Macropore and Micropore Effective Diffusion Coefficients from Dynamic Single-Pellet Experiments

Gülşen Doğu, Aliye Keskin
Department of Chemical Engineering
Middle East Technical University
Ankara, Turkey

Timur Doğu
Faculty of Sciences
Ankara University
Ankara, Turkey

In many catalytic and noncatalytic gas-solid reactions, the solid possesses a bidisperse pore structure. For such systems, the observed reaction rate depends on the rates of diffusion of reactants and products both in the macro- and micropore regions, as well as on the reaction rate (Örs and Doğu, 1979). In catalyst pellets, which are formed by compacting fine microporous particles, macropores are formed between the agglomerated particles. A similar pore structure was observed for activated soda pellets (Doğu et al., 1986) used for the removal of SO_2 from flue gas. The differential pore size distribution curve for soda pellet activated at 200°C is shown in Figure 1.

Hashimoto and Smith (1974), and Haynes and Sarma (1973) suggested chromatographic methods for the determination of macro- and micropore effective diffusivities in a bidisperse porous solid. In these methods the response peak to an injected pulse of tracer was influenced by axial dispersion and interpellet rate parameters as well as intraparticle rate parameters. With the single-pellet moment method, which was used for the evaluation of effective diffusion coefficients in monodisperse porous catalysts (Doğu and Smith, 1975), interparticle transport effects were eliminated and intraparticle rate parameters could in principle be evaluated more effectively. The method was later used for the analysis of adsorption on bidisperse porous catalysts (Doğu and Ercan, 1983).

In the present work, it was illustrated that both macro- and micropore diffusion coefficients could be determined accurately and quickly from two sets of single-pellet experiments carried out with pellets of identical physical properties but of different lengths. A schematic diagram of the apparatus is shown in Figure 2; details of the experimental system are reported elsewhere (Doğu and Smith, 1975, 1976). The method was applied for the evaluation of diffusion coefficients of an inert tracer (nitrogen in helium) in activated soda pellets. A pulse of nitrogen tracer was injected into the carrier gas (helium) flowing past the upper face of a cylindrical soda pellet. The response peak was measured at the outlet of the lower stream carrier gas (helium). Experimental values of the first absolute and second central moments were then determined from the observed response peaks.

For a bidisperse porous solid, first absolute and second central moment expressions were reported by Hashimoto et al. (1976). The rearranged form of the second central moment expression for an inert tracer is:

$$\mu_2' = \frac{L^4(\epsilon_i + \epsilon_a)^2}{6D_a^2} \frac{\left[\frac{1}{15}F^2 + \frac{2}{5}\frac{AD_a}{L}F + \left(\frac{AD_a}{L}\right)^2\right]}{\left[F + \frac{AD_a}{L}\right]^2} + \frac{L^2\epsilon_i^2 r_o^2}{15D_aD_i(1-\epsilon_a)} \cdot \frac{\left[\frac{1}{3}F^2 + \frac{4}{3}\frac{AD_a}{L}F + \left(\frac{AD_a}{L}\right)^2\right]}{\left[F + \frac{AD_a}{L}\right]^2} \tag{1}$$

For large values of the lower stream flow rate, the limiting forms

---

Gülşen Doğu is presently at Gazi University, Ankara, Turkey.

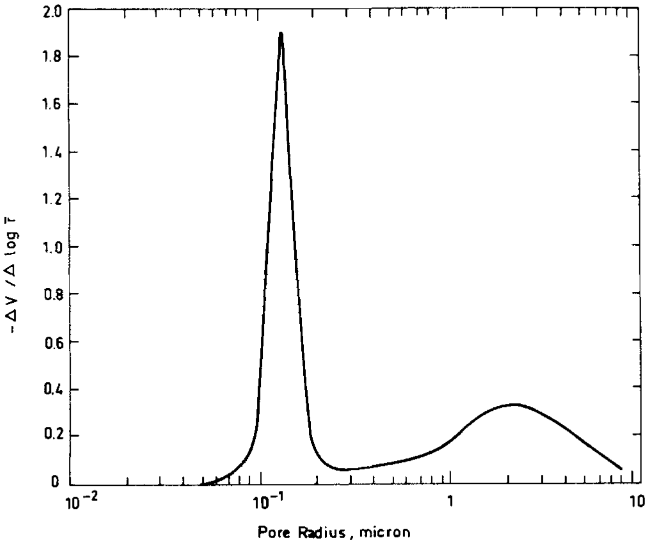

Figure 1. Differential pore size distribution curve for an activated soda pellet (Keskin, 1985).

of first obsolute moment (μ_1) and second central moment (μ_2') expressions become:

$$\mu_{1\infty} = \frac{L^2(\epsilon_i + \epsilon_a)}{6D_a} \qquad (2)$$

$$\mu_{2\infty}' = \frac{L^4(\epsilon_i + \epsilon_a)^2}{90D_a^2} + \frac{L^2\epsilon_i^2 r_o^2}{45D_aD_i(1 - \epsilon_a)} \qquad (3)$$

Experimental

Soda pellets were prepared by compressing sodium bicarbonate powder (99.7% pure) in a cylindrical stainless steel mold. The powder was moistened by keeping it in contact with saturated air in a closed vessel at 40°C prior to the pelleting process. Pellets were placed into the diffusion cell and were activated at 473 K for 2 h while both upper and lower carrier gas streams were flowing at a rate of 3.33 cm^3/s. As a result of this heating process, sodium bicarbonate was decomposed and micropores were formed within the activated soda (Na_2CO_3) particles. The average diameter of the particles was determined from electron microscope photographs as 8.4 × 10^{-5} m (Keskin, 1985). A 30,000 psi (206.7 MPa) mercury intrusion porosimeter was used to determine the pore size distribution of pellets. Pores smaller than 0.26 micron in radius were considered to be micropores. This corresponds to the minimum in the pore size distribution, Figure 1.

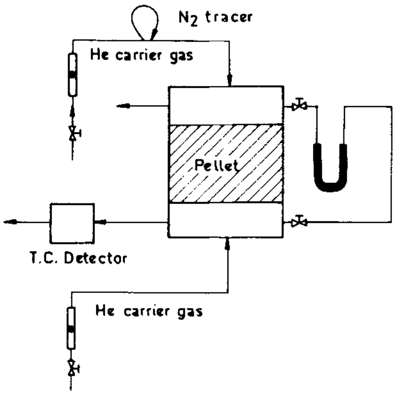

Figure 2. Experimental system.

Experimental moment values contain contributions from lower and upper dead volumes. Correct evaluation of the diffusion coefficients from the moment analysis requires the elimination of these factors. For this purpose, pulse-response experiments were carried out for two pellets of different lengths but with the same porosity. By analyzing the difference between the moments for the two pellets, more accurate values for the macro- and micropore diffusion coefficients were evaluated.

During the pulse-response experiments the pressure was maintained constant at both sides of the pellet. The flow rate of the upper stream was maintained at 5 cm^3/s while the flow rate of the lower carrier gas stream was changed. Pulse-response experiments were conducted at 200°C and atmospheric pressure. The experimental first absolute moment values for two pellets of different lengths but identical physical properties (microporosity 0.38, total porosity 0.47) and the difference of the moments are given in Figure 3. The second moment values for the same pellet pair are given in Figure 4.

Macropore and Micropore Diffusivities

The macropore diffusion coefficient was evaluated from the difference of the infinite flow rate first moment values. For this analysis, Eq. 2 was rearranged:

$$D_a = \frac{\epsilon_p(L_1^2 - L_2^2)}{6\Delta\mu_{1\infty}} \qquad (4)$$

On the other hand, the micropore diffusion coefficient was evaluated from the difference of infinite flow rate limits of second central moment values:

$$D_i = \frac{2\epsilon_i^2 r_o^2 \Delta\mu_{1\infty}}{15\epsilon_p(1 - \epsilon_a)\left[\Delta\mu_{2\infty}' - \frac{6}{15}(\Delta\mu_{1\infty})^2 \frac{(L_1^2 + L_2^2)}{(L_1^2 - L_2^2)}\right]} \qquad (5)$$

This equation was derived from Eqs. 3 and 4. The results of this

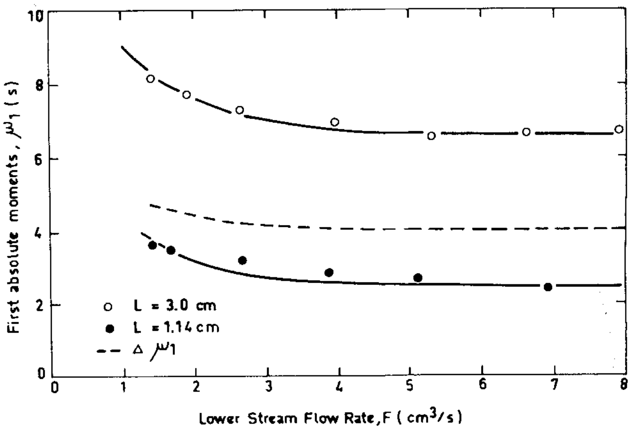

Figure 3. First absolute moment values of N_2 tracer for pellets of different lengths.

$\epsilon_p = 0.47$; $\epsilon_i = 0.38$

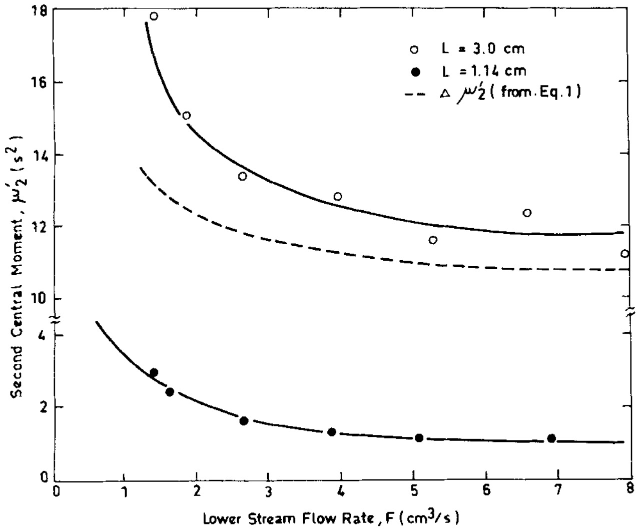

Figure 4. Second central moment values of N_2 tracer for pellets of different lengths.
$\epsilon_p = 0.47$; $\epsilon_i = 0.38$

analysis for two pellet pairs of different porosities are reported in Table 1.

In this analysis the nitrogen tracer is considered to be an inert tracer. A similar assumption was also made by Doğu et al. (1986). The surface area of the activated soda used is relatively small (about 5×10^4 cm²/g by mercury intrusion porosimeter measurement) and the reversible adsorption of N_2 is negligibly small at 200°C. In fact, the preliminary experiments conducted with helium tracer in nitrogen carrier gas gave approximately the same tortuosity factor value as the experimental result obtained with nitrogen tracer in helium.

The macropore and micropore effective diffusion coefficients evaluated from the high flow rate limits of first absolute and second central moments, using Eqs. 4 and 5, were then used to predict values of $\Delta\mu_1$ and $\Delta\mu_2'$, from Eq. 1, at different flow rates. The predicted curves and the experimental values show very good agreement, Figures 3 and 4.

The results in Table 1 show that the effective macropore diffusivity of pellet B was about three times larger than that of pellet A. On the other hand, the effective micropore diffusivity values were close to each other. The order of magnitude of D_i is in the range of effective micropore diffusivities reported in the literature. Both the total porosity and the macroporosity of pellet B are larger than the values for pellet A. The effective macropore diffusivity is expected to increase with macropore porosity. Experimental results are in agreement with this prediction. The ratio $\epsilon_i/(1 - \epsilon_a)$ is about the same for both pellets. This ratio corresponds to the porosity of the particles, and the effective micropore diffusivity is expected to be proportional to this ratio. All these results indicate that effective macro- and micropore diffusivities can be evaluated quickly and accurately following the experimental procedure outlined here.

Table 1. Macropore and Micropore Effective Diffusivities from Moment Analysis

	Pellet A	Pellet B
Total porosity, ϵ_p	0.47	0.71
Microporosity, ϵ_i	0.38	0.22
Macroporosity, ϵ_a	0.09	0.49
Macropore eff. diffus., D_a, cm²/s	0.15	0.48
Micropore eff. diffus., D_i, cm²/s	1.5×10^{-6}	1.2×10^{-6}

Notation

A = cross-sectional area of pellet
C_a = concentration in macropores
C_i = concentration in micropores
D_a = effective macropore diffusivity
D_i = effective micropore diffusivity
F = lower stream flow rate
L = length of the pellet
m_n = nth moment about origin
M = strength of input pulse
r_o = average particle radius of soda particles
t = time

Greek letters

ϵ_p = total porosity of pellet
ϵ_a = macropore porosity
ϵ_i = micropore porosity
μ_i = first absolute moment
$\mu_{1\infty}$ = infinite flow rate limit of μ_1
$\Delta\mu_{1\infty}$ = difference of $\mu_{1\infty}$ values for two pellets of different lengths
μ_2' = second central moment
$\mu_{2\infty}'$ = infinite flow rate limit of $\mu_{2\infty}'$
$\Delta\mu_{2\infty}'$ = difference of $\mu_{2\infty}'$ values for two pellets of different lengths
$\delta(t)$ = Dirac delta function

Literature cited

Doğu, G., and C. Ercan, "Dynamic Analysis of Adsorption on Bidisperse Porous Catalysts," *Can. J. Chem. Eng.*, **61**, 660 (1983).

Doğu, G., and J. M. Smith, "A Dynamic Method for Catalyst Diffusivities," *AIChE J.*, **21**, 58 (1975).

———, "Rate Parameters from Dynamic Experiments with Single-Catalyst Pellets," *Chem. Eng. Sci.*, **31**, 123 (1976).

Doğu, T., A. Keskin, G. Doğu, and J. M. Smith, "Single-Pellet Moment Method for Analysis of Gas-Solid Reactions," *AIChE J.*, **32** (1986).

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

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

Haynes, H. W., Jr., and P. N. Sarma, "A Model for the Application of Gas Chromatography to Measurements of Diffusion in Bidisperse Structured Catalyst," *AIChE J.*, **19**, 1043 (1973).

Keskin, A., "Single-Pellet Moment Technique for the Study of Noncatalytic Gas-Solid Reactions," M.S. Thesis, Middle Eastern Tech. Univ., Ankara, Turkey (1985).

Örs, N., and T. Doğu, "Effectiveness of Bidisperse Catalysts," *AIChE J.*, **25**, 723 (1979).

Manuscript received Feb. 10, 1986, and revision received May 7, 1986.