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Kinetics of asphaltenes conversion during hydrotreating of Maya crude

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Abstract

The kinetics of asphaltene conversion was studied during the hydrotreating of Maya heavy crude oil. Experimental tests were conducted in a pilot plant at the following reaction conditions: total pressure of 70–100 kg/cm^2, liquid hourly space-velocity (LHSV) of 0.33–1.5 h^{-1}, and reaction temperature of 380–420 °C at a constant hydrogen-to-oil ratio of 5000 ft^3/bbl. A commercial NiMo/Al$_2$O$_3$ catalyst was used in all experiments. Asphaltenes were precipitated from Maya crude and from hydrotreated products in a Parr Batch Reactor at 25 kg/cm^2 and 60 °C with *n*-heptane as solvent. Asphaltene hydrocracking data were used to estimate reaction orders and activation energy using a power-law model, and the average absolute error between experimental and calculated concentrations of asphaltenes was found to be less than 5%.

Keywords: Asphaltenes hydrocracking; Heavy oil; Kinetics

1. Introduction

Asphaltenes are well known to be coke precursors, as they are the most complex molecules present in petroleum and consist of condensed polynuclear aromatics carrying alkyl, cycloalkyl, and heteroatom constituents [1,2].

Asphaltenes are a solubility class of compounds that precipitate from oil when they are treated with a selected solvent. Asphaltenes are thought to be a complex mixture of high-boiling, polar, aromatic, high-molecular weight compounds containing metals, such as nickel and vanadium [3].

Asphaltenes are mainly responsible for catalyst deactivation during catalytic hydrotreating/hydrocracking of heavy distillates or residues due to their tendency to form coke. The low asphaltene conversion to non-asphaltenic molecules during hydrotreating enables the efficient use of residues to produce lighter hydrocarbons. Consequently, technologies for upgrading heavy residues will be influenced by how asphaltenes are treated [4].

In the particular case of hydrotreating (HDT) of heavy oils, asphaltenes affect the overall rate of HDT reactions; they precipitate on the catalyst surface and block the pore mouth, acting as a coke precursor which leads to the deactivation of the catalyst [5].

Because there are too many reactions involving both cracking and hydrogenation taking place during upgrading processes, it is difficult to give an overall description of them. During catalytic conversion, the reactor's temperature is increased and thermal cracking reactions become more pronounced. The high temperature toward end of run can lead to formation of insoluble material (sludge), which may cause catalyst deactivation. Hydrotreating can cause the asphaltenes to become less soluble, either by removing their aliphatic side chains or by hydrogenating the oil. The result is that it becomes a poor solvent for asphaltenes [6].

Asphaltene conversion mechanisms during hydrotreating are complex because different physical and chemical processes are present. Most of the studies in asphaltene hydrocracking have been focused on thermal decomposition, which involves several simultaneous reactions [7].

The most important reactions taking place in the thermal hydrocracking of asphaltenes are: (a) breakage of C–C and C–H bonds; (b) breakage of bonds with metals and heteroatoms; (c) aromatization; (d) alkylation; (e) condensation; and (f) hydrogenation–dehydrogenation. Recently, studies on asphaltene hydrocracking of various petroleum residues have indicated that during hydrocracking the hydrogenation and

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dealkylation of condensed polyaromatic rings are almost entirely suppressed [8].

Seki and Kumata [9] found that during hydrotreating shortening of alkyl side chains occurs. Nitrogen removal is considered to be hard to achieve, mainly because most of the nitrogen is contained in heteroaromatic rings which require hydrogenation prior to nitrogen removal. Hydrogenation of a nitrogen-containing aromatic ring is particularly difficult due to steric limitations. In addition, hydrogenation can yield condensed products which are harder to denitrify [10].

Callejas and Martínez [3] studied the intrinsic catalytic conversion kinetics of the asphaltenic fraction from a Maya residue which was carried out at temperatures between 375 and 415 °C and hydrogen pressure of 12.5 MPa in a perfectly mixed reactor in continuous operation. Asphaltenic fraction concentration data fit half-order removal kinetics, and the activation energy was 41.5 kcal/mol. Schueker [11] obtained a similar activation energy value by conducting some isothermal experiments to evaluate the asphaltene decomposition kinetics from the Arabian heavy vacuum residuum.

Philippopoulos and Papayannakos [12] used a commercial $CoMo/Al_2O_3$ catalyst (0.34 mm particle diameter) to obtain kinetic data of hydrocracking by using an integral trickle-bed reactor and a Greek atmospheric residue as feedstock at 5 MPa and 350–430 °C. Their results indicated that the power-law kinetic equation can describe in good manner the intrinsic rate equations for asphaltene hydrocracking, with a reaction order of 2 and activation energy of 27.8 kcal/mol.

The knowledge of kinetics as well as the influence of catalyst properties on diffusion limitations, together with other concepts (mass and heat transfer, thermodynamics, transport phenomena, etc.) permits the design of reactors not only for asphaltene hydrocracking but also for any catalytic reaction in which heavy petroleum fractions are involved. Kinetics also helps to obtain a better selection of suitable catalysts. Furthermore, catalyst selectivity does not only depend on the kinetics of each reaction, but also on the relative diffusivities of the reacting molecules, when diffusion limitations exist.

The main objective of this work is to present experimental information about hydrotreating of Maya crude to determine the kinetics of asphaltene hydrocracking at different reaction conditions using an integral trickle-bed reactor.

2. The kinetic model

To develop the kinetic model, the following assumptions were taken into account:

- Fluid velocities do not change along the reactor.
- Gas and liquid velocities are constant across the reactor.
- Radial and axial concentration gradients are neglected.
- The reactor is operated in a steady state.
- The reactor is kept at constant pressure and temperature.
- Chemical reactions only take place at the catalyst.

Asphaltene kinetics is proposed to be the following power-law model:

$$-\frac{dC_{\mathrm{Asph}}}{d(1/\mathrm{LHSV})} = kC_{\mathrm{Asph}}^{\alpha}C_{\mathrm{Hydrogen}}^{\beta} \tag{1}$$

where C_{Asph} is the concentration of asphaltenes and C_{Hydrogen}, the concentration of hydrogen which is in gas–liquid equilibrium; LHSV, the space-velocity; k, the intrinsic reaction rate coefficient; and α and β, the reaction orders for asphaltenes and hydrogen, respectively. Since the reactor operates under integral regime, Eq. (1) is integrated as follows:

$$\frac{C_{\mathrm{Asph}}^{1-\alpha} - C_{\mathrm{Asph_0}}^{1-\alpha}}{\alpha - 1} = \frac{kC_{\mathrm{Hydrogen}}^{\beta}}{\mathrm{LHSV}} \tag{2}$$

where C_{Aspho} corresponds to the initial concentration of asphaltenes. C_{Hydrogen} is calculated by using Henry's Law, which describes the gas–liquid equilibrium. The Henry coefficient H can be obtained from the solubility coefficient:

$$H = \frac{\upsilon_{\mathrm{N}}}{\lambda\rho_{\mathrm{L}}} \tag{3}$$

where υ_{N} is the molar gas volume at standard conditions and ρ_{L}, the density of the liquid under process conditions. The correlation used for calculating the hydrogen solubility in hydrocarbon mixtures (λ) is [13]:

$$\lambda = -0.559729 - 0.42947\times10^{-3}T + \frac{3.07539\times10^{-3}T}{\rho_{20\,^{\circ}\mathrm{C}}} + 1.94593\times10^{-6}T^2 + \frac{0.835783}{\rho_{20\,^{\circ}\mathrm{C}}^2} \tag{4}$$

where T is the temperature in Celsius degrees; $\rho_{20\,^{\circ}\mathrm{C}}$, the density at 20 °C in g/cm^3; and the hydrogen solubility is in $(NL_{H_2})/(kg_{oil}\ MPa)$. In Eq. (3), ρ_{L} is calculated as follows:

$$\rho_{\mathrm{L}} = \rho_{\mathrm{O}} + \Delta\rho_{\mathrm{P}} - \Delta\rho_{\mathrm{T}} \tag{5}$$

$$\Delta\rho_{\mathrm{P}} = \left[0.167 + 16.181\times10^{-0.0425\rho_{\mathrm{O}}}\right]\left[\frac{P}{1000}\right] - 0.01\left[0.299 + 263\times10^{-0.0603\rho_{\mathrm{O}}}\right]\left[\frac{P}{1000}\right]^2 \tag{6}$$

$$\Delta\rho_{\mathrm{T}} = \left[0.0133 + 152.4(\rho_{\mathrm{O}} + \Delta\rho_{\mathrm{P}})^{-2.45}\right][T - 520] - \left[8.1\times10^{-6} - 0.0622\times10^{-0.764(\rho_{\mathrm{O}}+\Delta\rho_{\mathrm{P}})}\right][T - 520]^2 \tag{7}$$

where ρ_{O} is the density at standard conditions (15.6 °C and 101.3 kPa) in lb/ft^3; P, the pressure in psia; and T, the temperature in Rankine degrees. Finally, C_{Hydrogen} is determined as follows:

$$C_{\mathrm{Hydrogen}} = \frac{P}{H} \tag{8}$$

For estimating the best values of kinetic parameters, the modified Levenberg–Marquardt's minimization method (DRNLIN routine of the IMSL 3.0 package) was used in order to obtain simultaneously the reaction orders, the activation energy, and the pre-exponential factor. The objective function (the sum of square errors between experimental and calculated asphaltene concentrations) used for minimization process was obtained from Eq. (2):

$$\mathrm{SSE} = \left| C_{\mathrm{Asph}}^{\mathrm{exp}} - C_{\mathrm{Asph}}^{\mathrm{calc}} \right|^2 = \left\{ C_{\mathrm{Asph}}^{\mathrm{exp}} - \left[\frac{A\mathrm{e}^{-E_{\mathrm{A}}/RT} C_{\mathrm{Hydrogen}}^{\beta} (\alpha + 1)}{\mathrm{LHSV}} + C_{\mathrm{Asph_0}}^{1-\alpha} \right]^{1/1-\alpha} \right\}^2 \qquad (9)$$

3. Experimental

3.1. Hydrotreating reactions

Maya crude oil was used as feedstock (20.9 API gravity, 3.44 wt% sulfur, 12.4 wt% asphaltenes). Catalytic hydrotreating of Maya crude oil was carried out in a pilot plant described elsewhere [14]. The central part of the pilot plant is an isothermal fixed-bed reactor. The reactor temperature was maintained at the desired level by using a three-zone electric furnace, which provides an isothermal temperature along the catalytic bed section. Catalytic bed temperature was measured during the experiments by three thermocouples located in a thermowell mounted at the center of the reactor.

The catalyst employed for hydrotreating reactions was a NiMo/Al_2O_3 commercial sample (175 m^2/g specific surface area, 0.56 cm^3/g pore volume, and 127 Å mean pore diameter). The catalyst was loaded into the reactor in the oxide form and it is sulfided in situ by using straight-run gas oil contaminated with dimethyl disulfide (1.0 wt% sulfur) at the conditions and procedure reported elsewhere [15].

Different tests were conducted in order to determine the magnitude and diminish the diffusion gradients. To do this, the catalyst was first crushed from its commercial size, and three different catalyst sizes were prepared: (a) 2.54 mm (commercial size); (b) 0.84 mm (mesh 20); and (c) 0.25 mm (mesh 60). Also, different feed flowrates were tested to examine the effect of mass velocity on conversion. Both internal and external diffusion limitations tests were evaluated at two different space-velocities, 0.33 and 1.0 h^{-1}, and temperatures of 360 and 400 °C.

The HDT experiments were done at the following reaction conditions: H_2-to-oil ratio of 5000 ft^3/bbl, total pressure of 70–100 kg/cm^2, reaction temperature of 380–420 °C, and liquid hourly space-velocity (LHSV) of 0.33–1.5 h^{-1}.

3.2. Asphaltene precipitation

Asphaltenes were precipitated from the feed and hydrotreated products by using a Parr Batch Reactor model 4842 and *n*-heptane as solvent. The solvent-to-oil ratio was 5:1 (v/w). The batch reactor was pressurized with N_2 as inert gas at 25 kg/cm^2, 60 °C, and a 750-rpm stirring rate during 0.5 h. After that, its content was settled for 0.5 h at room conditions, and finally, asphaltenes were recovered by filtering using a 1.6 μm pore diameter glass fiber paper. Asphaltenes were collected and washed with a sufficient amount of *n*-heptane to remove resins until the filtered solvent was colorless. Finally, the samples were dried at 105 °C for 0.5 h. The content of asphaltenes in the oil samples and conversion were determined as:

$$\text{Asphaltenes content (wt\%)} = \frac{\text{asphaltenes obtained (g)}}{\text{crude oil (g)}} \times 100 \qquad (10)$$

$$\text{Asphaltenes conversion (\%)} = \frac{\text{asphaltenes in feed} - \text{asphaltenes in product}}{\text{asphaltenes in feed}} \times 100 \qquad (11)$$

4. Results and discussion

4.1. Diffusion limitations

To operate under kinetic regime, it is necessary to minimize both internal and external diffusion limitations [16]. In order to diminish internal diffusion limitations, the catalyst was crushed to obtain different particle sizes. Fig. 1 shows how conversion changes as catalyst particle size is reduced. It is clearly seen that, compared with crushed catalysts, internal diffusion gradients are higher with the commercial catalyst size. At values of d*p* = 0.84 mm and lower (1/d*p* = 1.19 mm^{-1} and higher), asphaltene conversion remains constant, which means that diffusion limitations can be neglected by using a 0.84 mm diameter particle size. This behavior is observed at all reaction conditions. At the most severe LHSV and temperature (0.33 h^{-1} and 420 °C), higher conversions are obtained and the effect of particle size is not as clear as in the case of lower reaction severity. These results are in good agreement with others reported in batch reactor studies with lighter feeds, in which an effectiveness factor of 0.40–0.55 was obtained for commercial catalysts [17]. In order to assure that the reaction is within kinetic regime, in this work we used 0.25 mm diameter particles (mesh 60, 1/d*p* = 4 mm^{-1}).

To evaluate external diffusion limitations, the flowrate of feed was varied as well as the volume of the catalytic bed,

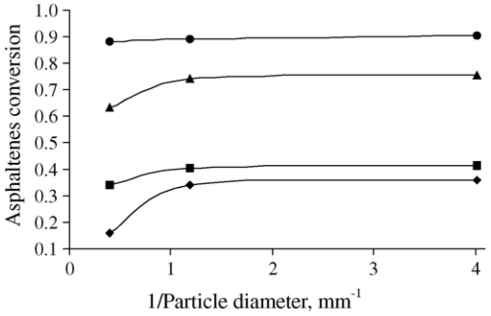

Fig. 1. Evaluation of internal diffusion limitations: (◆) 360 °C, LHSV = 1.0; (■) 360 °C, LHSV = 0.33; (▲) 420 °C, LHSV = 1.0; (●) 420 °C, LHSV = 0.33.

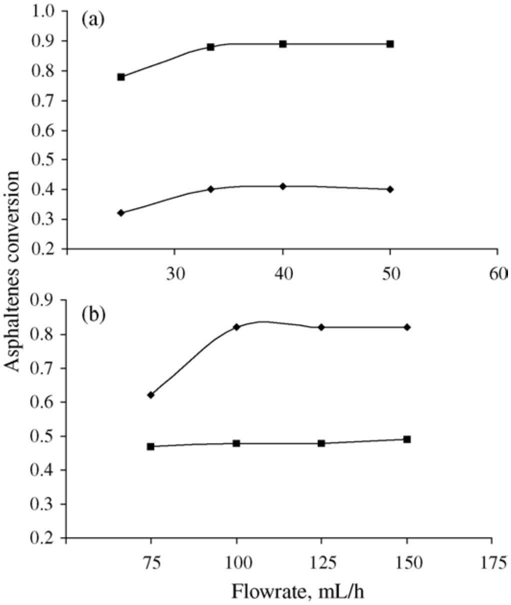

Fig. 2. Evaluation of external diffusion limitations: (a) (◆) 360 °C, LHSV = 0.33; (■) 420 °C, LHSV = 0.33. (b) (◆) 360 °C, LHSV = 1.0; (■) 420 °C, LHSV = 1.0.

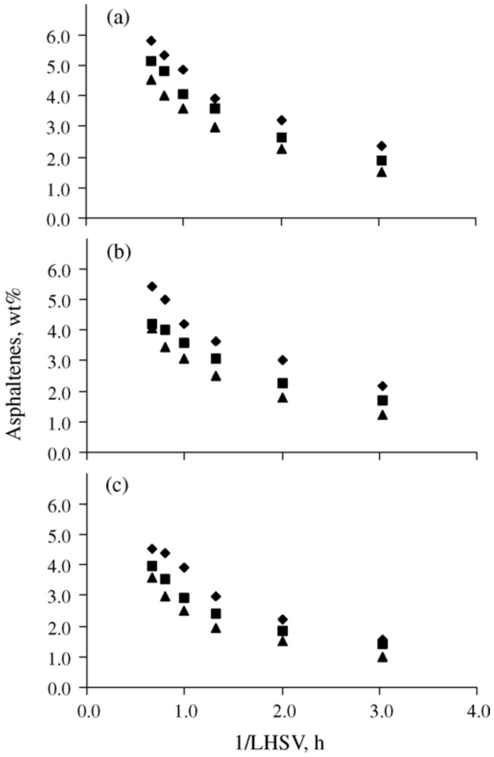

Fig. 3. Variation of asphaltene content in hydrotreated product as function of reaction conditions: (a) 70 kg/cm^2. (b) 85 kg/cm^2. (c) 100 kg/cm^2: (◆) 380 °C; (■) 400 °C; (▲) 420 °C.

keeping constant the space-velocity, and the asphaltene conversion was measured. Fig. 2 shows the asphaltene conversion obtained at two different space-velocities and temperatures. In Fig. 2a, space-velocity is lower than in the case of Fig. 2b, so that higher conversions are reached. Fig. 2a shows that asphaltene conversion is constant for a flow of Maya crude higher than 33 mL h^{-1}, which corresponds to 100 mL of catalytic bed for LHSV = 0.33 h^{-1}. This behavior is similar for both temperatures, 360 and 420 °C. In the other case (Fig. 2b), asphaltene conversion is constant from 100 mL h^{-1}, also corresponding to 100 mL of catalytic bed for LHSV = 1.0 h^{-1}. Based on these results, the minimum liquid flowrate that we considered for this work was 100 mL h^{-1} in order to minimize external diffusion limitations and operate under kinetic regime. These results are also in good agreement with others found with lighter feed in the same pilot reactor [18].

4.2. Hydrotreating experiments

Once both internal and external mass transfer gradients can be neglected, the reaction was carried out at different conditions. The effect of reaction conditions on asphaltene concentration in the hydrotreated products is shown in Fig. 3. The most severe reaction conditions yield the lower asphaltene content. The expected behavior is observed: the higher the temperature and pressure, and the lower the space-velocity are, the lower the asphaltene concentration. The most significant effect is observed at 420 °C and 100 kg/cm^2, since at these conditions the asphaltene content is the lowest.

It is important to highlight that the change in conversions is not proportional to every change in temperature. In other words, if the temperature is increased from 380 to 400 °C, asphaltene conversion increases at different rates than with other increments of temperature, which indicates that asphaltene hydrocracking is higher at an elevated temperature. At a low temperature, only dealkylation of side alkyl chains is observed, and at a higher temperature, asphaltene molecule hydrocracking is prominent. The hydrotreating temperature where the asphaltenes' structure changes also depends on other reaction conditions, such as hydrogen pressure and space-velocity.

It is also noted that at moderate pressure, hydrocracking is more pronounced at temperatures higher than 400 °C, whereas at high pressure, the temperature where hydrocracking is more severe is reduced. That is why different kinetic regimes have been proposed when developing kinetic models for hydrocracking of heavy oils [19,20].

4.3. Estimation of kinetic parameters

Experimental data of asphaltene content were used to estimate kinetic parameters by using the power-law model and the Arrhenius Equation. The best set of kinetic parameters was determined by minimizing the sum of square errors between experimental and calculated concentrations of asphaltenes (Eq. (9)) using Marquardt's algorithm. The kinetic model obtained by this means is:

$$(-r_{\mathrm{Asph}}) = 5.65 \times 10^{5} \mathrm{e}^{-10350/RT} C_{\mathrm{Asph}}^{2.1} C_{\mathrm{Hydrogen}}^{1.28} \qquad (12)$$

A comparison between calculated and experimental concentrations of asphaltenes is shown in Fig. 4. A very good correspondence was obtained between both concentrations with average absolute error less than 5%. Maximum deviation

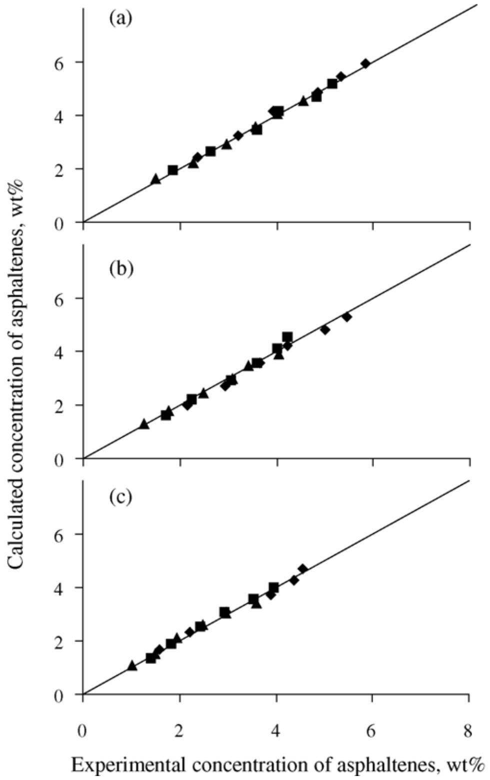

Fig. 4. Comparison between experimental and calculated concentrations of asphaltenes: (a) 70 kg/cm^2. (b) 85 kg/cm^2. (c) 100 kg/cm^2: (◆) 380 °C; (■) 400 °C; (▲) 420 °C.

between calculated and experimental asphaltene concentrations appears at the lowest space-velocity and highest temperature, which may be due to the change in hydrotreating selectivity from being hydrogenation-dominated to hydrocracking-dominated. This has been previously reported with asphaltene characterization studies [21].

The reaction order of hydrogen is more or less half of that for asphaltenes. This is a common behavior when estimating the reaction order of hydrotreating reactions; e.g., for hydrodesulfurization of vacuum gas oil, reaction orders for sulfur and hydrogen have been reported to be 1 and 0.45, respectively [13].

The activation energy value is low (10.35 kcal/mol). The possible explanations for this are the complexity of the asphaltenes' structure and the different path reactions that they can follow since Eq. (1) is averaging all these reactions and some of them can be more diffusion limited than others. In addition, Maya crude asphaltenes possess high molecular weight [22], and they tend to diminish the value of this parameter as severity of the reaction is increased. The structural parameters of asphaltenes also change significantly. Therefore, the nature of asphaltenes evidently changes, confirming the explanation given earlier.

Finally, it is important to mention that developing simple kinetic models (e.g., power-law model) for complex catalytic reactions is a common approach which can give basic information for catalyst screening and reactor design. More sophisticated and detailed kinetic models are being developed for various research groups, but they also require more detailed experimental data.

5. Conclusions

Catalytic hydrotreating of Maya crude experiments were conducted at different reaction conditions, showing the asphaltene content in hydrotreated products diminishing as pressure and temperature were increased and liquid hourly space-velocity was decreased.

The experimental data of asphaltene hydrocracking were described well by a power-law model. The reaction orders of asphaltenes and hydrogen were 2.1 and 1.28, respectively. The activation energy was 10.35 kcal/mol. The low value of activation energy was attributed to the complexity of the asphaltenes and to the change in selectivity at the reaction conditions used in this work.

Low asphaltene content in the hydrotreated products could indicate a higher hydrocracking of asphaltenes, but more characterization is needed in order to get more information about how the asphaltene structure is modified after hydrotreating.

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