

* = in polymer solution

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Simple Method for Solution of a Class of Reaction-Diffusion Problems

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In reaction-diffusion systems, one is frequently faced with a physical situation the mathematical description of which requires the solution of nonlinear coupled differential equations. The nonlinearity in these equations exists either in the source term (e.g., reaction rate), in the derivative term (e.g., when volume changes exist), in the coefficients of the governing equations (concentration temperature dependencies of transport parameters), or in the boundary conditions.

It is possible in a given situation to have part or all of these nonlinearities present simultaneously. No analytical solution can be found in such cases and resort to numerical analysis has to be taken. Over the years, a number of papers have appeared that attempt to solve these problems with less effort in computation, and many of the methods proposed have been successful and are now widely used (Kubicek et al., 1970, 1971a,b,c; Hanna, 1980; Hall and Watt, 1976; Hornbeck, 1975; Weisz and Hicks, 1962; Finlayson, 1974).

The present paper is concerned with problems which typically involve nonlinearity in the source term and coupled boundary conditions. Such a physical situation is encountered in gas-solid catalytic reactions in pellets having bimodal pore structure. In gas-solid noncatalytic reaction, this situation arises when particle-pellet (grain) type of models are used to describe the behavior. Besides, in many biochemical systems involving encapsulated enzymes, such a situation is fairly common.

The problem thus appears to be fairly general, and we present below the methodology for solving such problems by considering

a specific example: calculation of the effectiveness factor for a catalyst pellet with bimodal pore distribution. The problem is the same as that considered by Ors and Dogu (1979), who have, however, restricted the solution to a linear reaction rate situation. Kulkarni et al. (1981) have also considered this problem, and for a pellet with regular geometry obtained an asymptotic expression for effectiveness factor for nonlinear rate terms. The use of the present method allows one to compute the effectiveness factor over the entire range of Thiele modulus with considerable saving in computation time.

The conservation equations in dimensionless form can be written as

$$\frac{d^2 C_i}{dx^2} + \frac{2}{x} \frac{dC_i}{dx} = \phi^2 [C_i]^n \quad (1)$$

$$\frac{d^2 C_a}{dy^2} + \frac{2}{y} \frac{dC_a}{dy} = \alpha \left(\frac{dC_i}{dx} \right)_{x=1} \quad (2)$$

with the boundary conditions

$$x = 0, \quad \frac{dC_i}{dx} = 0 \quad (3)$$

$$x = 1, \quad C_i = C_a \quad (4)$$

$$y = 0, \quad \frac{dC_a}{dy} = 0 \quad (5)$$

$$y = 1, \quad C_a = 1 \quad (6)$$

where the various dimensionless terms are defined in the notation.

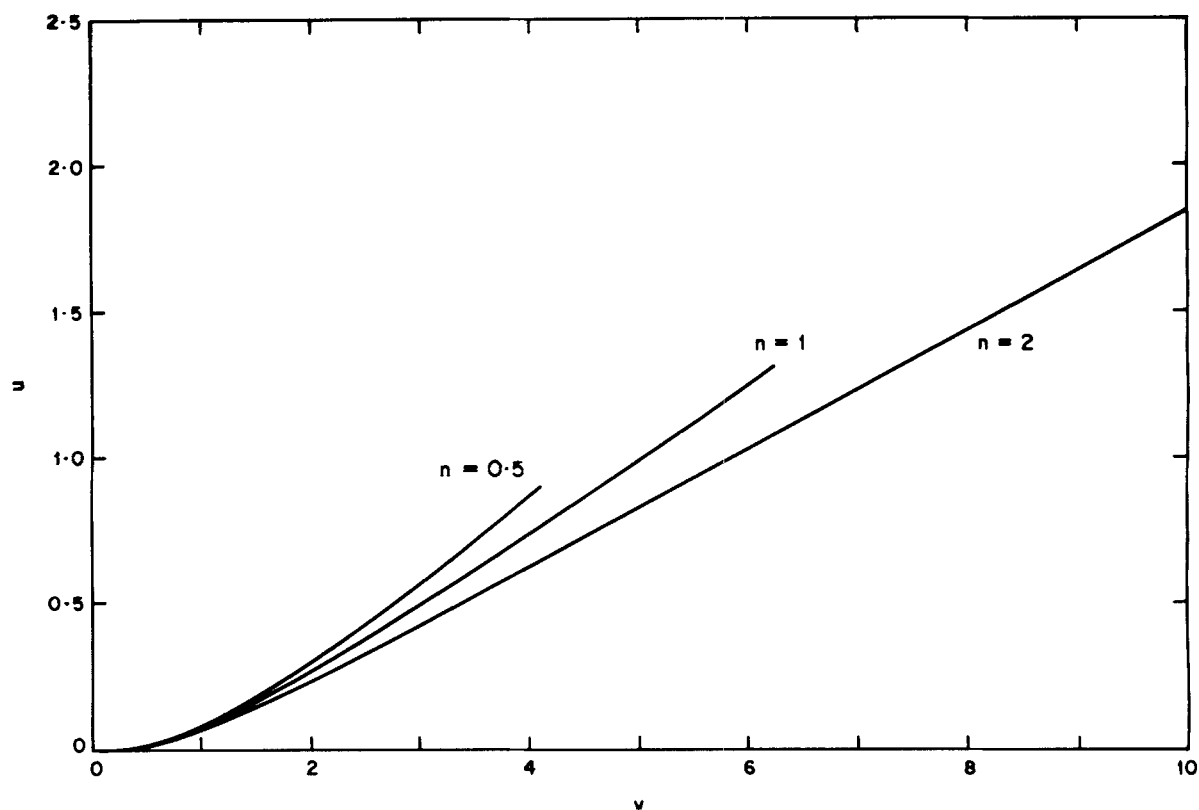


Figure 1. Phase plane plots for various orders of reaction.

The set of equations are nonlinear in the source term and involve the coupled boundary condition given by Eq. 4. The conventional method of solution requires trial and error on both Eqs. 1 and 2 such that the boundary conditions are satisfied. Generally, a large amount of computer time is required to obtain the desired solu-

tion.

In the proposed method, it seems feasible to reduce the trial and error considerably by converting the boundary value problem given by Eqs. 1, 3, and 4 to the corresponding initial value problem. For this purpose, we define the transformation (Ibanez, 1979).

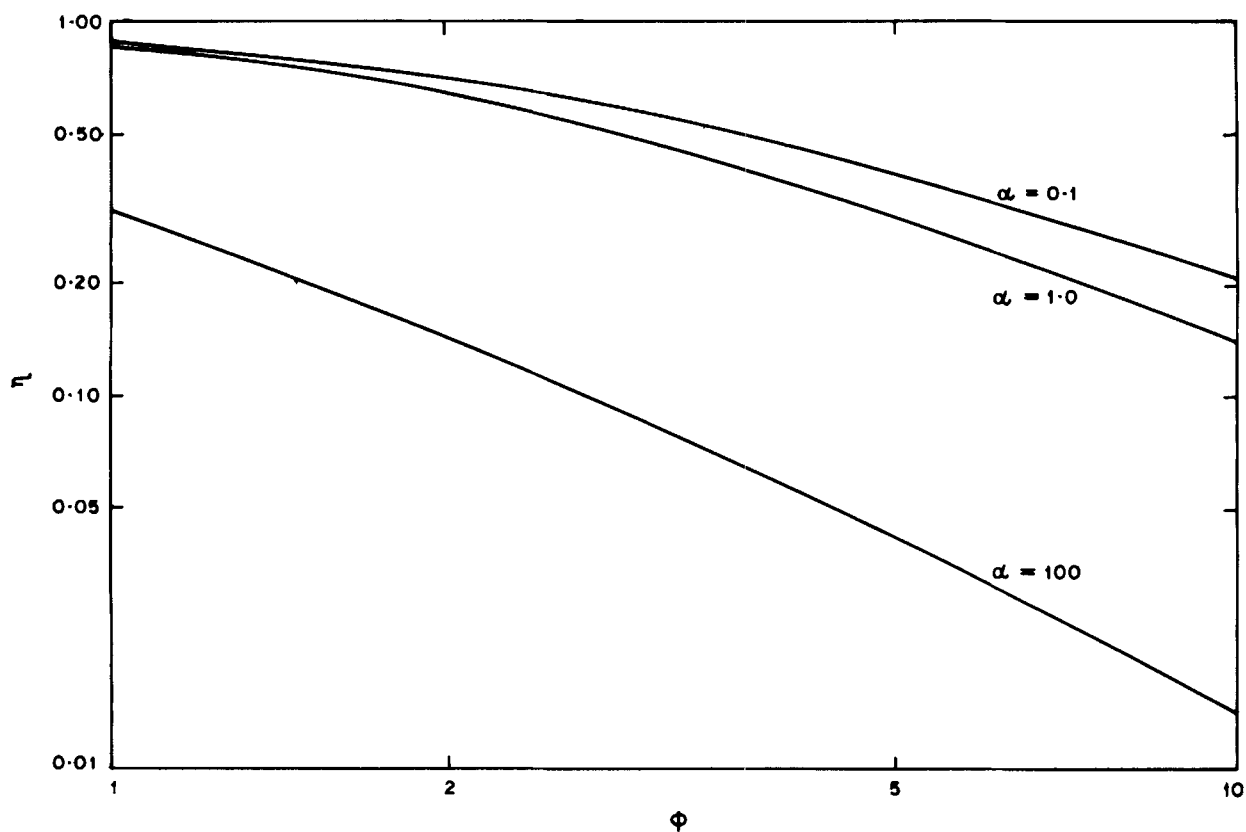


Figure 2. Plots of effectiveness factor vs. Thiele modulus for three values of α .

$$u = \frac{x}{C_i} \frac{dC_i}{dx}, \quad v = \phi^2 x^2 C_i^{n-1} w = \ln \frac{C_i}{C_{io}} \quad (7)$$

and convert Eq. 1 into two differential equations of reduced order as

$$\frac{du}{dw} = \frac{v}{u} - u - 1 \quad (8)$$

$$\frac{dv}{dw} = \frac{2v}{u} + [n - 1]v \quad (9)$$

The initial conditions to these equations can be written, taking into consideration Eq. 7:

$$u = v = 0 \quad \text{at } w = 0 \quad (10)$$

The set of Eqs. 8 and 9, however, possess a singularity at $w = 0$. This can be got rid of by evaluating (v/u) as $w \rightarrow 0$ using the definition given by Eq. 7. The use of L'Hospital's rule leads to the value $(v/u)_{w \rightarrow 0} = 3$. The set of Eqs. 8–10 can now be integrated; the results are displayed in Figure 1 in the form of a phase plot. It is interesting to note that all the variations of ϕ for a given system are condensed along a single curve which now depends only on the order of reaction, n . A further point to note in this figure is the fact that for $n > 1$ the curve $u - v$ continues to increase with increase in the value of w , while for $n < 1$ it attains a finite value that does not further change with increase in w .

SOLUTION

The results obtained in Figure 1 can be interpolated to obtain $(dC_i/dx)_{x=1}$ required in Eq. 2. This equation can now be solved so as to satisfy conditions 5 and 6. The trial and error involved is thus considerably reduced. The detailed procedure for calculating the effectiveness factor is given below.

Step 1. Assume a value of C_a at the center of the pellet [$y = 0$]; for a micropore situated at the center the value of C_i at the pore mouth [$x = 1$] is thus fixed [$C_i = C_a$].

Step 2. For this value of C_i [$= C_a$], Eq. 7 gives $v = \phi^2 C_a^{n-1}$. For a fixed value of ϕ and assumed value of C_a in Step 1, the value of v is therefore fixed. Obtain the corresponding value of u using Figure 1 or by interpolation.

Step 3. This value of u gives the gradient at the surface (using Eq. 7) as $(dC_i/dx)_{x=1} = uC_a$.

Step 4. Use the value of the gradient in Eq. 2 and integrate the equation subject to Eq. 5 and assumed value of C_a in Step 1, to obtain C_a at the end of the first increment in y .

Step 5. Continue integration repeating this procedure until $y = 1$ to check the condition given by Eq. 6. If the condition is not satisfied change suitably the value of C_a assumed in Step 1 and repeat the subsequent steps.

Step 6. Finally obtain the effectiveness factor as

$$\eta = \frac{9}{\phi^2 \alpha} \left(\frac{dC_a}{dy} \right)_{y=1}$$

The results obtained using this procedure are displayed in Figure 2 as plot of effectiveness factor vs. Thiele modulus for several values of α for a second-order reaction. The values of the effectiveness factor match with those obtained using the asymptotic expression of Kulkarni et al. (1981) in the region of high Thiele modulus.

The use of the method to the solution of this problem suggests that the complete trial-and-error procedure required in the use of the conventional method can be avoided, at least partially, thus rendering this method considerably more efficient. On the order of magnitude estimate, it is expected that the present method will be at least tenfold faster than the more conventional trial-and-error method. The only limitation of the method is that it is applicable to a nonlinear rate form of the type of n th order rate expression. Modifications will have to be made for other nonlinear rate forms such as Langmuir-Hinshelwood rate expression or for the general n th order reactions with volume change.

NOTATION

C_a	= dimensionless concentration in the macropore
C_i	= dimensionless concentration in the micropore
C_{io}	= the value of $C_i _{x=0}$
n	= order of reaction
u, v, w	= defined in Eq. 7
x	= distance parameter in the micropore
y	= distance parameter in the macropore
Greek Letters	
α	= ratio of micro-macropore diffusivities
η	= effectiveness factor
ϕ	= thiele modulus

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