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A Novel Interpretation of Temperature versus Time Curves for Deactivating Catalyst Systems

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A mathematical development of the relationship between the fundamental kinetics and the temperature versus time curves for catalyst deactivation is presented. It is demonstrated that a very large reaction order for fouling, which decreases as the catalyst fouls, can account for typically observed S-shaped temperature versus time curves for reactions involving hydrocarbons under reducing conditions. © 1986 Academic Press, Inc.

INTRODUCTION

In industrial reactors the inlet temperature is raised to compensate for catalyst deactivation. This allows a constant amount of feedstock to be processed by a catalytic reactor over a given length of time, despite the deactivation phenomena. In general, the temperature versus time history is a monotonically increasing function, $T = T(t)$. The second derivative of the T versus t curve may be either positive or negative. In many cases the curvature is initially negative, but increases with time, resulting in an inflection point prior to a region of positive curvature. There are many examples of this phenomenon in the literature (*1–7*).

Catalyst deactivation is often modeled using simple separable power-law activity factors (*8, 9*). This technique is extremely useful; however, there are limitations on the applicability of this model. In order to explain a wide range of fouling data on a single model system with a separable power-law model, it was necessary to allow the "order of deactivation" to depend on the activity (*10*). This variable reaction order can be rationalized on the basis of a simple multiplet model, in which catalyst fouling occurs on successively smaller site ensembles as the catalyst fouls (*11*). It is a reasonable consequence of the extinction of large site ensembles prior to that of smaller site ensembles, as anticipated by Herrington and Rideal (*12*).

The purpose of this paper is to demonstrate the relationship between the fundamental kinetic parameters used in the separable power-law models and the general shape of empirical temperature versus time curves for deactivating systems.

DEACTIVATION OF A WELL-MIXED REACTOR (CSTR)

The following items serve as a description of the reaction engineering system initially analyzed and form the basis for the mathematical treatment. In subsequent systems certain of these constraints are relaxed.

1. The temperature is raised to maintain a constant conversion in a heterogeneous catalytic reactor undergoing deactivation.
2. The reactant feedrate is held constant throughout the entire catalyst life cycle.
3. The reactor is well-mixed, held at uniform temperature, and continuously fed (Ideal CSTR) with respect to the fluid phase, and a well-mixed batch reactor (Ideal STR) with respect to the solid catalyst phase.
4. Two reactions occur: the desired reaction and the deactivation reaction. The desired reaction is much faster than the deac-

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tivation reaction. Both reactions can be represented by simple power-law kinetics in parallel, a separable activity factor, and Arrhenius temperature dependence.

5. No deactivation occurs prior to reaching the initial steady-state conversion with a fresh catalyst.

6. There are no internal or external transport effects.

MATHEMATICAL DEVELOPMENT

The design equation for the system is shown in

$$a_n\left[\frac{k_n(T)}{k_n(T_0)}\right] = \frac{X_e}{(1 - X_e)^q\mathrm{Da}}, \tag{1}$$

where

$a_n \equiv$ separable activity factor for main reaction
$k_n(T) \equiv$ rate constant for main reaction at T
$T, T_0 \equiv$ reactant feed temperature after a period of deactivation, and the initial feed temperature, respectively.
$X_e \equiv$ fractional conversion of limiting reactant
$q \equiv$ order of main reaction with respect to the limiting reactant
$\mathrm{Da} \equiv$ Damkohler number for the main reaction at the initial temperature $(t_R k_n(T_0)\, C_0^{q-1})$
$t_R \equiv$ average residence time
$C_0 \equiv$ concentration of the limiting reactant in the reactor feed.

Initially, the left-hand side of Eq. (1) is unity because a_n is defined as unity. With the passage of time, the activity a_n, decreases. However, the right-hand side of Eq. (1) will remain constant at a value of unity even as the catalyst deactivates because we constrain the system to constant conversion. Therefore, the temperature must be increased to maintain the left-hand side to unity. Following appropriate substitution and rearrangement

$$\alpha^n \exp Y = 1, \tag{2}$$

where

$$a_n = \alpha^n \tag{3}$$

$$\frac{k_n(T)}{k_n(T_0)} = \exp\left\{\gamma_n \frac{\theta}{(1 + \theta)}\right\} \tag{4}$$

and

$$Y \equiv \frac{\gamma_n \theta}{1 + \theta}, \tag{5}$$

where

$\alpha \equiv$ fraction of catalyst sites unfouled
$n \equiv$ order of the main reaction with respect to active sites
$\theta \equiv$ dimensionless temperature rise, $(T - T_0)/T_0$
$\gamma_n \equiv$ activation energy number for the main reaction, $\Delta E_n/RT_0$
$\Delta E_n \equiv$ activation energy of the main reaction
$R \equiv$ gas law constant.

Equation (2) can be differentiated with respect to time, to obtain the more useful activity–temperature relationship

$$\frac{d\alpha}{dt} = -\frac{\alpha}{n}\frac{dY}{dt}. \tag{6}$$

Combining this differential relationship with a differential rate expression for the deactivation reaction, it is possible in general to relate temperature versus time data to the fundamental kinetic parameters. For example, consider the rate of loss of active sites governed by the simple separable power-law rate expression of the form

$$\frac{d\alpha}{dt} = -a_m \cdot k_m(T) \cdot C_0^p(1 - X_e)^p, \tag{7}$$

where

$a_m \equiv$ separable activity factor for deactivation reaction
$k_m(T) \equiv$ rate constant for the deactivation reaction at T
$p \equiv$ order of the deactivation reaction with respect to the limiting reactant for the main reaction.

As with the main reaction, the activity factor can be replaced by a power-law expression and the temperature dependence of the rate constant can be replaced by an Arrhenius factor to yield, respectively,

$$a_m = \alpha^m \tag{8}$$

and

$$\frac{k_m(T)}{k_m(T_0)} = \exp\left\{\gamma_m \frac{\theta}{(1+\theta)}\right\}. \tag{9}$$

Substituting Eqs. (8) and (9) into (7) gives

$$\frac{d\alpha}{dt} = -\alpha^m k_m(T_0) C_0^p (1 - X_e)^p \exp(\varepsilon Y), \tag{10}$$

where

$m \equiv$ order of the deactivation reaction with respect to active sites
$\gamma_m \equiv$ activation energy number for the deactivation reaction T_0, $\Delta E_m / RT_0$
$\Delta E_m \equiv$ activation energy of the deactivation reaction
$\varepsilon \equiv$ activation energy ratio $= \frac{\Delta E_m}{\Delta E_n} = \frac{\gamma_m}{\gamma_n}$.

From Eqs. (2), (6), and (10) we get

$$\frac{dY}{d\tau} = \exp(\delta Y), \tag{11}$$

where

$$\tau \equiv n \cdot k_m(T_0) C_0^p (1 - X_e)^p t \tag{12}$$

and

$$\delta \equiv \varepsilon - \left(\frac{m-1}{n}\right). \tag{13}$$

The dimensionless time, τ, is equal to the Damkohler number of the deactivation reaction, times the order of the main reaction n. δ is equal to a weighted difference in the activation energy numbers. The weighting factor $(m - 1)/n$ is a multiplier in front of the activation energy number for the main reaction γ_n.

Equation (11) can be integrated over time, using the initial condition of $Y = 0$ at $\tau = 0$, to give the resulting temperature versus time history

$$1 - e^{-\delta Y} = \delta\tau. \tag{14}$$

Alternately, Eq. (11) can be differentiated with respect to time and rearranged, to obtain the resulting equation for the curvature of the temperature versus time plot

$$\frac{d^2\theta}{d\tau^2} = [\delta\gamma_n + 2(1 + \theta)](1 + \theta)^2 \exp\left\{2\delta\gamma_n \frac{\theta}{1 + \theta}\right\}. \tag{15}$$

The only factor on the right-hand side of Eq. (15) that can be less than zero is that enclosed in brackets which we define here as, Δ, for convenience. In terms of real quantities

$$\Delta \equiv \gamma_n \left[\frac{\Delta E_m}{\Delta E_n} - \frac{m-1}{n} + 2\frac{T}{\gamma_n T_0}\right]. \tag{16}$$

There are three possible cases as shown by Ho (*13*):

$\Delta > 0$: the first derivative of T vs t increases monotonically (positive curvature)
$\Delta = 0$: the slope of T vs t is constant (zero curvature)
$\Delta > 0$: the slope of T vs t decreases monotonically (negative curvature).

Ho stated that if $m - 1/n > \varepsilon + (T/\gamma_n \tau_0)$, then the curve would begin with a negative curvature. Then as T increases, the term $T/\gamma_n T_0$ increases and would account for a positive curvature. However, the quantities $\Delta E_m / \Delta E_n$, m, and n are constants for power-law systems; T/T_0 varies in practical situations from about 1 to 1.2 during the lifetime of the catalyst; and the value of the Arrhenius number, γ_n, for the main reaction is of the order of 20. The terms in the brackets of Eq. (16) are $\Delta E_m / \Delta E_n \approx 2$–$4$, $m - 1 \approx 0$–5, and $2T/\gamma_n T_0 \approx 0.1$–$0.2$. The only term that changes during deactivation is $2T/\gamma_n T_0$ and it is too small to affect the magnitude of Δ for typical reaction parameters. Accordingly, the sign of Δ does not change during deactivation and the second derivative is essentially constant for systems having constant kinetic orders.

It is much more likely that a variation in one or more of the kinetic parameters in the first two terms of Eq. (16) accounts for the sign change. The quantity $(m - 1)/n$ varies with kinetic orders of the deactivation and main reactions. It has been noted elsewhere

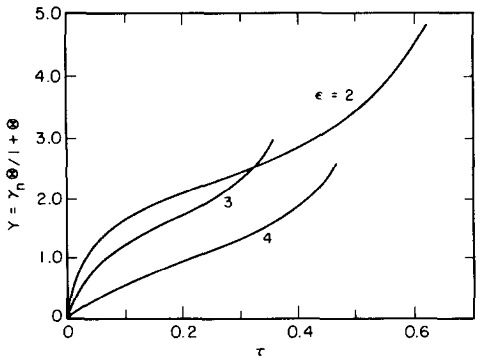

FIG. 1. Characteristic plot for multiplet model in a CSTR.

(*11*) that this quantity can start out at a value of about 5 for a fresh catalyst and decrease to a value of about 2 for a severely fouled catalyst where the main reaction is first order. This was based on a correlation of activity versus time data for a wide-range of reaction systems and conditions (*10*).

Using this model for a practical range of activation energies and temperatures, the value of $(m-1)/n$ is about 5 and Δ is a negative number, during the early stages of deactivation. Then, as the catalyst fouls, the value of $(m-1)/n$ decreases to about 2 and Δ becomes a positive number, resulting in an inflection point in the T versus t curve.

A deactivation law exhibiting these characteristics has the form (*11*)

$$\frac{d\alpha}{dt} = -(1-X)^p k_m(T) \sum_{m=2}^{6} \frac{\alpha^m}{\omega^{6-m}}, \qquad (17)$$

where

$\omega \equiv \exp(\lambda/RT)$
$\lambda \equiv$ bond energy with the surface.

From Eqs. (5), (6), (9), and (17) and simplifying, we get

$$\frac{dZ}{d\tau'} = -\sum_{m=2}^{6} Z^{m-\varepsilon}, \qquad (18)$$

where it is assumed that $n = 1$ and where

$$Z = \omega\alpha$$

$$\tau' = \frac{k(T_0)(1-X_e)^p C_0^p t}{\omega^{5-\varepsilon}}. \qquad (19)$$

The behavior of the multiplet model in a CSTR is shown in Fig. 1. Y is plotted as the ordinate instead of θ. However, in the range of the graph they are almost proportional. Note that the result depends only upon a single parameter ε which is the ratio of the activation energies for deactivation and the main reaction. The physical significance of the deactivation model (Eq. (18)), including factor ω, has been discussed elsewhere (*11*).

DEACTIVATION OF A PLUG FLOW REACTOR (PFR)

The previous treatment is of interest from the analytical point of view because it is simple to understand the behavior of a system in which the conditions in the reactor do not vary spacially. Most industrial catalytic reactors, however, exhibit spacial variation in reaction conditions.

The governing equations to describe the plug flow reactor are outlined analogous to those for the CSTR.

$$\frac{dx}{(1-X)^q} = \alpha^n \exp\left\{\frac{\gamma_n\theta}{1+\theta}\right\} \left\{\frac{k(T_0)C_0^{q-1}\,dl}{u}\right\}, \qquad (20)$$

where

$l \equiv$ reactor length coordinate
$u \equiv$ velocity,

where α^n is the activity in accordance with Eq. (3). When $t = 0$; $\theta = 0$ and $\alpha = 1$, it follows that

$$\int_0^{X_e} \frac{dx}{(1-X)^q} = \frac{k(T_0)C_0^{q-1}L}{u} \equiv \mathrm{Da}, \qquad (21)$$

where $L \equiv$ length of the PFR.

If the conversion X_e is fixed, then Da is known from the integration of the left-hand side of Eq. (21). Using the result, Eq. (20) can be written as

$$\frac{1}{\mathrm{Da}} \int_0^{X_e} \frac{dx}{(1-x)^q} = \exp\left\{\frac{\gamma_n\theta}{1+\theta}\right\} \int_0^1 \alpha^n\,dz = 1. \qquad (22)$$

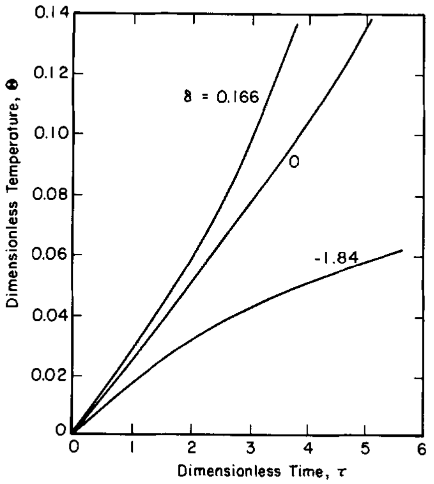

FIG. 2. Dependence of T versus t curves on δ.

In order to solve Eq. (22) we must, in general, know a deactivation rate law in order to express α as a function of z and time.

A particularly simple and useful solution obtains from a rate law of the form

$$\frac{d\alpha}{dt} = -k_m \alpha^m. \tag{23}$$

For this case α is not a function of z and the right-hand side of Eq. (22) becomes

$$\alpha^n \exp\left\{\frac{\gamma_n \theta}{1+\theta}\right\} = 1. \tag{24}$$

Differentiating Eq. (24) and substituting Eq. (23) for $d\alpha/dt$ and simplifying yields

$$\frac{dY}{d\tau'} = \exp(\delta Y), \tag{25}$$

where

$$\tau' \equiv \frac{n k_m (T_0) t}{\gamma_n}$$

and δ is defined by Eq. (13). Equation (25) is identical to Eq. (11) and therefore the same analysis applies to the behavior of this PFR and a CSTR.

More realistically the rate of deactivation should depend upon the local conversion such as that shown in Eq. (7). Equation (22) still applies, but the form of Eq. (7) dictates that α is a function of position in the reactor as well as time and an analytical solution is no longer apparent. A numerical integration of Eqs. (22) and (10) yields Fig. 2 in which it is apparent that the same criterion on the curvature holds approximately. This similar behavior between lumped parameter and distributed parameter systems is not uncommon. Therefore, we again learn that for both a PFR and a CSTR, no inflection can be observed in the θ versus τ curve for a constant value of m in the deactivation rate law.

If we now consider the PFR with the rate law of Eq. (17), then Eqs. (17) and (22) must be solved simultaneously. The procedure is as follows: initially α is unity for all positions, z, therefore, the conversion, X_e, can then be calculated as a function of z. In a time interval, $\Delta\tau$, the local values of α can then be calculated using Eq. (17). Then from Eq. (22), a new value of a θ can be calculated. Again, using Eq. (17) new local values of α can be again calculated. The new X profile can be calculated from Eq. (22). The computation is continued to obtain a plot of θ versus τ, as shown in Fig. 3 for selected values of γ_n and X_F, and for $\gamma_m = 65$.

Two points are obvious from Fig. 3. First, as conversion is increased, the lifetime of the catalyst increases. Second, as the activation energy of the main reaction increases, the lifetime on stream increases. Both result from the fact that the temperature does not need to be raised as much to maintain constant conversion thereby de-

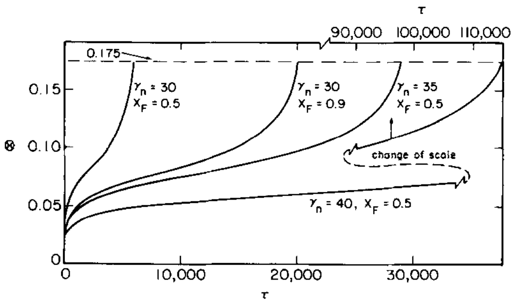

FIG. 3. Dependence of θ versus τ curves for PFR.

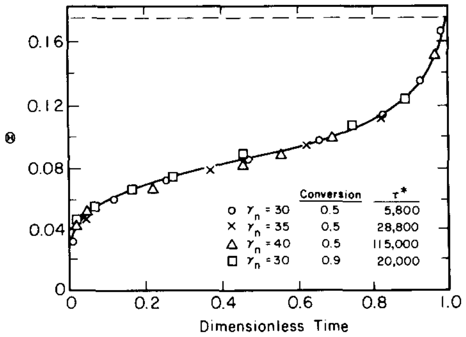

FIG. 4. Similarity temperature profiles for a PFR.

laying the onset of catastrophic deactivation.

It is interesting to normalize the time coordinate on Fig. 3 by the time necessary to raise θ to 0.175. Reploting them on Fig. 4 shows that the temperature–time profiles are remarkably similar.

Finally, some profiles were integrated to fit the data presented by Tamm *et al.* (6). The results are shown in Fig. 5. It is significant that from the results presented earlier in this paper that no constant power-law model can fit the curve. However, a good fit can be obtained using the multiplet model.

CONCLUSIONS

The complex shape of the temperature versus time curve that is found characteristic of constant conversion industrial operation can be easily and naturally explained and fit using the multiplet model of deactivation.

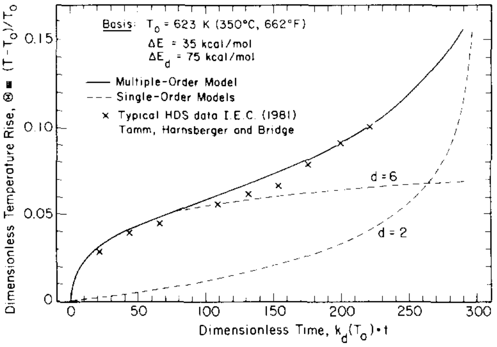

FIG. 5. Typical *T* versus *t* curves for various kinetic models.

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