The Catalytic Effectiveness Factor Under Nonisothermal Conditions

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The effectiveness factor for a porous-solid-catalyzed reaction is a measure of the extent to which species transport by Knudsen diffusion within the particle retards the over-all rate process. The literature reveals correlations based upon analytical solution of the appropriate equations when isothermal conditions prevail throughout the catalyst particle. Following Thiele's original work (5), Wheeler (8) and Weisz (7) have made significant contributions to the discussion of the isothermal effectiveness factor.

The problem of reaction heat release or abstraction within a catalyst particle has been recognized as a potentially serious one with respect to the influence of the resulting temperature gradient upon the effectiveness factor for both reactant and product. However analytical solution of the governing differential equations presents marked difficulties. Wheeler (8) and more recently Prater (2) have shown that for a simple first-order irreversible reaction the maximum temperature difference between the external and interior surface of the pellet is given by

$$\Delta T = \frac{(-\Delta H)\ (D)}{K}(C_o - C) \quad (1)$$

Valuable as the above relation is for purposes of estimating the maximum possible temperature gradient, the precise influence of the temperature gradient upon effectiveness remained, until recently, undefined.

Schilson and Amundson (3) were the first to undertake the task of solving the nonisothermal problem analytically. The heat-generation functions for a single reaction and for two simultaneous reactions were approximated by single linear functions and also by two linear relationships. Analytical solutions were then found by Schilson and Amundson in the form of an integral equation expressing temperature as a function of pellet radius. Specific cases were solved in terms of the effectiveness factor, the details of which can be found in their forthcoming publication (4).

Tinkler and Pigford (6) applied perturbation techniques to obtain an approximate analytical expression for the nonisothermal effectiveness factor in terms of the heat-generation function and the Nusselt number for heat transfer at the external surface. Their attention was focused upon a first-order irreversible reaction catalyzed by a spherical pellet.

The work reported in this communication embraces both first-and second-order irreversible catalytic reactions. Pellet geometry is not specified, since the model is written for a single pore. Aris (1) has shown that a proper definition of particle size ($L = 1/a$) renders the isothermal effectiveness factor virtually independent of particle shape, while Prater's derivation (2) proves that ΔT is also independent of geometry. Thus it is assumed here that the single-pore treatment (equivalent to flat-plate geometry) is of general applicability.

The following dimensionless equations are assumed to apply for kinetics of order n, where, in the case of second-order reaction, equality of species diffusivities is assumed. For mass

$$\frac{d^2 f}{dz^2} = L^2 \frac{k}{D} C^{n-1} f^n = \psi_o^2 f^n \exp\left[-E/RT_o\left(\frac{1}{y} - 1\right)\right] \quad (2)$$

For heat

$$\frac{d^2 y}{dz^2} = \beta \psi_o^2 f^n \exp \left[-E/RT_o\left(\frac{1}{y} - 1\right)\right] \quad (3)$$

where

$$\beta = -\frac{C_o}{T_o}\frac{\Delta H D}{K};\ k = k_o \exp \left[-E/RT_o\left(\frac{1}{y} - 1\right)\right] \quad (4)$$

and

$$\psi_o^2 = \frac{L^2 k_o}{D} C_o^{n-1}$$

The boundary conditions, in terms of the bulk phase Nusselt numbers for heat and mass transport, $(N_{Nu})_h$ and $(N_{Nu})_m$, respectively, are

$$z = 1 \begin{cases} f = 1 - \dfrac{1}{(N_{Nu})_m}(df/dz) \\ y = 1 - \dfrac{1}{(N_{Nu})_h}(dy/dz) \end{cases}$$

$$z = 0 \quad df/dz = dy/dz = 0$$

TABLE 1. INFLUENCE OF ΔH AND E UPON η AT CONSTANT VALUE OF α

	$-\Delta H$, kcal./mole	E, kcal./mole	ΔT, °C.	η
$\Psi = 0.85$	15	20	10.3	0.924
$\alpha = 1.0$	30	10	20.5	0.922
	60	5	41	0.918
$\Psi = 0.85$	180	5	197	1.39
$\alpha = 3$	18	50	28	1.87
$\Psi = 0.7$	30	40	53	3
$\alpha = 4$	60	20	92	2.6

$T_o = 300$°C.

The effectiveness factor is defined by

$$\eta = \frac{D\, dC/dx}{L\, k_o\, C_o^n} = \frac{df/dz}{\psi_o^2}$$

Equations (2) and (3) were solved simultaneously with an IBM-650 computer.

The results of computation are shown in Figures 1 and 2 in terms of the classical reaction-diffusion modulus, ψ_o, over a range of reaction exo and endothermicity ($\pm\,\alpha$), where

$$\alpha = -\left[\frac{C_o}{T_o}\frac{\Delta H}{K} D\right]\frac{E}{RT_o} \quad (5)$$

Figures 1 and 2 are based upon fluid film coefficients of heat and mass equal to infinity relative to the equivalent transport coefficients within the porous pellet. By definition of ΔH positive values of α signify exothermicity. The relation shown for $\alpha = 0$ corresponds to the classical isothermal effectiveness factor (1, 5).

An effectiveness greater than unity for positive values of α is a consequence of significant rate enhancement, due to a temperature rise within the pellet, in a region where the isothermal effectiveness is close to unity. In other words df/dz becomes greater than ψ_o^2. This result emphasizes the inadequacy of the traditional notion of catalytic effectiveness in which η is understood to be the ratio of actual surface area utilization to the total area of the catalyst.

The parameter α does not uniquely govern the nonisothermal relationship between η and ψ_o, for $\psi_o < 2$, as may be seen in Table 1, where computed values of η are shown over a range of ΔH and E at constant α and for values of ψ_o of 0.85 and 0.7. Obviously a more complex parameter exists which would assemble the computed data more concisely; however in view of the limited accuracy with which the reaction and diffusion coefficients are generally known the indicated manner of correlation is deemed adequate. For $\psi_o >$

TABLE 2. INFLUENCE OF BULK HEAT AND MASS TRANSFER UPON η

$\alpha = 2$ $\Psi = 0.83$

$(N_{Nu})_h = \infty$		$(N_{Nu})_m = \infty$	
$(N_{Nu})_m$	η	$(N_{Nu})_h$	η
∞	1.17	∞	1.17
500	1.16	100	1.2
50	1.13	10	1.4
5	0.7	5	1.8
		1	10

$(N_{Nu})_h$	$(N_{Nu})_m$	η
10	50	1.33
10	5	0.9
1	5	2.0

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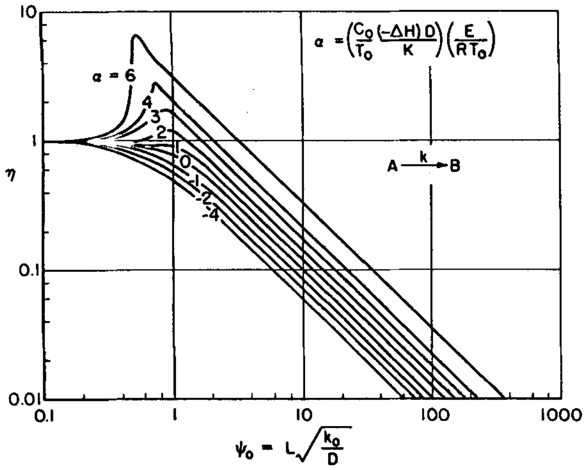

Fig. 1. Nonisothermal catalytic effectiveness factor.

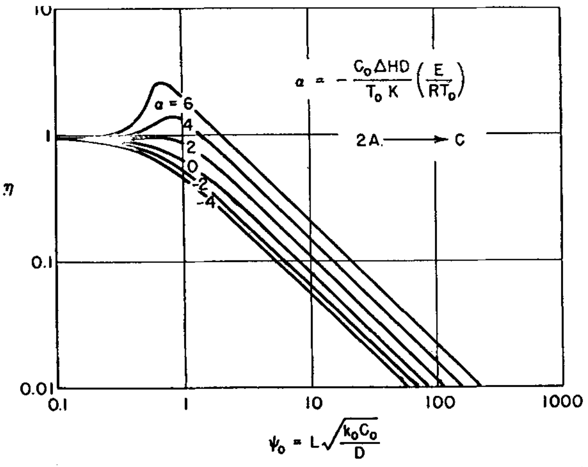

Fig. 2. Nonisothermal catalytic effectiveness factor (second-order reaction).

2.5 the effectiveness factor for a first-order exothermic reaction is given by

$$\eta = \eta_o \exp\,[\alpha/5] = \exp \frac{[\alpha/5]}{\psi_o}$$

Of significant importance is the influence upon η of finite heat and mass transfer resistances at the external surface of the particle. In Table 2 a few results are shown which illustrate the influence of both bulk mass and heat transfer upon the nonisothermal effectiveness factor. The Nusselt numbers are defined:

$$\text{for heat, } (N_{Nu})_h = \frac{hL}{K}$$

$$\frac{\text{conductivity of fluid film}}{\text{conductivity of solid}}$$

$$\text{for mass, } (N_{Nu})_m = \frac{k_g L}{D}$$

$$\frac{\text{diffusivity in fluid film}}{\text{diffusivity in solid}}$$

An assessment of the bulk mass transport contribution is readily made, in the case of first-order kinetics, by equating the surface rate to that of bulk mass transport. There results an over-all rate coefficient given by

$$\overline{k} = \frac{\eta k}{1 + \dfrac{\eta k}{k_g a}} \tag{6}$$

TABLE 3. INFLUENCE OF HEAT RELEASE UPON YIELD

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$\Psi_1 = 1.0$	$\Psi_2 = 0.5$	$(A/B)_o = 10$
α_1	α_2	Yield of B%
0	0	93
0.5	0.5	92
1.0	1.0	89
2.0	2.0	70

A suggested criterion for determining whether bulk transport can be considered negligible relative to surface-reaction kinetics is

$$\frac{\eta k}{k_g a} \leqq 0.1 \tag{7}$$

A number of consequences may be inferred from the results presented. While it might appear that a high effectiveness factor is desirable ($\eta > 1$), it must be realized that high values of η resulting from large values of $-\Delta H$ are associated with considerable temperature gradients. When the reaction product is heat sensitive, degradation is enhanced under such circumstances. In addition a high effectiveness factor due to exothermicity may ultimately render the catalyst inactive by virtue of sintering or site deactivation via phase and/or chemical transformation.

An appreciation of the influence of intraparticle exothermicity upon yield may be gathered from Table 3, where the yield of product B is shown as a function of α for the reaction sequence $A \rightarrow B \rightarrow C$.

With respect to measurement of activation energy it becomes apparent that, whereas diffusion retardation leads to an observed activation energy of one-half the true value under isothermal conditions (8), the opposite effect becomes manifest for $\eta > 1$; that is the apparent measured activation energy will be greater than the true value.

NOTATION

a = external surface to volume ratio of a particle, cm.$^{-1}$
C = species concentration, moles/cc.
D = Knudsen diffusivity, sq. cm./sec.
E = activation energy, cal./mole
f = dimensionless concentration, C/C_o
h = heat transfer coefficient, bulk phase, cal./sq. cm. sec., °C.
ΔH = reaction enthalpy change
k_g = mass transfer coefficient, cm./sec.
k = rate constant, sec.$^{-1}$ (moles/cc.)$^{-(n-1)}$
$\overline{k}$ = over-all rate coefficient, Equation (6)
K = thermal conductivity of particle, cal./°C. cm. sec.
L = characteristic particle radius, cm.
n = reaction order
$(N_{Nu})_h$ = Nusselt number for heat transfer, hL/K
$(N_{Nu})_m$ = Nusselt number for mass transfer, $k_g L/D$
R = gas constant, cal./mole, °K.
T = temperature, °K.
x = distance variable, cm.
y = dimensionless temperature, T/T_o
z = dimensionless distance, x/L
α = thermal parameter, Equation (5)
β = heat generation term, Equation (4)
η = catalyst effectiveness factor
ψ = diffusion, reaction modulus, Equation (4)

Subscripts

o = bulk-phase conditions

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