stratifications of the sandstone structure identified. It is evident from this preliminary investigation that CAT scanning is an effective means of observing the mechanism involved in immiscible displacement processes. Further studies are being undertaken to differentiate the variables affecting the oil recovery processes.

NOTATION

x_{ij} = oil fraction (volume fraction) of fluid mixture occupying the void space at element (i,j), δ

ϕ_{ij} = volume fraction of the void space at element (i,j), δ

μ_{ij} = X-ray attenuation coefficient of volume element (i,j), cm^{-1}

$\mu_{oil, 1 M KI}$ = X-ray attenuation coefficient of pure oil, 1 M KI solution, respectively, cm^{-1}

$\mu_{oil\ core}^{1\ M\ KI\ core}$ = X-ray attenuation coefficient of volume element (i,j) of the porous material when completely filled with oil, pure 1 M KI solution, respectively, cm^{-1}

Note: μ_{oil} and $\mu_{oil\ core}$ are different in that μ_{oil} is a physical property of pure oil and $\mu_{oil\ core}$ expresses the combining X-ray attenuation effect of both oil and the solid porous structure.

LITERATURE CITED

Ambrose, J., "Computerized Transverse Axial Scanning (Tomography). Part II. Clinical Application," *Brit. J. Radiol.*, **46**, 1023 (1973).

Brooks, R. A., and G. DiChiro, "Theory of Image Reconstruction in Computed Tomography," *Radiology*, **117**, 561 (1975).

Castellana, F. S., J. L. Spencer, and A. Cartolano, "Application of the Gamma Camera to Studies of Flow and Mixing in Reactor Vessels," *Ind. Eng. Chem. Fund.*, **19**, 222 (1980).

Genant, H. K., and D. Boyd, "Quantitative Bone Mineral Analysis Using Dual Energy Computed Tomography," *Invest. Radiol.*, **12**, 545 (1977).

Leverett, M. C., "Flow of Oil-Water Mixtures through Unconsolidated Sands," *Trans. AIME*, **132**, 149 (1939).

McCullough, E., et al., "Performance Evaluation and Quality Assurance of Computed Tomography Scanners with Illustrations from the EMI, ACTA and DELTA Scanners," *Radiology*, **120**, 173 (1976).

van Meurs, P., "The Use of Transparent Three-Dimensional Models for Studying the Mechanism of Flow Process in Oil Reservoirs," *Trans. AIME*, **210**, 295 (1957).

Parsons, R. W., "Microwave Attenuation—A New Tool for Monitoring Saturation in Laboratory Flooding Experiments," *Soc. Petrol. Engrs. J.*, **15**, 302 (1975).

Slobod, R. L., and B. H. Caudle, "X-Ray Shadowgraph Studies of Areal Sweepout Efficiencies," *Trans. AIME*, **195**, 265 (1952).

Single-Pellet Reactor for Bidisperse Porous Catalysts

DEEPAK KUNZRU

**Department of Chemical Engineering
Indian Institute of Technology, Kanpur
Kanpur 208016, India**

A single-pellet reactor has been shown to be an elegant method for determining the intrinsic rate constant, effective diffusivity and the effectiveness factor for monodisperse catalysts. In addition, by measuring the center plane concentration with time for a deactivating catalyst, information can be obtained on the mechanism and kinetics of the poisoning process. The experimental and analytical details of a single-pellet reactor have been discussed elsewhere (Hegedus and Peterson, 1974).

Very often the catalyst is formed by pelletizing small microspherical porous particles resulting in a bidisperse porous catalyst. Diffusion in both the macropores and the micropores affects the overall effectiveness factor. Generally, the effectiveness factor for the particles is assumed to be unity and, with this approximation, the expressions for the effectiveness factor for mono- and bidisperse catalysts become identical. However, if the reaction is fast, the effectiveness factor for the particles can be less than unity and the above approximation is no longer valid. Örs and Dŏgu (1979) discussed the effectiveness factor of bidisperse catalysts and the error involved if this is approximated as monodisperse. A procedure for incorporating the pore size distribution in the macro- and micropores in calculating effectiveness factors is available (Mingle and

Smith, 1961). Effectiveness factors for reversible reactions in bidisperse catalysts have also been presented (Carberry, 1962). Dynamic methods for determining macropore and micropore diffusivities in bidisperse catalysts have been discussed earlier (Hashimoto and Smith, 1974).

This note discusses the use of a single-pellet reactor for determining the diffusivities, effectiveness factor and the intrinsic rate constant for bidisperse catalysts and the error involved in the determination of the intrinsic rate constant if the bidisperse porous catalyst is approximated as monodisperse.

THEORETICAL ANALYSIS

It will be assumed that the reaction is isothermal, irreversible and first order, and the cylindrical pellet is made from spherical particles. The dimensionless conservation equations presented earlier for spherical pellets (Örs and Dŏgu, 1979) modified for a cylindrical pellet exposed to the reactant on one plane surface are

Micropore Balance

$$\frac{1}{\zeta^2}\frac{d}{d\zeta}\left(\zeta^2\frac{d\varphi_i}{d\zeta}\right) - h^2\varphi_i = 0 \qquad (1)$$

The boundary conditions in the micropore region are

$$\zeta = 0, \quad \frac{d\varphi_i}{d\zeta} = 0 \qquad (2)$$

$$\zeta = 1, \quad \varphi_i = \varphi_M \qquad (3)$$

where h, the Thiele parameter for the micropores, is defined as

$$h = r_o \sqrt{\left(\frac{\rho'_P S_g k_s}{D_{ei}}\right)} \qquad (4)$$

Macropore Balance

The conservation balance for the reactant in a cylindrical pellet can be written as

$$\frac{d^2\varphi_M}{d\theta^2} - \alpha\left(\frac{d\varphi_i}{d\zeta}\right)_{\zeta=1} = 0 \qquad (5)$$

where

$$\alpha = 3(1 - \epsilon_M)\frac{D_{ei}}{D_{eM}}\frac{L^2}{r_0^2} \qquad (6)$$

The macropore boundary conditions for a single-pellet reactor, assuming that the external gas film resistance is negligible, are:

$$\theta = 0, \quad \varphi_M = 1 \qquad (7)$$

$$\theta = 1, \quad \frac{d\varphi_M}{d\theta} = 0 \qquad (8)$$

Solving Eq. 1, we obtain

$$\frac{\varphi_i}{\varphi_M} = \frac{1}{\zeta}\frac{\sinh(h\zeta)}{\sinh(h)} \qquad (9)$$

Solving Eq. 5 together with Eqs. 7, 8 and 9, we obtain

$$\varphi_M = \cos hm\theta - \tan hm(\sin hm\theta) \qquad (10)$$

where

$$m = \left[\left(\frac{h - \tanh(h)}{\tanh(h)}\right)\alpha\right]^{1/2} \qquad (11)$$

In a single-pellet reactor, the concentration at $\theta = 1$ is measured experimentally. From Eq. 10

$$\varphi_M(1) = \frac{1}{\cosh m} \qquad (12)$$

The overall effectiveness factor for a bidisperse catalyst can be written as

$$\eta = \frac{-D_{eM}A\left(\dfrac{dC_M}{dx}\right)_{x=0}}{AL(1 - \epsilon_M)\rho'_p S_g k_s C_{Mo}} \qquad (13a)$$

$$= -\frac{3}{h^2\alpha}\left(\frac{d\varphi_M}{d\theta}\right)_{\theta=0} \qquad (13b)$$

$$= \frac{3m}{h^2\alpha}\tan hm \qquad (13c)$$

It should be emphasized that use of this expression for the effectiveness factor is restricted to the case where the reactants can enter the catalyst only from one plane face of a cylindrical pellet. In a real reactor, the reactants can diffuse into the pellet from all external surfaces and Eq. 13c will not be applicable.

The variation of η with h and α is shown in Figure 1. A similar plot for spherical pellets completely surrounded by the reactant has been presented earlier (Ors and Dŏgu, 1979).

The observed rate of reaction can then be written as

$$R_{\text{obs}} = \eta AL(1 - \epsilon_M)\rho'_p S_g k_s C_{Mo} \quad (\text{mol/s}) \qquad (14a)$$

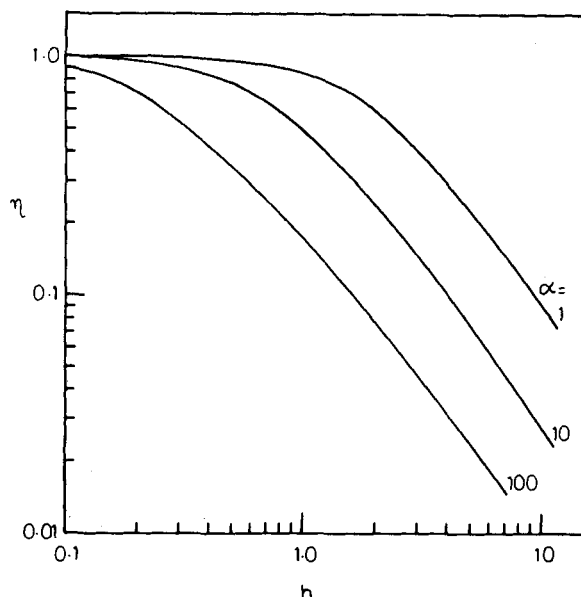$$= \frac{3m\tanh(m)}{h^2\alpha}AL(1 - \epsilon_M)\rho'_p S_g k_s C_{Mo} \quad (\text{mol/s}) \qquad (14b)$$

Figure 1. Variation of effectiveness factor with micropore Thiele parameter and α.

Substituting for $h^2\alpha$ from Eqs. 4 and 6, we get

$$R_{\text{obs}} = m\tanh(m)\frac{A}{L}D_{eM}C_{Mo} \quad (\text{mol/s}) \qquad (15)$$

DISCUSSION

In a single-pellet reactor, for each experiment $\varphi_M(1)$, R_{obs} and C_{Mo} are measured experimentally. Then, m can be obtained from Eq. 12. Knowing m and the pellet dimensions, D_{eM} can be calculated using Eq. 15. However, in order to calculate h, α, η and k_s it is necessary that D_{ei} be known. This can either be measured experimentally or estimated from available correlations. Since the micropores are relatively narrow. Knudson diffusion would be expected to predominate. Then,

$$D_{e_i} = D_{K_i}\frac{\epsilon_i}{\tau_i} \qquad (16)$$

From the model proposed by Wakao and Smith (1962)

$$D_{e_i} \approx \epsilon_i^2 D_{K_i} \qquad (17)$$

Knowing D_{e_i}, α can be calculated using Eq. 6. Since α and m are now known, h can be obtained from Eq. 11 by a simple trial-and-error or by using Figure 2 which shows a plot of m^2/α vs. h. Equations 13c and 4 then yield, η and k_s, respectively. The above analysis can be extended to nonlinear reactions; however, analytical solutions will not be possible.

It is worthwhile to estimate the error involved in the determination of the intrinsic rate constant in a single pellet reactor if the catalyst bidispersity is not accounted for. For a monodisperse catalyst, from the available results (Hegedus and Peterson, 1974), we have

$$\varphi_M(1) = \frac{1}{\cosh(h')} \qquad (18)$$

$$\eta = \frac{\tanh(h')}{h'} \qquad (19)$$

and

$$R_{\text{obs}} = \frac{\tanh(h')}{h'}AL\rho'_p(1 - \epsilon_M)S_g k_s C_{Mo} \quad (\text{mol/s}) \qquad (20)$$

where

$$h' = L\left[\frac{\rho'_p(1 - \epsilon_M)S_g k_s}{D_{eM}}\right]^{1/2} \qquad (21)$$
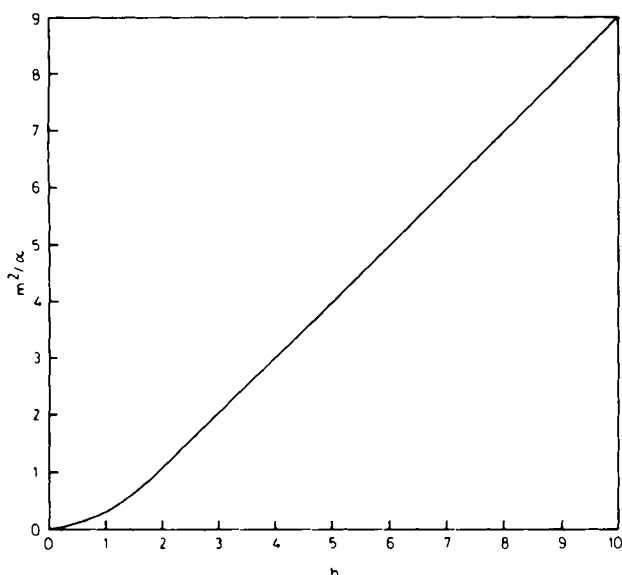
Figure 2. Variation of m^2/α with micropore Thiele parameter.

TABLE 1. VARIATION OF $k_{s,m}/k_s$ WITH MICROPORE THIELE PARAMETER

h	0.1	0.5	1.0	2.0	5.0
$k_{s,m}/k_s$	0.99	0.98	0.94	0.81	0.48

For the same experiment, for the mono- and bidisperse catalyst analysis, h' will be equal to m and equating Eqs. 20 and 14b, we obtain

$$\frac{k_{s,m}}{k_s} = \frac{3m^2}{h^2\alpha} \tag{22a}$$

$$= \frac{3}{h^2}\frac{[h - \tanh(h)]}{\tanh(h)} \tag{22b}$$

where $k_{s,m}$ is the intrinsic rate constant calculated assuming the catalyst to be monodisperse. The variation of $k_{s,m}/k_s$ with h is shown in Table 1. As can be seen from Table 1, the error in the intrinsic rate constant is insignificant for h less than unity but for higher values of h, $k_{s,m}$ can be significantly less than the actual intrinsic rate constant.

In conclusion, if the effective micropore diffusivity is known, a single-pellet reactor can be used to determine the effective macropore diffusivity, effectiveness factor, micropore Thiele parameter and the intrinsic rate constant for a bidisperse catalyst. For h larger than unity, significant errors can result in the intrinsic rate constant if the bidisperse catalyst is approximated as monodisperse.

NOTATION

A	= cross-sectional area of the pellet
C_i	= concentration of reactant in the micropores
C_M	= concentration of reactant in the macropores
C_{Mo}	= external surface concentration of reactant
D_{ei}	= effective diffusivity in the micropores
D_{eM}	= effective diffusivity in the macropores
K_{Ki}	= Knudsen diffusivity in the micropores
h	= Thiele parameter for the micropores
h'	= Thiele parameter for a monodisperse catalyst
k_s	= intrinsic reaction rate constant
L	= length of cylindrical pellet
m	= parameter defined in Eq. 11
r	= radial coordinate of the particle
r_o	= radius of the particle
S_g	= surface area per unit mass of catalyst
x	= axial coordinate of the pellet

Greek Letters

α	= parameter defined in Eq. 6
ϵ_i	= micropore porosity
ϵ_M	= macropore porosity
η	= effectiveness factor
θ	= dimensionless axial coordinate for the pellet, x/L
ρ_p	= $\rho_p(1 - \epsilon_M)$ = pellet density
ρ'_p	= particle density
τ_i	= micropore tortuosity
ζ	= dimensionless radial coordinate for the particle, r/r_o
φ_i	= dimensionless concentration in the micropores, C_i/C_{Mo}
φ_M	= dimensionless concentration in the macropores, C_M/C_{Mo}

LITERATURE CITED

Carberry, J. J., "The Micro-Macro Effectiveness Factor for the Reversible Catalytic Reaction," *AIChE J.*, 8, p. 557 (1962).

Hashimoto, N., A. J. Moffat, and J. M. Smith, "Diffusivities in Catalyst Pellets with Bidisperse Pores," *Ibid.*, 22, p. 944 (1976).

Hegedus, L. L., and E. E. Petersen, "The Single Pellet Diffusion Reactor: Theory and Applications," *Cat. Rev. Sci. and Eng.*, 9, p. 245 (1974).

Mingle, J. O., and J. M. Smith, "Effectiveness Factors for Porous Catalysts," *AIChE J.*, 7, p. 243 (1962).

Ors, N., and T. Dŏgu, "Effectiveness of Bidisperse Catalysts," *Ibid.*, 24, p. 723 (1979).

Wakao, N., and J. M. Smith, "Diffusion in Catalyst Pellets," *Chem. Eng. Sci.*, 17, p. 825 (1962).