D = gas diffusivity, sq.cm./sec.
$\mathcal{D}_j^{eff}$ = effective diffusivity of species j in porous iron layer, sq.cm./sec.
F = fractional reduction
f = weight fraction of iron in wustite
G = mass velocity of approaching gas, g./(sq.cm.)(sec.)
K_e = equilibrium constant for iron-wustite equilibrium, $H_2O/H_{2\,eq}$
k_j^m = mass transfer coefficient for gas j, cm./sec.
k_r = specific rate constant for surface reaction
$\dot{n}_O$ = molar consumption of atomic oxygen, g.-atoms/sec.
$\dot{n}_j$ = molar flow of species j, moles/sec.
N_{Re} = Reynolds number = $2x_oG/\mu$
N_{Sc} = Schmidt number = $\mu/\rho\mathcal{D}$
N_{Sh} = Sherwood number = $2x_ok_j^m/D$
p_j = partial pressure of species j, atm.
R = gas constant, 82.06, (cc.)(atm.)/(mole)(°K.)
T = temperature, °K. unless otherwise noted
t = reduction time, sec.
V = void fraction in phase
x = distance from the origin in spherical coordinates, cm.
x_i = core radius; distance from origin to reaction interface, cm.
x_o = external radius of oxide sphere, cm.
x_s = radius of pellet initially, cm.

Greek Letters

α = coefficient defined by Equation (13)
$\bar{\alpha}$ = integrated average value of α from $\theta = 0$ to $\theta = \theta$
α^* = $\bar{\alpha}/x_o$
β = coefficient defined by Equation (14)
γ = expansion factor defined by Equation (17)
μ = gas-phase viscosity, poise
ρ = gas-phase density, g./cc.

Superscripts

b = bulk phase value
i = value at reactions interface
m = reduced shell value
s = value at outer surface of pellet
Fe = refers to value for reduced iron shell
F = refers to value for unreduced wustite core

Subscripts

CO = value for carbon monoxide
CO_2 = value for carbon dioxide

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On the Cyclic Operation of Tubular Reactors

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In some cases it may be advantageous to operate a chemical reactor in the unsteady state. Douglas and Rippin (*1*) studied the cyclic operation of a back mix reactor with second-order kinetics and showed that for some values of system parameters the time average conversion of reactant was higher if the reactant concentration in the feed stream varied sinusoidally than if the concentration were held constant at the mean value of the fluctuations. We wish to consider the general problem of cyclic operation of isothermal tubular reactors with back mixing in contrast to their operation in the steady state.

THE UNSTEADY STATE AXIAL DISPERSION MODEL

In this study we are concerned with the isothermal axial dispersion model. This model seems to have been proposed first by Hulburt (*2*) and Danckwerts (*3*), but their analyses were limited to the steady state, although Danckwerts gave a solution to the unsteady state diffusion equation for the case of equimolar counterdiffusion and no reaction. Wehner and Wilhelm (*4*), in their extension of Danckwerts's analysis of the steady state dispersed flow reactor, discussed the applicability of the boundary conditions to the unsteady state as well, but did not give sample solutions. Kramers and Alberda (*5*) reported on the frequency response of the axial diffusion model for plug and laminar flow cases giving input-output amplitude ratio and phase lag diagrams. An alternate formulation of the entrance boundary condition leading to the same approximate solution was published by McHenry and Wilhelm (*6*).

Our formulation follows that of Danckwerts. By assuming constant overall fluid density and constant velocity, the equation of continuity in dimensionless form for a reactant species with second-order kinetics may be written as

$$N_{Pe}^{-1}\frac{\partial^2 x}{\partial \eta^2} - \frac{\partial x}{\partial \eta} - R_{(2)}\, x^2 = N_{Pe}^{-1}\frac{\partial x}{\partial \theta} \tag{1}$$

For a constant flow rate feed with a sinusoidally varying reactant concentration, a material balance on an infinitesimally thin section around the reactor entrance gives

$$1 + a\sin\omega\,\theta = x(0,\theta) - N_{Pe}^{-1}\frac{\partial}{\partial \eta}x(0,\theta) \tag{2}$$

Similarly, at the exit

$$\frac{\partial}{\partial \eta}x(1,\theta) = 0 \tag{3}$$

Essentially similar boundary conditions were assumed by Schmeal and Amundson (*7*) in their study of the dynamics of tubular reactors with recycle.

Note that the exit condition implies plug flow in the reactor outlet and is tantamount to requiring the concentration fluctuations to vanish, as $\eta \rightarrow 1$, in the axial dimension η but not in the time dimension θ. Our motivation for this commonly assumed (*5* to *7*) constraint is mostly practical; its relaxation would complicate the numerical solution of the problem prohibitively. We recognize, however, that it is a somewhat unrealistic restriction and that its theoretical justification for the unsteady state problem is not entirely satisfactory.

A numerical solution of Equation (1) was obtained on the digital computer for the case of $N_{Pe} = 1$ and $R_{(2)} = 12$, representing a system with moderately fast reaction and a considerable degree of back mixing, a system dynamically and kinetically similar to the reactor analyzed by Douglas and Rippin (*1*) except, of course, for the nonzero Peclet number. A representative set of physical parameters for the problem is given in Table 1. The steady state solution of Equation (1) was imposed as the initial condition $x(\eta, 0)$ about which the perturbation y, defined as

$$y(\eta, \theta) = x(\eta, \theta) - x(\eta, 0) \qquad (4)$$

was measured.

Since the time-average outlet perturbation $\bar{y}$ is expected to be quite small (limiting ideal reactor solutions) and thus especially susceptible to calculation errors, some remarks on the numerical solution of Equation (1) are in order. The presence of the quadratic reaction rate term requires that the finite-difference equations approximating Equation (1) be solved either by an explicit or by an iterative implicit scheme. In the present case, both schemes were found to be somewhat deficient, the explicit scheme because of the excessively small time steps necessary for stability and the iterative implicit scheme because of its slow convergence, probably caused by the relatively weak numerical feedback from the Newmann type of boundary condition at the outlet. Therefore, the finite-difference form of the quadratic term was linearized by expanding $x\,(\eta + \Delta\eta,\ \theta + \Delta\theta)^2$ about $x\,(\eta + \Delta\eta,\ \theta)$ by a Taylor series or by letting $x\,(\eta + \Delta\eta,\ \theta + \Delta\theta)^2 \cong x\,(\eta + \Delta\eta,\ \theta + \Delta\theta)\ x\,(\eta + \Delta\eta,\ \theta)$ and the equations solved simultaneously by the method of Thomas (*8*). All numerical work was done by using double precision arithmetic. Both time and distance grids were varied fourfold to check convergence.

ASYMPTOTIC SOLUTIONS

Asymptotic solutions for very slow disturbances ($\omega \rightarrow 0$) were calculated from the corresponding ideal reactor equations

$$x = (1 + R_{(2)})^{-1} \qquad \text{Plug flow, } N_{Pe} = \infty \qquad (5)$$

$$x = [(1 + 4\,R_{(2)})^{1/2} - 1]/(2R_{(2)}) \qquad \text{Back mix flow, } N_{Pe} = 0 \qquad (6)$$

TABLE 1. PHYSICAL PARAMETERS CORRESPONDING TO $N_{Pe} = 1,\ R_{(2)} = 12$

$u = 1, L = 10, k = 1.2, c(0,0) = 1, D = 10$

Steady state solutions:

$x(1,0) = 0.07692$	(Plug flow, $N_{Pe} = \infty$)
$x(1,0) = 0.1845$	($N_{Pe} = 1$)
$x(1,0) = 0.25$	(Back mix flow, $N_{Pe} = 0$)

by the successive substitution of the step function input

$$c(0, t) = c(0, 0)\ [1 \pm a/\sqrt{2}] \qquad (7)$$

for $c(0, 0)$ in both x and $R_{(2)}$.

We now consider the unsteady state case. The solution for back mix flow was obtained by Douglas and Rippin (*1*) for several values of the parameters of the system.

The corresponding result for the plug flow reactor does not seem to be available in the literature. Our result is

$$x = [1 + kc(0, 0)\ \tau]^{-1} \qquad t < \tau \qquad (8)$$

$$x = [1 + a \sin \omega\,(t - \tau)]\ \{1 + kc(0, 0)\tau\ [1 + a \sin \omega\,(t - \tau)]\}^{-1} \qquad t > \tau \qquad (9)$$

The above limiting solutions were used to check the validity of the numerical solutions, and some are plotted in Figure 1. It is seen that our numerical solutions of Equation (1) for $N_{Pe} = 100$ and $N_{Pe} = 0.01$ do indeed converge to the respective ideal reactor results, Equations (5) and (6).

We attempted to calculate the back mixing flow result of Douglas and Rippin (*1*) by letting $N_{Pe} = 0.01$ in Equation (1), but agreement of that solution with a numerical integration of their lumped parameter model was rather poor. In our problem, time was made dimensionless by dividing by L^2/D. Since D becomes small with $N_{Pe} \rightarrow 0$, an alternative formulation was tried. Time t in Equation (1) was now made dimensionless by using $\theta' = ut/L$, giving

$$N_{Pe}^{-1}\,\frac{\partial^2 x}{\partial \eta^2} - \frac{\partial x}{\partial \eta} - R_{(2)}\,x^2 = \frac{\partial x}{\partial \theta} \qquad (1a)$$

Solutions of this equation for several ω with $a = 0.25$ were almost identical to those of Equation (1) for $N_{Pe} = 1$ but were lower by a factor of 3 than the results of Douglas and Rippin. There is a question as to whether our unsteady state model approaches the Douglas and Rippin back mix flow model as $N_{Pe} \rightarrow 0$, since extension of Wehner and Wilhelm's reasoning to the cyclic operation case especially for limiting values of N_{Pe} is not as straightforward as may seem at first.

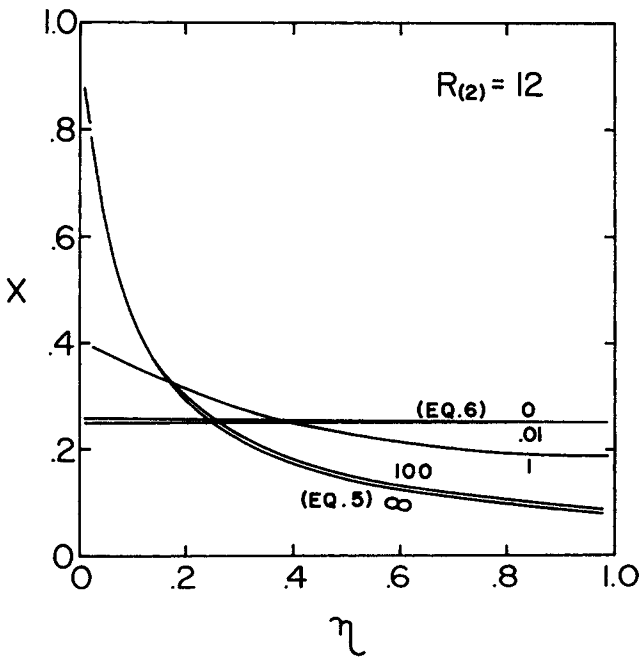

Fig. 1. Ideal reactor asymptotes and steady state solutions of Equation (1).

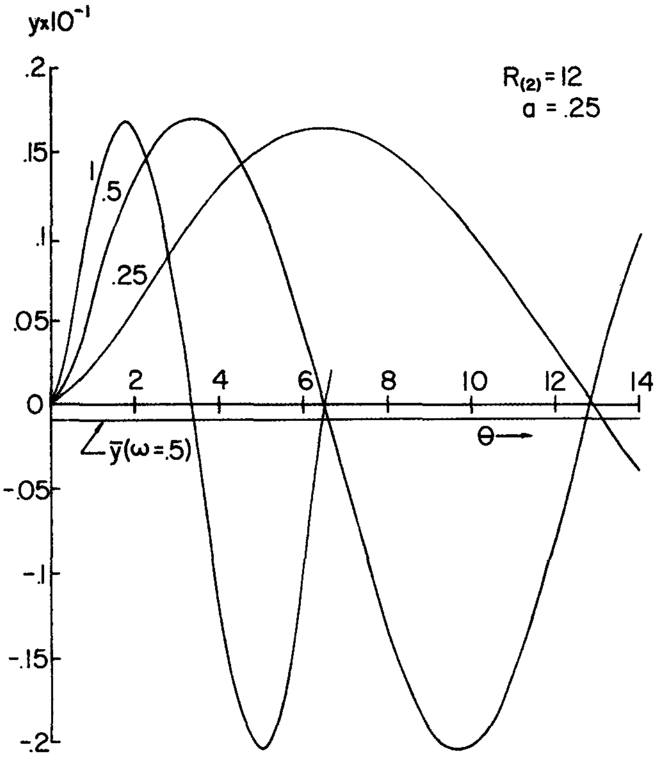

Fig. 2. Response of the reactor to cyclic input for several values of input frequency.

RESULTS AND CONCLUSIONS

The results are most conveniently presented in terms of $\bar{y}$, the time-average concentration perturbation at the reactor exit. The time variation of y is only approximately sinusoidal (Figure 2), and its mean value is not very different from zero even for large amplitude disturbances. This aspect places unusually stringent convergence requirements on the numerical solution in order for $\bar{y}$ to be known even within order-of-magnitude accuracy. In our solution to the problem, we have tried to strike a balance between computation cost and the numerical accuracy required to reveal trends and obtain meaningful results from the standpoint of reactor engineering.

If $\bar{y} < 0$, a higher conversion is obtainable from cyclic operation in comparison with steady state operation. All our solutions show this to be true for the axial dispersion reactor. The conversion difference seems to be enhanced by lower fluctuation frequency (Figure 3), but the effect borders our calculation error. Considering reactors with identical volumes, kinetics, and feed characteristics (that is, having the same value of R) and varying only in the degree of back mixing, we find that the effect of back mixing is to favor cyclic operation. By considering reactors with identical average conversions, a simple calculation with the ideal reactor Equations (5) and (6) used shows that back mixing has negligible effect on $\bar{y}$.

It is concluded that for the general tubular reactor for which this model is an adequate approximation, higher operating efficiency or improved conversion on a time-average basis may be obtained if the feed concentration is not rigidly controlled at the design value, but naturally occurring fluctuations about the design value are instead allowed to enter the process. To put the matter in perspective, the conversion improvement resulting from cyclic operation is quite small even for large amplitude disturbances.

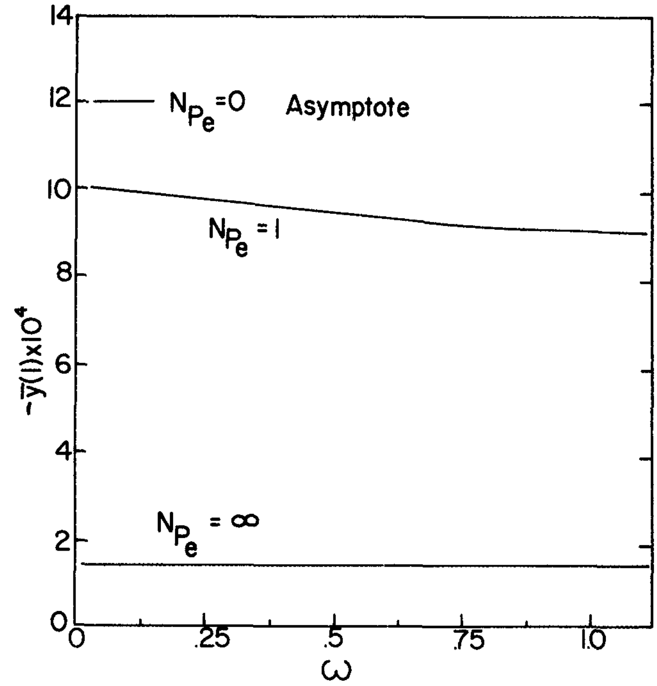

Fig. 3. Effect of frequency on mean conversion difference at reactor outlet.

NOTATION

a = amplitude of variation of in reactant concentration at reactor inlet
c = reactant concentration
D = effective dispersion coefficient
k = rate constant
L = reactor length
N_{Pe} = Peclet number, uL/D
n = reaction order
$R_{(n)}$ = reduced reaction rate group, $k[c(0,0)]^{n-1}L/u$
t = time
u = velocity of fluid
x = dimensionless reactant concentration, $c(z,t)/c(0,0)$
y = dimensionless perturbation from steady state concentration, defined by Equation (4)
$\bar{y}$ = time-average value of y at reactor outlet
z = axial dimension

Greek Letters

η = dimensionless axial coordinate, z/L
θ = dimensionless time, Dt/L^2
θ' = dimensionless time, ut/L
τ = space time, z/u
ω = radian frequency of variation in reactant concentration at reactor inlet

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