Catalyst Effectiveness Factors for Complex Reaction Mechanisms

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The subject of diffusion of reactants and products within a porous catalyst has been discussed many times in the literature. The majority of this work follows the approach of Thiele (1939) and considers only simple reaction mechanisms such as a first-order, irreversible, gas-phase reaction. Only a few workers have considered more complex reaction mechanisms. Chu and Hougen (1962) discuss two irreversible, heterogeneous models of the Hougen-Watson type. One reaction was combined with a flat plate model for the catalyst structure, and the other employed a spherical catalyst model. Both cases lead to second-order differential equations with nonhomogeneous boundary conditions. The resulting differential equations were solved by trial and error with a digital computer. This approach was applied to different reactions by Roberts and Satterfield (1965, 1966) and Knudsen et al. (1966).

For a spherical catalyst particle and a single reaction, the differential equation resulting from a steady state mass balance is

$$\frac{d^2C}{dr^2} + \frac{2}{r}\frac{dC}{dr} + \frac{R_A}{D} = 0 \tag{1}$$

This equation is derived in most texts on kinetics, such as Satterfield and Sherwood (1963). The known boundary conditions are the surface concentration and the concentration gradient at the center of the particle:

$$C = C_s \text{ at } r = R \tag{2}$$

$$\frac{dC}{dr} = 0 \text{ at } r = 0 \tag{3}$$

A trial-and-error solution of Equation (1) can be rather time consuming, even with a digital computer. Also, the second term presents computational problems when $r = 0$. This can be side-stepped by applying L'Hopital's rule. This paper will present a new method of solving Equation (1), which gives a reasonable solution in a minimum of computing time and is easily applied to any reaction model.

The method is based on a concept known as invarient imbedding. The concept of applying invarient imbedding to a two-point boundary-value problem has been discussed by Lee (1968). Essentially, this approach considers the original problem to be part of a family of problems. By application of this concept, the missing boundary condition dC/dr at $r = R$ can be found, thus converting the original problem to an initial value problem. In the original problem, the concentration gradient dC/dr is a function of position. As part of the more general problem, consider the gradient to be a function of both position and concentration

$$\frac{dC}{dr} = S(C, r) \tag{4}$$

Equation (1) may be rewritten as

$$\frac{dC}{dr} = X = S(C, r) \tag{5}$$

$$\frac{dX}{dr} = -\frac{2}{r}X - \frac{R_A}{D} \tag{6}$$

By using a Taylor series expansion, with higher-order terms truncated, the gradient at two positons, separated by Δ, can be related:

$$X(r + \Delta) = X(r) + X'(r)\Delta \tag{7}$$

or

$$S\,[C + S(C, r)\Delta, r + \Delta] = S(C, r) + \left[-\frac{2}{r}S(C, r) - \frac{R_A}{D}\right]\Delta \tag{8}$$

$$S\,[C + S(C, r)\Delta, r + \Delta] = S(C, r)\left(1 - \frac{2\Delta}{r}\right) - \frac{R_A\Delta}{D} \tag{9}$$

$$S(C, r) = \frac{r}{r - 2\Delta}\left[S\,[C + S(C, r)\Delta, r + \Delta] + \frac{R_A\Delta}{D}\right] \tag{10}$$

For small values of Δ

$$S\,[C + S(C, r)\Delta, r + \Delta] = S\,[C + S(C, r + \Delta)\Delta, r + \Delta] \tag{11}$$

Thus

$$S(C, r) = \frac{r}{r - 2\Delta}\left[S\,[C + S(C, r + \Delta)\Delta, r + \Delta] + \frac{R_A\Delta}{D}\right] \tag{12}$$

The missing initial condition may now be found by using Equation (12) and by allowing C to vary from 0 to C_S with increments of δ. At the center of the particle, $r = 0$, the gradient is zero for all values of C:

$$S(C, 0) = 0 \tag{13}$$

At the next position outward, $r = -\Delta$, the gradient may be calculated as a function of concentration and the gradient at the center:

$$S(C, -\Delta) = \frac{1}{3}\left[S\,[C + S(C, 0)\Delta, 0] + \frac{R_A\Delta}{D}\right] \tag{14}$$

$$S(C, -\Delta) = \frac{1}{3}\left[\frac{R_A\Delta}{D}\right] \tag{15}$$

At this point the gradient is calculated for values of $C = 0, \delta, 2\delta, 3\delta, , , , C_S$. At the next position, Equation (12) becomes

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$$S(C, -2\Delta) = \frac{1}{2}\left[S\,[C + S(C, -\Delta)\Delta, -\Delta] + \frac{R_A\Delta}{D} \right] \quad (16)$$

The process is continued until the missing initial condition $S(C_S, R)$ is found. The result is a matrix containing concentration gradients as a function of concentration and position. With this information, the concentration profile, effectiveness factor, and effective rate of reaction may be found.

Chu and Hougen (1962) calculated the effectiveness factor for the catalytic oxidation of nitric oxide over a spherical carbon catalyst. They assumed commercial conditions of 56°C and a total pressure of 1.11 atm. The feed contained 1.5% nitric oxide with a dew point of −30°C. The catalyst density was 711 kg/m^3, and an effective diffusion coefficient of 2.20×10^{-6} m^2/s was used. Their rate equation, based on earlier work, was

$$R_A' = \frac{P^2_{NO}\,P_{O2}}{a + bP^2_{NO} + cP_{NO2} + wP_{H2O}} \quad (17)$$

The constants were given as follows:

$$a = 0.000181$$
$$b = 0.916$$
$$c = 0.00982$$
$$w = 0.0564$$

Using the Runge-Kutta method, they calculated the effectiveness factor for a particle diameter of 3 mm and conversion of 0 to be about 0.32. Equation (12) was programmed for this reaction by using thirty increments of radius and ten increments of concentration. The effectiveness factor was calculated to be 0.33 or about 3% difference. The calculation took about 4 s on an EAI Pacer computer.

This method offers several advantages over previous trial-and-error methods. This straightforward approach should reduce computation time. The indeterminate term in Equation (1) is eliminated. Equation (12) is relatively simple to program, and, once having done so, it is a trivial matter to change the reaction model. Thus, several mechanisms can be investigated in a fairly short time. Also, the concept of invarient imbedding can be applied to many more complicated cases. In this short note, only the case of a single isothermal reaction has been discussed. More complicated mechanisms involving two reactions have been studied by Likins (1970) and the concept should be applicable to nonisothermal cases.

NOTATION

C = concentration, moles/vol.
D = effective diffusion coefficient
r = radial position within particle
R = catalyst effective radius
R_A = rate of reaction, moles/time-vol. catalyst
R_A' = rate of reaction, moles/time-mass catalyst
S = concentration gradient
Δ = increment of radius
δ = increment of concentration

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An Efficient General Purpose Method for the Integration of Stiff Ordinary Differential Equations

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Explicit methods such as the classical fourth-order Runge-Kutta method are known to be unsuitable for the integration of stiff systems, that is, systems with a large spread in the magnitude of the local eigenvalues. Stability of such methods requires that the step length is inversely proportional to the largest eigenvalue throughout the integration, and thus a prohibitively large number of steps is often required.

Simple semi-implicit methods exist which are stable for any step length; however published results with such methods used (Seinfeld et al., 1970; Caillaud and Padmanabhan, 1971) are somewhat disappointing from an accuracy point of view, and recent work (Aiken and Lapidus; 1974) points to singular perturbation methods as preferable alternatives.

Although such methods may be useful in certain extreme cases, they are unattractive as general purpose methods since a large effort is required for their use in each individual case.

It seems, however, that the apparently unsatisfactory behavior of the semi-implicit Runge-Kutta methods is entirely due to an insufficient utilization of their potential.