



Modeling catalyst deactivation during hydrocracking of atmospheric residue by using the continuous kinetic lumping model



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ABSTRACT

The kinetics of the hydrocracking of residue and catalyst deactivation were studied by using the continuous kinetic lumping approach. Catalyst activity decay was represented with an empirical equation. Experimental information was obtained in a continuous stirred tank reactor at liquid-hourly space velocity of 0.5 h^{-1} , three reactor temperatures (380, 400 and $410 \text{ }^\circ\text{C}$), 9.8 MPa of pressure, 5000 ft^3/bbl of H_2 -to-oil ratio and 200 h of time on stream. The parameters of the continuous kinetic model showed dependence with time on stream and temperature. Due to the marked changes on catalyst activity during time on stream, it was proposed that some pore blockage occurs apart from catalyst deactivation by site coverage.

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1. Introduction

The processing of non-conventional crude oils is increasing, and this trend will continue in the next years. Among all the commercially available technologies hydrotreatment and hydrocracking are excellent options to upgrade the heavy petroleum [1,2]. Because heavy oil and residua contain significant amounts of asphaltenes, the main problems associated with their processing are the excessive coke deposit on catalyst at the first hours of time on stream (TOS) and the difficulty for contact of these complex molecules with active sites due to mass transfer limitations [3], which in turn provokes the catalytic deactivation. For longer TOS, metal-bearing species are the main cause of permanent deactivation of catalyst [4–7].

The deposits of coke and metals cause loss of catalytic surface area and decrease of mean pore diameter and volume [8,9]. The effective diffusivity shows stronger correlation with coke content because the more the deposited coke, the more difficult the access to pores in which the chemical transformation is carried out. As a consequence, a decrease in effectiveness factor is observed [10].

Modeling these changes and other aspects of catalyst deactivation during heavy oil processing is not an easy task. Different approaches to model the deactivation in different reactions have appeared in the literature. For instance, Moustafa and Froment [11] have related the

loss of catalyst activity to coke deposition on catalyst surface, while others have used the time on stream [12,13]. Recently Jiménez-García et al. [14] have correlated the catalytic deactivation with the effectiveness factor in FCC process. They argue that as coke is deposited on catalyst surface, the smallest molecules present in the feed exhibit the easiest access to catalytic pores, and the contrary behavior is expected for larger ones. That behavior changes as catalyst pore diameter is reduced by effect of coke deposition. Galiasso [15,16] has also found that even for light cycle oil (LCO), rapid loss of activity is observed during hydrocracking, and this change on activity was related to loss of weak acid sites. Similar observations were pointed out by Castaño et al. [17] and Gutiérrez et al. [18], who confirm that some plugging of small catalytic pores together with loss of acid sites are responsible for catalyst deactivation due to the hydrocracking of LCO.

Beckman and Froment [19] have developed deactivation models for coke deposition on catalyst surface that proceeds following two mechanisms: site coverage and pore blockage, both limiting the diffusion of reactants to enter into the pore structure. Also, experimental information confirms the fact that under the hydrocracking of liquid hydrocarbons, both site coverage and pore blockage are responsible for loss of activity during the initial deactivation period [20].

Another important feature associated with the hydrocracking of heavy oils is the kinetic approach. On the one hand, very simple kinetics is used when modeling catalyst deactivation even if the employed feed is complex in nature, and on the other hand, if complex kinetic approach is used, no deactivation effects are taken into account. In previous publications, it has been demonstrated that the hydrocracking of crude oils and residua can be properly modeled by the continuous kinetic lumping approach [21,22]. The main attractiveness of such a model is the use of

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fixed reaction order and the accurate predictions of the entire boiling point curve with few parameters. Also, because the use of modern chromatographic apparatus for simulated distillation allows for obtaining almost the entire distillation curve of hydrocracked products, it is desirable to use a kinetic model compatible with those experimental results.

The use of continuous lumping approach for the hydrocracking of heavy oils is relatively new, and up until now, it has been applied to experiments collected at steady-state conditions, but nothing has been reported for its application to the hydrocracking of heavy oil experiments affected by catalyst deactivation. It is then the aim of the present contribution to use the continuous lumping to represent the reaction kinetics and catalyst deactivation of the hydrocracking of heavy oil at moderate reaction conditions.

2. The models

2.1. Consideration to develop the model

Relating catalyst deactivation with coke formation requires considerable amount of long-term experiments to measure the amount of coke deposited on catalyst to collect representative samples for characterization than in case of relating deactivation phenomenon with time on stream. Although the first approach is a rational way of modeling the catalyst deactivation high cost of experiments limits their use apart from other features of that approach, such as the ex situ analysis of coke content on catalyst that could be different than that deposited at reaction conditions.

The simplest way to take into account the loss of catalyst activity is by means of averaged power deactivation function that relates activity coefficient with time on stream. It is assumed generally that a simple function allows for modeling the deactivation by coke during the first hours of TOS without distinction between sites coverage and pore blockage. Another assumption frequently done is that the final activity reduces to zero, which is not the case for deactivation by coke in hydrocracking reactions according experimental evidence [17,18,20,23,24].

2.2. Kinetic model

The rate of reaction for species with reactivity “ k ” can be written as [25]

$$-r_A = k \cdot c(k, \tau) - \int_k^{k_{\max}} [p(k, x) \cdot x \cdot c(x, \tau) \cdot D(x)] dx \quad (1)$$

The first term of the right-hand side (rhs) of Eq. (1) allows for representing the rate of the hydrocracking of species with reactivity “ k ”, whereas the second term accounts for the species that being longer produces the species in question by hydrocracking. τ is the reciprocal of space velocity.

The yield species distribution ($p(k, K)$) is given by

$$p(k, K) = \frac{1}{S_0 \sqrt{2\pi}} \left[e^{-\left\{ \frac{(k/K)^3 - 0.5}{a_1} \right\}^2} - A + B \right] \quad (2)$$

where A and B are given by the following expressions:

$$A = e^{-(0.5/a_1)^2} \quad (3)$$

$$B = \delta [1 - (k/K)] \quad (4)$$

and S_0 is calculated as

$$S_0 = \int_0^K \frac{1}{\sqrt{2\pi}} \left[e^{-\left\{ \frac{(k/K)^3 - 0.5}{a_1} \right\}^2} - A + B \right] \cdot D(x) \cdot dx \quad (5)$$

Eq. (2) accounts for the amount of formation of species with reactivity k from species of reactivity K (being K greater than k).

Other features related to $p(k, K)$ are [25]:

Table 1

Complementary equations for the hydrocracking kinetic model.

$$\theta = \frac{TBP - TBP(I)}{TBP(N) - TBP(I)} \quad (8)$$

$$\frac{k_{\max}}{k_{\max}} = \theta^{1/\alpha} \quad (9)$$

$$S_0 = \int_0^K \frac{1}{\sqrt{2\pi}} \left[e^{-\left\{ \frac{(x/K)^3 - 0.5}{a_1} \right\}^2} - A + B \right] \cdot D(x) \cdot dx \quad (10)$$

$$C_{1,2} = \int_{k_1}^{k_2} c(x, \tau) \cdot D(x) \cdot dx \quad (11)$$

$$\frac{1}{N} \int_0^{k_{\max}} D(x) \cdot dx = 1 \quad (12)$$

- equal to zero for $k = K$.
- satisfies the mass balance criterion:

$$\int_0^K p(x, K) D(x) dx = 1 \quad (6)$$

- a positive function between the ranges of validity of model parameters.
- a yield distribution biased toward the reactivity of crackate K .
- $p(k, K) = 0$ if $k > K$, which means that dimerization effects are not significant.

a_0 and a_1 are model parameters that determine the position of peak on the interval $k \in (0, K)$ and δ is a small finite value that warranties that $p(k, K)$ takes a finite value when $k = 0$. All these model parameters are dependent on feed impurities (sulfur, metals content, heaviness of feed, etc.), catalyst activity and operating conditions.

The species-type distribution or change factor from discrete to continuous approach is given by the following relationship:

$$D(k) = \frac{N\alpha}{k^{\alpha} \frac{\delta}{m \Delta x}} k^{\alpha-1} \quad (7)$$

Such a relationship permits to keep the invariance during transforming discrete mixture to a continuous one. Physically, $D(k)$ expresses the interdependence between the reactivity of the various components [26]. Table 1 reports complementary equations of the kinetic model. The description of each variable is given in the Nomenclature section. In the continuous kinetic model, α , a_0 , a_1 , δ and k_{\max} are the model parameters.

2.3. Reactor model

The experiments were carried out in a continuous stirred tank reactor (CSTR). A pseudohomogeneous model is used to represent the reactor. Proper care has been taken to minimize the fluid-to-particle mass transfer resistance. Thus, kinetic information is affected only by intra-particle mass transfer resistance. Based on this, the CSTR model is used as follows [27]:

$$\tau = \frac{C_{A0} - C_{A1}}{-r_A|_{C_A=C_{A1}}} \quad (13)$$

Substituting Eq. (1) in Eq. (13),

$$\tau = \frac{c(k, 0) - c(k, \tau)}{k \cdot c(k, \tau) - \int k k_{\max} [p(k, x) \cdot x \cdot c(x, \tau) \cdot D(x)] dx} \quad (14)$$

Solving for hydrocracking product concentration, one arrives at [28,29]

$$c(k, \tau) = \frac{c(k, 0) + \tau \int k k_{\max} [p(k, x) \cdot x \cdot c(x, \tau) \cdot D(x)] dx}{1 + k \cdot \tau} \quad (15)$$

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