Analysis of Three-Phase Packed-Bed Reactors

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Three-phase reactors involving a solid catalyst are normally used for production of product or removal of impurity. Equations are presented for these two measures of reactor performance for a first-order, reversible or irreversible reaction in an isothermal reactor. The results are presented in terms of dimensionless groups of the pertinent mass transfer, kinetic, and equilibrium (solubility) properties, and the gas and liquid flow rates. From the equations given, it is possible to predict the relative performance of concurrent (trickle bed) and countercurrent flow reactors and also the effect of mixing in the gas or liquid streams on performance.

SCOPE

Three-phase reactors are used for chemical processes that involve a solid catalyst and gas and liquid reactants, or gaseous reactants in a liquid phase. Hydrotreating processes, such as desulfurization of petroleum fractions, polymerization of ethylene and propylene, and hydrogenation of oils are established examples, but other applications are developing, as noted in the reviews by Ostergaard (1968) and by Goto et al. (1977).

More transport steps are required in such systems so that reactor analysis necessitates careful study of the interaction between intrinsic kinetics and interphase and intraparticle transfer. For packed beds of catalyst particles, with either concurrent downflow (trickle beds) or countercurrent flow, there have been several analyses of reactor performance. Sylvester and Pitayagulsarn (1973) used available theory for two-phase, gas-solid catalytic systems to analyze first-order reactions in trickle-bed reactors. Also, Sylvester et al. (1975) defined a local reactor effectiveness which combined mass transfer and intrinsic kinetics for trickle-bed and slurry reactors. Goto (1975) modified the development to include the effect of liquid flow rate. Goto and Smith (1975) and Levec and Smith (1976) predicted the performance of trickle-bed reactors taking into account gas-liquid, liquid-particle, and intraparticle mass transfer effects. The results were compared with experimental measurements for the air oxidation of formic and acetic acid solutions. Because intrinsic kinetics were nonlinear, numerical solutions were required so that the effect of pertinent variables could not be directly displayed. Goto et al. (1976) obtained explicit solutions for the conversion in a trickle-bed reactor, with first-order kinetics, under the restriction that the concentration of reactant in the gas stream was constant. This restriction is satisfactory for a pure gas phase, a very high gas flow rate, or where the gaseous reactant is slightly soluble in the liquid phase; it is not suitable when the reactor is used for gas purification.

The chief objective of the present work is to present a more general development applicable for a variety of conditions. The procedure could be used for any form of kinetics, but the equations are given for a first-order, reversible reaction since explicit solutions are possible. A second objective is to use the theory to compare expected performance for trickle-bed and countercurrent flow reactors and to examine effects of mixing in the flow streams. Data for the hydrogenation of α-methylstyrene (Satterfield et al., 1969) are used as an illustration at conditions such that the gas phase concentration of hydrogen is not constant.

The results are applicable for isothermal, steady state conditions involving a catalytic reaction. Thus, the theory would not be suitable to dynamic problems such as the adsorption of a gaseous component on adsorbent particles.

CONCLUSIONS AND SIGNIFICANCE

Three-phase reactors may be used for several purposes: production of a reaction product (for example, polymerization of gases in a solvent), purification of a liquid feed stream (desulfurization of petroleum fractions), and purification of a gas feed stream. Accordingly, results are given for a first-order reversible reaction for either fractional removal x of the reactant from the gas phase or for the efficiency η_t of conversion of reactant to product in liquid or gas streams. For steady state, isothermal conditions explicit equations are given for these two quantities in terms of the mass transfer and kinetic parameters. The development is simplified by introducing effectiveness factors η, η_l, and η_b for intraparticle, liquid-particle, and gas-liquid mass transfer, respectively. Dimensionless solutions show what groupings of the many variables are important. Results are displayed as functions of gas and liquid flow rates (Damkoehler numbers Da_g and Da_l), mixing Peclet numbers (Pe_g and Pe_l), effectiveness factors, and gas solubilities (Henry's law constants H). Solutions are also given for specific cases such as irreversible reaction, nonvolatile reaction product, rapid reaction, and extreme flow rates.

The analysis shows that for conversion to desirable product, high gas rates and concurrent operation are preferred. For gas purification, countercurrent operation is preferable as long as the liquid feed contains none of the gaseous impurity. However, the differences due to flow direction are not large except for plug flow conditions. These conclusions were determined by using mass transfer coefficients that are the same for concurrent and countercurrent flow, that is, equal values of η_l and of η_b. The data of Goto et al. (1975) give similar values for mass transfer coefficients for the two flow arrangements. As expected, the results show that mixing of either gas or liquid stream

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reduces the performance of the reactor. Extension of this conclusion indicates that a packed-bed reactor could be more desirable than a continuous slurry reactor as far as purification is concerned, since the liquid phase is likely to be well mixed. Again, this conclusion is based upon the same values of mass transfer coefficients, which is not likely to be valid in comparing slurries and packed beds. Hence, the adverse effect of mixing in the liquid phase in the slurry reactor would have to be weighed against the advantage of a larger intraparticle effectiveness factor η and different values of mass transfer coefficients. There are large differences between trickle bed and countercurrent flow when mixing is poor (high Peclet numbers). Under these conditions, the countercurrent arrangement gives much higher fractions of reactant removed from gas phase.

The objective of the theory is to predict the concentration changes of reactant, and hence the conversion, in concurrent or countercurrent packed-bed reactors. A first-order, reversible reaction

$$A \rightleftharpoons R$$

is assumed to occur at an interior site on the catalyst. Reactions with more complicated kinetics could be analyzed with the same type of equations. In the general solution, the reactant is present in both gas and liquid feed streams. Solutions are also given for special cases, such as irreversible reaction, reactant present only in the gaseous feed, and for various mixing conditions in the flowing streams. Other assumptions are:

1. Isothermal, steady-state operation.
2. Physical properties, flow rates, and mass transfer coefficients are constant throughout the reactor.
3. Deviations from plug flow of gas or liquid phases can be accounted for by an axial dispersion term. Thus, holdup does not directly appear in the development. The mixing extremes from plug flow to stirred tank are considered by varying the axial Peclet number.

The equations are based upon the following series of steps: mass transfer of gaseous reactant from gas to bulk liquid, mass transport from bulk liquid to outer surface of catalyst particle, intraparticle diffusion, and reaction at an interior site on the pore surface.

THEORY

Basic Equations

For the given operating conditions and restrictions, mass conservation equations for concurrent and countercurrent flow of gas and liquid, applied to a differential reactor volume, are as follows:

$$E_g \frac{d^2C_{gA}}{dz^2} \mp u_g \frac{dC_{gA}}{dz} - N_{lA} = 0 \tag{1}$$

$$E_l \frac{d^2C_{lA}}{dz^2} - u_l \frac{dC_{lA}}{dz} + N_{lA} - N_{sA} = 0 \tag{2}$$

$$N_{sA} = R_V = -N_{sR} \tag{3}$$

$$E_l \frac{d^2C_{lR}}{dz^2} - u_l \frac{dC_{lR}}{dz} + N_{lR} - N_{sR} = 0 \tag{4}$$

$$E_g \frac{d^2C_{gR}}{dz^2} \mp u_g \frac{dC_{gR}}{dz} - N_{lR} = 0 \tag{5}$$

where N_{lA}, N_{sA}, N_{sR}, and N_{lR} are the interphase mass transport rates and R_V is the reaction rate. Since the reaction is reversible, these equations allow for mass transfer of product R from solid to liquid to gas phase. In Equations (1) and (5), $-u_g$ indicates concurrent flow and $+u_g$ countercurrent flow. Assuming no dispersion in the feed streams, boundary conditions for the concurrent flow system are

$$\text{at} \quad z = 0; \quad E_g \frac{dC_{gA}}{dz} = u_g(C_{gA} - C_{gA,f}) \tag{6}$$

$$E_l \frac{dC_{lA}}{dz} = u_l(C_{lA} - C_{lA,f}) \tag{7}$$

$$E_l \frac{dC_{lR}}{dz} = u_l(C_{lR} - C_{lR,f}) \tag{8}$$

$$E_g \frac{dC_{gR}}{dz} = u_g(C_{gR} - C_{gR,f}) \tag{9}$$

$$\text{at} \quad z = z_B; \quad E_g \frac{dC_{gA}}{dz} = 0 \tag{10}$$

$$E_l \frac{dC_{lA}}{dz} = 0 \tag{11}$$

$$E_l \frac{dC_{lR}}{dz} = 0 \tag{12}$$

$$E_g \frac{dC_{gR}}{dz} = 0 \tag{13}$$

For the countercurrent flow system Equations (6), (9), (10), and (13) are replaced by

$$\text{at} \quad z = 0; \quad E_g \frac{dC_{gA}}{dz} = 0 \tag{14}$$

$$E_g \frac{dC_{gR}}{dz} = 0 \tag{15}$$

$$\text{at} \quad z = z_B; \quad E_g \frac{dC_{gA}}{dz} = u_g(C_{gA,f} - C_{gA}) \tag{16}$$

$$E_g \frac{dC_{gR}}{dz} = u_g(C_{gR,f} - C_{gR}) \tag{17}$$

On the basis of the two-film concept at the gas-liquid interphase, the mass transport rate of A from gas to liquid can be expressed in terms of the gas and liquid side mass transfer coefficients; that is

$$N_{lA} = (ka)_{gA}(C_{gA} - C_{i,gA}) = (ka)_{lA}(C_{i,lA} - C_{lA}) \tag{18}$$

If it is assumed that Henry's law holds between $C_{i,gA}$ and $C_{i,lA}$, that is

$$C_{i,gA} = H_A^* C_{i,lA} \tag{19}$$

then Equation (18) may be written

$$N_{lA} = (ka)_{lA}\eta_{bA}(C_{gA}/H_A^* - C_{lA}) \tag{20}$$

Here η_{bA}, the gas-liquid effectiveness for transport of A, is given by

$$\eta_{bA} = 1/[1 + (ka)_{lA}/(ka)_{gA}H_A^*] \tag{21}$$

The mass transport rate of product R, N_{lR}, and the gas-liquid effectiveness of R, η_{bR}, are obtained by replacing subscript A with R in Equations (20) and (21):

$$N_{lR} = (ka)_{lR}\eta_{bR}(C_{gR}/H_R^* - C_{lR}) \tag{22}$$

$$\eta_{bR} = 1/[1 + (ka)_{lR}/(ka)_{gR}H_R^*] \tag{23}$$

The mass transport rates of A and R from liquid to solid are defined in terms of the corresponding mass transport coefficients by the expressions

$$N_{sA} = (ka)_{sA}(C_{lA} - C_{sA}) \tag{24}$$

$$N_{sR} = (ka)_{sR}(C_{lR} - C_{sR}) \tag{25}$$

The global rate of the first-order reaction per unit volume of reactor, and in terms of the catalytic effectiveness factor η, is

$$R_V = k\eta(1 - \epsilon_B)(C_{sA} - C_{sR}/K) \tag{26}$$

where η is dependent on the Thiele modulus ϕ. For a first-order reversible reaction, ϕ is

$$\phi = \frac{V_P}{S_P}\sqrt{\frac{k}{D_{eA}}\left(1 + \frac{1}{K}\frac{D_{eA}}{D_{eR}}\right)} \tag{27}$$

Introduction of the bed void fraction ϵ_B means that k is the rate constant referred to the volume of catalyst particles. We can combine Equations (24) to (26) to eliminate surface concentrations, giving

$$N_{sA} = R_V = -N_{sR} = k\eta\eta_l(1 - \epsilon_B)(C_{lA} - C_{lR}/K) \tag{28}$$

where η_l is the liquid-particle effectiveness, defined as

$$\eta_l = \frac{1}{1 + k\eta(1 - \epsilon_B)/(ka)_{sA} + k\eta(1 - \epsilon_B)/(ka)_{sR}K} \tag{29}$$

The transverse accumulation rate of A in the liquid phase $(N_{lA} - N_{sA})$ for substitution in Equation (2) may be expressed in terms of concentrations of A and R by using Equations (20) and (28). Thus

$$N_{lA} - N_{sA} = (ka)_{lA}\eta_{bA}[C_{gA}/H_A^* - C_{lA}/\eta_{oA} + C_{lR}(1 - \eta_{oA})/\eta_{oA}K] \tag{30}$$

Here, η_{oA} is the overall effectiveness of A, defined as

$$\eta_{oA} = 1/\{1 + k\eta\eta_l(1 - \epsilon_B)/(ka)_{lA}\eta_{bA}\} \tag{31}$$

Similarly, from Equations (22) and (28), $(N_{lR} - N_{sR})$ in Equation (4) may be expressed as

$$N_{lR} - N_{sR} = (ka)_{lR}\eta_{bR}[(1 - \eta_{oR})KC_{lA}/\eta_{oR} - C_{lR}/\eta_{oR} + C_{gR}/H_R^*] \tag{32}$$

where η_{oR} is the overall effectiveness of R:

$$\eta_{oR} = 1/\{1 + k\eta\eta_l(1 - \epsilon_B)/(ka)_{lR}\eta_{bR}K\} \tag{33}$$

Substituting Equations (20), (22), (30), and (32) into Equations (1), (2), (4), and (5), and using dimensionless variables, we get

$$\frac{1}{Pe_g}\frac{d^2y_{gA}}{d\zeta^2} \mp \frac{dy_{gA}}{d\zeta} - Da_g(y_{gA} - y_{lA}) = 0 \tag{34}$$

$$\frac{1}{Pe_l}\frac{d^2y_{lA}}{d\zeta^2} - \frac{dy_{lA}}{d\zeta} + Da_l\left[y_{gA} - \frac{y_{lA}}{\eta_{oA}} + \frac{(1 - \eta_{oA})y_{lR}}{\eta_{oA}}\right] = 0 \tag{35}$$

$$\frac{1}{Pe_l}\frac{d^2y_{lR}}{d\zeta^2} - \frac{dy_{lR}}{d\zeta} + Da_lQ_{RA}\left[y_{gR} - \frac{y_{lR}}{\eta_{oR}} + \frac{(1 - \eta_{oR})y_{lA}}{\eta_{oR}}\right] = 0 \tag{36}$$

$$\frac{1}{Pe_g}\frac{d^2y_{gR}}{d\zeta^2} \mp \frac{dy_{gR}}{d\zeta} - \frac{Da_gQ_{RA}}{H_{RA}}(y_{gR} - y_{lR}) = 0 \tag{37}$$

Boundary conditions for the concurrent flow system [Equations (6) to (13)] may be rewritten as

$$\text{at}\quad \zeta = 0;\quad \frac{1}{Pe_g}\frac{dy_{gA}}{d\zeta} = y_{gA} - 1 \tag{38}$$

$$\frac{1}{Pe_l}\frac{dy_{lA}}{d\zeta} = y_{lA} - y_{lA,f} \tag{39}$$

$$\frac{1}{Pe_l}\frac{dy_{lR}}{d\zeta} = y_{lR} - y_{lR,f} \tag{40}$$

$$\frac{1}{Pe_g}\frac{dy_{gR}}{d\zeta} = y_{gR} - y_{gR,f} \tag{41}$$

$$\text{at}\quad \zeta = 1;\quad \frac{1}{Pe_g}\frac{dy_{gA}}{d\zeta} = 0 \tag{42}$$

$$\frac{1}{Pe_l}\frac{dy_{lA}}{d\zeta} = 0 \tag{43}$$

$$\frac{1}{Pe_l}\frac{dy_{lR}}{d\zeta} = 0 \tag{44}$$

$$\frac{1}{Pe_g}\frac{dy_{gR}}{d\zeta} = 0 \tag{45}$$

Similar expressions can be formulated for countercurrent flow from Equations (14) to (17).

Solution

Combination of Equations (34) to (37) to eliminate y_{lA}, y_{lR}, and y_{gR} gives an eighth-order, linear, differential equation for y_{gA} as a function of ζ:

$$a_1\frac{d^8y_{gA}}{d\zeta^8} + a_2\frac{d^7y_{gA}}{d\zeta^7} + a_3\frac{d^6y_{gA}}{d\zeta^6} + a_4\frac{d^5y_{gA}}{d\zeta^5} + a_5\frac{d^4y_{gA}}{d\zeta^4} + a_6\frac{d^3y_{gA}}{d\zeta^3} + a_7\frac{d^2y_{gA}}{d\zeta^2} + a_8\frac{dy_{gA}}{d\zeta} + a_9y_{gA} = 0 \tag{46}$$

The development of Equation (46) and definitions of the constant coefficients a_1 to a_9 are given in Appendix A. These coefficients are functions of the mass transport coefficients $(ka)_g$, $(ka)_l$, $(ka)_s$, other rate and equilibrium parameters, and the liquid and gas flow rates.

Solution of Equation (46) gives the concentration of reactant A in the gas phase as a function of reactor length. Using the notation of a differential operator $D = d/d\zeta$, the differential equation may be written as the following eighth-degree polynomial:

$$a_1D^8 + a_2D^7 + a_3D^6 + a_4D^5 + a_5D^4 + a_6D^3 + a_7D^2 + a_8D + a_9 = 0 \tag{47}$$

The solution of Equation (46) may be formulated in terms of the eight roots $\lambda_1, \lambda_2 \ldots\ldots \lambda_8$ of Equation (47). Thus

$$y_{gA} = \sum_{i=1}^{8} \alpha_i \exp(\lambda_i\zeta) \tag{48}$$

The other dimensionless concentrations y_{lA}, y_{lR}, and y_{gR}, which with y_{gA} determine the performance of the reactor, can be expressed in the form of equation (48):

$$y_{lA} = \sum_{i=1}^{8} \beta_i \alpha_i \exp(\lambda_i \zeta) \tag{49}$$

$$y_{lR} = \sum_{i=1}^{8} \gamma_i \alpha_i \exp(\lambda_i \zeta) \tag{50}$$

$$y_{gR} = \sum_{i=1}^{8} \delta_i \alpha_i \exp(\lambda_i \zeta) \tag{51}$$

Equations for the constants β_i, γ_i, and δ_i ($i = 1, 2, \ldots 8$) which are functions of λ_i and the rate and equilibrium parameters of the system are given in Appendix B. The constants $\alpha_1, \alpha_2, \ldots, \alpha_8$ are determined from the eight boundary conditions. For concurrent flow, using Equations (38) to (45)

$$\sum_{i=1}^{8} (Pe_g - \lambda_i)\alpha_i = Pe_g \tag{52}$$

$$\sum_{i=1}^{8} \lambda_i \exp(\lambda_i)\alpha_i = 0 \tag{53}$$

$$\sum_{i=1}^{8} \beta_i (Pe_l - \lambda_i)\alpha_i = Pe_l y_{lA,f} \tag{54}$$

$$\sum_{i=1}^{8} \beta_i \lambda_i \exp(\lambda_i)\alpha_i = 0 \tag{55}$$

$$\sum_{i=1}^{8} \gamma_i (Pe_l - \lambda_i)\alpha_i = Pe_l y_{lR,f} \tag{56}$$

$$\sum_{i=1}^{8} \gamma_i \lambda_i \exp(\lambda_i)\alpha_i = 0 \tag{57}$$

$$\sum_{i=1}^{8} \delta_i (Pe_g - \lambda_i)\alpha_i = Pe_g y_{gR,f} \tag{58}$$

$$\sum_{i=1}^{8} \delta_i \lambda_i \exp(\lambda_i)\alpha_i = 0 \tag{59}$$

For countercurrent flow, Equations (52), (53), (58), and (59) are replaced by

$$\sum_{i=1}^{8} (Pe_g + \lambda_i)\exp(\lambda_i)\alpha_i = Pe_g \tag{60}$$

$$\sum_{i=1}^{8} \lambda_i \alpha_i = 0 \tag{61}$$

$$\sum_{i=1}^{8} \delta_i (Pe_g + \lambda_i)\exp(\lambda_i)\alpha_i = Pe_g y_{gR,f} \tag{62}$$

$$\sum_{i=1}^{8} \delta_i \lambda_i \alpha_i = 0 \tag{63}$$

For concurrent flow of gas and liquid, the concentrations at the exit of reactor are obtained by setting ζ in Equations (48) to (51) equal to unity; that is

$$y_{gA,e} = \sum_{i=1}^{8} \alpha_i \exp(\lambda_i) \tag{64}$$

$$y_{lA,e} = \sum_{i=1}^{8} \beta_i \alpha_i \exp(\lambda_i) \tag{65}$$

$$y_{lR,e} = \sum_{i=1}^{8} \gamma_i \alpha_i \exp(\lambda_i) \tag{66}$$

$$y_{gR,e} = \sum_{i=1}^{8} \delta_i \alpha_i \exp(\lambda_i) \tag{67}$$

For countercurrent flow, Equations (64) and (67) are replaced by

$$y_{gA,e} = \sum_{i=1}^{8} \alpha_i \tag{68}$$

$$y_{gR,e} = \sum_{i=1}^{8} \delta_i \alpha_i \tag{69}$$

Two measures of reactor performance were used. The first is the fraction x of reactant removed from the gas phase. Once $y_{gA,e}$ is obtained from Equation (64) or (68), this fraction is given by

$$x = 1 - y_{gA,e} \tag{70}$$

The value of x is important when the reactor is used for the removal of gaseous reactant, that is, for purification of air. The second measure is the efficiency of the three-phase reactor η_t defined as the ratio of the actual consumption rate of A to the intrinsic reaction rate, where concentrations in the porous catalyst particles are set equal to those in the liquid phase in equilibrium with the gas phase at feed conditions. This efficiency may be expressed by the equation

$$\eta_t = \frac{[(C_{gA,f} - C_{gA,e})u_g + (C_{lA,f} - C_{lA,e})u_l]/z_B}{k(1 - \epsilon_B)(C_{gA,f}/H_A^* - C_{gR,f}/KH_R^*)}$$

or, in terms of dimensionless parameters, as

$$\frac{\eta_t}{\eta\eta_l} = \frac{\eta_{oA}}{(1 - \eta_{oA})(1 - y_{gR,f})} \left(\frac{1 - y_{gA,e}}{Da_g} + \frac{y_{lA,f} - y_{lA,e}}{Da_l} \right) \tag{71}$$

The value of η_t is important when the reactor is used to produce product R.

COMPUTATIONAL PROCEDURE

In calculating reactor performance, it is assumed that the feed streams contain no reaction product, so that $y_{lR,f} = y_{gR,f} = 0$. Then, for a reversible reaction, $y_{gA,e}$ and $y_{lA,e}$, and hence x or η_t are functions of $y_{lA,f}$, η_{oA}, η_{oR}, Da_g, Da_l, Pe_g, Pe_l, Q_{RA}, and H_{RA}. The values of $y_{lA,f}$, η_{oA} and η_{oR} can vary from 0 to 1.0 and the others from 0 to infinity. In these ranges Equation (47) has real roots λ_i, but sometimes two roots are identical. Equations (49) to (69) are applicable when the roots are distinct. For multiple roots, the equations become more complex and are not included here. The roots are equivalent to the eigenvalues of the companion matrix of Equation (47) (Ralston and Wilf, 1960). Such eigenvalues were computed by the QR method described by Gard and Brebner (1968). The constants $\alpha_1 \ldots \alpha_8$ were computed by the Gauss elimination procedure (Wylie, 1966) for simultaneous linear equations, Equations (52) to (59) for concurrent flow and (54) to (57) and (60) to (63) for countercurrent flow. Then dimensionless effluent concentrations and x and $\eta_t/\eta\eta_l$ were evaluated from Equations (64) to (71).

SPECIAL CASES

Restrictions in the reaction system, and flow and mixing conditions, reduce the computations for solving Equations (70) and (71). Several of these special cases are described in the following paragraphs.

Irreversible Reaction

For $K = \infty$, Equation (33) shows that $\eta_{oR} = 1$. Also, Equations (36), (37), (40), (41), (44), and (45) are not needed, nor are H_{RA} or Q_{RA} involved, since the product R does not affect reactor performance. With these simplifications, Equation (46) becomes but a fourth-degree equation, and x or η_t is a function of $y_{lA,f}$, η_{oA}, Da_g, Da_l, Pe_g, and Pe_l.

If the irreversible reaction rate is extremely high, and also mass transfer from gas to liquid is the rate controlling step, $\eta_{bA} \rightarrow 0$ from Equation (21). Also, Equation (31) shows that η_{oA} is zero. In addition, y_{lA} approaches zero. Then Equation (34) only is necessary, and this may be solved (with $y_{lA} = 0$) for y_{gA} using boundary conditions given by Equations (38) and (42). The result is

$$y_{gA,e} = \frac{Pe_g(\lambda_1 - \lambda_2)}{\lambda_1^2 e^{-\lambda_2} - \lambda_2^2 e^{-\lambda_1}} \tag{72}$$

where

$$\lambda_1 = \frac{1}{2}\{Pe_g + [Pe_g(Pe_g + 4Da_g)]^{1/2}\} \tag{73}$$

$$\lambda_2 = \frac{1}{2}\{Pe_g - [Pe_g(Pe_g + 4Da_g)]^{1/2}\} \tag{74}$$

Very High Gas Rate

When the gas flow rate is extremely high, $Da_g \rightarrow 0$ and the concentrations of A and R in the gas phase are constant throughout the reactor and identical to the feed concentrations. Then, $y_{gA} = 1$ and $y_{gR} = y_{gR,f}$. Concurrent and countercurrent flow give the same results, and Equations (34), (37), (38), (41), (42), and (45) are not needed. An analytic solution is possible for an irreversible reaction. The equation for the efficiency, which also has been obtained earlier by Goto (1976), may be written

$$\frac{\eta_t}{\eta\eta_l} = \eta_{oA} + \frac{\eta_{oA}(y_{lA,f} - \eta_{oA})}{Da_l} \left[1 - \frac{Pe_l(\lambda_1 - \lambda_2)\exp(Pe_l)}{\lambda_1^2 \exp(\lambda_1) - \lambda_2^2 \exp(\lambda_2)}\right] \tag{75}$$

where

$$\lambda_1 = Pe_l(1 + \sqrt{1 + 4Da_l/Pe_l\eta_{oA}})/2 \tag{76}$$

$$\lambda_2 = Pe_l(1 - \sqrt{1 + 4Da_l/Pe_l\eta_{oA}})/2 \tag{77}$$

Extreme Mixing Conditions

According to the model used, plug flow conditions correspond to infinite Peclet numbers and complete mixing to $Pe = 0$. Explicit results can be obtained for an irreversible reaction for these special cases.

For plug flow of both liquid and gas, the first terms on the left side of Equations (34) to (37) disappear as well as the terms involving Pe_g or Pe_l in the boundary conditions, Equations (38) to (45). The analytic solution for the exit concentrations for an irreversible reaction is, for concurrent flow

$$y_{g,Ae} = \frac{(\mu - \lambda_2)\exp(\lambda_1) - (\mu - \lambda_1)\exp(\lambda_2)}{(\lambda_1 - \lambda_2)} \tag{78}$$

$$y_{lA,e} = \frac{(\mu - \lambda_2)(Da_g + \lambda_1)\exp(\lambda_1) - (\mu - \lambda_1)(Da_g + \lambda_2)\exp(\lambda_2)}{Da_g(\lambda_1 - \lambda_2)} \tag{79}$$

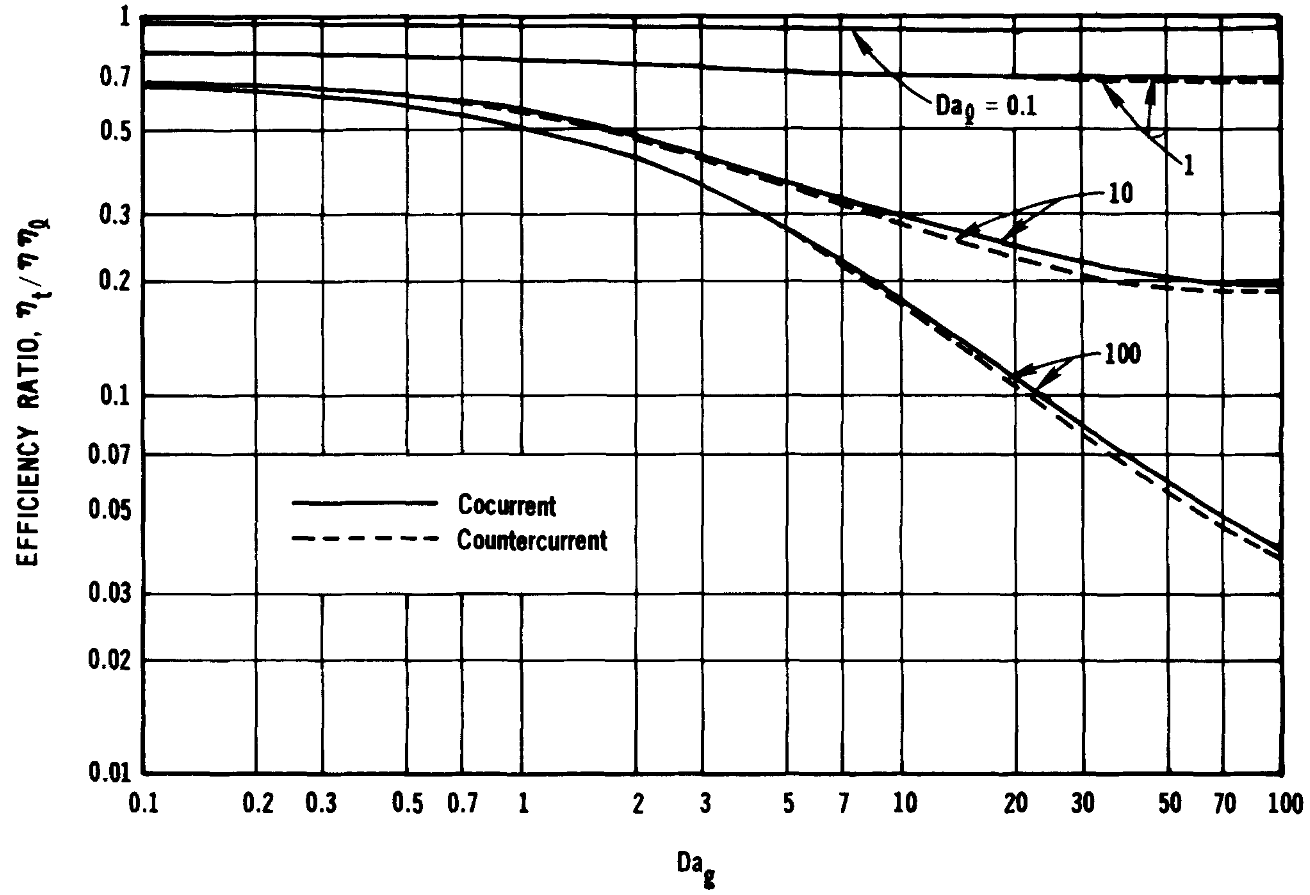

Fig. 1. Effect of Da_l on $\eta_t/\eta\eta_l$ at $y_{lA,f} = 1$, $\eta_{oA} = \eta_{oR} = 0.8$, $Pe_g = Pe_l = 1$, $Q_{RA} = H_{RA} = 1$.

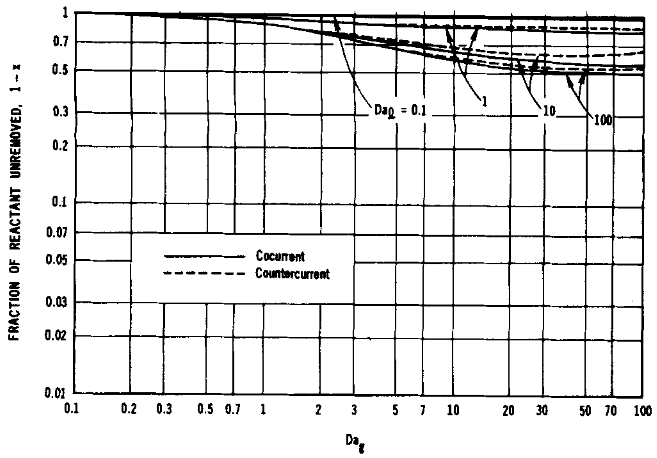

Fig. 2. Effect of Da_l on $(1 - x)$ at $y_{lA,f} = 1$, $\eta_{oA} = \eta_{oR} = 0.8$, $Pe_g = Pe_l = 1$, $Q_{RA} = H_{RA} = 1$.

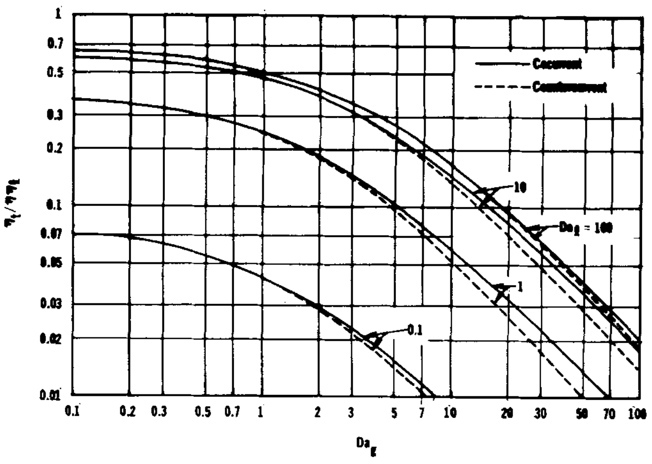

Fig. 3. Effect of Da_l on $\eta_t/\eta\eta_l$ at $y_{lA,f} = 0$, $\eta_{oA} = \eta_{oR} = 0.8$, $Pe_g = Pe_l = 1$, $Q_{RA} = H_{RA} = 1$.

where

$$\lambda_1 = [- Da_l/\eta_{oA} - Da_g + \sqrt{(Da_l/\eta_{oA} - Da_g)^2 + 4Da_gDa_l}]/2 \quad (80)$$

$$\lambda_2 = [- Da_l/\eta_{oA} - Da_g - \sqrt{(Da_l/\eta_{oA} - Da_g)^2 + 4Da_gDa_l}]/2 \quad (81)$$

$$\mu = Da_g(y_{lA,f} - 1) \quad (82)$$

For countercurrent flow, the solution is

$$y_{gA,e} = \frac{\lambda_1 - \lambda_2 + y_{lA,f}Da_g[\exp(\lambda_1) - \exp(\lambda_2)]}{(Da_g - \lambda_2)\exp(\lambda_1) - (Da_g - \lambda_1)\exp(\lambda_2)} \quad (83)$$

$$y_{lA,e} = \frac{(Da_g - \lambda_1)(Da_g - \lambda_2)[\exp(\lambda_1) - \exp(\lambda_2)] + y_{lA,f}Da_g(\lambda_1 - \lambda_2)\exp(\lambda_1 + \lambda_2)}{Da_g[(Da_g - \lambda_2)\exp(\lambda_1) - (Da_g - \lambda_1)\exp(\lambda_2)]} \quad (84)$$

where

$$\lambda_1 = [- Da_l/\eta_{oA} + Da_g + \sqrt{(Da_l/\eta_{oA} + Da_g)^2 - 4Da_gDa_l}]/2 \quad (85)$$

$$\lambda_2 = [- Da_l/\eta_{oA} + Da_g - \sqrt{(Da_l/\eta_{oA} + Da_g)^2 - 4Da_gDa_l}]/2 \quad (86)$$

For complete mixing of gas and liquid, the mass conservation equations corresponding to Equations (1), (2), (4), and (5) become algebraic expressions in terms of exit concentrations. With our dimensionless variables, these expressions are

$$1 - y_{gA,e} - Da_g(y_{gA,e} - y_{lA,e}) = 0 \quad (87)$$

$$y_{lA,f} - y_{lA,e} + Da_l[y_{gA,e} - y_{lA,e}/\eta_{oA} + (1 - \eta_{oA})y_{lR,e}/\eta_{oA}] = 0 \quad (88)$$

$$y_{lR,f} - y_{lR,e} + Da_lQ_{RA}[y_{gR,e} - y_{lR,e}/\eta_{oR} + (1 - \eta_{oR})y_{lA,e}/\eta_{oR}] = 0 \quad (89)$$

$$y_{gR,f} - y_{gR,e} + (Da_lQ_{RA}/H_{RA})(y_{gR,e} - y_{lR,e}) = 0 \quad (90)$$

For an irreversible reaction, solution of Equations (87) and (88) with $y_{lR,e} = 0$ is

$$y_{gA,e} = \frac{Da_l + \eta_{oA} + y_{lA,f}Da_g\eta_{oA}}{(1 - Da_g)(\eta_{oA} + Da_l) - Da_gDa_l\eta_{oA}} \quad (91)$$

$$y_{lA,e} = \frac{\eta_{oA}(Da_l + y_{lA,f} + y_{lA,f}Da_g)}{(1 + Da_g)(\eta_{oA} + Da_l) - Da_gDa_l\eta_{oA}} \quad (92)$$

In a slurry reactor, where bubbles of gas rise through the liquid, plug flow of gas and complete mixing of liquid may be the most realistic of the extreme mixing cases. For this case, the conservation expressions consist of Equations (34) and (37), with $Pe_g = \infty$ for the gas phase. For the liquid phase, $Pe_l = 0$, and Equations (88) and (89) are applicable, with $y_{gA,e}$ and $y_{gR,e}$ replaced by average values $\overline{y}_{gA}$ and $\overline{y}_{gR}$. The average concentration is defined as

$$\overline{y} = \int_0^1 y(\zeta)d\zeta \quad (93)$$

For an irreversible reaction, the solution for the exit concentrations is

$$y_{lA,e} = \frac{Da_l[1 - \exp(-Da_g)] + y_{lA,f}Da_g}{Da_g(1 - Da_l + Da_l/\eta_{oA}) + Da_l[1 - \exp(-Da_g)]} \quad (94)$$

$$y_{gA,e} = y_{lA,e} + (1 - y_{lA,e})\exp(-Da_g) \quad (95)$$

A solution for the reverse case, complete mixing of the gas phase and plug flow of liquid, although not likely to be practical, could be formulated in a similar way.

RESULTS

Figures 1 and 2 illustrate the results by showing x and $\eta_t/\eta\eta_l$ vs. Da_g at different values of Da_l for specific values of the other parameters. These results are for a liquid feed saturated with reactant ($y_{lA,f} = 1$). Through the effect on Da_l, these figures show how increasing the liquid rate (u_l) increases the reactor efficiency (Figure 1) for producing product but reduces the fraction of reactant removed from the gas (Figure 2). Increasing the gas rate (that is, decreasing Da_g) increases the efficiency $\eta_t/\eta\eta_l$ but decreases x. The more likely condition when the reactor is used to purify a gas stream would be for the liquid to contain no reactant $y_{Al,f} = 0$. Figures 3 and 4 are for this condition and for the same values of the other parameters as used in Figures 1 and 2. Here, the fractional removals x are much larger, and the effect of increased liquid rate is to increase x (Figure 4), in contrast to the case when $y_{Al,f} = 1$ (Figure 2). Efficiencies

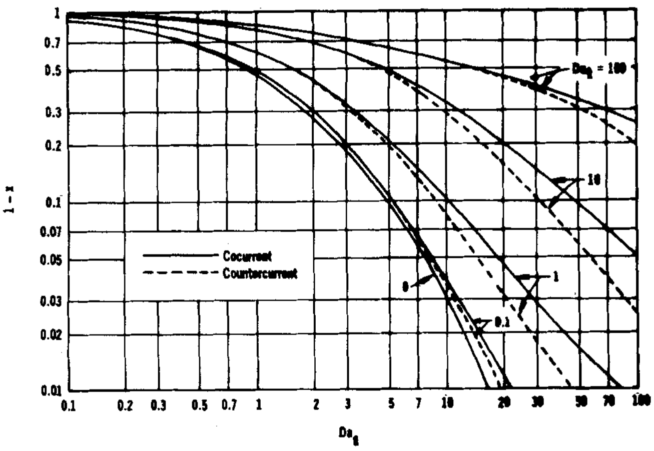

Fig. 4. Effect of Da_l on $(1 - x)$ at $y_{lA,f} = 0$, $\eta_{oA} = \eta_{oR} = 0.8$, $Pe_g = Pe_l = 1$, $Q_{RA} = H_{RA} = 1$.

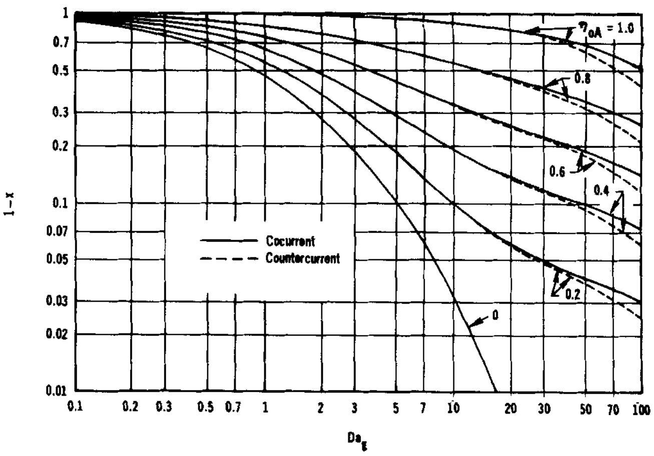

Fig. 5. Effect of η_{oA} on $(1 - x)$ at $y_{lA,f} = 0$, $\eta_{oR} = 0.8$, $Da_l = 100$, $Pe_g = Pe_l = 1$, $Q_{RA} = H_{RA} = 1$.

are much lower in Figure 3 than for Figure 1, indicating that for efficient production of product the liquid feed should contain reactant. If this is not possible, the liquid flow rate should be as low as possible.

The curves for concurrent and countercurrent flow are not greatly different for the intermediate values of Pe_g and Pe_l used. As noted later, flow direction has a large effect on x when plug flow conditions are approached. Also, the results in Figures 1 to 4 are based upon equal values for the mass transfer coefficients, since the figures are for the same values of η_{oA} and η_{oR}. The dotted and solid curves could be further displaced from each other should the mass transfer rates for countercurrent and concurrent flow be different. Available data (for example, Goto et al., 1975) suggest that $(ka)_g$, $(ka)_l$, and $(ka)_s$ are not particularly sensitive to the direction of flow. Figure 4 does indicate that the fraction of reactant removed from the gas is significantly higher for countercurrent flow, particularly at low gas rates and when the liquid feed contains no reactant.

The effect of reaction rate on the fraction removed is shown in Figure 5 through the parameter η_{oA}. Equation (31) indicates that as k increases, η_{oA} decreases from unity toward zero, with the resultant increase in x displayed in Figure 5. When $k = 0$, reactant A would be removed from the gas phase only by absorption in the liquid. This case is represented by the curve for $\eta_{oA} = 1$ in Figure 5. Hence, the difference between $(1 - x)$ from this curve and the one for any specific reaction rate is a measure of the effect of reaction on removing the reactant. For three examples of oxidation and hydrogenation in trickle-bed reactors, η_{oA} was found to be of the order of 0.8 (Goto et al., 1976).

The effect of reversibility of the reaction on reactor performance is determined by the parameter η_{oR} through Equation (33). When $\eta_{oR} = 1.0$, the reaction is irreversible and x has a maximum value, as displayed in Figure 6. These curves show that there is little difference between concurrent and countercurrent flow. Both Figures 5 and 6 are for no reactant in the liquid feed $y_{lA,f} = 0$ and for $\eta_{oA} = 0.8$.

If the reaction product is nonvolatile, the gas phase contains no R, and the parameter H_{RA} (ratio of Henry's law constants) becomes zero. Figure 7 shows that x increases as the volatility of the product increases. This is because the transfer of product from liquid to gas phase decreases C_{lR} and reduces the rate of the reverse reaction. The curves for $H_{RA} = \infty$, infinite volatility of product, in Figure 7 are the same as the curves for irreversible reaction ($\eta_{oR} = 1.0$) in Figure 6.

Figure 8 displays the effect of axial dispersion on fraction of reactant removed from the gas for a reactant-free liquid feed and for typical values of the various parameters, for example, $\eta_{oA} = \eta_{oR} = 0.8$ and $Q_{RA} = H_{RA} = 1$. For simplicity in presenting the results, the figure applies for equal values of Pe_g and Pe_l. The fraction removed increases proceeding from complete mixing toward plug flow. Also, this figure shows that large differences between concurrent and countercurrent flow occur as plug flow is approached. Where plug flow conditions

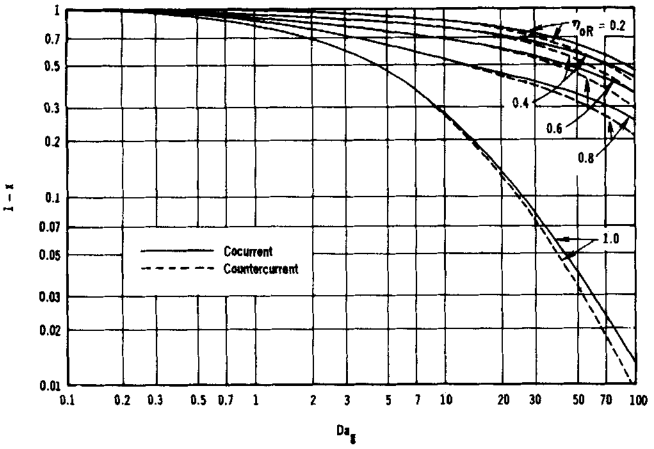

Fig. 6. Effect of η_{oR} on $(1 - x)$ at $y_{lA,f} = 0$, $\eta_{oA} = 0.8$, $Da_l = 100$, $Pe_g = Pe_l = 1$, $Q_{RA} = H_{RA} = 1$.

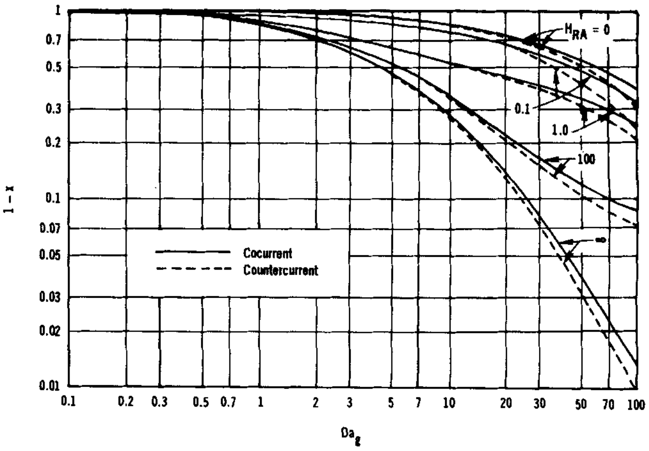

Fig. 7. Effect of H_{RA} on $(1 - x)$ at $y_{lA,f} = 0$, $\eta_{oA} = \eta_{oR} = 0.8$, $Da_l = 100$, $Pe_g = Pe_l = 1$, $Q_{RA} = 1$.

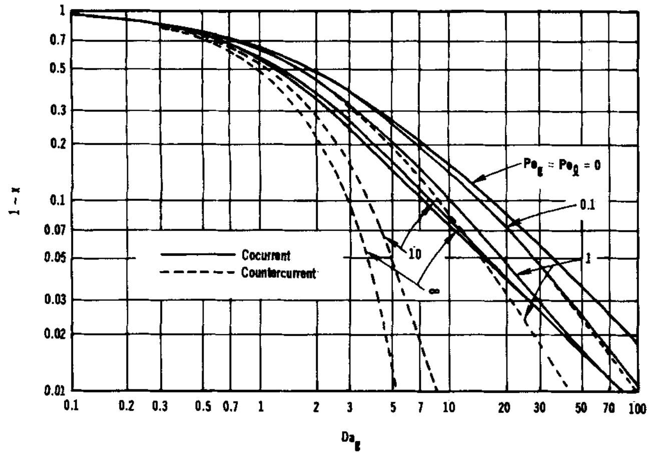

Fig. 8. Effect of Pe_g ($= Pe_l$) on $(1 - x)$ at $y_{lA,f} = 0$, $\eta_{oA} = \eta_{oR} = 0.8$, $Da_l = 1$, $Q_{RA} = H_{RA} = 1$.

Table 1. Model Parameters for Hydrogenation of α-Methyl Styrene (Satterfield et al., 1969)

t, °C	50
H^*	10.6
k, s^{-1}	16.8
η	5.75×10^{-3}
η_{bA}	1.0
η_l	0.678
η_{oA}	0.756
η_{oR}	1.0 (irreversible reaction)
$y_{lA,f}$	0.0
$y_{gA,f}$	1.0
Da_l	3.38

are approached, as in many conditions of trickle-bed operation, countercurrent flow is preferable for removing a gaseous contaminant by reaction.

APPLICATION OF THEORY

Satterfield et al. (1969) measured intrinsic kinetics for the hydrogenation of α-methyl styrene at 1 atm pressure. They also used the same catalyst for trickle-bed measurements in a single column of catalyst pellets which had a diameter of slightly more than one pellet diameter. The results showed considerable intraparticle diffusion resistance and also a significant retardation of the rate due to liquid-to-particle mass transfer. Accordingly, this system, with its large intrinsic, first-order irreversible rate, is a suitable one for evaluating the effects of reactor operating conditions according to the theory presented in this paper.

In Satterfield's work, an ample supply of pure hydrogen gas was used. Here we change the gas feed to contain a limited amount of hydrogen (in an inert gas) and the liquid feed to be free of hydrogen ($y_{lA,f} = 0$). Then, the fraction x of hydrogen removed from the gas was evaluated at 50°C as a function of gas flow rate (Da_g) for various operating conditions. Table 1 gives the properties of the reaction system and values of parameters. The fraction x was evaluated for concurrent and for countercurrent plug flow of gas and liquid from Equations (78) and (83), for complete mixing of both flows from Equation (91), and for plug flow of gas and completely mixed liquid from Equation (95), and also from equations (not shown) for completely mixed gas and plug flow of liquid. The results are shown as curves A to E in Figure 9. The largest removal of hydrogen from the gas is given at any gas rate by operating with countercurrent, plug flow of gas and liquid (curve B), while the least desirable performance corresponds to completely mixed gas and liquid phases.

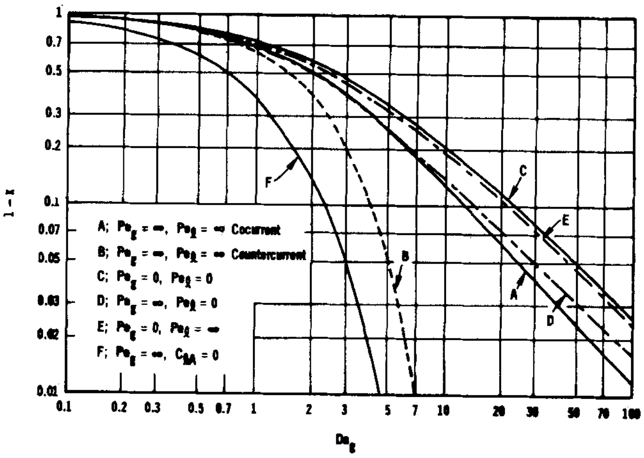

Fig. 9. Fraction x of gaseous reactant removed for various mixing conditions [based upon data of Satterfield, et al (1969); $y_{lA,f} = 0$, $\eta_{oA} = 0.756$, $\eta_{oR} = 1$, $Da_l = 3.38$].

Curve F represents a maximum attainable value of x for feasible operating conditions. This curve corresponds to plug flow of gas and a zero concentration of reactant in the liquid phase. Such a zero concentration ($y_{lA} = 0$) could be approached at a high liquid rate or for a very fast reaction ($\eta_{oA} = 0$). Figure 9 shows the results of different operating conditions as predicted by the theory presented here. The figure does not compare experimental and predicted results.

ACKNOWLEDGMENT

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NOTATION

C = concentration, mole/cm^3

Da_g = Damkoehler number based on gas flow rate, $(ka)_{lA}\eta_{bA}z_B/u_gH_A{}^*$

Da_l = Damkoehler number based on liquid flow rate, $(ka)_{lA}\eta_{bA}z_B/u_l$

D_e = effective intraparticle diffusivity, cm^2/s

E = axial dispersion coefficient, cm^2/s

H^* = Henry's law constant, C_g/C_l

H_{RA} = $H_R{}^*/H_A{}^*$

K = equilibrium constant for first-order reversible reaction

k = forward reaction rate constant, s^{-1}

$(ka)_g$ = volumetric gas-phase mass transfer coefficient (in gas-to-liquid transport), s^{-1}

$(ka)_l$ = volumetric, liquid-phase mass transfer coefficient (in gas-to-liquid transport), s^{-1}

$(ka)_s$ = volumetric, liquid-phase mass transfer coefficient (in liquid-to-solid transport), s^{-1}

N_l = rate of mass transport from gas to liquid, mole/(s)(cm^3 of bed)

N_s = rate of mass transport from liquid to solid, mole/(s)(cm^3 of bed)

Pe_g = Peclet number in gas phase, z_Bu_g/E_g

Pe_l = Peclet number in liquid phase, z_Bu_l/E_l

Q_{RA} = $(ka)_{lR}\eta_{bR}/(ka)_{lA}\eta_{bA}$

R_v = global rate based on volume of bed, mole/(s)(cm^3 of bed)

S_p = external surface area of particle, cm^2

u = superficial velocity, cm/s

V_p = volume of particle, cm^3

x = fraction of reactant removed from gas phase, Equation (70)

y_{gA} = dimensionless gas-phase concentration, $C_{gA}/C_{gA,f}$

y_{gR} = $C_{gR}H_A{}^*/C_{gA,f}H_R{}^*K$
y_{lA} = dimensionless liquid-phase concentration $C_{lA}H_A{}^*/C_{gA,f}$
y_{lR} = $C_{lR}H_A{}^*/C_{gA,f}K$
$\overline{y}$ = average dimensionless concentration defined by Equation (93)
z = axial coordinate in bed, cm
z_B = total length of bed, cm

Greek Letters

ϵ_B = void fraction in bed
ζ = dimensionless axial coordinate in reactor, z/z_B
η = catalytic effectiveness factor
η_{bA} = gas-liquid effectiveness of reactant, Equation (21)
η_{bR} = gas-liquid effectiveness of product, Equation (23)
η_l = liquid-particle effectiveness, Equation (29)
η_{oA} = overall effectiveness of reactant, Equation (31)
η_{oR} = overall effectiveness of product, Equation (33)
η_t = efficiency of three-phase reactor, Equation (71)
ϕ = Thiele modulus for first-order, reversible reaction, Equation (27)

Subscripts

A = reactant
e = exit
f = feed
g = gas phase
i = interphase
l = liquid phase
R = product
s = outer surface of solid particle

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APPENDIX A

Equations (34) to (37) may be written as

$$y_{lA} = y_{gA} + b_1 \frac{dy_{gA}}{d\zeta} + b_2 \frac{d^2y_{gA}}{d\zeta^2} \tag{A1}$$

$$y_{lR} = b_3 y_{gA} + b_4 y_{lA} + b_5 \frac{dy_{lA}}{d\zeta} + b_6 \frac{d^2y_{lA}}{d\zeta^2} \tag{A2}$$

$$y_{gR} = b_7 y_{lA} + b_8 y_{lR} + b_9 \frac{dy_{lR}}{d\zeta} + b_{10} \frac{d^2y_{lR}}{d\zeta^2} \tag{A3}$$

$$b_{11} \frac{d^2y_{gR}}{d\zeta^2} + b_{12} \frac{dy_{gR}}{d\zeta} + y_{gR} - y_{lR} = 0 \tag{A4}$$

where the coefficients $b_1, b_2, \ldots, b_{12}$ are given by the expressions

$$b_1 = \pm 1/Da_g, \quad b_2 = -1/Da_g Pe_g, \quad b_3 = -\eta_{oA}/(1-\eta_{oA}),$$
$$b_4 = 1/(1-\eta_{oA}), \quad b_5 = \eta_{oA}/(1-\eta_{oA})Da_l,$$
$$b_6 = -\eta_{oA}/(1-\eta_{oA})Da_l Pe_l, \quad b_7 = -(1-\eta_{oR})/\eta_{oR},$$
$$b_8 = 1/\eta_{oR}, \quad b_9 = 1/Da_l Q_{RA}, \quad b_{10} = -1/Da_l Q_{RA} Pe_l,$$
$$b_{11} = -H_{RA}/Da_g Q_{RA} Pe_g, \quad b_{12} = \pm H_{RA}/Da_g Q_{RA}$$

In the expressions for b_1 and b_{12}, a positive sign designates concurrent flow, and a negative sign indicates countercurrent flow.

Using Equation (A1) to eliminate y_{lA} in Equation (A2), we get

$$y_{lR} = y_{gA} + c_1 \frac{dy_{gA}}{d\zeta} + c_2 \frac{d^2y_{gA}}{d\zeta^2} + c_3 \frac{d^3y_{gA}}{d\zeta^3} + c_4 \frac{d^4y_{gA}}{d\zeta^4} \tag{A5}$$

where

$$c_1 = b_4 b_1 + b_5, \quad c_2 = b_4 b_2 + b_5 b_1 + b_6, \quad c_3 = b_5 b_2 + b_6 b_1, \quad c_4 = b_6 b_2$$

Eliminating y_{lA} and y_{lR} from Equation (A3) by using Equations (A1) and (A2), we get

$$y_{gR} = y_{gA} + d_1 \frac{dy_{gA}}{d\zeta} + d_2 \frac{d^2y_{gA}}{d\zeta^2} + d_3 \frac{d^3y_{gA}}{d\zeta^3} + d_4 \frac{d^4y_{gA}}{d\zeta^4} + d_5 \frac{d^5y_{gA}}{d\zeta^5} + d_6 \frac{d^6y_{gA}}{d\zeta^6} \tag{A6}$$

where

$$d_1 = b_7 b_1 + b_8 c_1 + b_9, \quad d_2 = b_7 b_2 + b_8 c_2 + b_9 c_1 + b_{10}$$
$$d_3 = b_8 c_3 + b_9 c_2 + b_{10} c_1, \quad d_4 = b_8 c_4 + b_9 c_3 + b_{10} c_2$$
$$d_5 = b_9 c_4 + b_{10} c_3, \quad d_6 = b_{10} c_4$$

Finally, substitution of Equations (A5) and (A6) into Equation (A4) yields Equation (46) in terms of y_{gA} and the constant coefficients $a_1, a_2, \ldots, a_9$. The values of the constants are

$$a_1 = b_{11} d_6, \quad a_2 = b_{11} d_5 + b_{12} d_6, \quad a_3 = b_{11} d_4 + b_{12} d_5 + d_6,$$
$$a_4 = b_{11} d_3 + b_{12} d_4 + d_5, \quad a_5 = b_{11} d_2 + b_{12} d_3 + d_4 - c_4,$$
$$a_6 = b_{11} d_1 + b_{12} d_2 + d_3 - c_3, \quad a_7 = b_{11} + b_{12} d_1 + d_2 - c_2$$
$$a_8 = b_{12} + d_1 - c_1, \quad a_9 = 0$$

APPENDIX B

Substituting Equation (48) for y_{gA} into Equations (A1), (A5), and (A6), we get Equations (49) to (51), respectively. The constants β_i, γ_i, and δ_i ($i = 1, 2, \ldots 8$) in these latter three equations have the values

$$\beta_i = 1 + b_1 \lambda_i + b_2 \lambda_i^2 \tag{B1}$$

$$\gamma_i = 1 + c_1 \lambda_i + c_2 \lambda_i^2 + c_3 \lambda_i^3 + c_4 \lambda_i^4 \tag{B2}$$

$$\delta_i = 1 + d_1 \lambda_i + d_2 \lambda_i^2 + d_3 \lambda_i^3 + d_4 \lambda_i^4 + d_5 \lambda_i^5 + d_6 \lambda_i^6 \tag{B3}$$

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