Kinetics of asphaltene hydrocracking in a batch reactor

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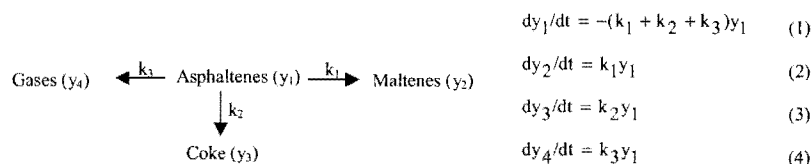México. Fax: (+52 55) 9175 8418. [*]E-mail: jancheyt@imp.mx*

Abstract
Catalytic hydrocracking of hexadecane dissolved Maya crude asphaltenes was carried out in a
batch reactor at 380, 400 and 410°C with varying the reaction time from 0 to 60 min over an
alumina-based NiMo commercial catalyst at hydrogen pressure of 2 MPa. Reaction products
were separated into four fractions (asphaltenes, maltenes, coke and gases) based on their
solubility properties. A four-lump reaction scheme comprising irreversible parallel reactions
fitted well the experimental data.

1. Introduction
Asphaltenes are complex molecules present in heavy crude and residue which are constituted by
aromatic rings having alkyl chains and naphthenes linked to the core, turning the asphaltenes into
the most difficult fraction to be processed when upgrading heavy crudes. During hydrotreating of
heavy crude, asphaltenes are responsible for reducing the reaction rate of HDS, tend to form coke
which deactivates the catalyst and are the main cause of sludge and sediment formation [1-3].
Asphaltenes suffer a number of reactions which transforms their chemical structure, such as the
cleavage of alkyl chains. Free radicals are involved in the conversion of asphaltenes especially by
attacking alkyl chains; however, when a catalyst is present, the yield toward maltenes is
improved by means of hydrogenation of oil using the hydrogen in a better way and reducing the
formation of free radicals which limits coke formation [4]. In this work hydrocracking of
asphaltenes was studied in a batch reactor, and hexadecane was used for dispersing asphaltenes in
the presence of a catalyst and hydrogen pressure.

2. Experimental
Asphaltenes, previously precipitated from Maya crude and purified by Soxhlet washing, were
used as reactant. Hexadecane was employed for maintaining asphaltenes dispersed inside the
batch reactor and an *ex situ* sulfided alumina-supported NiMo commercial catalyst was utilized.
The ratios of hexadecane-to-asphaltenes and asphaltenes-to-catalyst were kept constant at 40
(wt/wt) and 5 (wt/wt), respectively. Reaction began when temperature of 380, 400 and 420°C at 2
MPa was reached. Reaction time was from 0 to 60 min. During heating of reactor up to the
desired temperature, some degree of asphaltenes conversion was achieved and said conversion
was considered in the kinetic modeling. After reaction, the reactor content was poured and
separated into four components based on their solubility properties. Gases were analyzed by gas
chromatography containing mainly H_2S and unreacted H_2. Unreacted asphaltenes were defined as
toluene-solubles and C_7-insolubles; maltenes as C_7-solubles and coke as toluene-insolubles. A
four-lump kinetic model was used for fitting the experimental data by solving simultaneously
Equations (1) to (4) as shown below.

$$dy_1/dt = -(k_1 + k_2 + k_3)y_1 \quad (1)$$

$$\text{Gases }(y_4) \xleftarrow{\ k_3\ } \text{Asphaltenes }(y_1) \xrightarrow{\ k_1\ } \text{Maltenes }(y_2)$$

$$dy_2/dt = k_1 y_1 \quad (2)$$

$$\Big\downarrow k_2$$

$$dy_3/dt = k_2 y_1 \quad (3)$$

$$\text{Coke }(y_3)$$

$$dy_4/dt = k_3 y_1 \quad (4)$$

3. Results and discussion

Some experimental results are shown in Figure 1. In all cases, it was observed that the amount of asphaltenes diminished as reaction time increased. At the same time, coke and gases yields are increased. Coke reaches its higher yield at the highest temperature because of faster decomposition of asphaltenes whereas the amount of maltenes increased slightly. Not only higher temperature increases the amount of coke but also the influence of solvent plays a key role. In this case, hexadecane is a poor hydrogen donor and favors condensation reactions. Gases only increased steadily with increasing temperature and reaction time. GC analysis indicated the presence of unreacted H_2 and H_2S. H_2S is originated from thermally labile bonds and is formed from thiophenic sulfur present in asphaltenes.
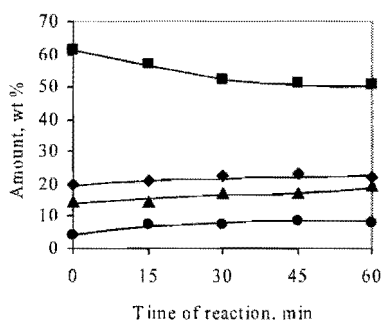

Figure 1. Distribution of products at 380°C
(■) Asphaltenes; (♦) Maltenes; (▲) Coke; (●) Gases

Figure 2. Calculated *versus* experimental values of each fraction at different temperatures

Table 1. Kinetic constants of the 4-lump model

Parameter	k_1	k_2	k_3
A (min⁻¹)	8.15×10^3	5.86×10^9	8.17×10^3
E_A (kcal/mol)	19.6	37.5	21.0

Experimental data were well fitted to the 4-lump model and kinetic parameters are shown in Table 1. It is observed that maltenes and gases (k_1 and k_3) are formed almost at the same reaction rate. Nevertheless coke formation rate (k_2) was almost twice. The high value of the activation energy of coke formation is an indication that reaction proceeded by free radicals originated by the cleavage of alkyl chains. The remaining asphaltenes are difficult to hydrogenate and the preferred pathway they follow is the condensation into larger molecules originating the formation of coke. Predicted values of each fraction and experimental values are compared in Figure 2. A good agreement between both values is observed. Correlation coefficient (r^2) was 0.978 and the residual values were randomly distributed.

In conclusion, the high activation energy and amount of coke are the result of a free radicals mechanism. For improving the hydrogenation of asphaltenes, it is desirable the use of a hydrogen donor solvent such as tetralin or 1-methyl-naphthalene. The presence of a good solvent along with higher hydrogen pressure and a catalyst would be capable of converting asphaltenes into maltenes with minimum amount of coke and gases.

References

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