Experimental and Theoretical Investigation of the Validity of Asymptotic Lumped Kinetics

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Continuum approximation is often used to treat problems involving reaction mixtures of a vast number of species. Previous studies predicted that in many situations the lumped kinetics of a continuum of reactions, regardless of their kinetics, are of the power law form after a long time. In this article we present experimental support for such asymptotic power law kinetics. The system considered is catalytic deep desulfurization of a petroleum distillate. In addition, a theoretical analysis is made to establish the condition under which the continuum approximation is valid in the long-time limit. The condition turns out not to be very stringent for practical purposes.

Introduction

In many technologically important areas, one deals with a mixture made of a very large number of reacting species. These include oils refining, polymerization, air pollution, and biological processes, to name a few. In such situations one often wants to know the aggregate behavior of the individual species. Recently, a great deal of theoretical work has been devoted to addressing the question of whether or not an overall, lumped kinetics can be developed to describe the mixture's behavior as a whole. To render the problem analytically tractable, much of prior work has assumed that the number of species is so large that the mixture may be idealized as a continuum. The idea of continuous mixtures first conceived by deDonder (1931) was propounded in the context of reaction kinetics by Aris and Gavalas (1966) and Aris (1968). Conceptually, in a continuous mixture the concentration of each constitutent species is infinitesimally small, and adjacent species are virtually indistinguishable. Recent developments in continuous mixtures can be found in Astarita and Sandler (1991) and Sapre and Krambeck (1991). The continuous mixture approach has been shown to be an effective and simple tool for experimentalists to analyze and correlate kinetic data on complex reaction mixtures (Prasad et al., 1986ab; Wang et al., 1994).

An important outcome of the continuum theory is the development of asymptotic kinetics at long reaction times (Krambeck, 1984; Ho and Aris, 1987; Chou and Ho, 1988, 1989; Aris, 1989; Ho et al., 1990). It turns out that for many classes of reactions mixtures, regardless of their initial compositions, there appears to be a universal "law," that is, the lumped kinetics after a long time takes a power-law form asymptotically (for a few exceptions, see Ho et al., 1990). Development of such asymptotic kinetics is very desirable from a practical viewpoint, since in many processes one often wants to achieve the highest permissible conversion. Moreover, the asymptotic kinetics can be used to construct a one-parameter model for global kinetics and to establish an upper bound on the mixture's kinetic behavior (Ho, 1991).

It should be stressed that the existence of a continuum of species is an idealization. A remaining question is whether the asymptotic power law kinetics can indeed be observed in the real world. Since the asymptotic kinetics are developed for long times, it is also important to address the question of when the long-time asymptotics and the continuum approximation are both valid. One can use the following simple argument to see that the continuum approximation must break down for very long times. Consider a first-order reaction mixture. After a sufficiently long time, the mixture behaves as if there were only one species which decays exponentially, since the concentrations of all other species are exponentially smaller. This is at variance with the power-law decay predicted by the continuum theory. Thus, in order for the continuum theory to be valid, time cannot be unconditionally long.

In light of the above, we provide here some experimental evidence for the asymptotic power law kinetics in the case of hydrodesulfurization (HDS) of a cracked distillate over three different catalysts. In addition, we attempt to put the asymp-

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totic kinetics on a firmer theoretical basis. An analysis is made to define the condition under which the continuum theory and the asymptotic power law are simultaneously valid. Finally, an estimate of the domain of validity of the asymptotic power law kinetics is provided by analyzing literature data obtained from pure-compound experiments.

HDS Kinetics

It is useful at the outset to briefly discuss HDS kinetics with pure compounds and with petroleum feedstocks. In analyzing HDS kinetics data, one customarily incorporates the hydrogen concentration term in the rate constant because hydrogen is present in large excess. Experiments using single-component feeds have indicated that when an organosulfur species desulfurizes in the absence of any other sulfur species, the reaction rate is pseudo-first order (Girgis and Gates, 1991). When the feed is a mixture of many sulfur species, the individual HDS kinetics take the Langmuir-Hinshelwood form because of competitive adsorption. The overall HDS kinetics with a petroleum feedstock is the sum of a vast number of HDS reactions of widely different rates. Let S and S_f be the total sulfur contents of the oil at space time t and zero, respectively. What has been observed in HDS of many petroleum feedstocks is that the plot of $ln(S/S_f)$ vs. t over a wide conversion range is concave upward. Such behavior is characteristic of high-order kinetics and has been interpreted as arising from the presence of a multitude of sulfur species with widely different reactivities. Our attention here is focused on the behavior of the mixture at deep HDS levels, that is, near the tail of the $ln(S/S_f)$ vs. t curve. In this regard, we remark that under the recent U.S. Clean Air Act Amendments, the sulfur specification in diesel oils has been lowered from 0.2 – 0.3 wt % to 0.05 wt %. Considerable effort has been expended on extending existing HDS process to meet the new and much stricter emission requirement.

Asymptotic Kinetics

The feed to the HDS reactor is thought of as comprising a continuum of sulfur-containing species with finite adsorptivities. Different sulfur species are labeled by their reactivity k (pseudo-first-order rate constant) in the interval $[0, \infty]$. Assuming plug flow, one can show for a Langmuir-Hinshelwood reaction mixture that as t become sufficiently large, the fractional sulfur remaining $C = S/S_f$ is given by a very simple equation (Ho, 1991), namely,

$$C \sim \frac{h}{t^z} \quad t \to \infty \tag{1}$$

where h and z are determined by the reactivity-concentration spectrum of the feed near $k = 0$. Equation 1 is valid whether or not the feed contains unconvertibles. It also implies the following lumped kinetics:

$$\frac{dC}{dt} \sim -zh^{-1/z}C^{1+1/z}, \quad 1+\frac{1}{z} > 1. \tag{2}$$

That is to say, according to the continuum theory, deep HDS is governed by high-order kinetics. In catalyst exploratory and development studies, HDS data are necessarily gathered at high HDS levels. It is important (for example, for catalyst ranking purposes) to know the kinetics in this regime.

Table 1. Properties of Catalysts Tested

Catalyst	wt. % Mo	Co	Ni	BET Surface Area, m^2/g	Pore Vol. cm^3/g
A	11.6	3.01	—	225	0.463
B	13.6	—	2.96	162	0.351
C	11.4	3.15	—	217	0.424

Experimental Studies

Catalysts

Three supported catalysts, designated as A, B, and C, were used in this study. Their properties are listed in Table 1. These catalysts were presulfided in situ at 360°C and ambient pressure for one hour with a 10% H_2S-in-H_2 gas mixture.

Feedstock

A light catalytic cycle oil with an API gravity [at 60°F (16°C)] of 16.5 was used. This feed contains 1.35 wt. % total sulfur and 715 wppm total nitrogen. Aliphatic sulfur compounds are known to be more reactive than aromatic sulfur compounds. The aromatic sulfur compounds are almost exclusively of the benzo- and dibenzothiophene (DBT) types, with roughly a 60-40 split in favor of benzothiophenes. About 47% of DBTs have a sterically hindered sulfur atom. These are very refractory species (Houalla et al., 1980; Girgis and Gates, 1991; Amorelli et al., 1991). The most refractory ones are 4,6 dimethyl DBT and its derivatives, since the sulfur hetroatom is doubly hindered.

Procedure

The experiments were conducted in an upflow, fixed-bed unit consisting of several independent reactors disposed in a common sand bath. Figure 1 depicts the key component of the unit. Each reactor [made of 3/8-in. (9.5-mm)-ID 316 stainless steel pipe] was packed with 6 cc of catalyst (14-35 mesh granules) in the central zone and denstone in the fore and aft zones. The reaction under a particular set of conditions was allowed to proceed for at least 20 h before the first product sample was analyzed. After purging with nitrogen, the liquid products were analyzed for total sulfur by X-ray fluorescence using external standards. Reaction conditions were 330°C, 2.31 MPa, and 1,500 SCF/B (standard cubic feet of H_2 per barrel of oil). Three liquid hourly space velocities (LHSV = $1/t$, in units of cm^3 feed/cm^3 catalyst/h) were used: 1.7, 0.85, and 0.5. These give high HDS levels ranging from 90% to 95.4% for catalyst A and 83% to 91.6% for catalyst B. The activity of catalyst C is in between those of catalysts A and B. It should be noted that the 0.05 wt% sulfur specification corresponds to a 96.3% HDS.

Analysis of Experimental Results

No signs of catalyst deactivation were noted throughout the study. Figure 2 plots lnC vs. 1/LHSV. Even over this

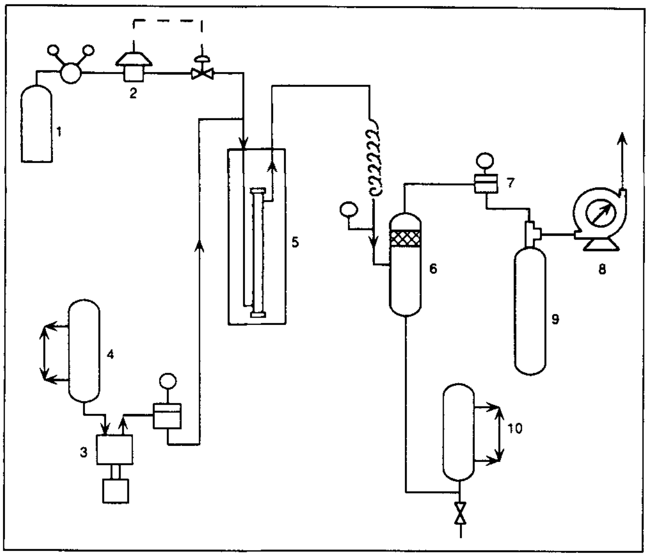

Figure 1. Main components of the reactor unit.

(1) hydrogen source; (2) flow controller; (3) liquid pump; (4) liquid feed tank; (5) reactor tube in sand bath; (6) gas-liquid separator; (7) pressure controller; (8) gas meter; (9) H_2S scrubber; (10) product liquid collector.

narrow conversion range, all three plots show a curvature which is convex towards the origin, indicative of higher-than-first-order kinetics. For instance, catalyst A attained a 90% HDS at a 1/LHSV of about 0.6; further HDS becomes increasingly slow (the slope of the curves becomes progressively less negative). The solid curves in Figure 2 were obtained from regression. According to Eq. 1, the plot of *lnC* vs. *lnt* should be a straight line with a slope equal to $-z$. As Figure 3 shows, this is indeed the case. The results of linear regression indicate that the values of z are slightly different for the three catalysts, but $z = 0.65$ provides an acceptable representation in all cases. This considerably simplifies data interpretation and suggests that the catalysts interact with the oil more or less in a similar fashion. One can say that all three catalysts are not particularly active for HDS of the family of sterically-hindered organosulfur compounds.

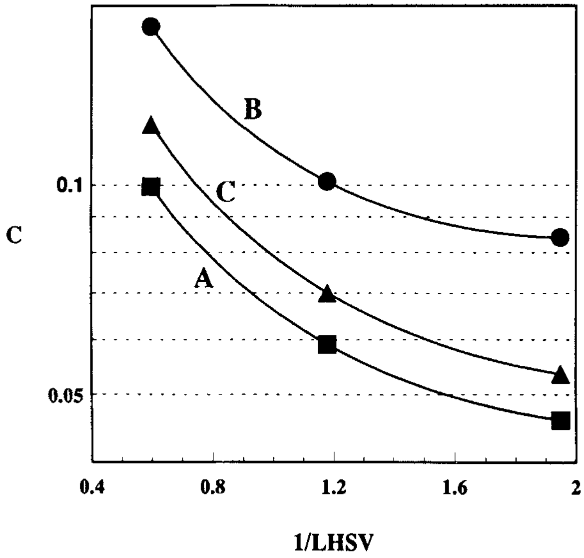

Figure 2. *C* vs. 1/LHSV for different catalysts.

●: catalyst B; ▲: catalyst C; ■: catalyst A; 330°C, 2.31 MPa, 1,500 S/B.

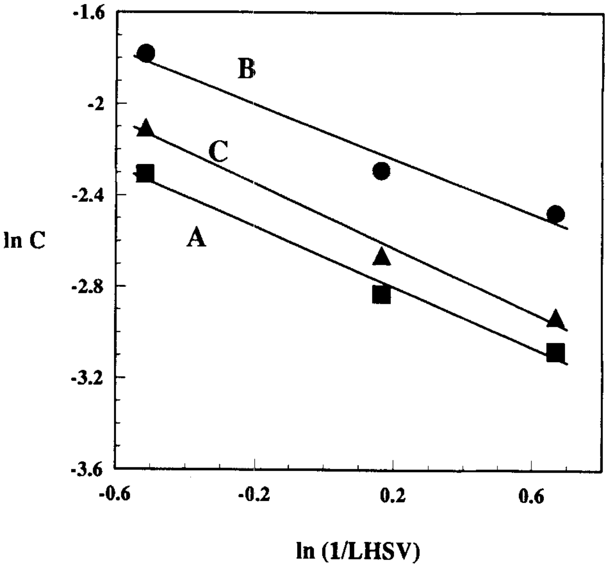

Figure 3. *lnC* vs. *ln*(1/LHSV) for different catalysts.

●: catalyst B; ▲: catalyst C; ■: catalyst A; 330°C, 2.31 MPa, 1,500 S/B.

The above analysis is valid only at large space times. In what follows we want to define the asymptotic condition, that is, what is meant by "large time." For simplicity only the case of first-order reactions is considered. This simplification can be justified because at long times competitive adsorption becomes less important due to diminishing concentrations.

Long-Time Theory

Continuous vs. discrete mixtures

With the rate constant k as the label, the total concentration in the continuous mixture (denoted by the subscript c) can be calculated as

$$C_c = \int_0^\infty c_o(k) e^{-kt} dk \tag{3}$$

where $c_o(k)$ is a smooth distribution of the constituent species in the feed, that is, $c_o(k)dk$ is the concentration of all species with k between k and $k + dk$. For practical purposes, $c_o(k)$ can be assumed to approach zero rapidly as $k \to \infty$. It should be pointed out that Eq. 3 serves the purposes of the present study, but it gives rise to some fundamental difficulties for kinetics of arbitrary nonlinearity (Ho and Aris, 1987). For ways of circumventing the difficulties, refer to Astarita and Ocone (1988), Chou and Ho (1988), and Aris (1989).

We now consider the underlying discrete mixture in which the first-order rate constant for the nth species is k_n. To simplify the analysis, we assume that all the k_ns are equally spaced, that is

$$k_n = n\delta \qquad n = 1, 2, \ldots. \tag{4}$$

The total concentration C_d is simply the sum of the individual concentrations

$$C_d(t;\delta,c_o)=\sum_{n=1}^{\infty} c_o(n\delta)\delta e^{-n\delta t}. \tag{5}$$

Here in order to link the discrete case to the continuous mixture, we have introduced a scale factor δ within the summation. Thus, $c_o(n\delta)\delta$, a very small quantity, is the concentration of the nth species in the feed. Had we not included δ within the summation in Eq. 5, we would have introduced a density-like function $D(k)$ in Eq. 3 and $c_o(k)$ becomes a concentration instead of a concentration distribution (Chou and Ho, 1988). $D(k)$ in the discrete case becomes a series of Dirac delta functions and accounts for the fact that the k_ns may not be equally spaced. Another point of note is that we could have included an unconvertible species in the discrete mixture by starting the summation from $n=0$, but this would not affect in any way the analysis or the final outcome, as will be seen later. Finally, we point out that Aris (1989) has shown for a discrete mixture of a special composition that the lumped kinetics of many nth-order reactions is also nth order at any time.

For fixed t, as $\delta \to 0$, C_c evidently is a satisfactory approximation to C_d because Eqs. 3 and 5 are merely the definition of the Riemann integral in elementary calculus. For fixed δ and $t \to \infty$, C_d decays exponentially (that is, asymptotic first-order kinetics) because it is governed by a single, most refractory species so that the continuum approximation is not valid (as alluded to in the Introduction). Here we investigate under what conditions both approximations can be valid as $\delta \to 0$ and $t \to \infty$. Since δt is dimensionless, one might expect it to be the controlling parameter. Indeed, we will show that the missing condition is that $\delta t \to 0$.

Let $\epsilon(t)$ be the difference between C_d and C_c, that is

$$\epsilon(t)=C_d(t)-C_c(t). \tag{6}$$

We will show under wide hypotheses on $c_o(k)$ that $C_d(t)$ will be asymptotic to $C_c(t)$ for large t and small grid δ if the product δt is small. Thus, time cannot be too long without the discrete nature of the sum manifesting itself, as perhaps expected intuitively. We will show the asymptotic relation $C_d \sim C_c$ by proving that $C_d/C_c \to 1$, or equivalently that $\epsilon/C_c \to 0$.

To this end, we use the Poisson summation formula (Carrier et al., 1966) which can be stated as follows. Let $F(\lambda)$ be the cosine transformation of a continuous function $f(k)$

$$F(\lambda)=\left(\frac{2}{\pi}\right)^{1/2}\int_o^{\infty} f(k)\cos(\lambda k)dk. \tag{7}$$

Then,

$$\sqrt{a}\left[f(0)/2+\sum_{n=1}^{\infty} f(na)\right]=\sqrt{b}\left[F(0)/2+\sum_{n=1}^{\infty} F(nb)\right] \tag{8}$$

where $ab=2\pi$. To apply the above summation formula, we let $f(k)=c_o(k)\delta e^{-kt}$ and $a=\delta$ (so $b=2\pi/\delta$). The cosine transformation then takes the form

$$F(\lambda)=\delta\left(\frac{2}{\pi}\right)^{1/2} Re\int_o^{\infty} c_o(k)e^{-(t+i\lambda)k}\,dk \tag{9}$$

where Re denotes the real part of a complex function or number. It follows that

$$C_d(t)=\sum_{n=1}^{\infty} f(na) \tag{10}$$

$$C_c(t)=\left(\frac{\pi}{2}\right)^{1/2} F(0)/\delta \tag{11}$$

and Eq. 8 gives the error introduced by the continuum approximation

$$\epsilon(t)=C_d(t)-C_c(t)=-\delta c_o(0)/2 \\ +2\,Re\sum_{n=1}^{\infty}\int_o^{\infty} c_o(k)e^{-z_n k}\,dk \tag{12}$$

in which

$$z_n \equiv t+i2n\pi/\delta=(t^2+4\pi^2n^2/\delta^2)^{1/2}\exp(i\theta_n) \tag{13}$$

where $\theta_n=\tan^{-1}[2\pi n/(\delta t)]$. Note that had we included an unconvertible species, the first term on the far right of Eq. 12 would have been positive. This change of sign has no effect at all on the outcome of the analysis, as evident from the following development.

Long-time behavior

The long-time behavior of C_c is dominated by refractory species with very small k. If $c_o(k)$ is bounded and has the leading behavior (Ho and Aris, 1987)

$$c_o(k)\sim \alpha k^{\beta} \quad \text{as} \quad k\to 0 \tag{14}$$

for some $\beta \geq 0$ and $\alpha \neq 0$, then by Watson's Lemma (Carrier et al., 1966)

$$C_c(t)\sim \tilde{C}(t)=\frac{\alpha\Gamma(\beta+1)}{t^{\beta+1}} \quad t\to\infty \tag{15}$$

where Γ is the gamma function. Note that Eq. 15 takes the form of Eq. 1, with $h=\alpha\Gamma(\beta+1)$ and $z=\beta+1$. The problem we wish to attack becomes that of finding the condition under which

$$\frac{\epsilon(t)}{\tilde{C}(t)}\to 0 \quad \text{as} \quad t\to\infty \tag{16}$$

since Eq. 16 implies that $\epsilon(t)/C_c(t)\to 0$ as $t\to\infty$.

In what follows our attention is focused on the right-hand side of Eq. 12. We start with the first term. Since $c_o(0)=0$

unless $\beta = 0$, we need to consider only the case $\beta = 0$, which gives $\tilde{C} = \alpha/t$. So the first term on the far righthand side of Eq. 12, when divided by $\tilde{C}$, becomes

$$\frac{-\delta c_o(0)/2}{\tilde{C}(t)} = -\frac{t\delta}{2}. \tag{17}$$

We thus see that for this term to vanish as $t \to \infty$, δ must go to zero sufficiently fast so that

$$\delta t \to 0. \tag{18}$$

To proceed further we define a function ϕ which is the second term on the far righthand side of Eq. 12 divided by $\tilde{C}(t)$, that is

$$\phi \equiv \frac{t^{\beta+1}}{\alpha\Gamma(\beta+1)} Re \sum_{n=1}^{\infty} \int_o^{\infty} c_o(k) e^{-z_n k}\, dk. \tag{19}$$

We shall show that as $t \to \infty$ and $\delta \to 0$, then $\phi \to 0$ if Eq. 18 is satisfied. This is done in four steps, increasingly generalizing $c_o(k)$.

Case 1: $c_o(k) = \alpha k^{\beta}$; $\beta \geq 0$, $\alpha > 0$

Substituting $c_o(k) = \alpha k^{\beta}$ into Eq. 19, performing the integration, and taking the real part of resulting complex function yields

$$\begin{aligned} \phi &= t^{\beta+1}\, Re \sum_{n=1}^{\infty} \frac{1}{z_n^{1+\beta}} \\ &= t^{1+\beta} \sum_{n=1}^{\infty} \frac{\cos[(1+\beta)\theta_n]}{(t^2 + 4\pi^2 n^2/\delta^2)^{(1+\beta)/2}}. \end{aligned} \tag{20}$$

Now for $\beta > 0$, we have

$$\begin{aligned} |\phi| &\leq t^{1+\beta} \sum_{n=1}^{\infty} \frac{1}{(4\pi^2 n^2/\delta^2)^{(1+\beta)/2}} \\ &= \left(\frac{\delta t}{2\pi}\right)^{1+\beta} \sum_{n=1}^{\infty} \frac{1}{n^{1+\beta}} \to 0 \end{aligned} \tag{21}$$

as $\delta t \to 0$ because the infinite series $\Sigma(1/n)^{1+\beta}$ converges.

In the $\beta = 0$ case, since $\cos\theta_n = \delta t/(\delta^2 t^2 + 4\pi^2 n^2)^{1/2}$, Eq. 20 becomes

$$\begin{aligned} \phi &= (\delta t)^2 \sum_{n=1}^{\infty} \frac{1}{(4\pi^2 n^2 + \delta^2 t^2)} \\ &\leq \frac{(\delta t)^2}{4\pi^2} \sum_{n=1}^{\infty} (1/n)^2 \to 0 \end{aligned} \tag{22}$$

as $\delta t \to 0$ since $\Sigma(1/n^2)$ converges.

Case 2: $c_o(k) = \alpha k^{\beta} + \sigma k^{\gamma}$, $\gamma > \beta$

Here ϕ can be written as

$$\phi = \phi_o + \phi_1 \tag{23}$$

where ϕ_o is obtained by setting $\sigma = 0$, and

$$\phi_1 = \frac{t^{\beta+1}}{\alpha\Gamma(\beta+1)} Re \sum_{n=1}^{\infty} \int_o^{\infty} \sigma k^{\gamma} e^{-z_n k}\, dk. \tag{24}$$

We have already shown in the previous case that $\phi_o \to 0$ as $t \to \infty$, $\delta \to 0$, and $\delta t \to 0$. To see that this is also the case with ϕ_1, we write after integration that

$$\phi_1 = v t^{\beta+1} \sum_{n=1}^{\infty} \frac{\cos[(1+\gamma)\theta_n]}{|z_n|^{1+\gamma}} \tag{25}$$

where $v \equiv \sigma\Gamma(\gamma+1)/[\alpha\Gamma(\beta+1)]$. Proceeding as before, ϕ_1 can be shown to approach zero as follows

$$\begin{aligned} |\phi_1| &\leq v t^{\beta+1} \delta^{1+\gamma} \sum_{n=1}^{\infty} \frac{1}{(4\pi^2 n^2 + \delta^2 t^2)^{(1+\gamma)/2}} \\ &\leq \frac{v}{(2\pi)^{1+\gamma}} \delta^{\gamma-\beta} (\delta t)^{1+\beta} \sum_{n=1}^{\infty} \frac{1}{n^{1+\gamma}} \to 0 \end{aligned} \tag{26}$$

since $\delta t \to 0$, $\delta \to 0$, $\gamma > \beta$ and $\Sigma(1/n^{1+\gamma}) < \infty$.

Case 3: $c_o(k) = \alpha k^{\beta} + \sum_{j=1}^{m} \sigma_j k^{\gamma_j}$, $\gamma_j > \beta \geq 0$

This is immediate, since by linearity each term is handled as before. With the above results, we are now in a position to consider the more general case, as discussed below.

Case 4: $c_o(k) = \alpha k^{\beta} + \sum_{j=1}^{m} \sigma_j k^{\gamma_j} + R(k)$, $\gamma_j > \beta \geq 0$

The restrictions on the remainder term $R(k)$ are

$$|R(k)|,\quad |R'(k)|,\quad \text{and}\quad |R''(k)| \leq q e^{st} \quad \text{for some } q \text{ and } s, \tag{27}$$

$$|R''(x)| \sim \omega k^{\gamma} \quad \text{as} \quad k \to 0,\ \gamma > \beta, \text{ and} \tag{28}$$

$$R(0) = R'(0) = 0 \tag{29}$$

where the prime denotes derivative with respect to k.

In the same vein as before, we let

$$\phi = \phi_o + \sum_{j=1}^{m} \phi_j + \hat{\phi} \tag{30}$$

where

$$\hat{\phi} \equiv \frac{t^{\beta+1}}{\alpha\Gamma(\beta+1)} Re \sum_{n=1}^{\infty} \int_o^{\infty} R(k) e^{-z_n k}\, dk. \tag{31}$$

Again by linearity, we need only consider the $\hat{\phi}$ term. Integrating by parts, we obtain

$$\int_o^{\infty} R(k) e^{-z_n k}\, dk = \frac{1}{z_n^2} \int_o^{\infty} R''(k) e^{-z_n k}\, dk. \tag{32}$$

Thus, with the aid of Eq. 28 and after some algebra

$$\left| Re \int_o^{\infty} R(k) e^{-z_n k}\, dk \right| \le \frac{1}{|z_n|^2} \left| \int_o^{\infty} R''(k) e^{-z_n k}\, dk \right|$$

$$\le \frac{1}{|z_n|^2} \frac{\omega \Gamma(1+\gamma)}{t^{1+\gamma}}. \qquad (33)$$

The last step follows from Watson's Lemma for $\omega > \overline{\omega}$ and sufficiently large t. Hence, for large t

$$|\hat{\phi}| \le \frac{\omega t^{\beta+1}}{\alpha \Gamma(\beta+1)} \sum_{n=1}^{\infty} \frac{\Gamma(\gamma+1)}{|z_n|^2 t^{1+\gamma}}$$

$$\le \frac{\delta^2 \omega \Gamma(\gamma+1)}{\alpha \Gamma(\beta+1)} \frac{1}{t^{\gamma-\beta}} \sum_{n=1}^{\infty} \frac{1}{n^2} \rightarrow 0 \qquad (34)$$

As a summary, what we have shown in this general case is that as $t \rightarrow \infty$ and $\delta \rightarrow 0$

$$\left| \frac{\epsilon(t)}{C_c(t)} \right| \rightarrow 0 \qquad (35)$$

as long as $\delta t \rightarrow 0$.

As can be seen, the results of the foregoing analysis are quite general, and therefore can be used for a wide variety of feeds characterized by $c_o(k)$.

Example

A versatile functional form for $c_o(k)$ which has been widely used in many prior studies is

$$c_o(k) = k^{\beta} e^{-\zeta k} \quad \beta \ge 0. \qquad (36)$$

To use the result developed in the preceding section, Eq. 36 is expanded as

$$c_o(k) = k^{\beta} - \zeta k^{\beta+1} + (\zeta^2/2) k^{\beta+2} + R(k) \qquad (37)$$

where

$$R(k) = \sum_{n=3}^{\infty} \frac{(-\zeta)^n}{n!} k^{n+\beta} = k^{\beta}(e^{-\zeta k} - 1 + \zeta k - \zeta^2 k^2/2). \qquad (38)$$

It can then be seen that Eq. 35 holds in this case because Eq. 38 satisfies the conditions discussed before. That is, $R(0) = R'(0) = 0$ and

$$R''(k) = k^{\beta} \sum_{n=1}^{\infty} \frac{(-\zeta)^{n+2}}{(n+2)!} (n+2+\beta)(n+1+\beta) k^n$$

$$\sim \frac{(3+\beta)(2+\beta)}{6} (-\zeta)^3 k^{1+\beta} \quad \text{as} \quad k \rightarrow 0. \qquad (39)$$

If β is a nonnegative integer, an alternative and easier treatment can be made. In this case,

$$C_d(t) = \sum_{n=1}^{\infty} (n\delta)^{\beta} \delta e^{-n\delta(t+\zeta)} \qquad (40)$$

and

$$C_c = \frac{\Gamma(1+\beta)}{(\zeta+t)^{1+\beta}}. \qquad (41)$$

C_d can be rewritten as

$$C_d(t) = \delta \left(-\frac{\partial}{\partial t} \right)^{\beta} \sum_{n=1}^{\infty} e^{-(t+\zeta)n\delta}$$

$$= (-1)^{\beta} \delta \left(\frac{\partial}{\partial t} \right)^{\beta} \frac{e^{-(t+\zeta)\delta}}{1 - e^{-(t+\zeta)\delta}}. \qquad (42)$$

Our task here is to verify that as $t \rightarrow \infty$, $C_d/C_c \rightarrow 1$ as $\delta \rightarrow 0$ and $\delta t \rightarrow 0$.

It can be shown after some algebra that

$$\frac{C_d(t)}{C_c(t)} = g_{\beta}[y(t, \delta)] \qquad (43)$$

where

$$y \equiv \delta(\zeta + t) \qquad (44)$$

and

$$g_{\beta}(y) \equiv \frac{(-1)^{\beta}}{\beta!} y^{1+\beta} \left(\frac{\partial}{\partial y} \right)^{\beta} \frac{1}{(e^y - 1)}. \qquad (45)$$

Since $y \rightarrow 0$ as $\delta \rightarrow 0$ and $\delta t \rightarrow 0$

$$\lim_{t \rightarrow \infty, \delta \rightarrow 0, \delta t \rightarrow 0} \frac{C_d(t)}{C_c(t)} = \lim_{y \rightarrow 0} g_{\beta}(y). \qquad (46)$$

Differentiating Eq. 45 yields

$$g_{\beta+1}(y) = g_{\beta}(y) - \frac{y}{(\beta+1)} g_{\beta}'(y) \qquad (47)$$

where the prime denotes the differentiation. Now $g_o(y) = y/(e^y - 1)$ is analytic for $|y| < 2\pi$ since $y = 0$ is a removable singularity. Therefore, by induction on Eq. 45, g_{β} is also analytic for $|y| < 2\pi$. In particular, then $y g_{\beta}'(y)$ vanishes for $y = 0$ and we have from Eq. 47 that

$$g_{\beta+1}(0) = g_{\beta}(0) = \cdots = g_o(0). \qquad (48)$$

Since $g_o(0) = 1$, then $g_{\beta}(0) = 1$ for all positive integer β.

Estimation of Region of Validity

The key message of the foregoing development is that the asymptotic power law kinetics are valid over *some long-time regime*. In what follows we illustrate how one can get a feel

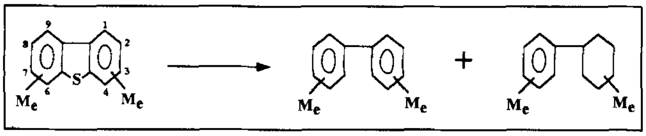

Figure 4. Major reaction products from HDS of methyl-substituted DBTs.

for the domain of validity for the asymptotic kinetics based on experimental results with pure compounds. Let k^* represent the characteristic scale of the rate constants for refractory species. Then for practical applications, the asymptotic kinetics derived from the continuum theory should be applicable over the following region

$$1/k^* \ll t \ll 1/\delta \tag{49}$$

To estimate the grid size δ and k^*, we use the data of Houalla et al. (1980) who studied HDS of DBT and four methyl-substituted DBTs over a sulfided Co-Mo/γ-Al_2O_3 catalyst at 300°C and 10.5 MPa. The major reaction products are the corresponding biphenyls and cyclohexylbenzenes, Figure 4.

As alluded to earlier, due to steric hindrance substitution in the 4 and 6 or 4 positions significantly decreases the HDS rate. Houalla et al. gave the pseudo-first-order rate constants (in units of cm^3 feed/g catalyst/h) for all five sulfur compounds at comparable feed concentrations. Based on the rate constants for 4-methyl DBT ($k = 23.9$) and 4, 6-dimethyl DBT ($k = 17.7$), $1/\delta$ is estimated to be 161×10^{-3} h·g cat./cm^3 feed. Note that a larger $1/\delta$ may be obtained if the rate constant for, say, 4-ethyl DBT is known.

The highest space time used by Houalla et al. is $t = 20 \times 10^{-3}$ h·g cat./cm^3 feed. At $t = 10 \times 10^{-3}$ h·g cat./cm^3 feed, about 94% of the parent molecule DBT is removed. In HDS of petroleum middle distillates, a high HDS level can often be attained once the bulk of DBT is removed. So we may take the rate constant for DBT ($k = 258.4$) as k^*.

Thus, if one were to desulfurize a middle distillate using the same conditions and catalyst as those used by Houalla et al., then the region of validity for the asymptotic power law kinetics, on the basis of inequality 49, is

$$3.87 \times 10^{-3} \ll t \ll 161 \times 10^{-3} \quad \text{h·g cat./cm}^3 \text{ feed} \tag{50}$$

Let us assume that the experiment of Houalla et al. is carried out up to $t = 100 \times 10^{-3}$ h·g cat./cm^3 feed so the $t \ll 1/\delta$ criterion is satisfied. Based on the rate constant for 4,6 dimethyl DBT, we calculate that the removal of this most refractory species is 83%. At this level, the HDS of many middle distillates is essentially complete.

The above analysis of pure-compound data together with our real-feed data indicate that the condition under which the continuum approximation is valid in the long-time limit is not very stringent. However, if one is interested in the regime of very long times ($t > 1/\delta$), a discrete approach may be preferable to a continuum one.

Conclusions

We have observed experimentally the high-conversion asymptotic power law that is predicted for lumped kinetics in the continuum approximation. We have also addressed a conceptual point essential to this power law, by establishing the condition under which both the continuum theory and its long-time limit are valid. On the basis of both real-feed and model-compound data, the condition is not very stringent.

Notation

$C = S/S_f$, total dimensionless concentration of reactants
C_c = total reactant concentration in continuous mixture
C_d = total reactant concentration in discrete mixture
$D(k)$ = reactant type distribution function
k = first-order rate constant
k^* = characteristic rate constant for refractory sulfur species
S_f = total sulfur concentration in feed
$S(t)$ = total sulfur concentration at space time t
z_n = defined as $z_n = t + i2n\pi/\delta$

Greek letters

α, β = parameters used in defining $c_o(k)$
δ = grid size, Eq. 4
ζ = parameter used for defining $c_o(k)$
σ, γ = parameters used for defining $c_o(k)$, case 2
σ_j, γ_j = parameters used for defining $c_o(k)$, case 3

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