Greek Letters

ϕ = helix angle
β_1 = parameter defined by Equation (4)
β_2 = parameter defined by Equation (9)
Δ = $\sqrt{\pi^2 d^2 + t^2} + (t_f Q/Wfh)$
δ = land clearance, in.
γ = fractional volatile removal from land film
λ_1 = parameter defined by Equation (12)

LITERATURE CITED

1. Bellman, R., and K. L. Cooke, "Differential-Difference Equations," Academic Press, New York (1963).
2. Bernhardt, E. C., ed., "Processing of Thermoplastic Materials," Reinhold, New York (1959).
3. Coughlin, R. W., and G. P. Canevari, *AIChE J.*, **15**, No. 4, 560 (1969).
4. Crank, J., "The Mathematics of Diffusion," Clarendon Press, Oxford, England (1956).
5. Latinen, G. A., *Adv. Chem. Ser.*, **34**, 235 (1959).
6. Luikov, A. V., "Analytical Heat Diffusion Theory," Academic Press, New York (1968).
7. Lundberg, J. L., M. B. Wilk, and M. J. Huyett, *Ind. Eng. Chem. Fundamentals*, **2**, No. 1, 37 (1963).
8. Moffatt, H. K., *J. Fluid Mech.*, **18**, 1 (1964).

Effect of Transport Processes on Conversion in a Fixed Bed Reactor

MOTOYUKI SUZUKI and J. M. SMITH

University of California, Davis, California

For a first-order reaction in an isothermal, fixed bed reactor, it is relatively simple to show the combined effects of axial dispersion, fluid-to-particle diffusion, intraparticle diffusion, and surface reaction on the conversion. Apparently this has not been done. Yet, for the purpose of evaluating the effect of transport resistances, many important catalytic reactions can be described with pseudo first-order kinetics. Therefore, relations which directly display these effects on conversion could be helpful both for interpretation of laboratory kinetic studies and for industrial design. Figure 1 has been prepared for this purpose. It is based upon Equations (11) to (14) which are developed in the following paragraphs.

Recently (*8*), equations have been derived for the zeroth, first, and second moments of the reactant concentration in the effluent from a fixed bed reactor in response to a pulse introduced into the feed. These equations include the effects of all transport resistances and are restricted to isothermal operation and to first-order surface processes. The equation for the zeroth moment can be related to the conversion x at steady state with the result

$$1 - x = \frac{C}{C_0} = \exp\left[-\frac{uz}{2E_z}(\gamma^{1/2} - 1)\right] \tag{1}$$

where

$$\gamma = 1 + \frac{4E_z k_f}{u^2}\left(\frac{3(1-\alpha)}{\alpha}\right)$$
$$\left\{1 - \frac{k_f R_p/D_e}{R_p\sqrt{k_r\beta/D_e}\coth\left(R_p\sqrt{k_r\beta/D_e}\right) - 1 + k_f R_p/D_e}\right\} \tag{2}$$

This result can also be obtained by solving the steady state version of the problem. The solution, Equations (1) and (2), can be written in the following form, which is more convenient for displaying the effects of the transport processes:

$$1 - x = e^{-\Lambda_3\omega} \tag{3}$$

$$\Lambda_3 = \frac{N_{Pe}}{2}\left[\sqrt{1 + 4\,\Lambda_2/N_{Pe}} - 1\right] \tag{4}$$

$$\Lambda_2 = \frac{1}{1/\Lambda_1 + 1/S} \tag{5}$$

$$\Lambda_1 = \frac{3}{F}\left[\sqrt{\Lambda_0 F}\coth\left(\sqrt{\Lambda_0 F}\right) - 1\right] \tag{6}$$

Here Λ_2 is a dimensionless global rate of reaction which includes the effects of external mass transfer (S), intraparticle diffusion (F), and surface rate (Λ_0).

When axial diffusion is negligible, N_{Pe} is large with respect to Λ_2 so that $\Lambda_3 \approx \Lambda_2$. If intraparticle diffusion resistance is negligible, F is so small that $\Lambda_1 \approx \Lambda_0$ from Equation (6). When external mass transfer resistance is negligible, S is large compared with Λ_1 so that $\Lambda_2 \approx \Lambda_1$. If all three transport resistances are negligible, $\Lambda_3 \approx \Lambda_0$, and Equation (3) is the usual expression for the conversion in terms solely of the kinetics of the reaction. In general, Λ_3 may be regarded as a pseudo global rate, which includes the effect of axial dispersion as well as the other transport processes.

Well known results for particular cases follow directly from Equations (3) to (6). For example, the effectiveness factor η of Thiele (*9*) is given by the ratio Λ_1/Λ_0. External diffusion has been included as an overall effectiveness factor η_{ov} by Carberry (*1*). This is given by the ratio Λ_2/Λ_0, modified to apply to flat plate geometry. Ruthven (*7*) included external diffusion by using a mass transfer factor η'. This is obtained from Equations (5) and (6) as the ratio Λ_2/Λ_1.

Figure 1 is a graphical representation of Equations (3) to (6), where each section displays the effect of a single transport resistance. Section A shows the relation between Λ_1 and Λ_0, or the importance of intraparticle diffusion; section B relates Λ_1 and Λ_2, indicating the importance of external diffusion; section C compares Λ_2 and Λ_3 and so gives the effect of axial dispersion. In using Figure 1 to evaluate the significance of the transport resistances, the kinetic constant k_r or k_B would be known so that Λ_0 can be calculated. Then the effect of each transport process could be estimated from estimates of F, S, and N_{Pe}. Section D of the figure shows the resultant effect of all the transport processes on the conversion in the effluent from the reactor. Figure 1 should also be useful for a rapid estimate of the kinetic constant from the observed conversion. In this case, x would be known, and the figure would be used in the reverse direction, proceeding from section D to C to B to A in order to eliminate the transport effects and arrive at Λ_0.

The oxidation of *o*-xylene to phthalic anhydride is used to illustrate the application of Figure 1 to a commercial scale reactor. Froment (*2*) provides rate constant (k_B) data for a specific catalyst. This and typical reactor variables (for example, approximately ⅛-in. catalyst particles) are shown in Table 1. From this information, Λ_0, F, S, and N_{Pe} are calculated as

$$\Lambda_0 = \left[\frac{(1-0.4)(1.5\times10^{-1})}{(2.3\times10^{2})}\right]\left[\frac{(0.18)(1)(82.1)(633)}{(1)}\right] = 3.7$$

$$F = \frac{(2.3\times10^{2})(1.5\times10^{-1})}{(0.01)(1-0.4)} = 5.7\times10^{3}$$

$$S = \frac{3(1-\alpha)k_f}{u} = \frac{3(1-\alpha)(N_{Sh})}{(N_{Sc})(N_{Re})}$$

$$= \frac{3(1-0.4)(36.8)}{(5.7)(117)} = 0.099$$

where the Sherwood number has been estimated by using Ranz' (*6*) equation:

$$N_{Sh} = 2.0 + 1.8\,(N_{Sc})^{1/3}\,(N_{Re})^{1/2}$$

In a gaseous system for $N_{Re} > 10^2$, the axial Peclet number $N_{Pe} = 1(4)$.

The dotted lines in Figure 1 show how these values of Λ_0, F, S, and N_{Pe} can be used to estimate the following values of Λ_1, Λ_2, and Λ_3:

$$\Lambda_1 = 0.076, \quad \Lambda_1/\Lambda_0 = 0.021$$

$$\Lambda_2 = 0.042, \quad \Lambda_2/\Lambda_1 = 0.55$$

$$\Lambda_3 = 0.040, \quad \Lambda_3/\Lambda_2 = 0.95$$

The ratios of Λ values indicate that, at commercial reactor conditions for this rapid surface reaction, intraparticle diffusion is very important (effectiveness factor = 0.021) and that gas-to-particle mass transfer resistance cannot be neglected. On the other hand, axial dispersion has only a small effect on the pseudo global rate Λ_3 and

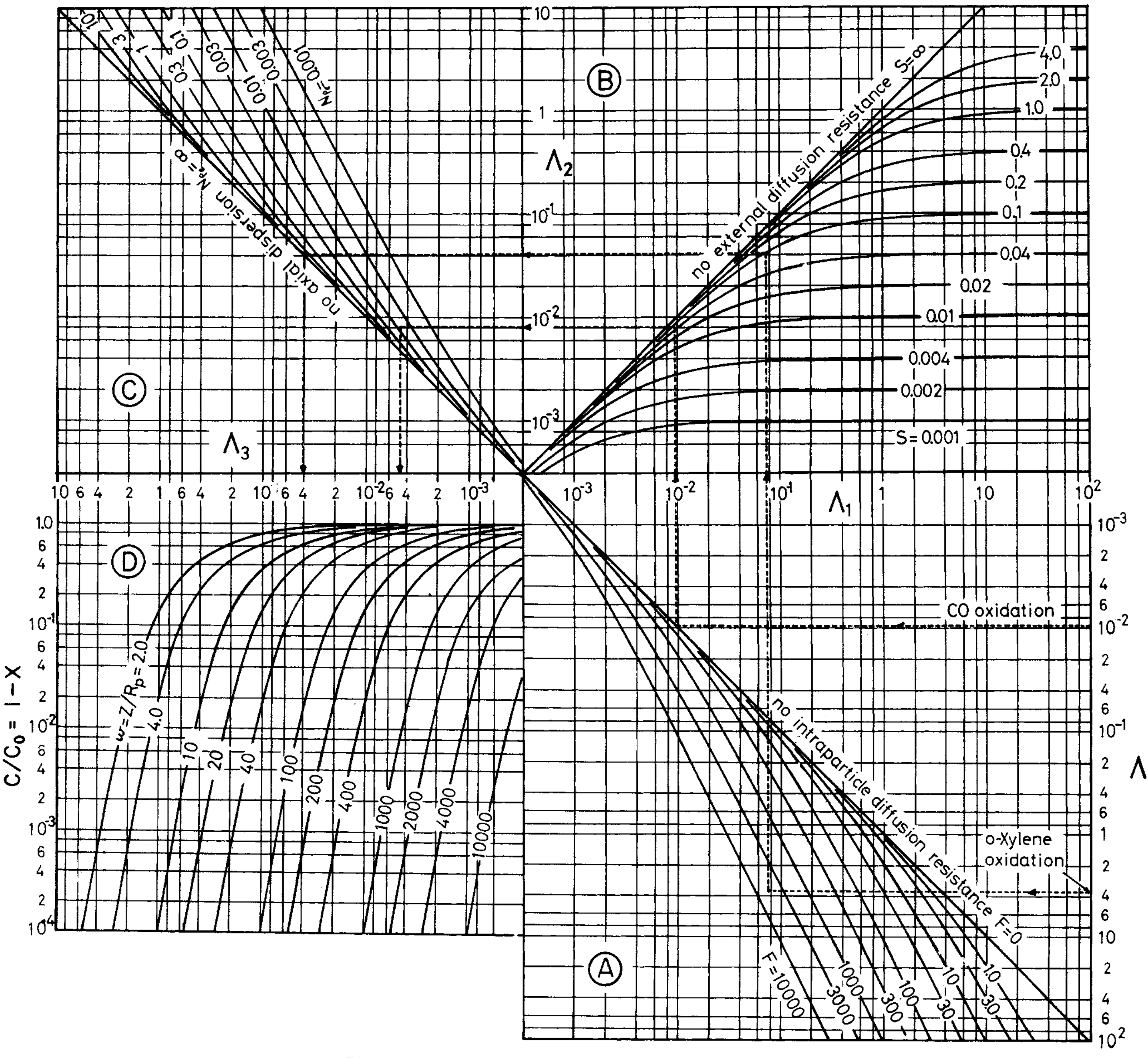

Fig. 1. Effect of transport processes in fixed bed reactors.

Table 1. Kinetic and Reactor Data for Oxidation of *o*-Xylene

Reactor conditions
Temperature = 360°C.
Pressure = 1 atm.
Catalyst particle diameter = 3×10^{-1} cm. (0.12 in.) (spherical)
Bed porosity, $\alpha = 0.4$
Gas velocity, $u = 2.3 \times 10^2$ cm./sec.

Gas properties*
$\rho_g = 0.57 \times 10^{-3}$ g./cc.
$D_{AB} = 0.10$ sq cm./sec. (diffusivity of *o*-xylene in air)
$\mu = 3.4 \times 10^{-4}$ poises
$N_{Sc} = 5.7$
$N_{Re} = 117$

Catalyst properties
$\rho_B = 1.0$ g./cc.
$D_e = 0.01$ sq. cm./sec.†

Kinetic constant
$k_B = 4.23 \times 10^8 \exp(-27{,}000/RT)$, (g. mole)/(sec.)(g. cat.)
$= 0.18$ (g. mole)/(sec.)(g. cat.) at 360°C.

* Since the reaction mixture considered by Froment (2) is more than 99% air, these properties are for air.
† Estimated.

Table 2. Kinetic and Reactor Data for Carbon Monoxide Oxidation

Temperature = 370°C.
Pressure = 1 atm.
Catalyst particle diameter = 0.1 mm. (0.004 in.)
Bed porosity $\alpha = 0.4$
Gas velocity $u = 0.15$ cm./sec.
$\rho_g = 0.61 \times 10^{-3}$ g./cc.
$D_{AB} = 0.20$ sq. cm./sec. (diffusivity of carbon monoxide in oxygen)
$\mu = 3.6 \times 10^{-4}$ poise
$N_{Sc} = 3.0$
$N_{Re} = 2.53 \times 10^{-3}$
Catalyst density, $\rho_B = 0.8$ g./cc.
$D_e = 0.1$ sq. cm./sec. [from Otani (5)]
$k_B = 1.1 \times 10^{-5}$ (g. mole).(g. cat.)(sec.)

on the conversion.

The laboratory data of Otani (5) for the catalytic oxidation of carbon monoxide on a nickel oxide/aluminum oxide catalyst in a bed of fine particles ($D_p = 0.1$ mm.) illustrate a different situation. Table 2 gives the data for this system which correspond to a feed gas consisting predominantly of oxygen. For this slow reaction, the gas velocity must be low in order to obtain significant conversion. Since the Reynolds number is very low, axial dispersion occurs by molecular diffusion, and E_z is approximately given by αD_{AB}. At this low gas velocity, k_f is best estimated from the Sherwood number correlation of Kunii and Suzuki (3). For spherical particles, their Equation (20) gives $N_{Sh} = 0.21 \times 10^{-3}$. From the data in Table 2

$\Lambda_0 = 9.6 \times 10^{-3}$
$F = 1.25 \times 10^{-2}$
$S = 0.05$
$N_{Pe} = 9.4 \times 10^{-3}$

Application of these parameters in Figure 1 (see dotted lines) gives

$$\Lambda_1 = 9.6 \times 10^{-3}, \quad \Lambda_1/\Lambda_0 = 1.0$$

$$\Lambda_2 = 8.0 \times 10^{-3}, \quad \Lambda_2/\Lambda_1 = 0.84$$

$$\Lambda_3 = 4.7 \times 10^{-3}, \quad \Lambda_3/\Lambda_2 = 0.59$$

In this example, the effectiveness factor is unity, but axial dispersion has a major effect on Λ_3 and would significantly affect the conversion in a reactor of short or moderate catalyst bed depth. Conversions could be estimated for various bed depths by continuing the dotted lines into section D of Figure 1.

NOTATION

C = concentration of reactant, (g.)(mole)/cc.
C_0 = concentration in the reactor feed, (g.)(mole)/cc.
C^1 = concentration in catalyst pore, (g.)(mole)/cc.
D_p = particle diameter, cm.
D_{AB} = molecular diffusivity in mixture of A and B, sq. cm./sec.
D_e = effective diffusivity in catalyst particle, sq.cm./sec.
E_z = axial dispersion coefficient, sq.cm./sec.
k_f = fluid-to-particle mass transfer coefficient, cm./sec.
k_r = reaction rate constant based on catalyst pore volume, sec.$^{-1}$
k_B = reaction rate constant based on mass of catalyst, (g.)(mole/(sec.)(g.)(cat.)
p = total pressure, atm.
R = gas constant
R_p = particle radius, cm.
r = radial position in a particle, cm.
T = temperature, °K.
x = conversion
u = superficial velocity, cm./sec.
z = axial distance from inlet to reactor, cm.

Greek Letters

α = porosity in catalyst bed
β = porosity of catalyst particle
η, η_{ov} = effectiveness factors
η' = mass transfer factor
μ = viscosity, g./(cm.)(sec.)
ρ_B = catalyst particle density, g./cc.
ρ_g = gas density, g./cc.
$\theta = r/R_p$
$\omega = z/R_p$

Dimensionless groups

$F = uR_p/D_e(1-\alpha)$
$N_{Pe} = R_p\, u/E_z$
$S = 3(1-\alpha)\, k_f/u$
$N_{Re} = D_p\, \rho_g u/\mu$
$N_{Sc} = \mu/\rho_g\, D_{AB}$
$N_{Sh} = k_f\, D_p/D_{AB}$
$\Lambda_0 = (1-\alpha)k_B\, \rho_B\, (RT/p)(R_p/u) = \dfrac{(1-\alpha)\beta k_r\, R_p}{u}$
$\Lambda_{1,2,3}$ = defined by Equations (4) to (6)

LITERATURE CITED

1. Carberry, J. J., *AIChE J.*, **8**, 557 (1962); *Ind. Eng. Chem.*, **58**, No. 10, 40 (1966).
2. Froment, G. F., *Ind. Eng. Chem.*, **59**, No. 2, 18 (1967).
3. Kunii, D., and M. Suzuki, *Intern. J. Heat Mass Transfer*, **10**, 845 (1967).
4. McHenry, K. W., and R. H. Wilhelm, *AIChE J.*, **3**, 83 (1957).
5. Otani, S., and J. M. Smith, *J. Catalysis*, **5**, 332 (1966).
6. Ranz, W. E., *Chem. Eng. Progr.*, **48**, No. 5, 247 (1952).
7. Ruthven, D. M., *Chem. Eng. Sci.*, **23**, 759 (1968).
8. Suzuki, M., and J. M. Smith, paper submitted to *Chem. Eng. Sci.*
9. Thiele, E. W., *Ind. Eng. Chem.*, **31**, 916 (1939).