New Method for Determining the Intrinsic Deactivation Rate Constant

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Analysis of immobilized enzyme deactivation is very important in designing continuous reactors. Often a first-order model

$$-\frac{dE}{dt} = k_d E \tag{1}$$

is sufficient to describe adequately the enzyme deactivation process. Many enzyme reactions obey a Michaelis-Menten kinetics, which simplifies to a first-order equation for $S \ll K_m$. Krishnaswamy and Kittrell (1981) have shown that for a first-order reaction in a single pellet, undergoing relatively slow (otherwise the system is economically unattractive) deactivation by a first order, the time-dependent effectiveness factor becomes

$$\eta(t) = \frac{3 \exp(-k_d t/2)}{\phi} \coth[\phi \exp(-k_d t/2)] - \frac{3}{\phi^2} \tag{2}$$

In order to estimate the magnitude of the intrinsic deactivation rate constant k_d, the following relationship was suggested by Krishnaswamy and Kittrell (1981):

$$k_{dp} = k_d \left[\frac{1}{2} + \frac{1}{2\phi \exp(-k_d t/2)}\right] \tag{3}$$

This relationship is difficult to utilize directly in analyzing experimental data and is valid only for $\phi \exp(-k_d t/2) > 3.0$.

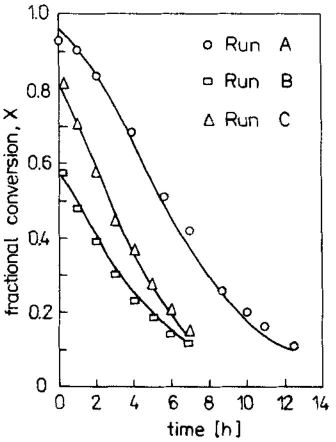

Figure 1. Thermal deactivation of immobilized catalase as a function of time.

	Run A	Run B	Run C
ϕ	120	30.7	20.7
k_d, h^{-1}	0.53	0.48	0.59

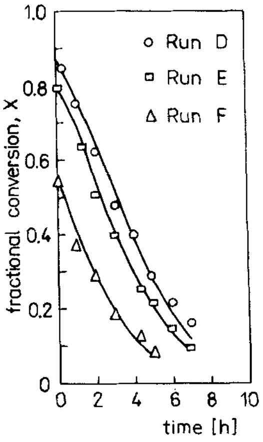

Figure 2. Thermal deactivation of immobilized catalase as a function of time.

	Run D	Run E	Run F
ϕ	6.2	3.9	2.9
k_d, h^{-1}	0.51	0.49	0.54

Here a method is presented for determining the intrinsic deactivation rate constant that is based on the concept of the average effectiveness factor. When reacting fluid flows through a deactivating catalyst and conditions change slowly with time, then the average effectiveness factor during a run can be found by calculating the steady state effectiveness factor at various times and summing

$$\eta_{av} = \frac{\int_0^{t_{run}} \eta(t)\, dt}{t_{run}} \tag{4}$$

Substituting Eq. 2 into Eq. 4 and integrating, one obtains

$$\eta_{av} = \frac{3}{k_d \phi^2 t_{run}} \ln \cdot \frac{2 - \exp(2\phi) - \exp(-2\phi)}{2 - \exp[2\phi \exp(-k_d t_{run}/2)] - \exp[-2\phi \exp(-k_d t_{run}/2)]} - \frac{3}{\phi^2} \tag{5}$$

On the other hand, the average effectiveness factor can be calculated for an isothermal packed-bed reactor as

$$\eta_{av} = \frac{\int_0^{t_{run}} \ln[1/1 - X(t)]\, dt}{k\tau t_{run}} \tag{5}$$

Using experimental conversion data X vs. time t, the integral in Eq. 5 can be evaluated numerically. Combining Eqs. 4 and 5 provides a nonlinear equation with one unknown, k_d. The solution can be reached easily by conventional methods.

Experimental data of Krishnaswamy and Kittrell (1982) on thermal deactivation of catalase immobilized on Kieselguhr were used to examine this procedure. Figures 1 and 2 show the predicted and observed fractional conversions using values of the intrinsic deactivation rate constant calculated by the procedure described above. The experimental points are in close agreement with the theoretical curve.

Notation

D = effective diffusivity of reactant
E = fractional enzyme activity
k = reaction rate constant
k_d = intrinsic deactivation rate constant
k_{dp} = pseudodeactivation rate constant
k_i = intrinsic reaction rate constant
R = radius of spherical particle
t = time

Greek letters

η = effectiveness factor
ϕ = Thiele modulus $= R\sqrt{k_i/D}$
τ = space time

Literature Cited

Krishnaswamy, S., and J. R. Kittrell, "Diffusion Influences on Deactivation Rates," *AIChE J.*, **27**, 120 (1981).

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