A Computer Model of the Fixed Bed Catalytic Reactor:

The Adiabatic and Quasi-adiabatic Cases

JAMES J. CARBERRY and MARTIN M. WENDEL
E. I. du Pont de Nemours & Company, Wilmington, Delaware

A digital computer model of the adiabatic-fixed bed catalytic reactor is developed which includes axial dispersion of heat and mass, interparticle heat and mass transport, and intraparticle diffusion of reacting species. The influence of these transport processes upon conversion and yield is discussed. The model is readily extended to nonisothermal, nonadiabatic cases in the absence of radial gradients.

The technique of computer solution avoids the inherent instability problem associated with explicit techniques as applied to flux boundary condition problems which involve flow, diffusion, and reaction.

A justifiable interest has been shown by numerous investigators in problems related to behavior of the fixed-bed catalytic reactor. The complex nature of the events which simultaneously occur in the typical nonisothermal unit has provoked much of the fixed-bed research in such areas as fluid-particle heat and mass transfer, fluid-wall heat transfer, radial dispersion of heat and mass, and most recently axial dispersion of mass in fixed beds.

In the instance of isothermal operation the influence of bulk mass transfer to and diffusion within the catalyst pellet may be readily assessed by application of criteria cited by Wheeler (*15*), Weisz (*14*), Aris (*2*), and Carberry (*8, 8a, 8b*). Axial dispersion, as it affects isothermal fixed-bed processes, has been discussed by Danckwerts (*9*), Hulburt (*11*), Wehner and Wilhelm (*13*), Levenspiel and Bischoff (*12*), and Carberry (*4*).

Isothermal operation of a fixed-bed catalytic process however is rarely possible and often not economically feasible, as it is both difficult and expensive to remove or add heat at the reactor wall in a fashion guaranteed to create temperature uniformity throughout the unit. Thus the nonisothermal and/or adiabatic operation of fixed-bed reactors represents the more typical practice. Under these circumstances the isothermal criteria suggested for an assessment of mass transfer, porous-solid diffusion, and axial-dispersion effects apply only at a point within the nonisothermal network. Since rates of mass transfer, pore diffusion, and surface reaction are each characterized by differing temperature and concentration dependencies, it might be anticipated that no single mode of rate control should necessarily prevail throughout a nonisothermally operated fixed bed. Indeed it may be safe to predict that varying degrees of mixed rate control will be realized between bed entrance and exit. Obviously a detailed description of the net rate process at various points throughout the reactor, and the extent to which reactor performance is affected by these point processes, is realized only by recourse to a computer solution of the appropriate equations which define the events. This paper describes the construction and digital computer solution of a model involving a catalytic reaction carried out in a fixed bed in which the following events are assumed to occur simultaneously: bulk mass transfer and heat transfer to or from the exterior pellet surface, species diffusion within the porous pellet, and axial dispersion of heat and mass.

The reaction considered is the first-order conversion of A to B, followed by the first-order decomposition of *B* to *C*; that is

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Hence an assessment of both yield and conversion is realized, since *C* may be viewed as an undesirable by-product.

The model is developed for two extremes of nonisothermal operation: adiabatic conditions and nonisothermal operation under circumstances where radial gradients of concentration and temperature are negligible. In brief the assumptions underlying the development are:

1. The absence of radial gradients of heat, mass, and momentum.
2. The absence of a temperature gradient within the catalyst pellet (*8*).
3. Constancy of coolant temperature as a function of reactor length in the nonadiabatic case.
4. A constant average heat capacity characterizes the reactant stream, and the heats of reaction are assumed independent of temperature.
5. Heat and mass transfer coefficients are uninfluenced by the surface reaction.
6. Gas velocity, density, and the axial-dispersion coefficient (a linear function of velocity) are functions of temperature as dictated by the ideal gas law.
7. Axial conduction of heat is confined to that dispersed by the fluid; that is conduction through the particles is assumed negligible.
8. The appearance of product *B* and its consumption to form *C* is a function only of the concentration of reactant *A*, the respective rate constants, and porous-solid diffusivity. In other words separate differential equations are not written for *B* and *C*, since it is assumed that no differences exist in their dispersive transport. In essence the assessment of yield is undertaken for plug flow conditions (negligible axial diffusion).
9. The diffusivities of *A* and *B* within the porous pellet are assumed equal and temperature independent. For Knudsen diffusion the diffusivity is actually proportional to $\sqrt{T/M}$. Since the chemical rate processes are expressed as exponential functions of temperature, it is deemed unnecessary to consider the temperature effects upon diffusion.

MATHEMATICAL MODEL

A differential material balance, in terms of gaseous reactant *A*, may be written for a first-order catalytic conversion as it occurs in a fixed bed:

$$\frac{d\left(-E\frac{dC_a}{dx}\right)}{dx}+\frac{d(uC_a)}{dx}+KC_a=0 \quad (1)$$

Reactant dispersion in the axial direction is governed by the dispersion

---

J. J. Carberry is at the University of Notre Dame, Notre Dame, Indiana. M. M. Wendel is with E. I. du Pont de Nemours and Company, Incorporated, Gibbstown, New Jersey.

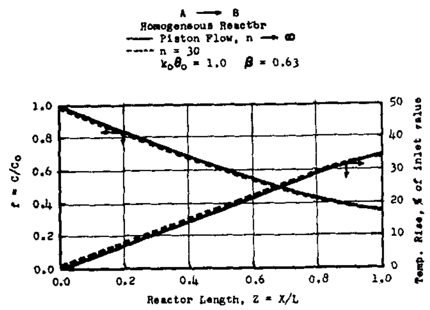

Fig. 1. Influence of axial mixing upon adiabatic profiles.

coefficient. On the assumption that heat is dispersed axially by virtue of mass dispersion only, the corresponding equation describing gas temperature in the bed is

$$\frac{d\left(-\rho C_p E \frac{dT}{dx}\right)}{dx} + \frac{d(u \rho C_p T)}{dx} + \bar{R}Q - h_w \frac{4}{D_t}(T - t_w) = 0 \quad (2)$$

where $h_w \frac{4}{D_t}(T - t_w)$ represents the heat transferred between the fluid and reactor wall for the quasiadiabatic case. The term $\bar{R}Q$ is the quantity of heat generated or consumed by virtue of surface reaction. In terms of the solids surface temperature t_s and the fluid-particle heat transfer coefficient h_p one may write

$$\bar{R}Q = -\Delta H_a K_1 C_a - \Delta H_b K_2 C_b = h_p a' (t_s - T) \quad (3)$$

The rate coefficients K_1 and K_2 are effective rate constants which are functions of solids temperature, the mass transfer coefficient, and pore diffusivity.

The governing equations are rendered dimensionless by the following substitution, where C_o is the initial concentration of A:

$(C/C_o)_a = f$; $Z = t_w/T_o$
$t_s/T_o = y$; $T/T_o = \tau$; $u = u_o \tau$
$\rho = \rho_o/\tau$; $z = x/L$; $E = E_o \tau$
and $E_o = Lu_o/2n$ (4)

Thus dispersion of heat and mass are readily described in terms of the number of equivalent perfect mixers n, where n is related to the axial Peclet number by (5, 6)

$$n = \frac{L}{2D_p} N_{Pe} \quad (5)$$

If one makes the specified substitutions, there results for the reactant f

$$\frac{d^2 f}{dz^2} + \frac{1}{\tau}\frac{d\tau}{dz}\frac{df}{dz} - 2n\frac{df}{dz} - \frac{2nf}{\tau}\frac{d\tau}{dz} - \frac{2n\theta_o}{\tau} K_1 f = 0 \quad (6)$$

where $\theta_o = L/u_o$, the contact time based upon inlet conditions. For the fluid temperature

$$\frac{1}{2n}\frac{d^2\tau}{dz^2} - \frac{d\tau}{dz} + \frac{h_p}{GC_p}\frac{6(1-\epsilon)L}{D_p}(y - \tau) - \frac{h_w}{GC_p}\frac{4L}{D_t}(\tau - Z) = 0 \quad (7)$$

The boundary conditions for the problem are, as shown by Wehner and Wilhelm (*13*)

$$z = 0, \text{ bed entrance } f = \frac{1}{\tau} + \frac{1}{2n}\frac{df}{dz}$$

$$\tau = 1 + \frac{1}{2n}\frac{d\tau}{dz} \quad (8)$$

$$z = 1, \text{ bed exit } \quad \frac{df}{dz} = \frac{d\tau}{dz} = 0$$

DEFINITIONS OF THE RATE PROCESSES

An effective rate coefficient K may be defined in terms of a surface reaction rate coefficient k, a mass transfer coefficient $k_g a'$, and porous catalyst effectiveness η. In terms of reactant concentration at the pellet exterior surface C_s the rate of bulk mass transfer must equal that of reaction; thus

$$k_g a' (C_g - C_s) = \eta k C_s \quad (9)$$

$$\text{where } a' = a(1 - \epsilon) \quad (10)$$

Solving for C_s one obtains for the effective rate

$$\eta k C_s = \frac{\eta k C_g}{1 + \eta k / k_g a'} = K_1 C_g \quad (11)$$

The various coefficients are expressed in terms of reduced solids temperature and the parameters governing the diffusive processes as

$$k = k_o \exp\left[\frac{-\alpha}{RT_o}\left(\frac{1}{y} - 1\right)\right] \quad (12)$$

$$\eta = \frac{\tanh\psi}{\psi} = \frac{1}{\psi}\left(\frac{1 - e^{-2\psi}}{1 + e^{-2\psi}}\right) \quad (13)$$

where

$$\psi = \frac{1}{a}\sqrt{\frac{k}{D}} \quad (14)$$

in which $1/a$ is the ratio of the volume to the external surface area of the pellet. Aris (*2*) has shown that specification of the characteristic particle length in this fashion $1/a$ renders the η — ψ relationship virtually independent of particle shape. The diffusivity is that which dictates the rate of species transport into the catalyst interior. For most active, high surface-area pellets Knudsen diffusion prevails, and D is generally some order of magnitude lower than the bulk diffusivity of the gas.

The heat and mass transfer coefficients are defined, for Reynolds number below 1,000, by a boundary layer j factor (*7*)

$$J_{BL} = \frac{h_p}{\rho u C_p} N_{Pr}^{2/3} = \frac{k_g}{u} N_{Sc}^{2/3} = 1.15\, N_{Re}^{-1/2} \quad (15)$$

This relationship has been found to be in substantial agreement with literature data representing a wide range of physical properties and processes.

PRODUCT DEGRADATION (WHEN n → ∞)

The yield with respect to B is assumed to be governed by the concentration of unreacted A, the ratio of rate coefficients $S = k_1/k_2$, and the extent to which diffusion within the catalyst promotes the formation of the degradation product C.

In the instance of a macroporous catalyst where species diffusion within the pellet is rapid relative to the surface reaction rate, the differential yield of B for the reaction $A \rightarrow B \rightarrow C$ is simply, for piston flow ($n \rightarrow \infty$)

$$-\frac{dB}{dA} = 1 - \frac{B}{SA} \quad (16)$$

When however the more typical case of catalysis by microporous pellets is encountered, the product B which is formed within the pores may undergo degradation to C in its diffusive journey out of the pores. Wheeler (*15*) has treated this situation in detail and has shown that the differential yield of B is given by

$$-\frac{dB}{dA} = \frac{S}{S-1} - \left(\frac{B}{A} + \frac{S}{S-1}\right)\frac{1 \tanh \psi/\sqrt{S}}{\sqrt{S}\tanh\psi} = \gamma \quad (17)$$

As ψ approaches zero, Equation (17) reduces to the diffusion-independent relation, Equation (16).

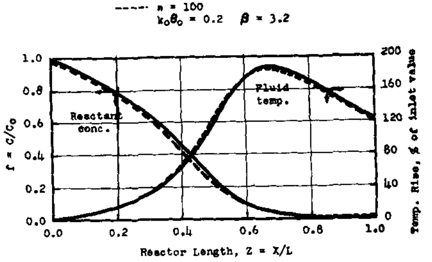

Fig. 2. Influence of axial mixing upon temperature and concentration profiles.

The yield of B at each point in the reactor is readily computed in terms of solids temperature, reactant concentrations, and the reaction-diffusion parameters at each point in the fixed-bed network. Thus writing Equation (17) in terms of degradation product C one obtains

$$\frac{dC}{dA} = \frac{S}{S-1} - \left(\frac{B}{A} + \frac{S}{S-1}\right)$$

$$\frac{1 \tanh \psi/\sqrt{S}}{\sqrt{S}\tanh \psi} - 1 \quad (18)$$

$$\frac{dC}{dA} = \gamma - 1$$

From Equation (3), since $dC/d\theta = dA/d\theta\ (\gamma - 1)$

$$h_p a\ (t_s - T) = -\Delta H_a \frac{dA}{d\theta} -$$

$$\Delta H_b \frac{dA}{d\theta} (\gamma - 1)$$

In dimensionless form

$$\left(\frac{h_p}{GC_p}\right) 6(1-\epsilon) \frac{L}{D_p} (y - \tau) =$$

$$\left[\frac{x_o(-\Delta H_a)}{C_p T_o} \theta_o K_1 f \left(1 + \frac{\Delta H_b}{\Delta H_a} (\gamma - 1) \right) \right] \quad (19)$$

TECHNIQUE OF COMPUTER SOLUTION

Others (*1*) have noted the stability difficulties that are encountered when equations of the type characterizing the model invoked here are subjected to explicit or marching techniques of computer solution. Since the explicit technique involves marching from reactor inlet toward the end of the reactor, the specification of df/dz and $d\tau/dz$, as demanded by the boundary conditions, leads to an inherent instability. Amundson and co-workers (*1*) have circumvented this difficulty by integrating from the outlet of the reactor (where df/dz and $d\tau/dz$ equal zero) toward the inlet. An assumed distribution of concentration and temperature, which was initially estimated by first treating the bed as a series of well-stirred reactors, is necessary. More recently Deans and Lapidus (*10*) presented a dynamic as well as steady state model of a fixed bed first-order surface rate controlled reaction where both axial and radial dispersion of heat and mass are handled by viewing the entire bed as composed of a series of well-stirred reactors in both the axial and radial directions.

The present solution is an implicit one, involving the solution of simultaneous finite difference equations which were used to approximate the differential equations. No initial estimate of the temperature and concentration distribution is required; that is τ, y, and f are assumed constant and equal to unity throughout the bed at the beginning of the computation. Employing an IBM-650, with the floating decimal adjunct, programming in machine language, and making use of the high-speed immediate access storage units, one requires approximately 10 min. of machine time to produce a converged solution. A fifty-one-point network including a point at the bed entrance $p = 0$ and a point at the bed exit $p = 50$ was employed in programming this problem, and the error found in comparing the calculated heat release to the calculated adiabatic temperature rise was less than 0.01%. A one hundred-point net yields identical results.

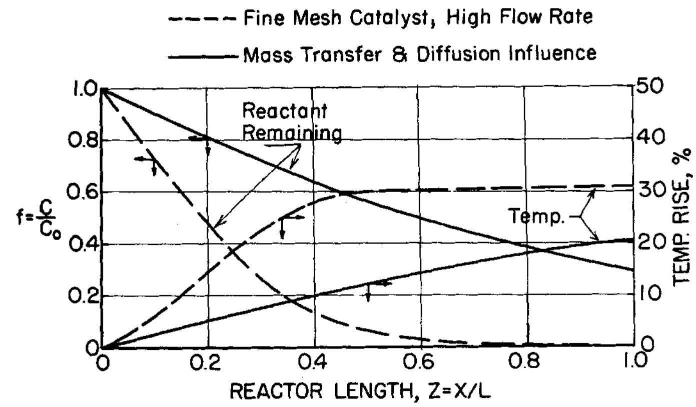

Fig. 3. Intraparticle diffusion and mass transfer influence.

NUMERICAL METHOD

The method of solution for the problem can be illustrated with the equation for the dimensionless concentration f [Equation (6)]:

$$\frac{d^2f}{dz^2} + \frac{1}{\tau}\frac{d\tau}{dz}\frac{df}{dz} - \frac{2ndf}{dz} -$$

$$\frac{2nf}{\tau}\frac{d\tau}{dz} - \frac{2n\theta_0 K_1 f}{\tau} = 0 \quad (20)$$

Substitution of finite difference approximations for the differential terms in this equation gives

$$f_{p-1} + f_p \left[-2 - \frac{2n\theta_0 \Delta z^2}{\tau_p} K_1 \right] +$$

$$f_{p+1} = \frac{n\Delta z}{\tau_p} \left\{ \tau_{p+1} \left[f_{p+1} - \frac{1}{2n} \right] - \tau_{p-1} \left[f_{p-1} - \frac{1}{2n} \right] \right\} \quad (21)$$

Relabeling terms in Equation (21) one finds

$$f_{p-1}\,\overline{A}_p + f_p\,\overline{B}_p + f_{p+1}\,\overline{C}_p = \overline{D}_p \quad (22)$$

This difference equation is centered at point p. The system of nonlinear simultaneous equations represented by Equation (22) for $p = 1$ to $p = 49$ forms a tridiagonal matrix. If assumed values of τ and f are used in the calculation of $\overline{B}_p$ and $\overline{D}_p$, the equations can be solved for f_p by a method described by Bruce et al. (3) and attributed by them to L. H. Thomas of the Watson Scientific Computing Laboratory. Bruce et al. (3) stated, "While the method is equivalent to plain Gaussian elimination, it avoids the error growth associated with the back solution of the elimination method and also minimizes the storage problems in machine computation."

The Thomas method applied to the solution of Equation (22) is as follows:

At $p = 1$: $f_0\overline{A}_1 + f_1\overline{B}_1 + f_2\overline{C}_1 = \overline{D}_1$ (23)

The boundary condition at the bed entrance states

$$f_0 = \frac{1}{\tau} + \frac{1}{2n}\left(\frac{df}{dz}\right)_{z=0} \quad (24)$$

Substituting Equation (24) in (23) and rearranging to conform to the algorithm of Thomas one finds

$$f_1\overline{B}_1 + f_2\overline{C}_1 = \overline{D}_1 - \left[\frac{1}{\tau} + \frac{1}{2n}\left(\frac{df}{dz}\right)_{z=0} \right] \overline{A}_1 \quad (25)$$

At $p = 49$: The last equation of the set is centered at $p = 49$:

$$f_{48}\overline{A}_{49} + f_{49}\overline{B}_{49} + f_{50}\overline{C}_{49} = \overline{D}_{49} \quad (26)$$

The boundary condition at the bed exit states

$$\left(\frac{df}{dz}\right)_{z=1} = \frac{f_{50} - f_{49}}{\Delta z} = 0 \quad (27)$$

Therefore $f_{49} = f_{50}$ and

$$f_{48}\overline{A}_{49} + f_{49}\,(\overline{B}_{49} + \overline{C}_{49}) = \overline{D}_{49} \quad (28)$$

At points other than $p = 1$ and 49

Equation (22) applies. In general the solution is obtained by letting

$$w_p = \bar{B}_p - \bar{A}_p b_{p-1}$$

$$b_p = \bar{C}_p / w_p \qquad (29)$$

$$g_p = \frac{\bar{D}_p - \bar{A}_p g_{p-1}}{w_p}.$$

For the first point

$$w_1 = \bar{B}_1$$

$$b_1 = \bar{C}_1 / w_1 = \bar{C}_1 / \bar{B}_1$$

$$g_1 = \frac{\bar{D}_1 - \left[\frac{1}{\tau} + \frac{1}{2n} \left(\frac{df}{dz} \right)_{z=0} \right] \bar{A}_1}{w_1}$$

For the forty-ninth point

$$w_{49} = (\bar{B}_{49} + \bar{C}_{49}) - \bar{A}_{49} b_{48}$$

$$g_{49} = \frac{\bar{D}_{49} - \bar{A}_{49} g_{48}}{w_{49}} \qquad (31)$$

The above relationships (30) and (31) follow by reason of the specified boundary conditions.

The solution to the equation is, as demonstrated earlier (3)

$$f_{49} = g_{49}$$

$$f_{48} = g_{48} - b_{48} f_{49} \qquad (32)$$

$$f_p = g_p - b_p f_{p+1}$$

and so on to f_1. This gives a set of values calculated from assumed sets of f and τ values. Therefore a trial-and-error calculation is required in which the calculated value of f is substituted into the terms $\bar{B}_p$ and $\bar{D}_p$ as the next assumption of f.

The solution of Equation (7) for τ is carried out concurrently with the solution for f by a method exactly analogous to that described above for f.

At the beginning of a complete iteration a set of values for f and τ is assumed. The same set is used in the solution for both f and τ and then changed to a new set for the next complete iteration. This new set is simply the calculated values of f and τ from the previous iteration. This method was applied until convergence of the trial-and-error calculation was achieved as indicated by the sum of the absolute values of the differences between assumed and calculated values of the variable. In the present study convergence was assumed when the sum of the absolute differences for fifty-one points became 0.01 or less for both the variables f and τ.

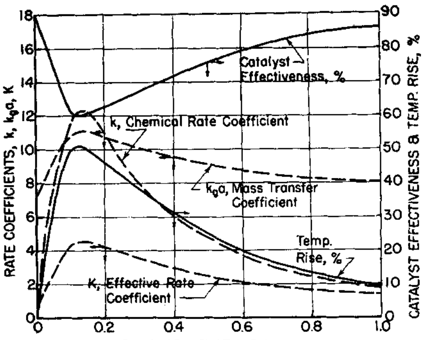

Fig. 4. Influence of temperature profile on rate parameters (nonadiabatic reactor).

Since the boundary conditions at the bed entrance

$$f_0 = \frac{1}{\tau} + \frac{1}{2n} \left(\frac{df}{dz} \right)_{z=0}$$

$$\tau_0 = 1 + \frac{1}{2n} \left(\frac{d\tau}{dz} \right)_{z=p}$$

have caused difficulty in the past (1), it is of interest to show how they were handled in the present study.

For the first trial-and-error iteration at the beginning of the solution distributions of f and τ throughout the bed were assumed. The gradients

$$\left(\frac{df}{dz} \right)_{z=0} \text{ and } \left(\frac{d\tau}{dz} \right)_{z=0}$$

could then be calculated with the finite difference approximations:

$$\left(\frac{df}{dz} \right)_{z=0} \cong \frac{-3f_0 + 4f_1 - f_2}{2\Delta z}$$

$$\left(\frac{d\tau}{dz} \right)_{z=0} \cong \frac{-3\tau_0 + 4\tau_1 - \tau_2}{2\Delta z}$$

Once calculated distributions of f and τ were obtained from an iteration, the gradients at $z = 0$ could be recalculated and used in the next iteration. Unlike most explicit or marching techniques a priori estimates of

$$\left(\frac{df}{dz} \right) \text{ and } \left(\frac{d\tau}{dz} \right)$$

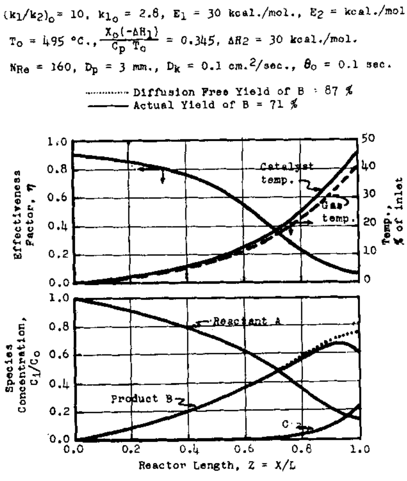

Fig. 5. Influence of transport factors on yield (adiabatic reactor) $A \xrightarrow{k_1} B$ (product) $\xrightarrow{k_2} C$.

at $z = 0$ were not required with this implicit method.

The stability of the method used in this study is illustrated by the fact that the initial f and τ distributions assumed for any given case to be solved were

$$f = 1.0$$

and

$$\tau = 1.0$$

at all values of z. In general this distribution was far removed from the final solution, but no instabilities developed and the solution converged very rapidly.

Precisely the same strategy as outlined above was employed to solve the problem of diffusion and reaction within nonisothermal porous catalyst pellets where a flux boundary condition due to interparticle diffusion was imposed (8).

DISCUSSION

Axial Mixing Effects

The influence of axial dispersion of heat and mass upon conversion appears, on the basis of computation, to be negligible so long as the bed depth is greater than about 50 particle diameters for $N_{Pe} = 2$. In other words the computed temperature and concentration profiles for piston flow ($n \to \infty$) are virtually indistinguishable from those profiles which result for a finite number of mixing stages equivalent to bed depths of 50 particle diameters. Thus the conclusions previously inferred from relationships for isothermal operation (4) appear to be borne out for adiabatic operation, as noted in Figures 1 and 2. Yield, involving as it does competitive conversions, will remain uninfluenced by axial diffusion unless low aspect ratios (L/D_p) characterize reactor design.

Bulk Mass Transfer and Pore-Diffusion Effects

As might be expected considerable differences in reactor performance may be encountered between cases involving small and large diameter pellets. This point is illustrated in Figure 3, where the computed concentration and gas temperature profiles for adiabatic fixed-bed operation are shown for two extreme modes of operation. In the first, pellet diameter is small and mass transfer rates quite high relative to the surface reaction rate. In the second case relatively large pellets are employed. The net result is of course a radical reduction in conversion for a given bed length as a result of rate retardation due to bulk mass transfer and diffusion within the porous pellets which reduces catalytic effectiveness.

A more dramatic illustration of mixed rate control and the influence of temperature upon rate control is given in Figure 4. This is a case of nonadiabatic, nonisothermal operation where radial gradients of heat and mass are assumed to be negligible. The figure specifies point values of the catalytic effectiveness, the surface rate constant, the mass transfer coefficient, and the resultant effective rate constant over a length of reactor in which the temperature varies considerably. A quantitative assessment of the contribution of each step to the overall rate process is given below.

$z = x/L$	Mass transfer resistance, %	Chemical rate k, sec.$^{-1}$	Effective rate K, sec.$^{-1}$	Catalytic effectiveness, %
0	10	1	0.83	92
0.125	41	13	4.5	60
0.25	38	9	4	64
0.5	29	5	2.7	75
0.75	23	3	2	81
1.0	18	2.3	1.5	85

Factors Affecting Yield

In the general reaction scheme considered the factor which most severely influences the yield in the sequence $A \rightarrow B \rightarrow C$ is the diffusivity of the species within the pores of the catalyst. While this has been clearly demonstrated by Wheeler's analytical solution, as might be expected, existence of exotherms within the bed seriously promotes the degradation of desired species B. In Figure 5 profiles for diffusion-free and diffusion-influenced adiabatic operation are displayed for a consecutive reaction scheme in which the intermediate B is the desired product.

CONCLUSIONS

The construction of a fixed-bed catalytic reactor model in which is incorporated various potential modes of transport illustrates the fact that the nonisothermal operation of a fixed bed is rarely characterized by one mode of rate control. Although only simple chemical kinetic expressions have been used, these conclusions are nevertheless valid no matter how complex the chemical transformation law may be. It is clear that axial dispersion of heat and mass exerts a negligible effect upon profiles unless one is dealing with extremely shallow bed reactors. It is therefore concluded that the chief detriment to high yield in the nonisothermal fixed-bed reactor is porous-solid diffusion. The question of temperature gradients within the particle, while not considered in this model, has been treated in a previous communication (8), and indeed an assessment of exothermicity within the bed as a whole and within individual particles must always be made when one is seeking a cause for the low yield of a thermally or catalytically sensitive product.

ACKNOWLEDGMENT

The authors are indebted to H. H. Rachford, Jr., and Professor R. L. Pigford for their beneficial comments on this work.

NOTATION

a = external surface to volume ratio for a particle, cm.$^{-1}$
a' = $a\ (1 - \epsilon)$
A, B, C = molecular species, moles
$\overline{A}, \overline{B}, \overline{C}, \overline{D}$ = coefficients in Thomas routine
C_i = concentration of species i, moles/cc.
C_g = bulk phase concentration moles/cc.
C_o = initial concentration moles/cc.
C_s = surface concentration moles/cc.
C_p = heat capacity, cal./mole °C.
D = diffusivity of species in porous pellet, sq. cm./sec.
D_m = bulk molecular diffusivity, sq. cm./sec.
D_t = reactor tube diameter, cm.
D_p = particle diameter, cm.
exp = exponential
E = axial-dispersion coefficient, sq. cm./sec.
f = $(C/C_o^s)_a$, reduced concentration of A
g = defined by Equation (26)
G = mass velocity, $u\rho$
h_p = fluid-particle heat transfer coefficient, cal./sec. sq. cm. °C.
h_w = fluid-wall heat transfer coefficient, cal./sec. sq. cm. °C.
ΔH = reaction enthalpy change, cal./mole
j = heat and mass transfer j factor, Equation (15)
k = surface reaction rate constant, sec.$^{-1}$
k_g = bulk mass transfer coefficient, cm./sec.
K = overall, effective rate constant, Equation (11), sec.$^{-1}$
L = reactor length, cm.
M = molecular weight
n = number of perfect mixers, Equation (5)
N_{Re} = Reynolds number, $D_p u/\nu$
N_{Pr} = Prandtl number, $C_p\mu/k$
N_{Pe} = Peclet number, $D_p u/E$
N_{Sc} = Schmidt number, ν/D_m
Q = heat released or abstracted owing to reaction, cal./mole
R = gas constant, cal./g. mole °K.
$\overline{R}$ = reaction rate, moles/(cc.)(sec.)
R' = defined by Equation (22)
S = selectivity, $= k_1/k_2$
T = gas temperature, °K.
T_o = inlet gas temperature, °K.
t_w = reactor wall temperature, °K.
t_s = catalyst temperature, °K.
u = average fluid velocity within bed, cm./sec.
u_o = superficial velocity $= u\,\epsilon$, cm./sec.
w = defined by Equation (26)
x = axial distance within reactor, cm.
x_c = initial mole fraction
y = reduced solids temperature, t_s/T_o
z = reduced bed length, x/L
Z = reduced wall temperature, t_w/T_o

Greek Letters

α = activation energy, cal./g.-mole
γ = selectivity function, Equation (17)
θ = contact time, $= \theta_o\tau$, sec.
τ = reduced gas temperature, T/T_o
ρ = gas density $= \rho_o/\tau$, g.-moles/cc.
η = catalytic effectiveness factor
ψ = diffusion-reaction modulus, Equation (14)
ϵ = void fraction
β = heat generation parameter, $\left(\dfrac{-\Delta H\, x_o}{C_p\, T_o}\right)$

Subscripts

a, b = molecular species A, B
o = feed conditions, T_o, C_o
p = net point in Thomas routine
s = solid
w = wall

LITERATURE CITED

1. Amundson, N. R., J. Costa, and D. Rudd, *Can. J. Chem. Eng.*, **39**, 149 (1961).
2. Aris, Rutherford, *Chem. Eng. Sci.*, **6**, 262 (1957).
3. Bruce, G. H., D. W. Peaceman, H. H. Rachford, and J. D. Rice, *Trans. Am. Inst. Mining, Met. Petrol. Engrs.*, **198**, 79 (1953).
4. Carberry, J. J., *Can. J. Chem. Eng.*, **36**, 207 (1958).
5. ———, and R. H. Bretton, *A.I.Ch.E. Journal*, **4**, 367 (1958).
6. Carberry, J. J., *ibid.*, p. 13M.
7. *Ibid.*, **6**, 460 (1960).
8. *Ibid.*, **7**, 350 (1961).

8*a*. *Ibid.*, **8**, 557 (1962).

8*b*. Carberry, J. J., *Chem. Eng. Sci.*, **17**, 675 (1962).

9. Danckwerts, P. V., *ibid.*, **2**, 1 (1953).
10. Deans, H. A., and Leon Lapidus, *A.I.Ch.E. Journal*, **6**, 656 (1960).
11. Hulburt, H. M., *Ind. Eng. Chem.*, **36**, 1012 (1944).
12. Levenspiel, O., and K. B. Bischoff, *ibid.*, **51** (1959).
13. Wehner, J. F., and R. H. Wilhelm, *Chem. Eng. Sci.*, **6**, 89 (1956).
14. Weisz, P. B., *Z. Physik Chem.*, *Neue Folge*, **11**, 1 (1957).
15. Wheeler, Ahlborn, "Catalysis," Vol. 2, P. H. Emmett, ed., Reinhold, New York (1955).

Manuscript received July 19, 1961; revision received June 6, 1962; paper accepted June 7, 1962. Paper presented at A.I.Ch.E. New York meeting.