The Dead Zone in a Catalyst Particle for Fractional-Order Reactions

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Diffusion and chemical reaction in a porous catalyst particle, when $n < 1$ is a conceptually different problem from those cases when $n > 1$—the latter having received far more attention (Aris, 1975). In the former case, a nonactive region within the particle may exist, the so-called "dead zone" (Temkin, 1975). For an isothermal particle of any geometry, diffusion and a chemical reaction of nth order are described by

$$X^{1-a}\frac{d}{dX}\left(X^{a-1}\frac{dC}{dX}\right) = h_0^2 \cdot C^n \tag{1}$$

with boundary conditions:

$$X = 0 \therefore \frac{dC}{dX} = 0 \tag{2}$$

$$X = 1 \therefore C = 1, \text{ or} \tag{3}$$

$$X = 1 \therefore \frac{dC}{dX} = Bi_M(1 - C_S) \tag{4}$$

As the diffusional resistance increases, the concentration falls with distance until, for $h_o = h_o^c$, C becomes null in the particle center. For $h_o > h_o^c$, the dead zone makes it necessary to change the boundary condition (Eq. 2), which is now (Aris, 1975; Temkin, 1982; Romero et al., 1987):

$$X = Z > 0 \therefore \frac{dC}{dX} = C = 0 \tag{5}$$

The solution of Eq. 1 is valid only for $1 > X > Z$, and the solution in $Z > X > 0$ is $C = 0$, thus avoiding the indeterminacy of that equation when $n < 0$ (Aris, 1975; Temkin, 1982).

The fractional-order reactions have not been studied widely. Most of the works deal with the zeroth-order reaction (Wheeler, 1951; Weekman and Gorring, 1965; Lin and Lih, 1971; Hu et al., 1985a; Romero et al., 1987), and only a few consider other reaction orders (Aris and Mehta, 1971; Aris, 1975; Temkin, 1982; Hu et al., 1985b).

In the present work, attention is given to the study of the dead zone. The critical values of Thiele modulus and effectiveness factor, h_o^c and η_o^c, are determined for any geometry and interphase mass and heat transfer resistances, considering the temperature inside the particle as constant.

Critical Thiele Modulus

To take into account the possible difference of temperatures between the surface particle and bulk fluid, and using a Thiele modulus referred to the bulk fluid conditions, Eq. 1 must be modified as follows:

$$X^{1-a}\frac{d}{dX}\left(X^{a-1} \cdot \frac{dC}{dX}\right) = h_o^2 \cdot \exp\left(\gamma - \frac{\gamma}{T_S}\right) C^n \tag{6}$$

with boundary conditions 2 and 4.

Equation 6, a special form of the Emden-Fowler equation (Aris, 1975; Temkin, 1982), presents an analytical solution for some values of a and n. For catalytic reactions, the solution is usually found for $a = 1$, 2 or 3, being explicit only for $n = 0$, 1 and 5. Because this last value is not considered in chemical kinetics, only zeroth and first order are analytically solved.

As shown by Temkin (1982), for $-1 < n < 1$, there exists a particular solution for Eq. 1. In a similar way, for Eq. 6, this particular solution is:

$$C = C_S \cdot X^m \tag{7}$$

being

$$m = \frac{2}{1 - n} \tag{8}$$

This can be easily demonstrated, substituting the first and second derivatives from Eq. 7, in Eq. 6. Thus, Eq. 8 is found as the only value of m satisfying the condition for any value of X.

Nevertheless, Eq. 7 is valid only when $C = 0$ in $X = 0$. Thus, Eq. 7 is a solution of Eq. 6 only for $h_o = h_o^c$ and not for any other value of h_o. In consequence, the critical value of h_o can be calculated:

$$h_o^c = \sqrt{\frac{m(m + a - 2)}{\exp\left(\gamma - \frac{\gamma}{T_S}\right) C_S^{n-1}}} \tag{9}$$

C_S can be substituted as:

$$Bi_M(1 - C_S) = m \cdot C_S \therefore C_S = \frac{Bi_M}{Bi_M + m} = \frac{1}{1 + \frac{m}{Bi_M}} \tag{10}$$

becoming:

$$h_o^c = \sqrt{\frac{(4n + 2a(1 - n))\left(1 + \frac{2}{(1 - n)Bi_M}\right)^{n-1}}{(1 - n)^2 \cdot \exp\left(\gamma - \frac{\gamma}{T_S}\right)}} \tag{11}$$

With T_S subject to an additional condition, a heat balance in the interphase:

$$T_S - 1 = \frac{\beta'}{Bi_M}\left(\frac{dC}{dX}\right)_{X=1} \tag{12}$$

This relation can be rewritten by substitution of Eq. 9 as:

$$\begin{aligned} T_S - 1 &= \frac{\beta'}{Bi_M}\frac{(h_o^c)^m \cdot m}{(m(m + a - 2))^{m/2}} \exp\left(\frac{m}{2}\left(\gamma - \frac{\gamma}{T_S}\right)\right) \\ &= Da_n^{\mathrm{IV},c} \exp\left(\frac{m}{2}\left(\gamma - \frac{\gamma}{T_S}\right)\right) \end{aligned} \tag{13}$$

Equation 11 can be simplified if heat and/or mass transfer in the interphase are not considered. When $T_S \rightarrow 1$ and $Bi_M \rightarrow \infty$, the following equation is obtained, as already quoted by Aris (1975).

$$h_o^c = \sqrt{\frac{4n + 2a(1 - n)}{(1 - n)^2}} = \sqrt{\frac{2(1 + n + (a - 1) \cdot (1 - n))}{(1 - n)^2}} \tag{14}$$

And, for $a = 3$, the equation given by Temkin (1982) is obtained:

$$h_o^c = \sqrt{\frac{6 - 2n}{(1 - n)^2}} \tag{15}$$

Equations 11, 14 and 15 are valid only for $1 > n > -1$. Outside that range, the equations are indetermined or yield meaningless values.

Critical Effectiveness Factor

The critical value of the effectiveness factor, when $h_o = h_o^c$, can be calculated by substitution in the differential definition of η_o, taking into account Eqs. 8 and 9:

$$\begin{aligned} \eta_o^c &= \frac{a \cdot m \cdot C_S \cdot C_S^{n-1}}{m(m + a - 2)} \exp\left(\gamma - \frac{\gamma}{T_S}\right) = \frac{a \cdot C_S^n \exp\left(\gamma - \frac{\gamma}{T_S}\right)}{m + a - 2} \\ &= a(1 - n) \cdot \exp\left(\gamma - \frac{\gamma}{T_S}\right) \Big/ \left\{\left(1 + \frac{2}{(1 - n)Bi_M}\right)^n \cdot (2n + a(1 - n))\right\} \end{aligned} \tag{16}$$

This equation can also be simplified for $T_S \rightarrow 1$ and $Bi_M \rightarrow \infty$, and particularized for a geometry. Under those conditions, for $a = 3$, the equation given by Temkin (1982) is obtained:

$$\eta_o^c = \frac{3(1 - n)}{3 - n} \tag{17}$$

Discussion

When $n \rightarrow 1$ the influence of the geometry, a, in h_o^c gradually disappears, while when n deviates from zero the effect of a in η_o^c increases. When $n \rightarrow 1$, the behavior of slabs is different from that of cylinders and spheres. This can be seen in Figure 1 where η_o^c is drawn vs. ϕ_o^c, being:

$$\phi_o^c = \frac{h_o^c}{a}\sqrt{\frac{n + 1}{2}} \tag{18}$$

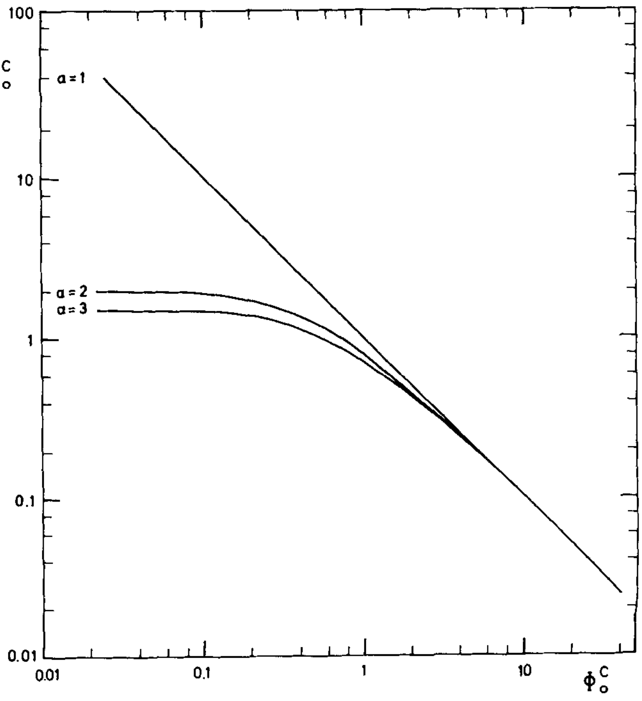

Figure 1. Critical effectiveness factor vs. critical Thiele modulus (generalized).

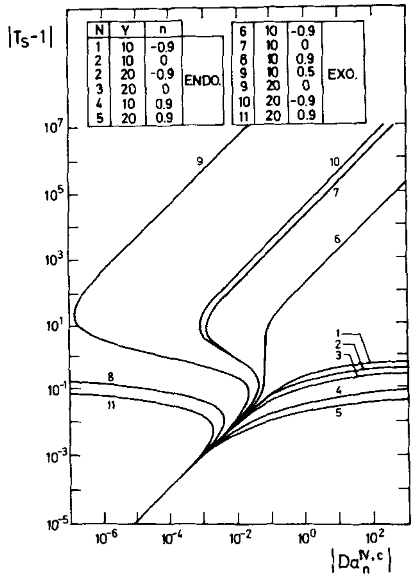

Figure 2. Surface temperature, $|T_S - 1|$, vs. critical Damköhler modified number, $|Da_n^{IV,c}|$.

Moreover the curves in Figure 1 must designate the limits between which the values of η_o vs. ϕ_o must fall for the different values of n; and for values of $\phi_o > \phi_o^c$ the variation of η_o vs. ϕ_o for any n value must be very close to the values of η_o^c vs. ϕ_o^c. Thus, this representation can be valid as an approximation to the general solution.

When mass transfer resistance in the interphase is considered, Bi_M and a values have a marked effect on h_o^c when $n < 0$, as long as $Bi_M < 10$. On the contrary, these variables have hardly any effect when $n \rightarrow 1$. Also, η_o^c is more affected by Bi_M and a when n deviates from zero.

If the heat transfer interphase resistance exists according to Eq. 13, steady-state multiplicity for exothermic reaction is to be expected. Figure 2 shows the variation of surface temperature, as $|T_S - 1|$, with $|Da_n^{IV,c}|$, the latter being also defined by Eq. 13. The $|Da_n^{IV,c}|$ interval where multiplicity is found increases as γ and n increase. For $n \rightarrow 1$, one of the solutions disappears.

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Notation

a = geometry (a = 1, slab; a = 2, cylinder; a = 3, sphere)
Bi_C = heat Biot number
Bi_M = mass Biot number
C = concentration
$Da_n^{IV,c}$ = Damkhöler modified number, Eq. 13
h = Thiele modulus
m = given by Eq. 8
n = reaction order
T = temperature
X = coordinate
Z = magnitude of dead zone
β' = Prater number
γ = Arrhenius number
η = effectiveness factor

Subscripts

0 = refered to the bulk fluid
s = value in the particle surface

Superscripts

c = critical value

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