Continuous Lumping Model for Simulation of Hydrocracking

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Hydrocracking of vacuum gas oil is an important chemical process involving complex reaction mixtures. The reaction is carried out in a trickle-bed reactor, considering reaction kinetics along with such hydrodynamic effects as mass transfer, intraparticle diffusion, and partial wetting. Since reaction kinetics is critical to modeling and simulation of a hydrocracking reactor, a modeling approach needs to capture the complex chemistry of the process, along with the elegance of the solution method. The complex chemistry of hydrocarbon is represented by an elegant continuous lumping approach to modeling. The true boiling point of the mixture is used as the characterization parameter. Since the rate constant of hydrocracking is assumed to be a monotonic function of the true boiling point, it is possible to reformulate mass-balance equations in terms of rate constant as a continuous variable. A novel distribution function p(k, K), which determines the fractional yield distribution of species, was formulated based on data from the cracking patterns of various model compounds. Resulting integrodifferential equations are solved numerically to obtain yields of various fractions as a function of reactor residence time. Model predictions are compared with limited published data to show the utility of the model.

Introduction

Hydrocracking is an important secondary process in the petroleum industry, and is generally used to process feed stocks ranging from vacuum gas oils (VGO) to residue. The process involves cracking of heavy petroleum fractions in the presence of hydrogen. The process is environmentally friendly and is tailored to various needs of the refineries in terms of maximization of middle distillates, gasoline, LPG and so forth.

Basically, hydrocracking catalysts are supported metal catalysts consisting of both cracking (e.g., silica/alumina, etc.) and hydrogenation components (noble metals, nonnoble metals of VIb and VIII groups). The hydrocracking of petroleum fractions involves complex chemistry, including various reactions, such as, hydrogenation–dehydrogenation, isomerization, C-C bond scission, hydrogen transfer, disproportionation, paring reaction and ring saturation, ring opening, and dealkylation.

Modeling of the complex hydrocracking kinetics has been necessary since the process began being used in the petroleum refining industry. Prediction of yields of various desired and undesired products at different operating conditions is required by the refineries for process optimization, control, design, catalyst selection, and so forth. Ideally the kinetic model should take into account various reactions and mechanisms that are involved with all the components in the petroleum reaction mixture. However, in actual practice, it is very difficult to keep track of each individual component and the reaction involved. As a result various researchers have viewed hydrocracking chemistry (kinetics) for petroleum fractions with respect to the hydrocracking of a set of model compounds or pseudocomponents. Various experimental yield distribution data on hydrocracking of several model compounds have been generated to be used as guiding factors for analyzing the chemistry of hydrocracking (Sullivan et al., 1964). Based on the product distribution patterns generated, some approaches (mostly in the category of discrete lumping approaches) have been proposed specifically for hydrocracking. However, as briefly discussed in the next section, several approaches that can be applied to hydrocracking, ranging from

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simple discrete lumping to sophisticated model compounds and structure-oriented lumping approaches, have been developed over the past few decades.

Different models based on the discrete lumping approach have been developed by Weekman and Nace (1970), Orochko et al. (1970), Quader (1970), Nace et al. (1971), Stangeland and Kittrell (1972), Zhorov (1971), Usami (1972) and Tom et al. (1972). All of these workers developed models based on some form of lumping of the compound types present in the feed stocks and products (e.g., lumps of LPG, gasoline, diesel, etc.), and devised various series and parallel reactions for their hydrocracking. In all the models just mentioned, the various individual reactions involved have been lumped and viewed as an overall hydrocracking reaction, which results in the distribution of a particular lump of a heavier petroleum fraction into lighter lumps. The success of the preceding models lies in choosing as many lumps as possible, which would basically mean a manyfold increase in the number of model parameters (e.g., rate constants, etc.).

Stangeland (1974) suggested a better and simpler approach for modeling hydrocracking kinetics, which used analogy of cracking with comminution of particles to develop a correlative method for predicting the entire TBP curve of the product for a specified set of operating conditions. However, computations for this approach would become difficult to handle, if a very large number of lumps are to be considered for better resolution. Moreover the approach is suitable only for consideration of first-order kinetics. It would be difficult to incorporate nonlinear kinetics of certain individual reactions, such as, cracking of poly aromatic hydrocarbons or hydroisomerization, which must be considered for better resolution and effectiveness of the model.

Krishna and Saxena (1989) suggested a different approach, one that considers hydrocracking analogous to axial dispersion. This is a simplistic model with a minimum number of parameters. The major drawback of the model is the significant skewness in model prediction at higher severities. However, the model may be useful for preliminary screening of hydrocracking catalysts.

Continuum theory of lumping

In contrast to the discrete lumping approaches (based on pseudocomponents, such as, products slate, "TBP cuts," carbon number, and molecular weight) proposed earlier, the continuum theory of lumping considers the reactive mixture to form a continuous mixture with respect to its species type, boiling point, molecular weight, and so forth.

The continuous mixture is so complex that it is no longer worth distinguishing individual chemical species. Instead, an index is chosen (e.g., TBP, reactivity). The notion of continuous mixture was first introduced by De Donder (1931). This idea has been applied to distillation (Amundson and Acrivos, 1955), thermodynamics (Briano and Glandt, 1988), polymerization (Zeeman and Amundson, 1965), froth flotation (Loveday, 1966), heterogeneity of catalytic sites (Malhotra and Sadana, 1987), reactions in continuous mixtures in general (Aris and Gavalas, 1966; Aris, 1968; Luss and Hutchinson, 1971; Weekman, 1979; Kemp and Wojciechowski, 1974; Krambeck, 1984; Astarita and Ocone, 1988; Chou and Ho, 1989; Prasad et al., 1986a,b), equilibrium-reversible oligomerization reactions (McCoy, 1993), coke formation from olefinic oligomers (McCoy and Balasubramaniam, 1995), chromatographic separation (McCoy and Goto, 1994), and thermolytic extraction of coal in supercritical fluid (Wang et al., 1994).

Continuum of parallel reactions in a continuous mixture has found its principal application in cracking of crude oil (Weekman, 1979). It explains that if individual species react in accordance to first-order kinetics, the resulting order of reaction of the total mixture would asymptotically approach second-order (also Aris, 1968; Ho and Aris, 1987; Krambeck, 1984).

Chou and Ho (1988) developed an approach for treating the continuum of nonlinear reaction mixtures. Subsequently, Ho et al. (1990) applied the approach to mixtures consisting of parallel *n*th-order reactions. Chou and Ho (1989) treated the continuous lumping of coupled nonlinear reactions. One of the advantages of a continuum theory of lumping is accurate estimation of the apparent overall order of reaction, which is an important requirement for reactor design. The methodology for apparent overall order of reaction has been well covered by Astarita (1989), and a simplistic expression was developed by Ho (1991) for modeling the collective behavior of a large number of reactions.

Cicarelli et al. (1992) have developed a methodology for modeling a catalytic cracking process using the continuum theory of lumping. The methodology involves the fragmentation approach and Langmuir Hinselwood kinetics for each species. The formulation assumes equal stoichiometric distribution of all crackates, which is a stronger assumption while depicting cracking of complex petroleum mixture. Also the formulation does not allow for the incorporation of higher-order kinetics.

McCoy and Wang (1994) have formulated a generalized fragmentation kinetics, which can address different stoichiometric distributions. Recently, the subject of complex reaction mixtures and the continuum theory of lumping has attracted a lot of industrial and academic interest [Mobil's symposium proceedings on continuous mixtures, edited by Krambeck and Spare (1994) and the ACS symposium proceedings edited by Astarita and Sandler (1991)]. The present trend is toward retaining as much molecular information as possible. Klein (1994) has developed a Monte-Carlo modeling approach for modeling complex reaction mixtures, which considers a large number of model compounds (about 10,000) reacting, and the reaction pathways are constructed according to a Monte-Carlo simulation approach. Quann and Jaffe (1992) proposed a novel and promising approach that appears to be refined and close to the chemistry of the process. The approach orients the lumping strategy toward the molecular structure, and is called structure-oriented lumping (SOL).

Although continuum theory of the lumping approach has attracted wide research attention, there is very little in the reported literature on its application to hydrocracking. Browarzik and Kehlen (1994) have developed a fragmentation-based approach for modeling the kinetics of *n*-alkane hydrocracking. This approach assumes that an *n*-alkane molecule of carbon number M undergoes a series of first-order parallel reactions, each of which results in a pair of cracked molecules of carbon number k and $M-k$ (k belongs to $(1,M)$). The mathematical formulation, however, does not apply to hydrocracking of petroleum fractions containing different components (iso- and n-paraffins, olefins, naphthenes, aromatics, etc.) that may have different stoichiometry. Moreover, the formulation does not allow for easy incorporation of nonlinear kinetics, for example, higher-order reactions, that would require an altogether different kind of approach.

Preliminary schemes for the application of the continuum theory of lumping approach for modeling hydrocracking kinetics have been formulated based on the comminution analogy Laxminarasimhan et al., 1991). The comminution analogy and fragmentation formulation (Browarzik and Kehlen, 1994; McCoy and Wang, 1994) are two subtly different approaches describing the same phenomenon of cracking that leads to a similar kind of mathematical equations to solve (Ziff, 1991). However, it would be elegant to adopt comminution analogy, as it represents the stoichiometric distribution of various components more easily and, due to the presence of a species-type distribution function, would be particularly useful while extending the approach from components cracking by first-order kinetics to components with higher-order cracking rates (Chou and Ho, 1988) (described in the following section). Also the comminution analogy allows for easy extension to multiple indices involving paraffinicity, naphthenicity, aromaticity, and so forth.

In the present article, a model has been developed for hydrocracking a petroleum mixture based on the continuum theory of lumping. Although the petroleum mixture in the model is characterized by the true boiling point (TBP), and individual first-order kinetics (based on the reported literature) is considered, the model formulation is flexible enough to allow for the incorporation of individual nonlinear reactions, such as, cracking of naphthenic and aromatic components. Moreover, the yield distribution function is a novel skewed-Gaussian type formulated to describe the yield and selectivity of the hydrocracking components (stoichiometry). The function has been developed from experimental data on the yield patterns of the hydrocracking of various model compounds reported in the literature (Sullivan et al., 1964; Langlois and Sullivan, 1969; Coonradt and Garwood, 1964; Liguras and Allen, 1989). Thus, the yield distribution function and the model structure, along with the solution methodology, are suitable for reasonably depicting the hydrocracking of any complex petroleum reaction mixture.

Model Formulation

The model formulation involves consideration of the characterization of the reaction mixture, the underlying pathways, and the associated selectivities of the different reactions. The characterization parameter of the mixture is basically the TBP. The mixture composition at any particular stage of the reaction is characterized by its TBP curve. During the course of the hydrocracking of a particular feed, the TBP distribution curve of the reaction mixture (corresponding to the feed TBP curve at the start of the reaction) changes continuously with the changing residence time of the reaction mixture in the reactor. As the residence time of reaction increases, more of the heavier components in the reaction mixture are converted into lighter components. As a result, the distribution curve of the mixture changes with the increased length of residence time, and shows an increased bias toward the lighter components. Like any other kinetic model, the present model formulation also attempts to determine the concentration distribution of the reaction mixture at any given residence time (reaction time).

Characterization of the reaction mixture

The TBP curve can be converted into a distribution function with the weight fraction of any component as a function of normalized TBP (θ). Let $C(\theta,t)$ be the value of the concentration distribution function corresponding to a normalized TBP θ at any given time t. Thus $C(\theta,t)\cdot d\theta$ will be a fraction of the species with a boiling point corresponding to the normalized TBP range of θ and $\theta + d\theta$. If the species (pseudocomponents) index in the reaction mixture is chosen as i, then the concentration of any pseudocomponent, i, can be designated as $C_i(t)\cdot di$, which equals $C(\theta,t)\cdot d\theta$. For all practical purposes i's are assumed to be equally spaced along the i-axis. Hence

$$C_i(t)\cdot di = C(\theta,t)\cdot d\theta. \tag{1}$$

It is useful here to define the normalized TBP as follows:

$$\theta = \frac{\text{TBP} - \text{TBP}(l)}{\text{TBP}(h) - \text{TBP}(l)}. \tag{2}$$

Here TBP(h) and TBP(l) represent, respectively, the highest and the lowest possible boiling points of the reaction mixture, which correspond to the heaviest and lightest possible components present in the mixture. The mixture composition changes with reaction time, and is duly represented by the continuous function $C(\theta,t)$ at any given instant t.

It has been widely reported in the literature that the hydrocracking rate constant is a monotonic function of TBP. In other words, molecules with a higher boiling point (heavier molecules) crack faster than molecules with a lower boiling point. Accordingly, the species of normalized TBP θ_i will have a rate constant defined as k_i. Since the components are treated as a continuous function (as mentioned earlier) of normalized TBP, the rate constants can also be treated as continuous variables, and the concentration of species i can also be expressed as a function of the rate constant variable. Although the model is formulated for a single characterization variable, the approach could be extended to develop models with multiple characterization variables, for example, reactivity along with paraffinicity and aromaticity, in the case of hydrocracking, which will be extremely useful in determining product yield as well as quality.

Reactivity and species-type distribution functions

The model equations for the reactor performance are formulated more conveniently in the c vs. k frame (Chou and Ho, 1988), and can be subsequently converted to C vs. θ coordinate system, as shown below.

At any instant t,

$$C(\theta,t)\cdot d\theta = c(k,t)\cdot D(k)\cdot dk, \tag{3}$$

where $D(k)$ is the species-type distribution function. $D(k) \cdot dk$ denotes the number of species with reactivity between k and $k + dk$. The major advantage of this approach is that there is no concentration distribution function involved while developing the kinetic expressions, as $c(k,t)$ is just the concentration of the component with reactivity k. It may be noted here that the distributive nature is shifted to the $D(k)$ function, which when multiplied with concentration function $c(k,t)$ (as in Eq. 3) gives the concentration of all the species with reactivity between k and $k + dk$.

The monotonic k vs. θ function is assumed to be a simple power law type. The functional description is as follows:

$$\frac{k}{k_{\max}} = \theta^{1/\alpha}, \tag{4}$$

where α is a model parameter. Here $k_{\max}$ is the rate constant of the species with highest TBP, that is, corresponding to $\theta = 1$. Also, an implicit assumption in Eq. 4 is that $k = 0$ at $\theta = 0$, that is, the cracking rate constant for the lowest possible boiling species is zero, which is a reasonable assumption. The preceding power law functional form for k vs. θ is chosen because it represents most of the reported experimental data. Other types of functional forms can also be used, and the methodology presented here can be easily extended. In practice, model compound studies can be used to determine a more precise form of relationship.

As described earlier, the concentration distribution function $C(\theta,t)$ must be remapped to the functional form $c(k,t)$ such that Eq. 3 is satisfied. The species-type distribution function $D(k)$ can be mathematically regarded as a Jacobian of $i-k$ coordinate transformation (where i is the species index), and is represented as

$$D(k) = \frac{di}{dk} = \frac{di}{d\theta} \cdot \frac{d\theta}{dk}. \tag{5}$$

By definition of the pseudocomponents with respect to θ, the species indices i's are equally spaced along the i-axis. Assuming that the total number of species in the mixture is N ($N \to \infty$), the term $di/d\theta$ can be approximated to N. Thus:

$$D(k) = \frac{N \cdot \alpha}{k_{\max}^{\alpha}} \cdot k^{\alpha - 1}. \tag{6}$$

It can be clearly seen that this function satisfies the following normalization criteria for a species-type distribution function:

$$\frac{1}{N} \cdot \int_0^{k_{\max}} D(k) \cdot dk = 1. \tag{7}$$

Material balance equation

With this background, the mass-balance equations for the species with reactivity k can be formulated elegantly in the k-plane as follows:

$$\frac{dc(k,t)}{dt} = - k \cdot c(k,t) + \int_k^{k_{\max}} p(k,K) \cdot K \cdot c(K,t) \cdot D(K) \cdot dK. \tag{8}$$

Here a yield distribution function $p(k,K)$ has been introduced that determines the amount of formation of species with reactivity k from the cracking of the species with reactivity K. Note that the species-type distribution function (Jacobian of the mapping) $D(K)$ is needed as a factor within the integral to account for the cracking of all species with reactivity K, since the mass balance is written in k space.

It may be noted that a similar kind of integrodifferential equation can be obtained through a formulation based on fragmentation kinetics (McCoy and Wang, 1994). However, it is known that with the just mentioned comminution type of formulation in k space, incorporation of nonlinear kinetics, for example, higher-order kinetics, or the Langmuir–Hinselwood rate model, becomes easy, as it involves almost direct substitution of the rate model for the terms $k \cdot c(k,t)$ and $K \cdot c(K,t)$. This is possible due to the concept of species-type distribution function.

The integrodifferential equation, Eq. 8, can be solved numerically to find the product distribution in the reactor as a function of residence time, provided one assumes a suitable form for the $p(k,K)$ function.

Form of p(k, K) function

The form of the $p(k,K)$ function chosen is now presented. The $p(k,K)$ function chosen should have the following properties:

(1) The value of $p(k,K)$ should be zero for $k = K$, since the species of reactivity k cannot yield to itself upon cracking. Also it is assumed that $P(k,K) = 0$ for $k > K$, as dimerization and other similar reactions are not so significant in hydrocracking. However, in principle, the $p(k,K)$ function can be extended to include the preceding cases.

(2) The $p(k,K)$ function should satisfy the following material balance criteria:

$$\int_0^K p(k,K) \cdot D(k) \cdot dk = 1. \tag{9}$$

(3) $p(k,K)$ should be a finite, small nonzero value when $k = 0$, which supports the experimental findings that when a component of reactivity K cracks, even the smallest reactivity components are formed in traces.

(4) $p(k,K)$ should always be a positive value, as negative $p(k,K)$ values do not have any significance in the preceding case.

Ideally, $p(k,K)$ is a kind of yield distribution function describing the formation of components of reactivity k ($k < K$) from primary cracking of components of reactivity K. Although it is very difficult to experimentally realize the primary hydrocracking yield distribution of, say, a model compound, because of data masking by fast secondary cracking reactions, certain guidance on the functional form of the $p(k,K)$ function can be obtained from the experimental data pertaining to hydrocracking of various paraffinic, olefinic, and aromatics model compounds (e.g., hexadecane, decane, and alkyl benzenes) reported by several researchers (Sullivan et al., 1964; Langalois and Sullivan, 1969; Vansina et al., 1983; Coonradt and Garwood, 1964; Liguras and Allen, 1989). On analysis of all the experimental data, it was found that without much loss of generality, a skewed Gaussian-type distribution function can be chosen to best depict the yield distributions. Normally, it is expected that the maximum yield distribution of the products of primary cracking of the component with reactivity K, would occur among components of reactivities just less than K, that is, most of the product components formed from primary cracking would be from immediately smaller reactivities compared to the reactivity of the crackates. This thus implies that the distribution curve would have a peak (maximum) closer to the reactivity of the crackate K (i.e., the distribution function would be biased toward K). The extent of bias may vary from component to component, and should be depicted by the $p(k, K)$ function.

Considering all of this, the $p(k, K)$ distribution function is described as follows:

$$p(k,K)=\frac{1}{S_0\cdot\sqrt{2\cdot\pi}}\cdot\left[\exp-[\{(k/K)^{a_0}-0.5\}/a_1]^2-A+B\right], \tag{10}$$

where

$$A=e^{-(0.5/a_1)^2} \tag{11}$$

$$B=\delta\cdot\left(1-\left(\frac{k}{K}\right)\right). \tag{12}$$

The parameters a_0 and a_1 of the $p(k, K)$ function defined by Eqs. 10, 11, and 12 determine the location of the peak (maximum of distribution) in the interval $k \in (0, K)$. The term A, defined by Eq. 11, comes from the following condition:

$$p(k,K)=0 \quad \text{at} \quad k=K. \tag{13}$$

When $k = 0$, it can be seen that

$$p(k,K)=\frac{\delta}{S_0\cdot\sqrt{2\cdot\pi}} \tag{14}$$

where δ (a small finite quantity) is a model parameter, which accounts for the fact that $p(k, K)$ should be a finite small quantity when $k = 0$ (condition (4) for the $p(k, K)$ function, as mentioned earlier). The parameters a_0, a_1, and δ are system specific, and are used as tuning parameters for the model, which are required to be determined by the experimental data set. Basically, these parameters could depend on the catalyst type, activity, and impurities (microconstituents) present in the feed.

The parameter S_0 is estimated from the integration criteria mentioned in Eq. 9, as follows:

$$S_0=\int_0^K\left[\frac{1}{\sqrt{2\cdot\pi}}\cdot\left(\exp-[\{(k/K)^{a_0}-0.5\}/a_1]^2-A+B\right)\right]\cdot D(k)\cdot dk. \tag{15}$$

As can be seen, the chosen $p(k, K)$ function satisfies all four of the previously mentioned requirements. In general, any kind of distribution function can be chosen that would satisfy all these properties and represent the yield distribution patterns from hydrocracking the model compounds. More complexities can also be introduced by introducing additional parameters in the model into the $p(k, K)$ function to account for the smaller auxiliary peaks of yield distribution which could increase the resolution of the model. However, it is felt that increasing the number of parameters would make the computations cumbersome. In light of this, the functional form chosen (which generates a single peak) is elegant and useful in reasonably approximating any kind of yield distributions, without increasing the computational time.

Although first-order hydrocracking reactions were used in formulating the model, the approach allows for easy incorporation of other aspects of hydrocracking (e.g., consideration of aromatics cracking, formation of poly aromatic hydrocarbons, isomerization, etc.) that involve nonlinear reaction kinetics, which are being considered in our subsequent efforts. This is possible because the species-type distribution function ensures that the continuous reaction mixture is kinetically consistent with the underlying discrete mixture. Moreover, the approach eliminates the mathematical inconsistencies faced during the formulation of nonlinear kinetics using the conventional approach, as described in the article by Chou and Ho (1988). Formulation of the model is within the framework described by Chou and Ho (1988), and satisfies the single-component identity test of Ho and Aris (1987).

Solution Methodology

Since it is apparent that an analytical solution of the preceding model is not possible, an elegant solution methodology was devised to numerically solve the integrodifferential equation, Eq. 8, for $c(k; t)$. The numerical solution consists of first solving the integral part, and then evaluating $c(k, t)$ in the differential equation by forward time marching approach. For this purpose, the integral part has to be solved at each instant of time throughout the K space (i.e., for each of the K species). Integration is best carried out by Gaussian quadrature, with a piecewise linearization of $c(K, t)$ function. The solution methodology is explained below.

The K-plane is divided into N nodes, and the difference equation (Eq. 8) for any ith node and small time step δt, is written as follows, assuming linear interpolation for the $c(K, t)$ function between two successive nodes:

$$\frac{(c(k_i,t)-c(k_i,t-\delta t))}{\delta t}=c(k_i,t)[-k_i+I_1(k_i,k_{i+1})]$$
$$+\sum_{j=i+1}^{N-1}c(k_j,t)\cdot I_1(k_j,k_{j+1})+\sum_{j=i+1}^{N-1}c(k_j,t)\cdot I_2(k_j,k_{j+1}), \tag{16}$$

where

$$I_1(k_j,k_{j+1}) = \int_{k_j}^{k_{j+1}} p(k_i,K)\cdot\frac{(K-k_{j+1})}{(k_i-k_{j+1})}\cdot D(K)\cdot dK \quad (17)$$

$$I_2(k_j,k_{j+1}) = \int_{k_j}^{k_{j+1}} p(k_i,K)\cdot\frac{(K-k_j)}{(k_{j+1}-k_i)}\cdot D(K)\cdot dK. \quad (18)$$

Initiation of the numerical solution in this case occurs at the Nth node (highest reactivity), as molecules of the highest reactivity just disappear (no formation of molecules of the highest reactivity is possible during cracking). Thus for each time step,

$$c(k_N,t) = c(k_N,t-\delta t)\cdot e^{-k_N\cdot\delta t}, \quad (19)$$

where $k_N = k_{\max}$.

The preceding difference equation is solved for all nodes and time steps to obtain $c(k,t)$. The solution can then be integrated to find the yield of any particular fraction (TBP cut) as follows:

$$C_{1,2}(t) = \int_{k_1}^{k_2} c(k,t)\cdot D(k)\cdot dk, \quad (20)$$

where k_1 and k_2 correspond to reactivities at initial and final boiling points, respectively, of the TBP cut of interest, and $C_{1,2}(t)$ is the weight fraction of the desired TBP cut (product). The solution methodology is effective and easy to implement. One can choose to use nonlinear interpolation of the $c(K,t)$ function between two successive nodes, but it has been found that there is no apparent advantage, because with linear interpolation itself, significant integration errors do not exist if N exceeds 25.

Results and Discussion

The model has been applied to two different sets of published pilot-plant data on VGO-hydrocracking (Bennett and Bourne, 1972; and El-Kardy, 1979).

Bennett and Bourne (1972) reported the product distribution of the hydrocracking of Kuwait VGO at four severity (residence time) levels: 0.383 h, 0.952 h, 1.724 h, and 2.5 h. The model parameters were tuned to fit the data at severity level 2.5 h. It may be noted that the model has five independent tuning parameters, α, a_0, a_1, δ, and $k_{\max}$. The parameters estimations was carried out using the Levenberg–Marquardt algorithm. The model parameters were estimated as $\alpha = 1.35$, $a_0 = 6.41$, $a_1 = 28.15$, $k_{\max} = 1.35\ \mathrm{h}^{-1}$, and $\delta = 2.6667\times10^{-5}$.

Subsequently, the model was used to predict the product distribution for other severities (prediction mode). Comparison of the model predictions with experimental data for all the severities (including the tuning case of severity 2.5 h) is shown in Figure 1 in the form of the TBP curves. The feed TBP curve is provided in Figure 2 to illustrate how the product distributions change as a function of residence time in the reactor.

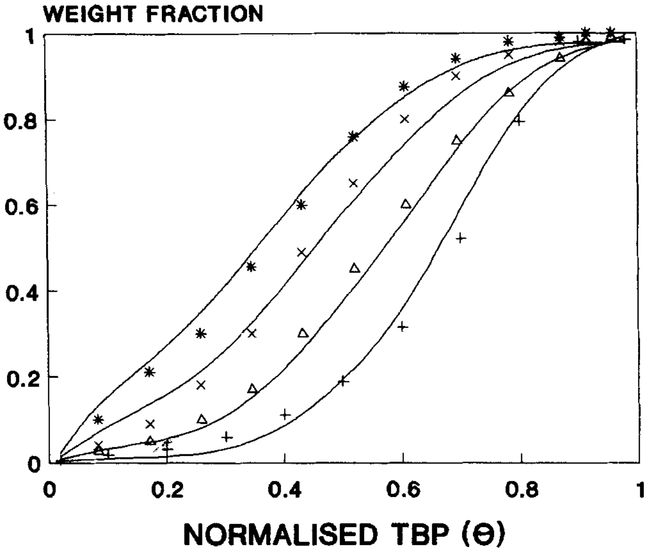

Figure 1. Yield predictions of the model.

A comparison with experimental data from Bennett and Bourne (1972) at different space/time. Key: + = exp(0.383 h); * = exp(2.5 h); × = exp(1.724 h); △ = exp(0.952 h).

El-Kardy (1979) has reported product distributions of VGO-hydrocracking at different severity levels (temperature and residence time). The preceding exercise of model tuning was carried out for El-Kardy's data set at 390°C and a residence time of 2.0 h. The model parameters were estimated as $\alpha = 0.77$, $a_0 = 3.67$, $a_1 = 22.86$, $k_{\max} = 0.88\mathrm{h}^{-1}$, and $\delta = 0.77\times10^{-9}$. Subsequently, the model was used to predict the product distributions reported at other residence times (viz., 0.6667 h and 1.0 h) for the same reaction temperature, 390°C. Figure 3 illustrates the comparison between the model predictions and the experimental data for the severities of

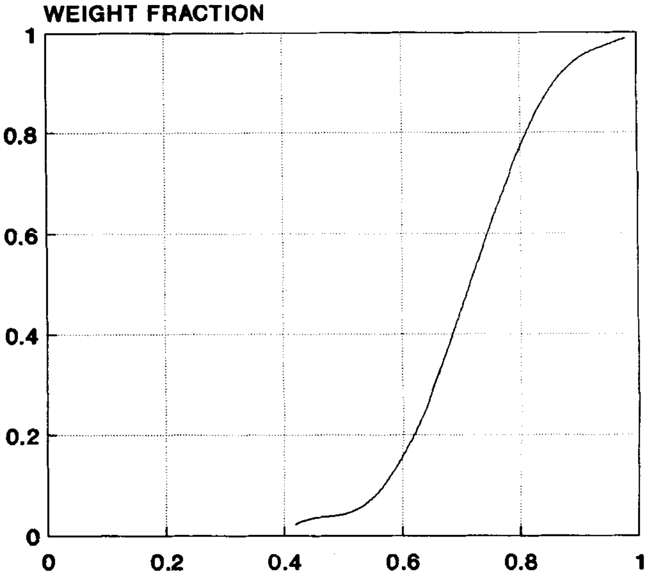

Figure 2. Feed data for the model; —— = feed data. (Data from Bennett and Bourne (1972)).

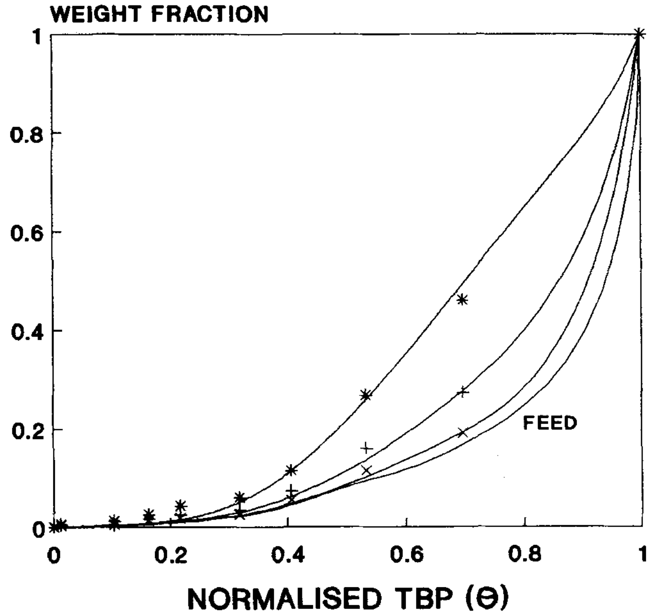

Figure 3. Yield predictions of the model.

Comparison with experimental data from El-Kardy (1978) at different space/times. * = exp(1.5 h); + = exp(1.0 h); × = exp(0.667 h).

0.6667, 1.5, and 2.0 h (tuned case), respectively (the feed distribution curve is also provided in the figure).

It can be seen from the preceding that normal hydrocracking trends with respect to the residence time are predicted well by the model, that is, as the hydrocracking proceeds, the distribution becomes wider and more pronounced toward lower TBP components.

Figures 4 and 5 give an idea of the typical yield distribution functions ($p(k, K)$) for $K = k_{\max}$ and $K = k_{\max}/50$, respectively (based on Bennett and Bourne's data). We can see in the plots that the yield distribution in the model is biased toward the reactivity of crackate K, which is in line with the usual assumption, as discussed earlier.

Tables 1 and 2 compare the product yields (gasoline and diesel) predicted by the model with those of the experimental data at different severities for the data sets of Bennett and Bourne (1972) and El-Kardy (1979). Here the gasoline fraction has a TBP range of (IBP–FBP) 30–150°C, middle distillates (MDS) fraction is in the range of 150 to 370°C, and the 370°C$^+$ fraction is classified as residue. The yields of these fractions are obtained by integrating the concentration function $c(k, t)$ over the rate constant limits corresponding to IBP and FBP of each of these fractions, as discussed earlier (Eq. 23). The corresponding experimental data of Bennett and Bourne (1972) are also shown for comparison. It can be found that the model predictions match well with the experimental data.

From the preceding model and data, one can also determine the overall apparent order of reaction of VGO cracking (370°C$^+$ material) by fitting a simple nth order rate expression to the concentration data of 370°C$^+$ with time. The overall apparent order of reaction is found to be 2.0 (although the order of reaction of individual species is found to be 1.0), which is in agreement with the findings of Krambeck (1984) and Aris (1968).

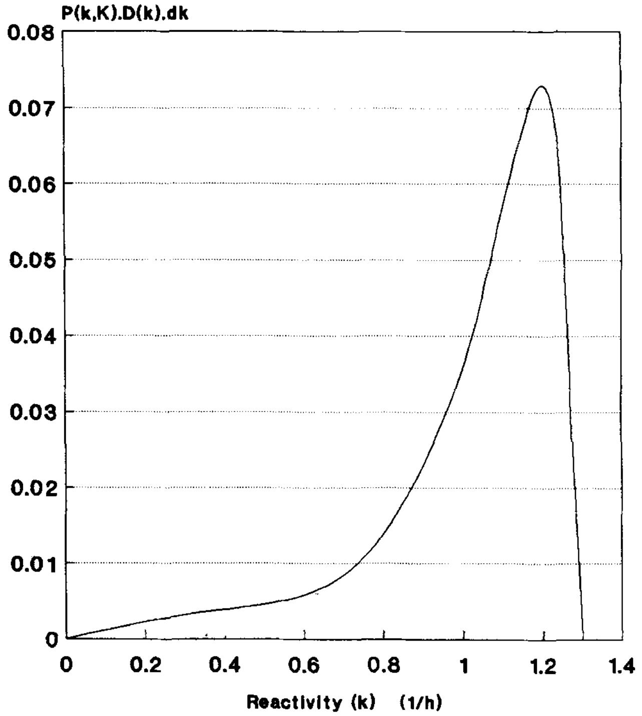

Figure 4. Yield distribution $P(k, K)$ function.

$K = k_{\max}$. Based on Bennett and Bourne (1972) data.

Summary

A model was developed for predicting hydrocracking kinetics based on the continuum theory of lumping. It has flexibility and features to incorporate nonlinear kinetics, if desired.

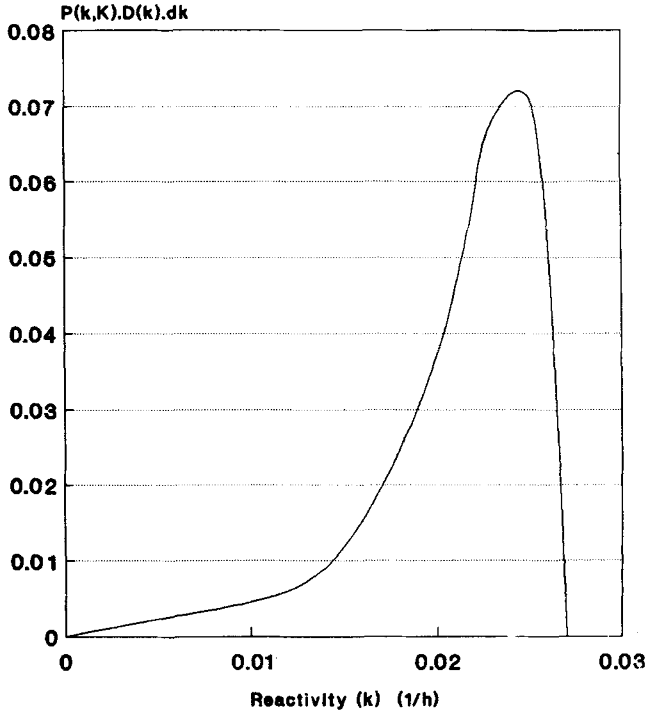

Figure 5. Yield distribution $P(k, K)$ function.

$K = k_{\max}/50$. Based on Bennett and Bourne (1972) data.

Table 1. Comparison of Model Predictions with Experimental Data

	Product Yields at Various Severities								
Residence Time (h)	0.383 (E)	0.383 (M)	0.952 (E)	0.952 (M)	1.724 (E)	1.724 (M)	2.5 (E)	2.5 (M)	Feed
Gasoline (30–150°C)	6.0	5.5	16.0	16.0	23.0	21.0	26.0	25.0	0
MDS (150–370°C)	45.0	52.0	51.0	53.0	61.0	59.0	39.0	35.0	41.0
370°C$^+$	35.0	40.0	25.0	25.0	9.0	11.0	5.0	7.5	59.0

Note: (E) = experimental data: (M) = model predictions.
From Bennett and Bourne (1972).

Table 2. Comparison of Model Predictions with Experimental Data

	Product Yields at Various Severities						
Residence Time (h)	0.667 (E)	0.667 (M)	1.0 (E)	1.0 (M)	2.0 (E)	2.0 (M)	Feed
Gasoline (30–150°C)	3.01	3.25	5.0	5.0	7.5	6.0	3.0
MDS (150–370°C)	14.0	13.9	23.0	24.0	36.0	39.0	13.5
370°C$^+$	80.0	79.6	70.0	70.0	54.0	51.0	82.5

Source: El-Kardy (1979) at temperature 390°C.
Note: (E) = experimental data: (M) = model predictions.

The model also has a novel skewed Gaussian distribution function to determine product yield distribution (stoichiometry) of hydrocracking reactions. The function is versatile and capable of depicting most of the yield distributions to a reasonable extent.

The model predictions have compared well with the reported experimental data. Hence there is significant potential for shaping the model for hydrocracker simulation applications.

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Notation

k_1 = reactivity of species at IBP, h^{-1}
k_2 = reactivity of species at FBP, h^{-1}
k_i = reactivity of species i, h^{-1}
θ_i = normalized TBP of species i

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