Multiplicity of Isothermal Reactions in a Stirred-Tank Reactor: Combined Influence of Residence Time, Inter- and Intra-particle Diffusion

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Isothermal reactions whose rate curve goes through a maximum can exhibit multiplicity and the necessary and sufficiency criteria for a number of reaction schemes have been published (Matsuura and Kato, 1969; Luss, 1971; Moo-Young and Kobayashi, 1972; Bruns et al., 1973; Wadiak and Carbonell, 1975; McGrath and Yang, 1975; Sadana et al., 1980; Ramachandran et al., 1981; Kulkarni and Ramachandran, 1980a,b; Oh et al., 1979; Schmitz, 1975; Slinko and Slinko, 1978).

The analysis are either for single particle with only internal diffusional gradients or for a CSTR in the absence of mass transfer gradients. Combined influence of residence time, inter- and intra-particle gradients does not appear to have been published. The motivation behind the present work is to present such an analysis which will be directly applicable for delineating the region of multiplicity in, say, a stirred catalytic-basket reactor or a stirred liquid-phase reactor with suspended catalyst or immobilized enzyme.

The behavior of a completely backmixed reactor without any significant transport resistances can be represented in dimensionless form as:

$$\alpha(1 - a_o) = f(a_o) \tag{1}$$

where a_o is the dimensionless outlet concentration, $f(a_o)$ represents the dimensionless rate and α represents the ratio $F/(Wk_1)$.

The conditions under which this system will exhibit multiple steady states have been published earlier. (For a summary, see Ramachandran et al., 1981.) The necessary condition is that the following equation should have two real roots in the interval $0 < a < 1$.

$$g(a) = f'(a) - \frac{f(a)}{a - 1} = 0 \tag{2}$$

The necessary condition depends only on the kinetic parameters of the system and not on the transport parameters.

The sufficiency condition can be stated as:

$$\alpha_- < \alpha < \alpha^+ \tag{3}$$

where

$$\alpha_- = \frac{f(a_1)}{1 - a_1} \tag{4}$$

and

$$\alpha^+ = \frac{f(a_2)}{1 - a_2} \tag{5}$$

where a_1 and a_2 are the roots of Eq. 2 in the interval 0 to 1. The parameter α_- and α^+ are dependent only on the kinetic scheme. The sufficiency condition is, however, dependent on the residence time in the reactor in view of Eq. 3.

The problem of multiplicity for a single particle with intraparticle diffusion was analyzed by Kulkarni and Ramachandran (1980a) who reduced the distributed parameter problem to an equivalent lumped problem by using a single interior point collocation. The sufficiency criterion was then obtained as:

$$\alpha_- < \frac{B_{12}}{\phi^2} < \alpha^+ \tag{6}$$

The use of single point collocation, though it makes the analysis somewhat approximate, has the advantage that an analytical criterion for the prediction of multiplicity is possible. The predictions of single point collocation, however, have been shown to lead to conservative estimates of the region of multiplicity (Hlavacek et al., 1971; Birnbaum and Lapidus, 1978).

In this paper, we shall obtain the criteria for multiplicity for the reactor including flow, and inter- and intra-particle gradients using single point collocation. Such an analysis will be very useful for practical design purposes.

COMBINED INFLUENCE OF INTER- AND INTRA-PARTICLE RESISTANCES

Consider a single particle with significant inter- and intra-particle gradients. The mass balance equation can be written as:

$$\nabla^2 a = \phi^2 f(a) \tag{7}$$

with the boundary conditions:

At $x = 1$

$$\frac{da}{dx} = Bi(1 - a) \tag{8}$$

and at $x = 0$,

$$\frac{da}{dx} = 0 \tag{9}$$

Applying the single point collocation to Eqs. 7 and 8 we obtain:

$$\frac{B_{12}Bi}{\phi^2(A_{22} + Bi)}(1 - a_1') = f(a_1') \tag{10}$$

where a_1' is the concentration at the interior collocation point. In view of the analogous nature of this equation with Eq. 1, the sufficiency condition given by Eq. 3 is directly applicable with α now being defined as $B_{12}Bi/\phi^2(A_{22} + Bi)$. The necessary condition remains unchanged as the form of Eq. 10 is identical to Eq. 1 and is seen to depend only on kinetic parameters.

ANALYSIS OF CSTR

The mass balance equation for the bulk fluid is:

$$\frac{F\rho_p R}{3k_g W}(1 - a_o) = a_o - a_s \tag{11}$$

where a_s is the concentration at the catalyst surface and k_g is the film mass transfer coefficient.

The equation for the particle is the same as Eq. 7. The boundary condition, condition 8 now gets modified as:

$$\frac{da}{dx} = Bi(a_o - a_s) \tag{12}$$

Applying single point collocation to Eq. 7 we have:

$$\frac{B_{12}}{\phi^2}(a_s - a_1') = f(a_1') \tag{13}$$

Similarly the boundary condition 12 yields:

$$a_s = \frac{Bia_o + A_{22}a_1'}{A_{22} + Bi} \tag{14}$$

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In deriving Eqs. 13 and 14, we have used the relations $B_{11} = -B_{12}$ and $A_{21} = -A_{22}$. Eliminating a_s and a_o by use of Eqs. 11 and 14, the following equation is obtained for a_1'

$$\frac{B_{12}}{\phi^2}\left[\frac{Bi\beta}{A_{22} + \beta(A_{22} + Bi)}\right](1 - a_1') = f(a_1') \qquad (15)$$

where

$$\beta = \frac{F\rho_p R}{3k_g W} \qquad (16)$$

The problem has now been reduced to an equivalent problem of CSTR with no gradients. Hence, the analysis published in the literature (condition of Eq. 3) can be directly used with the parameter α assuming the value of $B_{12}/\phi^2[Bi\beta/A_{22} + \beta(A_{22} + Bi)]$. As the quantity β is also equal to $F/k_1W\phi 2/3Bi)$ this quantity assumes the following value for a spherical pellet:

$$\alpha = \frac{\dfrac{F}{k_1W}}{1 + \dfrac{F}{k_1W}\phi^2\left(\dfrac{1}{3Bi} + \dfrac{1}{10.5}\right)} \qquad (17)$$

where, for the Jacobi polynomial the value of $B_{12} = 10.5$ and $A_{22} = 3.5$ have been used. Equation 17 thus provides a general definition of α in the presence of transport resistances. It also reduces to the correct asymptotic value of F/k_1W, when transport resistances are absent namely when $\phi \rightarrow 0$ and $Bi \rightarrow \infty$. The implication of Eq. 17 is that the region of multiplicity gets shifted in the presence of transport effects. Thus, in a stirred basket reactor, if the catalyst particle size is unchanged, the multiplicity may disappear or start appearing. to illustrate this point consider the following example:

$$\alpha_- = 0.08$$

$$\alpha^+ = 0.1031$$

$$Bi = 100$$

$$\frac{F}{k_1W} = 1$$

For $\phi = 10$ the value of α is 0.0921 indicating that multiple steady states are possible. If the particle size is reduced by half, the value of $\phi = 5$ and $\alpha = 2.886$. It is now seen that the reactor is now operating with only one steady state. The analysis presented here is useful in estimating such effects for practical situations.

NOTATION

a = dimensionless concentration of the reactant
a_o = dimensionless concentration of the reactant at the outlet
a_1,a_2 = dimensionless concentration of the reactant corresponding to the roots of Eq. 2
a_1' = concentration at the collocation point
a_s = dimensionless concentration at the catalyst surface
A_{22},B_{12} = collocation constants for the Jacobian polynomial
Bi = Biot number characterizing external transport resistance
$f(a),f(a_o)$ = the dimensionless rate function
$g(a)$ = function defined by Eq. 2
F = feed rate to the reactor
k_1 = reaction rate constant per unit weight of catalyst
k_g = mass transfer coefficient across the external film
R = radius of catalyst pellet
W = weight of catalyst
x = dimensionless radial coordinate for the particle
a = parameter defined by Eq. 17
α^+,α^- = upper and lower bound of α for the existence of multiplicity
β = dimensionless parameter defined by Eq. 16
ϕ = Thiele modulus characterizing internal transport resistance
ρ_p = bulk density of the catalyst

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Manuscript received September 14, 1981, and accepted December 2, 1981.