# Diffusional Influences on Deactivation Rates of Bidispersed Catalysts

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The combined effect of pore diffusion and deactivation on the activity of monodispersed catalysts has been investigated by several authors (Masamune and Smith, 1966; Sagara et al., 1967; Chu, 1968; Hegedus and Petersen, 1973). These studies show that in some cases diffusional resistances can reduce the effective deactivation rate of the catalyst. Levenspiel (1972) considered diffusion-free deactivating catalysts in a plug-flow reactor and showed that for a first-order concentration independent poisoning, the deactivation rate constant was equal to the slope of the ln ln $(1/1\text{-}x)$ vs. $t$ plot. Krishnaswamy and Kittrell (1981) extended Levenspiel's analysis to account for the effect of diffusion on the deactivation rate for monodispersed catalysts. It was shown that, in the limiting case of severe diffusional limitation for a catalyst deactivating by first-order concentration-independent poisoning, the apparent deactivation rate constant was half the true value.

Very often the catalyst is formed by pelletizing small microspherical porous particles resulting in a bidispersed porous catalyst. Örs and Dōgu (1979) discussed the effectiveness factors of bidispersed catalysts for first-order reactions and the error involved if this is approximated as monodispersed. Kulkarni et al. (1981) have presented asymptotic solutions for effectiveness factors of bidispersed catalysts for $n$th-order reactions.

This note discusses the effect of concentration-independent deactivation on the effectiveness factor of bidispersed catalysts and analyzes the combined effect of diffusion and deactivation on the performance of a plug-flow reactor utilizing a bidispersed catalyst.

## BIDISPERSE CATALYST EFFECTIVENESS FACTORS

It will be assumed that the reaction is isothermal and irreversible, and that the spherical pellet is made from microspherical particles. Moreover, the catalyst deactivation has been assumed to be first order, concentration independent, and slow compared to the main reaction so that the pseudo steady state assumption is justified.

The dimensionless conservation equations presented in a previous work for an $n$th order reaction in a bidispersed catalyst (Kulkarni et al., 1981) can be modified for the case of decreasing activity simply by replacing the Thiele modulus by a time-dependent Thiele moduls, $\phi'$, defined as

$$\phi' = \phi A \tag{1}$$

where

$$A = \exp(-\theta/2) \text{ and } \theta = k_d t$$

For first-order reactions, an analytical solution for the effectiveness factor, defined as the ratio of the rate of reaction at any time to the rate of reaction in the absence of diffusion at zero time, can be obtained and is

$$\eta = \frac{9}{\phi^2 \alpha} \left\{ \frac{\left[\alpha \left(\frac{\phi'}{\tanh\phi'} - 1\right)\right]^{1/2}}{\tanh\left[\alpha \left(\frac{\phi'}{\tanh\phi'} - 1\right)\right]^{1/2}} - 1 \right\} \tag{2}$$

where $\alpha$ is defined as

$$= 3(1 - \epsilon_M) \frac{D_{ei}}{D_{eM}} \frac{R_0^2}{r_0^2} \tag{3}$$

For higher order reactions, analytical expressions for $\eta$ are not possible and the coupled micro- and macropore conservation equations have to be solved numerically. The numerical computation is simplified by a change of variables (Ibáñez, 1979) and this variable transformation, together with a numerical integration procedure, was used to generate the $\eta$ vs. $\phi$ plots for higher orders.

The variation of $\eta$ with $\theta$ and $\phi$ for first- and second-order reactions with $\alpha = 1$ is shown in Figure 1. The trends of these plots are similar to those reported by Krishnaswamy and Kittrell (1981) for monodispersed catalysts. It should be noted that for large values of $\phi$, the diffusion limitations in the micropores (not necessarily in the macropores) become significant, since $\phi$ corresponds to the ratio of diffusion time in the micropores to the reaction time. On the other hand, $\alpha$ characterizes the ratio of diffusion times in the macro- and micropores. For a fixed value of $\phi$ and $\theta$, $\eta$ decreases with increasing $\alpha$. This is to be expected because, for a fixed $\phi$, $\alpha$ can be increased either by decreasing the effective macropore diffusivity or increasing the pellet radius, thus reducing the observed rate of reaction.

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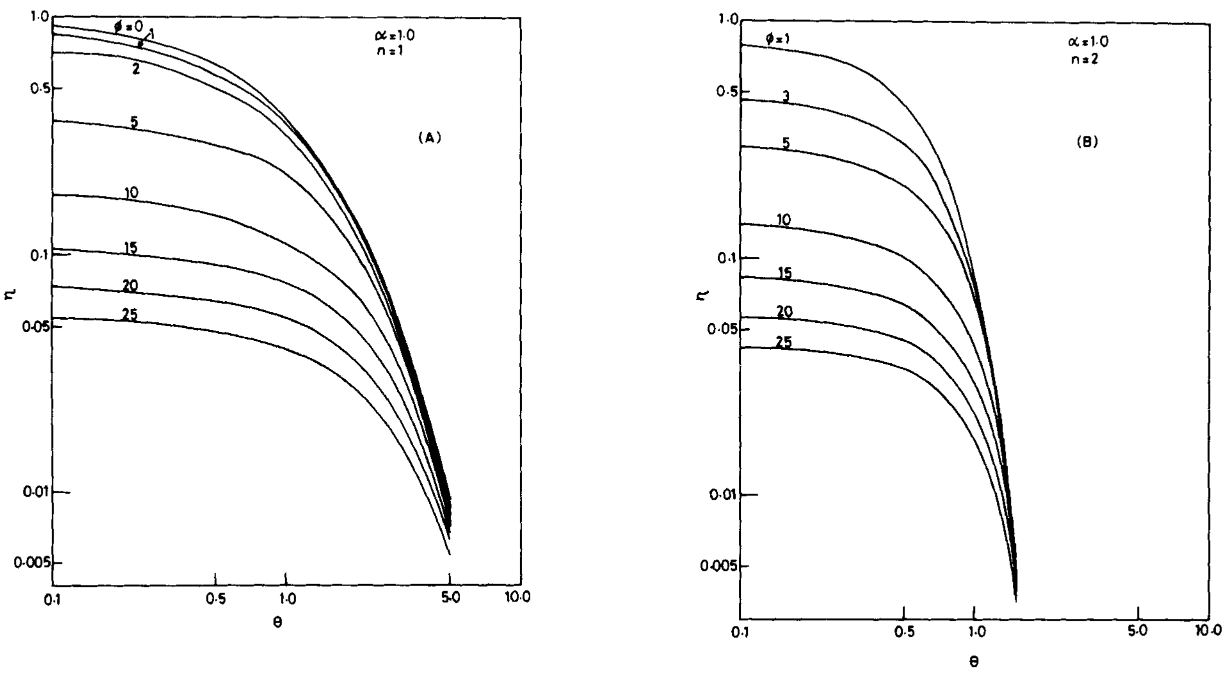

**Figure 1. Variation of effectiveness factor with Thiele modulus and dimensionless time.**

## INTERPRETATION OF CONVERSION DATA FROM A PLUG-FLOW REACTOR

### First-Order Reactions

As Krishnaswamy and Kittrell (1981) have shown, the variation of conversion with time for a first-order reaction in an isothermal plug-flow reactor can be written as

$$\ln \ln \left(\frac{1}{1-x}\right) = \ln(k\tau) + \ln\eta \qquad (4)$$

where the variation of $\eta$ with time is obtained from Eq. 2. For low values of $\phi A$

$$\coth(\phi A) \approx \frac{1}{\phi A} + \frac{\phi A}{3} \qquad (5)$$

and Eq. 2 simplifies to

$$\eta = A^2 = \exp(-k_d t) \qquad (6)$$

Substituting in Eq. 4, we obtain

$$\ln \ln \left(\frac{1}{1-x}\right) = \ln(k\tau) - k_d t \qquad (7)$$

which is identical to the relationship given by Levenspiel (1972) for a diffusion-free catalyst. For large values of $\phi$A, Eq. 2 can be approximately written as

$$\eta \cong \frac{9}{\phi^{3/2}\alpha^{1/2}} A^{1/2} \qquad (8a)$$

or

$$\eta = \eta_o A^{1/2} \qquad (8b)$$

where $\eta_o$ is the asymptotic effectiveness factor for a nondeactivating bidispersed catalyst. Then, for severe diffusional limitations, Eq. 4 becomes

$$\ln \ln \left(\frac{1}{1-x}\right) = \ln(\eta_o k\tau) - \left(\frac{k_d}{4}\right) t \qquad (9)$$

Hence, for large values of $\phi A$, the slope of the Levenspiel plot will be one-fourth the intrinsic deactivation rate constant compared to half the true value reported for monodispersed catalysts (Krishnaswamy and Kittrell, 1981). Thus, for intermediate and high values of $\phi$, the initial slope of the Levenspiel plot will only yield an apparent deactivation rate constant, $k_{dp}$. It should be emphasized that the Levenspiel plots for deactivating catalysts will not be linear because as $t$ increases, $\phi A$ decreases, and even for large $\phi$, the product $\phi A$ will eventually approach zero. Therefore, as $t \rightarrow \infty$, $k_{dp}$ will be equal to $k_d$ even for diffusion-influenced catalysts.

Figure 2 shows the variation of $k_{dp}/k_d$ as a function of Thiele modulus and $\alpha$. This plot will be the same for all values of $k\tau$. As discussed above, $k_{dp}$ decreases with increasing $\phi$ and for large values of $\phi$ is approximately equal to $k_d/4$. As $\alpha$ increases, the asymptotic value is approached at lower $\phi$.

## HIGHER-ORDER REACTIONS

The above analysis can also be extended to higher order reactions. The conversion vs. time relationship for $n$th-order reactions in a plug-flow reactor for the diffusion-free case becomes

$$\ln[(1-x)^{1-n} - 1] = \ln[k\tau C_o^{n-1}(n-1)] - k_d t \qquad (10)$$

For severe diffusional limitations, an expression for the asymptotic effectiveness factor for $n$th order reactions in nondeactivating bidispersed spherical catalysts has been developed by Kulkarni et al. (1981). For the case of a deactivating catalyst, this can be modified as

$$\eta \approx \left[\frac{\left(\frac{2}{n+1}\right)^{1/2}}{\frac{(n+3)}{4}}\right]^{1/2} 9\phi^{-3/2}\alpha^{-1/2}A^{1/2} \qquad (11a)$$

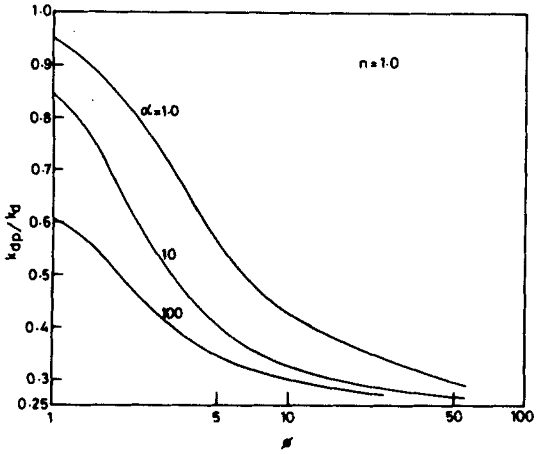

**Figure 2. Variation of apparent deactivation rate constant with Thiele modulus for a first-order reaction.**

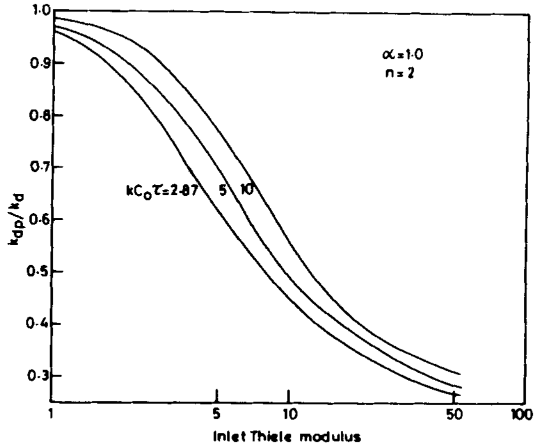

**Figure 3. Variation of apparent deactivation rate constant with Thiele modulus for a second-order reaction.**

$$= \eta_o A^{1/2} \tag{11b}$$

For an isothermal PFR

$$-\frac{dC}{d\tau} = \eta k C^n \tag{12}$$

where $\eta$ is a function of $C$. Substituting Eq. 11 into Eq. (12) and integrating, one can express the conversion time relationship for large $\phi A$ as

$$\ln\left[(1-x)^{\frac{1-n}{4}} - 1\right] = \ln\left[\frac{(n-1)}{4}\eta_{oi}k\tau C_o^{n-1}\right] - \frac{k_d t}{4} \tag{13}$$

where $\eta_{oi}$ is $\eta_o$ evaluated at the reactor inlet so that $C_R = C_o$. Therefore, in the diffusion-limited regime, even for higher order reactions, the deactivation rate constant as determined from plots analogous to Levenspiel plots would be one-fourth the true value. However, since the logarithmic conversion functions on the left-hand side of Eq. 10 and 13 are different, the problem arises as to which functionality to use to determine $k_{dp}$ of an operating catalyst for intermediate values of $\phi$. The problem can be overcome by using Eq. 13 to obtain the slope of $\ln[(1-x)^{1-n} - 1]$ vs. time plots for large $\phi A$. From Eq. (13), for large $\phi A$,

$$\ln[(1-x)^{1-n} - 1]$$
$$= \ln\left[\left\{1 + \frac{(n-1)}{4}\eta_{oi}k\tau C_o^{n-1}\exp\left(-\frac{k_d t}{4}\right)\right\}^4 - 1\right] \tag{14}$$

Differentiating Eq. 14 and using L'Hospital's rule, it can be shown that

$$\frac{d}{dt}\{\ln[(1-x)^{1-n} - 1]\}|_{t\to 0} = -k_d/4 \tag{15}$$

Thus $k_{dp}$, determined as the initial slope of $\ln[(1-x)^{1-n} - 1]$ vs. time plot, will vary from $k_d$ to $k_d/4$ as $\phi A$ increases from low to high values. At intermediate $\phi$ values, $k_{dp}$ will depend on $k\tau C_o^{n-1}$ and $\alpha$.

The variation of $k_{dp}/k_d$ as a function of the initial Thiele modulus and $k\tau C_o^{n-1}$ for a second-order reaction is shown in Figure 3. $k_{dp}$ values for different inlet $\phi$ were evaluated by numerically integrating Eq. 12 together with the known variation of $\eta$ with $\phi$ and $\theta$ (Figure 1). If the inlet Thiele modulus is known, Figure 3 can be employed for evaluating $k_d$ even when $\phi$ is in the intermediate region. Even if $\phi$ is not known a priori, two determinations with different $\phi$ but constant $kC_o\tau$ can be utilized to determine $k_d$ by trial and error.

In conclusion, the analyses of Levenspiel for diffusion-free catalysts and Krishnaswamy and of Kittrell (1981) for diffusion-influenced monodispersed catalysts have been extended to diffusion-affected bidispersed catalysts. Significant errors can result in the measured deactivation rate constant if the bidispersed nature of the catalyst is not taken into account. A limitation of this analysis is that since the deactivation has been assumed to be independent of concentration, the rate of deactivation is independent of position in the pellet and reactor.

## NOTATION

$A$ = $\exp(-k_d t/2)$
$C$ = bulk stream concentration of reactant, gmol/cm$^3$
$C_R$ = external surface concentration of reactant, gmol/cm$^3$
$C_o$ = bulk stream concentration at the reactor inlet, gmol/cm$^3$
$D_{ei}$ = effective diffusivity in the micropores, cm$^2$/s
$D_{eM}$ = effective diffusivity in the macropores, cm$^2$/s
$k$ = intrinsic reaction rate constant, (gmol/cm$^3$)$^{1-n}$ s$^{-1}$
$k_d$ = deactivation rate constant, h$^{-1}$
$k_{dp}$ = apparent deactivation rate constant, h$^{-1}$
$n$ = order of the main reaction
$R_o$ = radius of spherical pellet, cm
$r_o$ = radius of the particle, cm
$t$ = run time, h
$x$ = fractional conversion of reactant

### Greek Letters

$\alpha$ = parameter defined in Eq. 3
$\epsilon_M$ = macropore porosity
$\eta$ = effectiveness factor
$\eta_o$ = asymptotic effectiveness factor at zero time
$\eta_{oi}$ = $\eta_o$ evaluated at the inlet of the plug-flow reactor
$\theta$ = dimensionless time, = $k_d t$
$\phi$ = Thiele modulus, = $r_o(kC_R^{n-1}/D_{ei})^{1/2}$
$\phi'$ = modified Thiele modulus, = $\phi A$
$\tau$ = space time, s

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