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interact with and are influenced by the heat transport process in a way that may be considered nondynamic.

(2) Locally linear, plug-flow models are remarkably descriptive of the principle dynamic characteristics of these reactors, even with temperature excursions that cause a doubling of the chemical reaction rate (30°C in these experiments). Nonlinear effects that appear for larger excursions are simple in nature. These models require accurate modeling of the steady state, which implies care in representing heat exchange with surroundings and heat generation by reaction.

(3) Evidence of intraparticle diffusion limitations was found in the most reactive locations of the bed. However, these effects under dynamic conditions can be treated in a purely quasi-static manner.

(4) A major concern in choosing between a one- and a two-dimensional model is accuracy in representing the steady-state profiles. A two-dimensional representation seems necessary when radial temperature differences exceed 20% of the absolute tempreature level. The dynamic behavior in these experiments was represented well by a one-dimensional model because radial temperature gradients were small.

(5) The influence of a nonuniform fluid velocity across the bed radius was found to be negligible. Under dynamic conditions, coupling between temperature and fluid velocity owing to density changes was also found to be negligible.

(1) Sinai, J., Foss, A. S., *A.I.Ch.E. J.* (1970) **16**, 658.

Fixed Bed Reactor Analysis by Orthogonal Collocation

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Consider the equations governing a fixed bed catalytic reactor under the assumptions of constant physical properties and plug flow.

$$\frac{\partial c}{\partial z} = \alpha \frac{1}{r} \frac{\partial}{\partial r}\left(r \frac{\partial c}{\partial r}\right) + \beta R(c, T) \tag{1}$$

$$\frac{\partial T}{\partial z} = \alpha' \frac{1}{r} \frac{\partial}{\partial r}\left(r \frac{\partial T}{\partial r}\right) + \beta' R(c, T)$$

$$\frac{\partial c}{\partial r} = 0, \; -\frac{\partial T}{\partial r} = Bi(T - T_w) \text{ at } r = 1$$

where $\alpha = Ld_p/R^2Pe_M$, $\alpha' = Ld_p/R^2Pe_H$, L and R are the length and radius of the reactor, d_p is the particle diameter, $Pe_M = Gd_p/D_e\rho$ and $Pe_H = Gd_pC_p/k_e$ are the Peclet numbers for mass and heat, G is the mass flow rate, D_e and k_e are the effective diffusivity and conductivity. The Biot number h_wR/k_e is defined in terms of the effective thermal conductivity and tube radius, whereas the Nusselt number, h_wd_p/k_f is defined in terms of the particle diameter and fluid thermal conductivity.

The orthogonal collocation method is applied as outlined by Villadsen and Stewart (*1*) and Ferguson and Finlayson (*2*). It reduces the system of partial differential equations (*1*) to a set of ordinary differential equations in z, which are integrated numerically.

$$\frac{dc_j}{dz} = \alpha \sum_{i=1}^{N+1} B_{ji}c_i + \beta R_j \qquad j = 1,2, \ldots, N$$

$$\frac{dT_j}{dz} = \alpha' \sum_{i=1}^{N+1} B_{ji}c_i + \beta' R_j \tag{2}$$

$$-\sum_{i=1}^{N+1} A_{N+1,i}T_i = Bi(T_{N+1} - T_w)$$

$$\sum_{i=1}^{N+1} A_{N+1,i}c_i = 0$$

where T_j and c_j are the temperature and conversion at the collocation points and the matrices A and B are easily calculated (*1*). In the first approximation the equations are identical to a lumped parameter model (no radial variations in c and T) with the equivalent heat transfer coefficient, U.

$$\frac{1}{Nu'} = \frac{1}{2\alpha'}\left(\frac{1}{Bi} + \frac{1}{3}\right) \tag{3}$$

$$\frac{1}{U} = \frac{1}{h_w} + \frac{R}{3k_e} \text{ (Jacobi)} \tag{4}$$

$$\frac{1}{U} = \frac{1}{h_w} + \frac{R}{4k_e} \text{ (Legendre)} \tag{5}$$

where $Nu' = 2UL/GC_pR$. If Legendre polynomials (*2*) are used, in the first approximation the concentration is constant in r, the temperature is parabolic in r, and the reaction rate is evaluated at the average tempera-

ture. The equivalence (5) has been shown before for a parabolic temperature profile (*4, 5, 6, 7, 8, 9*).

The ratio of $1/Bi$ compared with $1/Bi + 1/3$ gives the percentage of the thermal resistance occurring at the boundary: $Bi = 1$, 75%; $Bi = 20$, 13%. Thus for small Biot numbers most of the resistance occurs at the wall, and only a one-dimensional treatment is necessary. Since the one-dimensional model corresponds to the first approximation in the collocation method, as Bi increases, the number of terms in the approximate solution can be increased to account for the two-dimensional nature of Equation 1.

Numerical computations were made for $Bi = 1$ or 20, $\alpha = \alpha' = 1$, $\beta = 0.3$, $\beta' = 0.2$, $R = (1 - c) \exp(\gamma - \gamma/T)$, $\gamma = 20$, $T_w = 0.92$ or 1. When $Bi = 1$, the first approximation predicted the hot spot within 2%. The Jacobi polynomials gave better results than Legendre polynomials in the first approximation, whereas the Legendre results converged faster (in higher approximations). A two-term collocation solution was as accurate and four times as fast as a six-term finite difference solution. For $Bi = 20$ the first approximation was less suitable, but a four-term collocation solution was as accurate and three times as fast as an eleven-term finite difference solution. When using 200 steps in the z direction, four collocation points, and the Runge-Kutta method of integrating the ordinary differential equations, the computation time on the CDC-6400 computer was 2.1 seconds.

Computations were also done using the experimental velocity profiles of Schwartz and Smith (*10*) for a 4-inch diameter tube, 80 inches long, packed with 5/32-inch diameter spheres. The effective diffusivity and conductivity were calculated using

$$G(r)d_p/D(r)\,\rho = 10 \tag{6}$$

$$k_e/k_f = 8.1 + 0.09\,Re\,Pr,\ Re = G(r)d_p/\mu \tag{7}$$

$$k_e/k_f = 6.9 + 0.01\,Re\,Pr, \text{ within } \tfrac{1}{2}\,d_p \text{ of wall} \tag{8}$$

Equation 6 and the form of Equation 7 have been verified experimentally by Schertz and Bischoff (*11*), while Equations 7 and 8 are predicted using the methods of Baddour and Yoon (*3*). Experimental comparisons are given by these authors and Yagi and Kunii (*12*).

When using Equation 8, the heat transfer resistance at the wall is accounted for by the lower value of k_e rather than a heat transfer coefficient. During the calculations, a Biot number was calculated using

$$Bi = \frac{-[\partial T/\partial r]_{r=1}}{\langle T \rangle - T_w} \tag{9}$$

where $<T>$ is the average temperature within one-half particle diameter of the wall. This distance was chosen because the void fraction rises rapidly from 0.4 to 1.0 there. This *Bi* varied only a few percent down the bed, and typical values are given in Table I. This *Bi* was then used in

Table I. Typical *Bi* Values

Re	$k_e(1)/k_{e,avg}$	*Bi*(predicted)
375	0.23	15
189	0.35	20
85	0.52	29

the model with a flat velocity profile and heat transfer resistance (Equation 1), and good agreement was obtained between the two models. This suggests that it may be possible to predict the heat transfer coefficient which causes the two mathematical models to agree.

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Oxidation of SO_2 in a Trickle-Bed Reactor Packed with Carbon

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Both the Lurgi "sulfacid" and the Hitachi processes for removing SO_2 from flue gas involve the reaction of SO_2 and oxygen at the surface of a carbon catalyst to form SO_3, which is washed away with water as sulfuric acid. The steady-state, continuous, countercurrent contacting of