Continuous Kinetic Lumping of Catalytic Cracking Processes

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Processes, in which a multicomponent mixture of chemically similar compounds undergoes cracking reactions governed by nonlinear kinetics, are analyzed. Cracking reactions in general imply cleavage of chemical bonds between monomeric units. The article focuses on the case of the "uniform" kinetics. To obtain an analytical solution of the kinetic equations describing this process, we present an approach based on a continuous description of the mixture. The resulting nonlinear integro-differential equation has been linearized by a warped time scale, and a formal solution has been obtained via a regular perturbation method. The perturbation parameter is twice the inverse of the initial average number of monomeric units in excess of the minimum number that can be cracked by the reactions considered.

Introduction

Mixtures containing a very large number of components are studied best by a continuous description that uses distribution functions. The idea was formulated by De Donder (1931) and has been formalized by Aris and Gavalas (1966). The latter authors also analyzed the overall kinetics of cracking reactions for the special case where the intrinsic kinetics are first-order. Cracking processes involve a comparatively complex topology of the reaction network, since every component of the mixture may be formed by cracking of higher molecular weight ones and is in turn consumed by cracking it into lower molecular weight ones.

Until very recently, the case of a multicomponent mixture, where the intrinsic kinetics are nonlinear, escaped attempts at formal solutions (Ho and Aris, 1987). In 1988, Astarita and Ocone provided a formal approach to such problems, based on the concept of uniform cooperative kinetics, which uses a warped time scale to transform the problem to a quasilinear one which can be solved formally. However, the approach of Astarita and Ocone was limited to the simple reaction network topology where a class of reactants transforms to a class of products that is not a reactant for subsequent reactions of the same type. In this article, we analyze the processes endowed with the reaction network topology of cracking for the intrinsic kinetics that are of the uniform nonlinear type considered by Astarita and Ocone (1988). While thermal cracking reactions are likely to be first-order, catalytic cracking reactions are not.

In a cracking reaction process, each component undergoes cleavage of bonds in a mixture of very many components (the I-mers), resulting in lower-molecular-weight oligomers, which may in turn undergo the same type of reaction. We first present a possible kinetic scheme for catalytic cracking (which may, perhaps by a stretch of imagination, be applied even to biochemical systems such as enzymatic hydrolysis of cellulose, see the Appendix). The kinetics used are nonlinear but of a very simple type, since the main purpose of this article is to present the methodology of approach to the class of problems considered. Next, we transform the equations to a continuous description, and we develop a formal perturbation scheme that yields in principle a complete formal solution. We develop the perturbation scheme in detail up to the first-order in the perturbation parameter. The latter is inversely proportional to the initial average number X^* of monomeric units in excess of the minimum value that can be the product of the class of reactions considered. It follows that our analysis is of significance for the (realistic) case where X^* is well in excess of unity.

The philosophy of this work is based on the following considerations taken from the work of Courant (1964): ". . a development will start from the concrete grounds, then discard ballast by abstraction and rise to the lofty layers of thin air where navigation and observation are easy; after this flight comes the crucial test of landing and reaching specific goals in the newly surveyed low plains of individual reality." We thus conclude the formal analysis with an estimate of the order of magnitude of the relevant effects, and an analysis of how the measurable quantities of interest are expected to evolve in time.

Stoichiometry and Kinetics

Consider a mixture of I-ers, $B(I)$, of some monomeric units $B(1)$ which may undergo cracking reactions of the following type:

$$B(I) \rightarrow B(J) + B(I-J);$$

$$I-J > M-1;\ J > M-1$$

where $B(M)$ is the lowest-molecular-weight species that can be produced by the class of reactions considered (which only includes those reactions described by the kinetics discussed below). M may well be unity (in the case, for instance, of the classical catalytic cracking of hydrocarbons that may produce as low an I-mer as $B(1)$, methane), but it does not need to be unity. For instance, in the enzymatic hydrolysis of cellulosic materials, where the monomer unit is glucose, $M=2$ for some of the classes of enzymatic reactions considered in the literature (see the Appendix). Also, the very simple kinetic equation that we use may break down at the low end of the molecular weight spectrum; in this case, M may be chosen so that $B(2M)$ is the lowest-molecular-weight species that still conforms to the assumed kinetics. In the following, species $B(K)$ with $K<2M$ will be called end products.

Let the kinetics of the reactions considered be dominated by the Langmuir isotherm adsorption, and let both the kinetic constant k and the adsorption constant P be the same for all reactants. This is, of course, a strong assumption, but, given the very similar chemical nature of all reactants, not an unreasonable one. (More complex kinetics could be considered, but we here wish to restrict attention to the simplest possible case of nonlinear kinetics.) With the assumptions stated and with $c(I)$ the concentration of species $B(I)$, the rate of cracking of species I is:

$$r(I) = kc(I) \Big/ \left[1 + P \sum_{2M}^{N} c(K) \right] \tag{1}$$

The intended sum is from $2M$ (the lowest value of I, for which reactions of the type considered may take place) to the largest value N of I. It is important to note that Eq. 1 describes uniform kinetics, in that the term multiplying $kc(I)$ on the righthand side of Eq. 1 does not depend on the current index I.

Keeping track of the topology of the reaction network forces the labeling of components: the index I is chosen as the number of monomeric units in species $B(I)$. When the topology is degenerately simple, it is more convenient (Astarita and Ocone, 1988) to scale the index so that it is proportional to the kinetic constant for species $B(I)$. One could develop the analysis below by allowing the kinetic constant to differ among different species, $k=k(I)$, but the mathematics involved would become untractable unless $k(I)$ is of the power-law form. The case where k is a unique constant still contains all the relevant features of the problem.

If the probability of any given bond being cleaved is the same for all the cleavable bonds, species $B(K)$, with $K=M, M+1, \ldots I-M$ which can be formed from species I are all produced in the same amounts. Permanence of atoms (or equivalently of monomeric units) then implies that the reactions can be written with the following equivalent stoichiometry:

$$B(I) \rightarrow \frac{2}{I+1-2M} \sum_{K=M}^{I-M} B(K)$$

Continuous Description

We first define the new index $X=I+1-2M$, so that the lowest-molecular-weight species which can undergo the reaction is $X=1$. The essence of the continuous description is that the label X is taken as a continuous variable (rather than being restricted to integer values); this is justified if actual values for species present in the mixture reach to large values of X, as is the case for most cracking reactions. Let $c(X,\tau)dX$ be the concentration at time τ of species in the interval from X to $X+dX$. The initial total concentration of monomers which may undergo the reactions considered, c_T, is, with square brackets indicating integration over the label range:

$$c_T = [c(X,0)] \tag{2}$$

It is useful to normalize all concentrations with respect to c_T:

$$g(X,\tau) = c(X,\tau)/c_T; \quad g(X,0) = A(X) \tag{3}$$

$$u(\tau) = [g(X,\tau)]; \quad u(0) = 1 \tag{4}$$

The initial average value of X, X^*, is the first moment of the initial concentration distribution:

$$X^* = [XA(X)] \tag{5}$$

The continuous form of Eq. 1 becomes with $Q=Pc_T$:

$$r(X) = kg(X,\tau)/[1+Qu(\tau)] \tag{6}$$

Since the kinetic constant k is independent of X, it is natural to normalize time with respect to it, $t=k\tau$. It is now possible to write an equation for the rate of change of $g(X,t)$. Species X is formed by all species from $X+M$ up, and is consumed itself; all relevant rates are given by Eq. 6. It follows that:

$$\frac{@g(X,t)}{@t} = \frac{1}{1+Qu(t)} \int_{X+M}^{\infty} \frac{2g(Y,t)}{Y}\, dY - g(X,t) \tag{7}$$

where Y is the label X when it is intended as a dummy variable.

Equation 7 is a nonlinear, partial integrodifferential equation, and some simplifications are in order. First of all, it is useful to rescale the label X with respect to its initial average value, $x=X/X^*$. Both the zeroth and the first moment of the initial concentration distribution function $A(x)$ are now required to be unity. Let $\epsilon=M/X^*$; in any realistic case, ϵ is significantly less than unity, and hence a perturbation solution in terms of the parameter ϵ can be sought. In terms of the normalized label x (indicated with y when it is intended as a dummy variable), Eq. 7 becomes:

$$\frac{\partial g(x,t)}{\partial t}=\frac{1}{1+Qu(t)}\left[\int_{x+\epsilon}^{\infty}\frac{2g(y,t)}{y}\,dy-g(x,t)\right] \tag{8}$$

Solution

The term in square brackets in Eq. 8 has a structure which is very similar to that by Aris and Gavalas (1966) describing thermal cracking of hydrocarbons. It is not surprising, since it is a cracking reaction, in which the term within square brackets essentially describes the stoichiometry of the reactions: the integral represents the formation of any given species from higher-order oligomers, and the other term represents the cleavage of the species considered. The fundamental difference between Eq. 8 and the Aris and Gavalas equation is in the term $1/(1+Qu)$, which makes the equation nonlinear. However, the important point is that the term $1/(1+Qu)$ does not depend on x: *it has the same value for all species.* Of course, it is because we assumed kinetics of the Langmuir isotherm type.

In the terminology of Astarita and Ocone (1988), the kinetic function on the righthand side of Eq. 8 describes uniform cooperative kinetics. They are cooperative in that the formation rate of species x depends (through the term containing u) on the whole spectrum of concentrations; they are uniform in that the term responsible for nonlinearity does not depend explicitly on x. Thus, the problem, following Astarita and Ocone, is a quasilinear one which can be attacked by defining a warped time scale $w(t)$, which is delivered by the solution of the following differential equation:

$$dw/dt=1/[1+Qu(t)]; \quad w(0)=0 \tag{9}$$

The derivative dw/dt is always positive, and hence $w(t)$ is invertible; its inverse $t(w)$ is delivered by:

$$dt/dw=1+Qu(w); \quad t(0)=0 \tag{10}$$

In terms of the warped time scale w, Eq. 8 becomes:

$$\frac{\partial g(x,w)}{\partial w}=\int_{x+\epsilon}^{\infty}\frac{2g(y,w)}{y}\,dy-g(x,w) \tag{11}$$

It is important to realize that the value of the adsorption constant, which determines the value of Q, influences only the relationship between the actual dimensionless time t and the warped time w, through Eq. 9. As will be seen below, the behavior in the warped time scale w is entirely independent of the value of Q. Before proceeding to a perturbation expansion, it is useful to calculate du/dw by integration of all terms in Eq. 11 over x from 0 to ∞. Let $2K(x,w)$ be the integral appearing in Eq. 11. One obtains:

$$du/dw=2[K(y,w)]-u \tag{12}$$

Integration by parts of the integral in Eq. 12 yields:

$$[K(y,w)]=u-\int_0^{\epsilon}g(y,w)dy-\epsilon\int_{\epsilon}^{\infty}\frac{g(y,w)}{y}\,dy \tag{13}$$

and thus finally:

$$du/dw=u-2\int_0^{\epsilon}g(y,w)dy-2\epsilon\int_{\epsilon}^{\infty}\frac{g(y,w)}{y}\,dy \tag{14}$$

Equation 14 should be discussed in some detail. The first term on the right simply reflects that as any of the reactions considered takes place, two species are formed from one, and therefore the total concentration increases proportionally to itself in the time scale w in which the kinetics are linear. While this is true for most of the elementary steps, it is not true for all of them, since some end products are produced that disappear from the spectrum of species being described. We will come back to this point later; here we simply observe that at zero-order in ϵ, Eq. 14 has the trivial solution:

$$u=e^{w} \tag{15}$$

If this is substituted into Eq. 10, one obtains the zero-order relationship between the actual and the warped time scales:

$$t=w+Q(e^{w}-1) \tag{16}$$

Perturbation Expansion

Laplace transformation of Eq. 11 furnishes the following Volterra integral equation for $G(x,s)$, the image of $g(x,w)$ in the Laplace domain:

$$\begin{aligned}G(x,s)&=A(x)/(s+1)+\frac{2}{s+1}\int_{x+\epsilon}^{\infty}\frac{G(y,s)}{y}\,dy\\&=A(x)/(s+1)+2H(x,s)/(s+1)\end{aligned} \tag{17}$$

This can be dealt with by differentiation of the function $H(x,s)$ with respect to x, which, when combined with Eq. 17, yields:

$$(s+1)(x+\epsilon)\partial H/\partial x+2H(x+\epsilon,s)=-A(x+\epsilon) \tag{18}$$

Should one set ϵ to zero, one would obtain essentially the Aris and Gavalas equation describing thermal cracking with, however, s the transform variable for the actual time t and not the warped time w. Since ϵ is necessarily a small number, a perturbation expansion can be set up as follows. First, function $H(x,s)$ is assumed to be expressed as:

$$H=H_o+H_1\epsilon+H_2\epsilon^2+\ldots \tag{19}$$

Next, both $A(x+\epsilon)$ and $H(x+\epsilon)$ are expressed by Taylor series expansions around x, and hence again as power series in ϵ. These expressions are then substituted in Eq. 18, terms of equal order in ϵ are collected, and the differential equation for the nth order of perturbation is obtained:

$$-(s+1)\partial H_n/\partial x-2H_n=(s+3)\partial H_{n-1}/\partial x$$
$$+2\sum_2^n \frac{1}{i!}\frac{\partial^i H_{n-2}}{\partial x^i}+\frac{1}{n!}\frac{d^nA}{dx^n}=F_n(x,s) \quad (20)$$

Equation 20, subject to $H_n(x,\infty)=0$, is a linear nonhomogeneous differential equation, because at any level of perturbation $F_n(x,s)$ is a known function obtained from the lower-order perturbations. The solution is:

$$H_n(x,s)=\frac{x^{-2/(s+1)}}{s+1}\int_x^\infty F_n(y,s)y^{(1-s)/(1+s)}dy \quad (21)$$

Substitution of Eq. 21 into Eq. 19, and then the result into Eq. 17 furnish a formal series representation of the Laplace transform of the concentration distribution:

$$G(x,s)=A(x)/(s+1)$$
$$+\frac{2x^{-2/(s+1)}}{(s+1)^2}\sum_0^\infty \epsilon^n\int_x^\infty F_n(y,s)y^{(1-s)/(1+s)}dy \quad (22)$$

Zero-Order Level

The zero-order-level equation is easily integrated to yield:

$$G_o(x,s)=A(x)/(s+1)$$
$$+\frac{2x^{-2/(s+1)}}{(s+1)^2}\int_x^\infty y^{(1-s)/(1+s)}A(y)dy \quad (23)$$

It takes some tedious algebra to integrate Eq. 23 over x from 0 to ∞ to obtain the zero-order Laplace image of the lumped concentration, $U_o(s)$; the result is:

$$U_o(s)=1/(s-1) \quad (24)$$

which is, of course, the Laplace transform of Eq. 15. Note that the result is entirely independent of the form of the initial concentration distribution function $A(x)$: *the temporal evolution of the lumped concentration is, at the zero-order level, independent of the form of the initial distribution of concentrations*. The result in Eq. 24 validates the analysis leading to Eq. 15, proving that the result is the correct zero-order level one. In particular, t and w are related to each other by Eq. 16.

Taking the inverse Laplace transform of Eq. 23 (Abramowitz and Stegun, 1968), the concentration distribution function $g_o(x,w)$ is, with $I_1(\ )$ the first-order modified Bessel function of the first kind:

$$e^w g_o(x,w)=A(x)+\{I_1(y)A[x\exp(y^2/8w)]\} \quad (25)$$

Equation 25 shows that the concentration distribution at the warped time w is a transform of the initial one: the first term represents simply an exponential decay of the initial concentration, and the second term is a transform of a distorted initial distribution.

It is now of interest to ascertain the range of (approximate) validity of the zero-order result. The differential equation for $G_o(x,s)$ is the Laplace image of the equation one would obtain by neglecting ϵ with respect to x in Eq. 11. Equivalently, the zero-order result has been shown to be equivalent to neglecting the two integrals on the righthand side of Eq. 14. It takes little analysis to realize that these approximations are justified, provided that the normalized first moment of the distribution $g(x,w)$, $[xg(x,w)]$, is larger then ϵ, a condition which is certainly satisfied at time zero when the first moment $[xg(x,0)]$ has been set to unity by the rescaling $x=X/X^*$.

The zero-order approximation, insofar as it produces Eq. 15, is based essentially on neglecting the formation of end products, and hence to within its validity, the total number of monomeric units in the spectrum of concentrations is constant in time. This implies that:

$$[xg(x,w)]=1/u+O(\epsilon) \quad (26)$$

Combining this with Eq. 15, the value of w_c, the critical warped time at which the zero-order approximation breaks down, is estimated as:

$$w_c=-\ln\epsilon \quad (27)$$

Even in the case of first-order kinetics, where $t=w$, the critical time would be $-\ln\epsilon$. It would be significantly larger than unity. The effect is even more marked when Q is not zero; substitution of Eq. 27 into Eq. 16 yields the estimate of the critical time t_c:

$$t_c=-\ln\epsilon+Q(1-\epsilon)/\epsilon>-\ln\epsilon \quad (28)$$

For small Q values (specifically, for $Q<<-\epsilon\ln\epsilon$), the critical time is $-\ln\epsilon$, which corresponds to first-order kinetics. One thus concludes that first-order kinetics are a reasonable approximation only at very low values of Q. For Q values in excess of $-\epsilon\ln\epsilon$, t_c approaches Q/ϵ. It is very important to conclude that *the zero-order approximation holds up to dimensionless times well in excess of unity*. Physically, there is a long induction time (significantly longer than the inverse of the kinetic constant) during which the reactions considered essentially reduce the average molecular weight of the mixture, without producing significant amounts of end products. Only after this induction period will the concentrations of end products become significant.

First-Order Level

The first-order-level differential equation for $G_1(x,s)$ can again be integrated explicitly, and the result can be inverse transformed (Abramowitz and Stegun, 1968) to yield $g_1(x,w)$. The result, with $I_l(\ )$ the lth-order modified Bessel function of the first kind, is:

$$-e^w g_1(x,w)=2wA(x)/x$$
$$+(8w/x)\{[I_2(y)/y]\exp(-y^2/8w)A[x\exp(y^2/8w)]\}$$
$$+[4w(4w+3)/x]\{e^{-y}\int_{2\sqrt{(wy)}}^\infty [I_3(z)/z^2]A[x\exp(z^2/8w)]dz\}$$
$$+(4w/x)\left\{e^{-y}\int_{2\sqrt{(wy)}}^\infty [dI_3(z)/dz]A(x\exp z^2/8w)]dz\right\} \quad (29)$$

This is not, by itself, of great interest, since if the first-order correction is of significance, a law of diminishing returns rapidly sets in: at w values slightly larger than w_c, the second-order corrections also becomes of importance, and so on. Formally, however, the solution at any level can be obtained explicitly in terms of transforms of the distorted initial concentration distribution involving modified Bessel functions of the first kind and their derivatives as kernels. Equation 29 can be integrated to yield $u_1(w)$, the first-order correction to the lumped concentration. At the same level, Eq. 10 becomes:

$$dt/dw = 1 + Qu_o(w) + \epsilon Qu_1(w) \qquad (30)$$

which integrates to:

$$t(w) = w + Q(e^w - 1) + Q\epsilon \int_0^w u_1(z)dz \qquad (31)$$

The last term on the righthand side is negative: u_o is an overestimate of u, since some end products are formed even at short times. To show that indeed $u_1 < 0$, one only needs to take the first-order expansion of Eq. 14, which yields:

$$du_1/dw = u_1 - (2/\epsilon)\int_0^\epsilon g_o(y,w)dy - 2\int_\epsilon^\infty [g_o(y,w)/y]dy \qquad (32)$$

Since this is subject to $u_1(0) = 0$ and the two integrals are positive, $u_1 < 0$ and its absolute value increases with increasing w.

The interest of the first-order-level solution lies in the following fact. The quantity $u_1(w)$ represents (to first order in ϵ) the total concentration of species which have disappeared from the spectrum considered: it represents the amount of end products formed from higher-molecular-weight oligomers (note that within zero order, no end products are formed, and hence that u_1 represents the lowest-order estimate, and the only significant one during the induction period). At t values exceeding t_c, even the first-order result cannot be used with confidence any more, and this leads to consideration of the long-time asymptotic behavior of the system considered, which is discussed in the next section.

Long-Time Asymptotic Behavior

Consider the (likely) case where Q is well in excess of $-\epsilon \ln \epsilon$ (in the converse case, the kinetics are essentially linear). The plot of the actual dimensionless time scale t vs. the warped time scale w is shown in Figure 1. The initial slope is $1 + Q$; the zero-order curve is the plot of Eq. 16. At $w = w_c$, the first-order correction becomes important; the $t(w)$ curve bends down away from the zero-order curve.

The behavior at very long times is easily ascertained. Most of the oligomers have been transformed to end products, and hence u has become very small as compared to $1/Q$; Eq. 10 then implies that dt/dw approaches the value of unity, hence:

$$t = t^* + w \qquad (33)$$

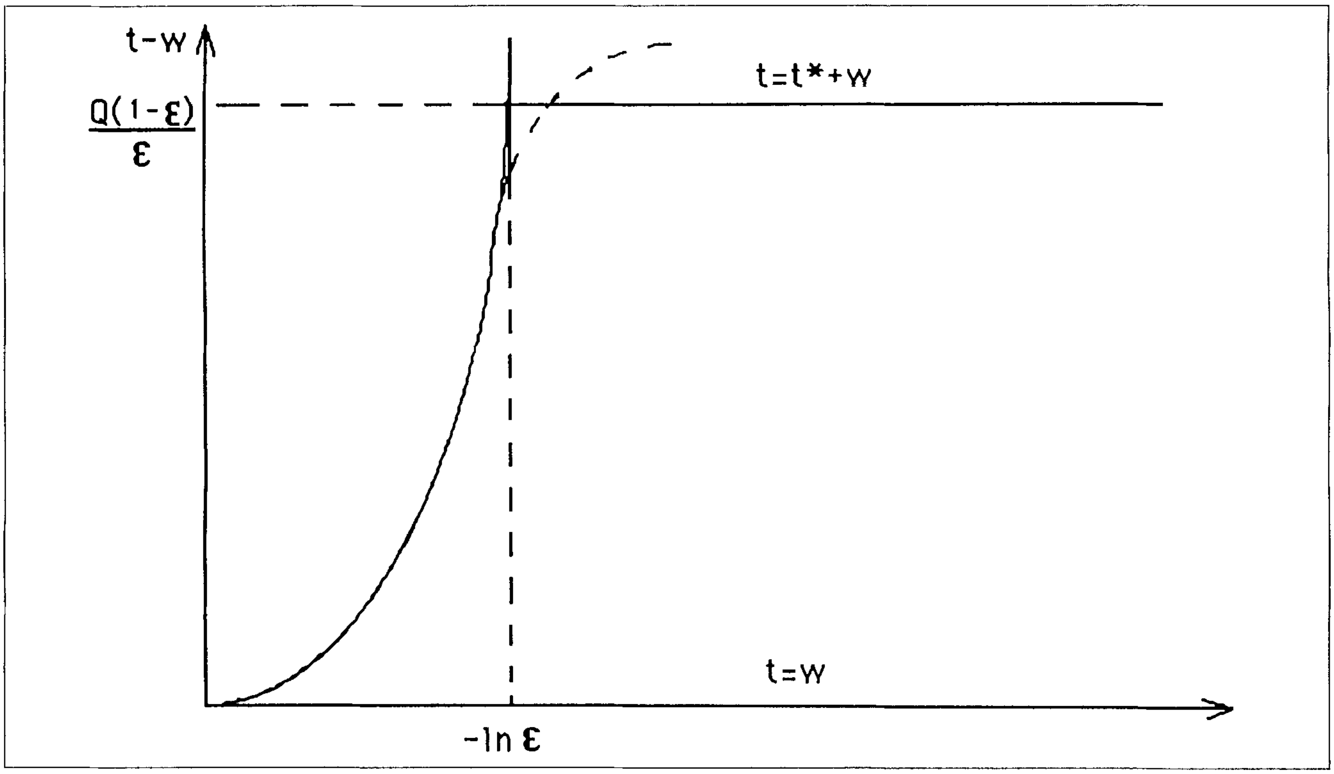

Figure 1. Qualitative plot of t vs. w.

The upper straight line is the large time asymptotic behavior. The full curve through the origin is the zero-order approximation. The dashed curved is the first-order approximation.

One now needs an estimate of the constant t^*. We have seen that significant deviations from the zero-order approximations occur when $[xg(x,w)]$ becomes of order ϵ: in this case, most of the oligomers in the spectrum are $B(2M)$ and $B(2M+1)$, which can only react to yield end products. Hence, in the warped time scale w, once $[xg(x,w)]$ has become of order ϵ, u decreases significantly over a w range of order unity. This is significantly less than w_c, and hence the long-time asymptotic behavior is approached shortly after the zero-order approximation fails to hold. It follows that a reasonable estimate of t^* can be obtained by requiring the straight line representing Eq. 33 to intersect the zero-order curve at $w = w_c$; this provides the following estimate for t^* (as used in Figure 1):

$$t^* = Q(1-\epsilon)/\epsilon \approx Q/\epsilon \qquad (34)$$

In the case of approximately first-order kinetics (Q smaller than $-\epsilon \ln \epsilon$), the induction time is of order $-\ln \epsilon$: it is larger than unity, but grows only logarithmically with $1/\epsilon$. In the case of nonnegligible values of Q (in excess of $-\epsilon \ln \epsilon$), t^* is even larger and grows linearly with $1/\epsilon$.

Conclusions

A system of cracking-type reactions governed by nonlinear kinetics has been analyzed by a continuous description, combining basic ideas developed by Aris and Gavalas (1966) and by Astarita and Ocone (1988). A formal solution based on a perturbation expansion has been obtained.

Two points about the formal solution are worth noting. First, all equations give actual concentration distributions in terms of linear transforms of the initial one; it follows that the equations hold for arbitrary initial distributions $A(x)$. Second, the equations, when expressed in terms of the warped time scale w, are independent of the value of the adsorption constant, which only enters in determining the relationship between the warped and actual time. The long-time asymptotic behavior has been analyzed in qualitative terms.

It is concluded that a cracking mixture with a large initial average molecular weight will exhibit an induction period before appreciable amounts of end products are formed; the induction time is well in excess of the reaction time scale of each individual cracking reaction, and it is larger in the case of Langmuir isotherm kinetics than it is for first-order kinetics.

Literature Cited

Abramowitz, M., and I. R. Stegun, *Handbook of Mathematical Functions*, Dover Publications, New York (1968).

Aris, R., and G. R. Gavalas, "On the Theory of Reactions in Continuous Systems," *Phil. Trans. Roy. Soc.*, **A260**, 351 (1966).

Astarita, G., and R. Ocone, "Lumping Nonlinear Kinetics," *AIChE J.*, **34**, 1299 (1988).

Courant, R., "Mathematics in the Modern World," *Sci. Amer.*, **211**(3), 41 (1964).

De Donder, Th., *L'affinité: Seconde Partie*, Gauthiers-Villars, Paris (1934).

Halliwell, G., and M. Griffin, "Nature and Mode of Action of the Cellulolytic Component C_1 of Trichoderma Koningii on Native Cellulose," *Biochem. J.*, **135**, 587 (1973).

Ho, T. C., and R. Aris, "On Apparent Second-Order Kinetics," *AIChE J.*, **33**, 1050 (1987).

King, K. W., and M. I. Vessal, "Enzymes of the Cellulase Complex," *Adv. Chem. Ser.*, **95**, 7 (1969).

Lee, S. E., W. B. Armiger, C. M. Watteeuw, and A. E. Humphrey, "A Theoretical Model for Enzymatic Hydrolysis of Cellulose," *Biotechn. Bioeng.*, **20**, 141 (1978).

Lee, Y., and L. T. Fan, "Properties and Mode of Action of Cellulase," *Advances in Biochemical Engineering*, p. 101, A. Fiechter, ed., Springer-Verlag, Berlin (1980).

Lee, Y., L. T. Fan, and L. Fan, "Kinetics of Hydrolysis of Insoluble Cellulose by Cellulase," *Advances in Biochemical Engineering*, p. 131, A. Fiechter, ed., Springer-Verlag, Berlin (1980).

Nisizawa, K., Y. Hashimoto, and T. Shibata, "Specificities of some Cellulases of the Random Type," *Advances in Enzymatic Hydrolysis of Cellulose and Related Materials*, E. T. Reese, ed., Pergamon Press, New York (1963).

Reese, E. T., and M. Mandels, *Series on High Polymers*, Vol. 5, p. 1079, N. M. Bikales and L. Segal, eds., Wiley, New York (1971).

Reese, E. T., R. G. H. Siu, and H. S. Levinson, "Biological Degradation of Soluble Cellulose Derivatives and its Relationship to the Mechanism of Cellulose Hydrolysis," *J. Bacteriol.*, **59**, 485 (1950).

Suga, K., G. van Dedem, and M. Moo-Young, "Degradation of Polysaccharides by Endo- and Exo-Enzymes: a Theoretical Analysis," *Biotechn. Bioeng.*, **17**, 433 (1975).

Appendix

We have discussed a cracking mixture, without specifically addressing its chemistry. The analysis presented is relevant to at least some possible processes of catalytic cracking. Another process that may have been described, at least in part, by our equations is the enzymatic hydrolysis of cellulosic materials to produce glucose.

Cellulose can be hydrolized to a mixture of glucose and its oligomers by attack of enzymatic complexes generically named cellulases. Suppose that all the glucans, which constitute the cellulosic material, are available for enzymatic attack at time zero which may or may not be a realistic assumption, depending on circumstances. The reactions which glucans undergo are cracking reactions with the monomeric unit being glucose. Mechanisms for the enzymatic breakdown of cellulose have been proposed as early as 1950 by Reese et al. Halliwell and Griffin (1973) have identified in the β-1,4-glucan cellobiohydrolase, the agent which has some hydrolytic activity and removes cellobiose.

The main hydrolytic activity, however, is performed by endo- and exo-components, that are present in almost all cellulases studied so far. Exo-β-1,4-glucanase removes glucose units from nonreducing ends of the chain, acting most rapidly on soluble glucans of four to seven units (Nisizawa et al., 1963). Endo-β-1,4-glucanases randomly attack high-molecular-weight glucans, playing a key role in the overall degradation of the polymer; these only cleave bonds that are not end ones. Should the role of these enzymes be isolated from the analysis as if other enzymes were not present, one would have a stoichiometry of the type discussed in this article. In fact, whenever few, long glucose chains are present, there are too few ends to obtain appreciable hydrolysis rates by exo-enzymes alone (Reese and Mandels, 1971). Finally, β-glucosidases hydrolyze cellobiose and cellotriose, and do not act on higher-molecular-weight glucans (King and Vessal, 1969); so, from the viewpoint of this article, the latter enzymes would attack only the end products.

Several models have been proposed to describe enzymatic hydrolysis of cellulose. Many of these adopt classical Michaelis Menten kinetics, or combine it with equations describing enzyme adsorption onto the material. A very comprehensive review is available (Lee et al., 1980). There are also depolymerization models: Suga et al. (1975) considered the action of endo- and exo-enzymes alone, and studied the combined effect of the two components. They postulated Michaelis Menten kinetics and integrated the equations by quasi-steady-state approximations. Lee et al. (1978) considered a cellulase complex containing all four components; they integrated numerically the model equations and gave some theoretical distributions of molecular weight of oligomers as a function of process time.

The important point to be noted is that Michaelis Menten kinetics are, from a mathematical viewpoint, undistinguishable from Langmuir isotherm adsorption ones, and hence that an analysis of the type presented here could, under appropriate qualifying conditions, be applied to a preliminary analysis of cellulose hydrolysis.

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