Hydroprocessing; Heavy crude

1. Introduction

Heavy crude oils are complex hydrocarbon mixtures and their physical and chemical composition and properties vary depending on the type and origin. Their constituents are from the lightest hydrocarbons like gases to the complex molecular structures like asphaltenes. In general, heavy crude oils are characterized by their processing complexity due to the high concentration of heteroatoms such as Ramsbottom carbon, metals (Ni and V), sulfur, nitrogen and asphaltenes [1].

To convert heavy oils, e.g. atmospheric or vacuum residua, into light products hydroprocessing has been extensively used. Different type of catalyst (NiMo, CoMo, etc.), reactor configuration (single reactor, reactors in series, one catalytic bed with various catalysts, etc.), reaction system (fixed bed, ebullated bed, slurry) and severity of reaction are employed depending on the complexity of the feed and on the needed level of removal of undesirable components and conversion.

In the last decades hydrotreating process has taken great importance in the refining industry because it transforms high molecular weight hydrocarbons into valuable products by removal of the diverse heteroatoms. The removal of the undesirable components is generally accompanied by hydrocracking reactions in order to reduce the molecular size as well as the boiling point of hydrotreated products.

The presence of asphaltenes in heavy crude oils causes various problems during hydrotreating (HDT). Asphaltenes are the precursors of coke formation because they are formed from large molecules that have high coke forming tendencies that inevitable ends up in HDT catalysts deactivation. They also cause variations in the relative rates of catalytic reactions such as hydrodesulfurization [2–4].

Asphaltene constituents are very complex molecules believed to consist of associated systems of polynuclear aromatics bearing alkyl side chains; organic molecules containing oxygen, nitrogen, and sulfur as well as vanadium and nickel porphyrins are also present in asphaltenes [4]. The exact molecular structure of asphaltene constituents is not known because of their chemical complexity. Therefore, the

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definition of asphaltenes is based on their solubility. Asphaltenes are, broadly speaking, the fraction of oil that is insoluble in *n*-heptane or *n*-pentane and soluble in benzene/toluene. But the properties of the asphaltene constituents allow reaction progress to be followed on a relative basis thereby offering insights into the chemical events that occur during processing.

Since asphaltenes make catalytic hydrotreating very difficult, it is very important to know more detailed information about the properties and changes of asphaltenes structure during hydrotreating reactions. This kind of information gives more tools to development of upgrading technology and catalysts for higher heteroatoms content feedstocks [5].

The characterization techniques frequently used to determine the properties and molecular structure of the asphaltenes are nuclear magnetic resonance (NMR), elemental analysis (EA), vapor pressure osmometry (VPO), gel permeation chromatography (GPC) or size-exclusion chromatography (SEC), electron spin resonance (ESR), among others. For example, the use of NMR allows for elucidating different structural parameters such as aromaticity factor, average number of carbons per alkyl side chain, percent of substitution of aromatic rings and aromatic ring number. To analyze the molecular weight of asphaltenes, GPC (or SEC) and VPO methods have been employed.

Asaoka et al. concluded that asphaltenes obtained from Boscan crude, Athabasca bitumen and a Khafji vacuum residue presented a particular cracking mechanism. It was clarified that the main reactions were the destruction of asphaltenes aggregates caused by vanadium removal, and depolymerization of asphaltenes molecules by removal of heteroatoms such as sulfur. This conclusion was based on the use of ESR and X-ray characterization techniques [5].

Ancheyta et al. have reported that the asphaltenes precipitated from Maya heavy crude oil exhibit different changes in composition and properties during catalytic hydrotreating. They found that at temperatures lower than 420 °C, only dealkylation of side alkyl chains was observed and at higher temperatures (440 °C) the structural parameters of asphaltenes from hydrotreated products change substantially [3].

In previous papers, we reported deactivation studies during hydrotreating of Maya crude, in which the effect of time-on-stream on product quality was studied at constant [6] and variable [7] reaction temperature.

The present work is the third part of this deactivation study and deals with the characterization of asphaltenes precipitated from hydrotreated products obtained at different temperature and time-on-stream [7].

2. Experimental

2.1. Hydrotreating experiments

Maya heavy crude oil was used as feed for this study and its main properties are summarized in Table 1. The catalytic hydrotreating tests were carried out in a pilot plant described elsewhere [8]. The pilot reactor operates in isothermal mode and fixed bed scheme. The isothermal condition inside the reactor was controlled across three-zone electric furnace, which guarantees the desired temperature inside the catalytic bed during the experiments.

Table 1
Properties of Maya heavy crude oil

API gravity	20.9
Sulfur (wt%)	3.4
Total nitrogen (wppm)	3700
Asphaltenes in *n*-C_7 (wt%)	12.4
Vanadium (wppm)	298.9
Nickel (wppm)	54.8

For all hydrotreating experiments a commercial (NiMo/γ-Al_2O_3) catalyst sample was utilized (specific surface area of 175 m^2/g, mean pore diameter of 127 Å, pore volume of 0.56 cm^3/g). The catalyst is loaded into the reactor and before starting the hydrotreating test, the catalyst is sulfided to transform the metal oxides to metal sulfides. This step is conducted in situ by employing desulfurized naphtha contaminated with 0.8 wt% carbon disulfide. The catalyst sulfiding was done at the following conditions: pressure of 54 kg/cm^2, H_2-to-oil ratio of 2000 ft^3/bbl, liquid hourly space-velocity of 3.2 h^{-1} and temperature of 230 °C, during 18 h.

When sulfiding was completed pressure, H_2-to-oil ratio and liquid hourly space-velocity (LHSV) were adjusted to the start-of-run conditions (70 kg/cm^2, 5000 ft^3/bbl and 1.0 h^{-1}, respectively). The start-of-run temperature was 400 °C and it was increased to 420 °C and finally to 430 °C in order to compensate for catalyst deactivation.

2.2. Precipitation of asphaltenes

Asphaltenes were obtained by *n*-heptane solvent precipitation from Maya crude oil and from hydrotreated products using the traditional ASTM-D-3279 method. The asphaltenes fraction was isolated by addition of a 100:1 (mL of solvent: g of sample) excess of *n*-heptane to the crude oil or HDT products.

Briefly, the asphaltenes were recovered by using a small amount of sample of virgin and hydrotreated crude oil (1 g). Each sample was mixed with 100 mL of *n*-heptane in a 250 mL round-bottom flask with magnetic stirred. The resulting solution was stirred gently for 20 min and heated by using a magnetic stirrer hot plate with reflux (92 °C), and then the mixture was allowed for cooling at room temperature for 1 h. Afterwards, the suspension was filtered employing glass filter pads (Whatman 934-AH, circles of 24 mm diameter). Previously, the glass fiber pads were pretreated in an oven at about 107 °C for 15 min, and allowed for cooling in a desiccator. The precipitate was washed with three volumes of *n*-heptane of about 10 mL each.

Asphaltenes from Maya crude oil required up to 50 mL of *n*-C_7 during washing procedure. The *n*-heptane was used in the washing in order to drain out the precipitate coating the flask wall and to recover all solids obtained on the filter. The filtered asphaltenes were dried in the same oven used for pretreating glass fiber pads step at 107 °C during 20 min. Finally, the sample was weighted for determining asphaltenes content as insolubles in *n*-heptane.

To obtain enough amount of sample for asphaltenes characterization, various precipitations were needed, especially with hydrotreated products where asphaltenes content was very low.

2.3. Characterization of asphaltenes

The different techniques used to characterize Maya heavy crude oil and hydrotreated products are described in previous works [6–8].

The following methods were employed to analyze asphaltenes composition:

(a) Elemental analysis: the composition of the asphaltenes was determined by elemental analysis by combustion at 950 °C in an ELEMENTAR VARIO EL model analyzer. The major constituents observed in this technique were C, H, and N.
(b) Sulfur content was determined by using a LECO SC-444 model analyzer. This element was analyzed in the asphaltenes by combustion at 1350 °C.
(c) Oxygen content was obtained by difference then it is less accurate than the others.
(d) Metal content (Ni, V) of the asphaltenes samples used in this study was determined by atomic absorption in a Perkin-Elmer 5000 model spectrophotometer.

In addition the following techniques were employed to analyze the structural parameters of asphaltenes:

(e) Molecular weight was determined on a Corona Wescan 232A equipment by vapor pressure osmometry using toluene solvent at 25 °C.
(f) Liquid State ^{1}H and ^{13}C nuclear magnetic resonance (NMR). The main molecular parameters from NMR were determined in a JEOL Eclipse 300 spectrometer operating at ^{1}H resonance frequency of 300 MHz and ^{13}C resonance frequency of 75 MHz.

3. Results and discussion

Asphaltenes are the highest molecular weight and most polar fractions found in crude oil. The characteristics of the asphaltenes and the amount of them in oil depend to a greater or lesser extent on the crude source. During refining, asphaltenes are converted to lower boiling products and also to coke. During hydrotreating, the yield of liquid products from asphaltenes is often increased but the coke is laid down on the catalyst thereby shortening catalyst activity and life.

There have been many attempts to define the thermal chemistry of the asphaltene constituents of crude oil [1 and references cited therein] but the chemical behavior of asphaltene constituents during hydrotreating processes is less well understood. The data provided by this work presents indications of asphaltene behavior and chemistry during hydrotreating processes.

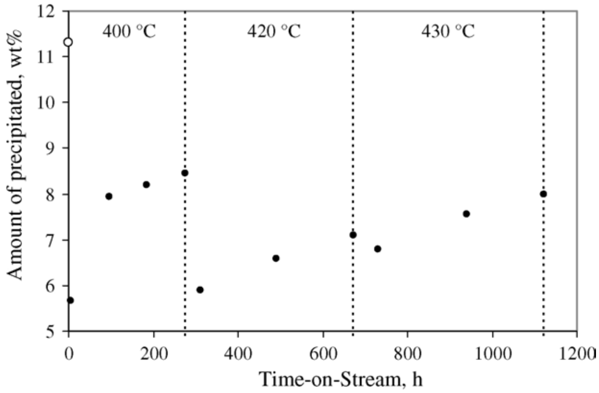

Fig. 1. Amount of precipitated using *n*-heptane solvent vs. time-on-stream: (○) Maya; (●) hydrotreated products.

3.1. Effect of hydrotreating on asphaltene content

During the initial stages of the hydrotreating process (up to 300-h on-stream), there is an increase in the amount of asphaltenes precipitated before a decrease in the amount of precipitate is observed (Fig. 1). This indicates that in the early stages of the process resin constituents are being converted to asphaltene material by aromatization and by some dealkylation. In addition, aromatization and dealkylation of the original asphaltene constituents yields asphaltene products that are of higher polarity and lower molecular weight that their original asphaltene constituents. This produces an overall asphaltene fraction that is more polar material and also of lower molecular weight (Fig. 2).

As the hydrotreating process proceeds and on-stream times in excess of 300 h are logged (Fig. 1), the amount of asphaltenes precipitated decreased due to conversion of the asphaltene constituents to products. At more prolonged time-on-stream there is a steady increase in the yield of the asphaltenes. This is accompanied by a general increase in the molecular weight of the precipitated material.

These observations are in keeping with observations for the thermal reactions of asphaltene constituents in the absence in hydrogen where the initial events are a reduction in the molecular weight of the asphaltenes leading to lower molecular weight by more polar products that are derived from the

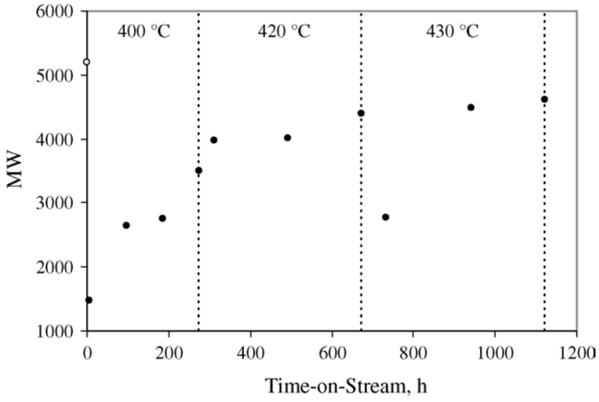

Fig. 2. Molecular weight of asphaltenes: (○) Maya; (●) hydrotreated products.

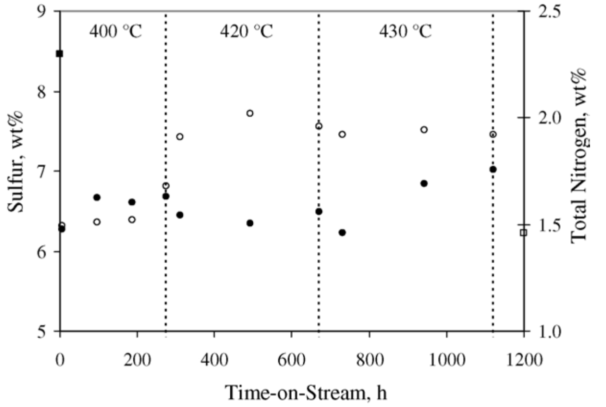

Fig. 3. Sulfur and nitrogen contents in asphaltenes: (■) sulfur (Maya); (□) nitrogen (Maya); (●) sulfur (hydrotreated products); (○) nitrogen (hydrotreated products).

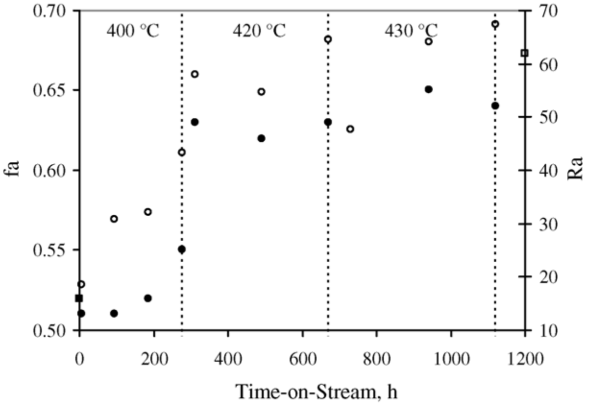

Fig. 5. Aromaticity factor (fa) and number of aromatic carbons of asphaltenes (Ra): (■) fa (Maya); (□) Ra (Maya); (●) fa (hydrotreated products); (○) Ra (hydrotreated products).

asphaltene constituents but are often referred to as *carbenes* and *carboids* [1,4, and references cited therein, 8]. As the reaction progresses, these derived products increase in molecular weight and eventually become insoluble in the reaction medium, deposit on the catalyst, and form coke [9].

3.2. *Effect of hydrotreating on asphaltene properties*

In keeping with the nature of the hydrotreating process, sulfur is reduced with time-on-stream relative to the original asphaltene constituents. However, an apparently slight rise in the sulfur content with on-stream time is consistent with part of the original asphaltene sulfur being concentrated in the carbenes, carboids, and coke [10,11]. There is a similar concentration effect of nitrogen in the reacted products (Fig. 3). This again, is in keeping with part or all of the original asphaltene nitrogen being concentrated in the carbenes, carboids, and coke [10,11].

As predicted from the chemistry of the thermal reactions of the asphaltene constituents [10,11], there is a steady increase in aromaticity (reflected as a decrease in the hydrogen/carbon atomic ratio) (Fig. 4) with time-on-stream. This is due to following reasons [1,4]:

(1) Aromatization of naphthene ring system that are present in asphaltene constituents.
(2) Cyclodehydrogenation of alkyl chains to form other naphthene ring systems.
(3) Dehydrogenation of the new naphthene ring systems to form more aromatic rings.
(4) Dealkylation of aromatic ring systems.

The increase in the aromatization and the increase in the number of aromatic ring systems (reflected by the increase in aromatic carbon atoms) are confirmed by the data shown in Fig. 5.

As the reaction progresses the aromatic carbon atoms in the asphaltene constituents show a general increase and the degree of substitution of the aromatic rings decreases (Fig. 6). Again this is in keeping with the formation of products from the original asphaltene constituents (carbenes, carboid, and eventually coke) that have an increased aromaticity and decreased number of alkyl chains as well as a decrease in the alkyl chain length. Thus, as the reaction progresses with increased on-stream time, *new* asphaltene constituents are formed that, relative to the original asphaltene constituents, the *new* species have increased aromaticity coupled with a lesser

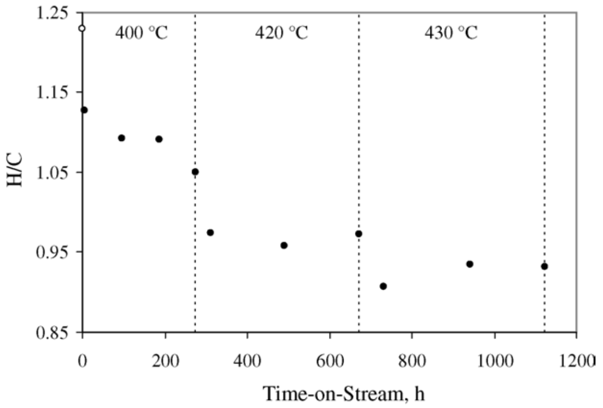

Fig. 4. H/C atomic ratio of asphaltenes: (○) Maya; (●) hydrotreated products.

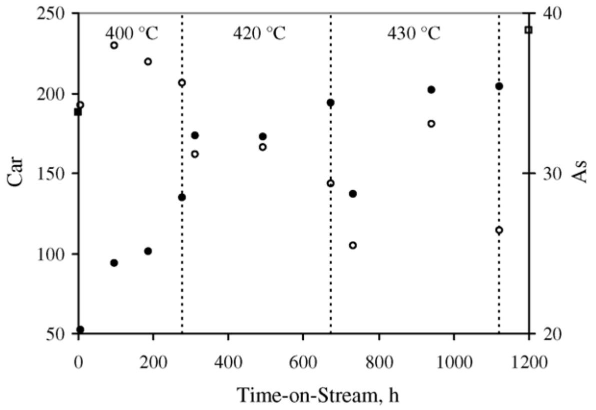

Fig. 6. Number of aromatic carbons (Car) and percent of substitution of aromatic rings of asphaltenes (As): (■) Car (Maya); (□) As (Maya); (●) Car (hydrotreated products); (○) As (hydrotreated products).

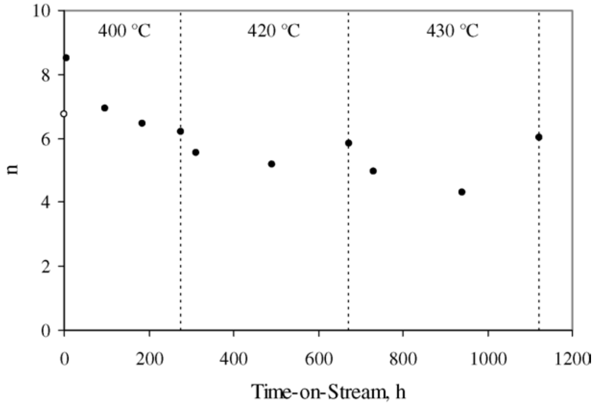

Fig. 7. Average number of carbons per alkyl side chain of asphaltenes (*n*): (○) Maya; (●) hydrotreated products.

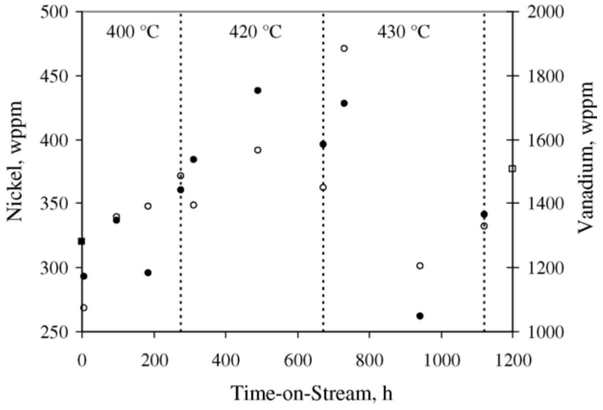

Fig. 8. Nickel and vanadium contents in asphaltenes: (■) Ni (Maya); (□) V (Maya); (●) Ni (hydrotreated products); (○) V (hydrotreated products).

number of alkyl chains that are shorter than the original alkyl chains (Fig. 7).

Finally, a comment must be made on the fate of the nickel and vanadium porphyrins that are separated with asphaltene constituents and measured by the nickel and vanadium content.

As the reaction progresses (Fig. 8), both metals concentrate in the asphaltene fraction, but only to a point (up to 700-h on-stream). After this time, the nickel and vanadium content of the asphaltene fraction is reduced presumably because the nickel and vanadium concentrate on the coke that is laid down on the catalyst.

4. Conclusions

The behavior of the asphaltene constituents during hydrotreating Maya crude oil has been followed by monitoring a series of physical parameters. In keeping with the thermal behavior of the asphaltenes constituents, the observations are:

1. As the hydrotreating process proceeds and on-stream times in excess of 300 h are logged, the amount of asphaltenes precipitated decreased but at more prolonged time-on-stream there is a steady increase in the yield of the asphaltenes. This is accompanied by a general increase in the molecular weight of the precipitated material.
2. Initially, sulfur is reduced with time-on-stream relative to the original asphaltene constituents but as the on-stream time increases the rise in sulfur content is consistent with sulfur species being concentrated in asphaltene constituents giving rise to sulfur in the carbenes, carboids, and coke.
3. There is a similar concentration effect of nitrogen in the reacted products.
4. There is a steady increase in aromaticity (reflected as a decrease in the hydrogen/carbon atomic ratio) with on-stream time that is also reflected by the increase in aromatic carbon atoms.
5. As the reaction progresses the aromatic carbon atoms in the asphaltene constituents show a general increase and the degree of substitution of the aromatic rings decreases.
6. As the on-stream time increases, there is decrease in the length of the alkyl chains within the asphaltene constituents.
7. As the reaction progresses, the nickel and vanadium concentrate in the asphaltene fraction, but only to a point (up to 700-h on-stream). After 700-h on-stream, the nickel and vanadium content of the asphaltene fraction is reduced presumably because the nickel and vanadium concentrate on the coke that is laid down on the catalyst.

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