between the data and the single straight line is encouraging, particularly in view of the different solid mixing conditions in the two runs. Some scatter in the data is to be expected, principally because of the large percentage error in the  $\Delta TC$  measurement when  $\Delta T\bar{C}$  is small. Estimation of the film density as 1.05 g/cm<sup>3</sup> gives A = 0.16 which, with the slope of the line in Figure 2 and the measured value of n (4.55), gives  $\rho = 53600$ mg/l. Thus, the abscissa of Figure 2 goes to approximately  $\bar{x} = 1.4$ . The slight curvature shown by the data from the first run at large  $\bar{x}$  is as would be expected from the model (see Figure 1).

### CONCLUSIONS

The growth of biomass in a liquid fluidized bed causes it to expand in a predictable way. In general, the expansion will depend on the way the biomass is distributed over the bed particles and on the solids mixing condition. However, it can be approximated over a wide range by a linear function which is independent of these factors. This function should prove useful both for inferring the quantity of biomass in a bed and for predicting the bed height.

#### **ACKNOWLEDGMENT**

Part of this investigation was performed under grant #ENG 76-16415, National Science Foundation.

### **HOTATION**

= buoyant density of bacterial film/buoyant density of clean particle

g(x) = distribution function of bacterial film

= bed height

= exponent in the Richardson-Zaki correlation

 $\Delta TC$  = inlet total carbon concentration-outlet total carbon concentration

= time, hr

= particle settling velocity = clean particle volume

= bed volume

= particle volume/liquid volume in reactor containing no bacterial film

= film volume/clean particle volume

 $\bar{x}$ = mean value of g(x)

= fraction of clean particle volume below a point in the bed

= bed porosity  $\epsilon$ 

= mg carbon/l bacterial film

= space time of reactor containing clean particles

### Subscripts

= bed of clean particles = condition at time zero max = maximum value

### LITERATURE CITED

Freidman, L. D., W. J. Weber, R. Bloom, and C. B. Hopkins, "Improving Granular Carbon Treatment," Water Pollution Control Research Series #17020 GDN 07/71, Environment

Protection Agency (1971).

Hoehn, R. C., and A. D. Ray, "Effects of Thickness on Bacterial Film," J. Water Poll. Control Fed., 45, 2302 (1973).

Lee, D. D., and C. D. Scott, "A Tapered, Fluidised-Bed Bioreactor for Treatment of Aqueous Effluents from Coal Conversion Processes," paper presented at AIChE 70th Annual Meeting, New York (1977).

Richardson, J. F., and W. N. Zaki, "Sedimentation and Fluidisation," Trans. Inst. Chem. Eng. (London), 32, 35 (1954).

Manuscript received February 20, 1978; revision received August 11, and accepted August 25, 1978.

## Effectiveness of Bidisperse Catalysts

### NURAN ORS and TIMUR DOGU

Chemical Engineering Department Middle East Technical University Ankara, Turkey

Many of the supported porous catalysts have a bidisperse pore structure. Such catalyst pellets are formed by the agglomeration of porous particles. Pores within these particles are usually called micropores, and pores between the agglomerated particles are called macropores. In such catalysts, most of the active centers lie within the particles in the micropore region. Hashimoto et al. (1976) presented a method to predict the effective diffusivities both in the macro and micropore regions of bidisperse catalysts. It has also been shown by Uyanik (1977) that both macro and micropore diffusivities can be determined by the method of single pellet chromatography which is originally developed by Doğu and Smith (1975). Diffusion and adsorption in bidisperse porous catalysts are studied by Hashimoto and Smith (1974). Wakao and Smith (1964) derived an expression for the effective diffusivity for diffusion in bidisperse porous catalyst pellets under

0001-1541-79-1888-0723-\$00.75. © The American Institute of Chemical Engineers, 1979.

reaction conditions. They showed that this diffusivity is a function of the effectiveness factor of the microporous particles. They also discussed the need of knowledge of the pore size distributions to predict the effectiveness factors. Silveston and Hashimoto (1971) incorporated the pore size distribution into the evaluation of effectiveness factors. Mingle and Smith (1961) derived the microeffectiveness factors for several pore distribution functions for a nonisothermal pellet. Carberry (1962) evaluated the effectiveness factor for the reversible first-order reaction. Diffusion and reaction in porous catalysts are reviewed by Aris (1975) in detail.

The effectiveness of bidisperse catalysts depend upon the rate of diffusion of reactants and products both in the macro and micropore regions as well as the rate of reaction. This implies that the prediction of the effectiveness factor of such catalysts from a single parameter, namely, the Thiele modulus (Petersen, 1965), may give erroneous results.

Assuming that the microporous particles are spherical, and considering an  $n^{\text{th}}$  order surface reaction, we can write the volume averaged pseudo homogeneous conservation equation for these particles as

$$\frac{D_i}{r^2} \frac{d}{dr} \left( r^2 \frac{dC_i}{dr} \right) - \rho_p S k_r C_i^n = 0 \tag{1}$$

The volume averaged pseudo homogeneous conservation equation for the macroporous region can be written as (the pellet geometry is also assumed to be spherical)

$$\frac{D_a}{R^2} \frac{d}{dR} \left( R^2 \frac{dC_a}{dR} \right) - \frac{3(1 - \epsilon_a)}{r_o} D_i \left( \frac{dC_i}{dr} \right)_{r=r_o} = 0$$
(2)

Equations (1) and (2) and the suitable boundary conditions are written in dimensionless form as

$$\frac{1}{\xi^2} \frac{d}{d\xi} \left( \xi^2 \frac{d\psi_i}{d\xi} \right) - \phi^2_{i,n} \psi^n = 0 \tag{3}$$

$$\frac{1}{\ell^2} \frac{d}{d\ell} \left( \zeta^2 \frac{d\psi_a}{d\ell} \right) - \alpha \left( \frac{d\psi_i}{d\xi} \right)_{\xi=1} = 0 \tag{4}$$

at 
$$\xi = 0$$
;  $\frac{d\psi_i}{d\xi} = 0$  (5)

at 
$$\xi = 1$$
;  $\psi_i = \psi_a$  (6)

at 
$$\zeta = 0$$
;  $\frac{d\psi_a}{d\zeta} = 0$  (7)

at 
$$\zeta = 1$$
;  $\psi_a = 1$  (8)

where

$$\phi_{i,n} = r_o \left( \frac{\rho_p' S k_r C_o^{n-1}}{D_i} \right)^{1/2}$$
 (9)

$$\alpha = 3(1 - \epsilon_a) \frac{D_i}{D_a} \frac{R_o^2}{r_o^2} \tag{10}$$

 $R_o$  is the pellet radius and  $C_o$  is the surface concentration which may be assumed as bulk gas phase concentration if the mass transfer resistance from fluid to the external surface of the pellet is negligible. Looking at these equations, one can predict that the behavior of this system depends upon the numerical magnitudes of two parameters (Thiele modulus)  $\phi_{i,n}$  and  $\alpha$ .

If we consider a first-order reaction (n = 1), the solution of this system of equations is possible (Ors, 1977):

$$\psi_{i} = \frac{1}{\xi} \left( \frac{\psi_{\alpha}}{\sinh(\phi_{i,1})} \right) \sinh(\phi_{i,1}\xi)$$
 (11)

$$\psi_{a} = \frac{1}{\zeta \sinh\left[\alpha \left(\frac{\phi_{i,1}}{\tanh(\phi_{i,1})} - 1\right)\right]^{\frac{1}{2}}}$$
$$\sinh\left[\left[\alpha \left(\frac{\phi_{i,1}}{\tanh(\phi_{i,1})} - 1\right)\right]^{\frac{1}{2}} \zeta\right] \quad (12)$$

For a first-order irreversible reaction in a single spherical porous catalyst pellet, the effectiveness factor  $\eta$  can be predicted from

$$\eta = \frac{9}{\phi_{i,1}^{2}\alpha} \left(\frac{d\psi_{a}}{d\zeta}\right)_{r=1} \tag{13}$$

By substituting  $\psi_a$  from Equation (12) into Equation (13), the effectiveness factor expression for an isothermal first-order reaction taking place in a bidisperse catalyst is obtained:

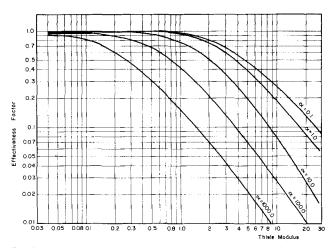


Fig. 1. Dependence of effectiveness factor on Thiele modulus and the parameter  $\alpha$ .

Table 1. The Variation of the Ratio,  $\eta/\eta'$  with the Parameter  $\alpha$  for  $\phi_{i,1}=4.0$ 

$$\eta = \frac{9}{\phi_{i,1}^{2}\alpha} \left\{ \frac{\left[ \alpha \left( \frac{\phi_{i,1}}{\tanh(\phi_{i,1})} - 1 \right) \right]^{\frac{1}{2}}}{\tanh\left[ \alpha \left( \frac{\phi_{i,1}}{\tanh(\phi_{i,1})} - 1 \right) \right]^{\frac{1}{2}}} - 1 \right\}$$
(14)

The variation of effectiveness factor as predicted from Equation (14) with respect to Thiele modulus  $\phi_{i,1}$  for different values of  $\alpha$  is given in Figure 1.

It is obvious from Figure 1 that in the prediction of effectiveness factor of bidisperse catalysts, it is necessary to know the magnitude of  $\alpha$  in addition to the Thiele modulus. The magnitude of  $\alpha$  is actually determined by the ratio of diffusion times in the macro and micropore regions. It appears that a very wide range of values is possible for the parameter a. The magnitude of ratio of effective gas diffusivities in the micro and macropore regions is in the range of  $10^{-1}$  to  $10^{-2}$  for most industrially important catalysts. Of course, this ratio depends upon the pore size distributions of the pellets. Hashimoto and Smith (1974) have determined this ratio as  $1.25 \times 10^{-2}$ at 30°C for the diffusion of n-butane in alumina pellets with macro and micro mean pore radii of 1 200 and 17 A, respectively. The ratio of pellet radius to particle radius lies within a wider range of values, but for most industrially important catalysts, the value of this ratio is between 10 and 100. For the pellets used by Hashimoto and Smith (1974), this ratio is about 10. If we consider these, it can be said that for most practical catalysts, the value of parameter  $\alpha$  lies between 1 and 1 000. The value of  $\alpha$  is about 2.5 for the pellets used by Hashimoto and Smith.

The ratios of effectiveness factor values evaluated from this model and from conventional methods are given in Table 1 for different  $\alpha$  values having  $\phi_{i,1}=4.0$ . At this value of Thiele modulus, diffusion is at least as important as reaction.

As expected, as the value of  $\alpha$  increases, the difference between the effectiveness factors predicted from this

model and the conventional model becomes smaller and smaller. At a fixed value of  $\alpha$ , the ratio  $\eta/\eta'$  decreases as  $\phi_{i,1}$  increases. For example, for  $\alpha = 0.1$  and  $\phi_{i,1} =$ 10.0, this ratio becomes 0.32, while the same ratio is 0.6 for  $\phi_{i,1} = 4.0$ .

In conclusion, one can say that the prediction of the effectiveness factors from the conventional methods would give overestimated values, especially for small  $\alpha$ .

The approach described here can also be applied to nonisothermal systems (Örs, 1977) and for other pellet geometries.

### **HOTATION**

= concentration of reactant A in the macropores = concentration of reactant A in the micropores  $C_i$  $C_o$ = external surface concentration of reactant A  $D_a$ = effective macropore diffusion coefficient  $D_i$ = effective micropore diffusion coefficient

 $k_r$ = surface reaction rate constant R= radial coordinate for the pellet

= radius of the pellet  $R_o$ 

= radial coordinate for the particle

= radius of the particle  $r_o$ 

= surface area per unit mass of the catalyst

### **Greek Letters**

= defined by Equation (9) α

= macropore porosity €a = effectiveness factor

= effectiveness factor of bidisperse pellet considerη ing it as a monodisperse one

ζ = dimensionless radial coordinate for the pellet,

 $= \rho_p'(1 - \epsilon_a) = \text{pellet density}$  $\rho_p$ 

= particle density

= Thiele modulus for an  $n^{th}$  order reaction

= dimensionless concentration in the macropores,

= dimensionless concentration in the micropores,  $C_i/C_o$ 

= dimensionless radial coordinate for the particle,

### LITERATURE CITED

Aris, R., The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts, Clarendon Press, Oxford, London, England (1975).

Carberry, J. J., "The Micro-Macro Effectiveness Factor for the Reversible Catalytic Reaction," AIChE J., 8, 557 (1962). Doğu, G., and J. M. Smith, "A Dynamic Method for Catalyst Diffusivities," ibid., 21, 58 (1975).

Hashimoto, N., A. J. Moffat, and J. M. Smith, "Diffusivities in Catalyst Pellets with Bidisperse Pores," ibid., 22, 944

Hashimoto, N., and J. M. Smith, "Diffusion in Bidisperse Porous Catalyst Pellets," Ind. Eng. Chem. Fundamentals, 13, 115 (1974).

Mingle, J. O., and J. M. Smith, "Effectiveness Factors for Porous Catalysts," AIChE J., 7, 243 (1961).

Ors, N., "Effectiveness of Bidisperse Porous Catalysts," M.S. thesis, Middle East Technical Univ., Ankara, Turkey (1977).

Petersen, E. E., Chemical Reaction Analysis, Prentice Hall,

Englewood Cliffs, N.J. (1965).

Silveston, P. L., and K. Hashimoto, "An Effectiveness Factor Approximation for Pore Size Distributions," AIChE J., 17, 745 (1971).

Uyanik, Ö., "Effect of Micropores on Gaseous Diffusion in Bidisperse Porous Catalysts," M.S. thesis, Middle East Technical Univ., Ankara, Turkey (1977).

Wakao, N., and J. M. Smith, "Diffusion and Reaction in Porous Catalysts," Ind. Eng. Chem. Fundamentals, 3, 123

(1964).

Manuscript received February 27, 1978; revision received August 11, and accepted August 25, 1978.

# Collocation Solution of Creeping Newtonian Flow Through Sinusoidal Tubes

### MARIANO A. NEIRA and ALKIVIADES C. PAYATAKES

**Chemical Engineering Department** University of Houston Houston, Texas 77004

Laminar flow through periodically constricted tubes is usually employed as a modeling device in the study of transfer processes in porous media (Payatakes, Tien and Turian, 1973a, 1974a, b; Slattery, 1974; Oh and Slattery, 1976; Sheffield and Metzner, 1976; Stegermeier, 1976; Payatakes, Brown and Tien, 1977; Payatakes and Neira, 1977; Fedkiw and Newman, 1977; Payatakes, Flumerfelt, and Ng, 1977).

The problem of laminar Newtonian flow through periodically constricted tubes was solved by Payatakes, Tien and Turian (1973b) with a finite-difference method of the stream function-vorticity type. This method has two substantial advantages. First, it applies to tubes of arbitrary

etc.) so long as the wall radius is a single-valued function of the axial coordinate. Second, it retains the non-linear inertial terms of the equation of motion, which are shown to become important at relatively low values of the Reynolds number (say, larger than 1 to 30). On the other hand, the finite difference method suffers from the disadvantages of 1) requiring large mentory to achieve satisfactory accuracy, and 2) rendering the solution in matrix form, namely only on the network nodes. Stream function, velocity and pressure values at off-node points have to be calculated with two-dimensional interpolation techniques.

shape (allowing for wall discontinuities such as cusps,

Hence, there are great incentives to develop analytical approximate solutions for this type of problem.

Dodson, Townsend and Walters (1971) developed

<sup>0001-1541-79-9954-0725-\$00.75. ©</sup> The American Institute of Chem-