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Effect of Flow Direction on Conversion in Isothermal Radial Flow Fixed-Bed Reactors

Singular perturbation solutions are used to derive criteria predicting the influence of change in flow direction on the conversion in an isothermal radial-flow, fixed-bed reactor. It is shown that when the reaction does not involve a change in the number of moles, the outward flow direction is the preferred one for any reaction with a convex rate expression. The inward flow direction is a better choice for any reaction with a concave rate expression. A more intricate behavior occurs for reactions involving a change in volume. Analytical approximations and numerical solutions indicate that the influence of flow direction on the conversion is rather small.

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SCOPE

Cylindrical or spherical radial-flow, packed-bed reactors (RFBR) are used in several important industrial processes. Previous studies (Raskin et al., 1968; Hlavacek and Kubicek, 1972; Calo, 1978) pointed out that when an exothermic reaction is carried out in these reactors, the conversion as well as the yield of a desired product depend on the direction of flow. Duduković and Lamba (1975) used numerical solutions to show that when an isothermal n-th order reaction ($n \neq 1$) is carried out in a cylindrical RFBR, the conversion depends on the flow direction.

Analysis of the governing steady-state equations indicates that the flow direction affects the conversion only when the axial dispersion is important. When the reaction does not involve a change in volume, the flow direction affects the conversion for all kinetic rate expressions except for a first and a zeroth-order reaction. When the reaction involves a change in volume, the conversion is dependent on the flow direction for all rate expressions except for a zeroth-order reaction.

The purpose of this work is to enhance our understanding of the causes and magnitude of the influence of flow direction on the conversion in a RFBR. The method of matched asymptotic expansions is used to obtain approximate solutions of the governing nonlinear differential equations and to derive criteria predicting the pereferred flow direction for reactions with no change in the number of moles. Numerical simulations are used to find the preferred flow direction for reactions involving a change in volume.

CONCLUSIONS AND SIGNIFICANCE

It is shown that for all isothermal reactions, which do not involve a change in volume, the outward RFBR yields a higher conversion than the inward RFBR for reactions with convex rate expressions, such as n-th order reactions with $n > 1$. The inward RFBR is preferred when the kinetic expression is concave. For large Peclet numbers (small deviation from plug flow), simple criteria are derived predicting the difference in conversion between the two flow directions for any kinetic rate expression when either the Bodenstein number is a constant (Eq. 44) or the radial dispersion coefficient is a constant (Eq. 54). For an n-th order reaction, these expressions become Eqs. 55 and 56, respectively.

It is shown that for a first-order reaction involving an increase in the number of moles, the outward flow gives a higher conversion than the inward flow. The converse is true for a first-order reaction with a decrease in the number of moles.

The above findings lead to the prediction that the outward flow direction is preferred for any reaction with a convex rate expression which involves an increase in volume. Similarly, the inward flow is the preferred direction for any reaction with a

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concave rate expression which involves a decrease in volume. In all other cases, the preferred flow direction depends on the magnitude of the kinetic parameters and the radial Peclet number. Numerical simulations are used to verify these predictions.

Analytical approximations and numerical solutions indicate that the change in the conversion upon a flow reversal in an isothermal RFBR is rather small (at most, a few percent). This additional conversion may be attained with no additional operation or equipment expenses and should be exploited, whenever it is possible.

Cylindrical or spherical radial flow packed-bed reactors are used for a variety of industrial applications such as ammonia and methanol synthesis, catalytic reforming and vapor-phase desulfurization (Strauss and Budde, 1978). These reactors enable a reduction in the pressure drop, which in turn facilitates use of smaller catalytic pellets with higher effectiveness factors and increased production rate per unit volume of the reactor. The advantages of a RFBR were discussed by Raskin et al. (1968), Hlavacek and Kubicek (1972), Duduković and Lamba (1975), and Strauss and Budde (1978).

A typical RFBR consists of a hollow cylindrical or spherical vessel packed with catalytic particles. When an exothermic reaction is carried out in a RFBR, the conversion and yield often depend on the direction of the flow (Raskin et al., 1968; Hlavacek and Kubicek, 1972; Calo, 1978). Duduković and Lamba (1975) used numerical simulations to show that when an isothermal n-th order reaction ($n \neq 1$) is carried out in a cylindrical RFBR, the conversion depends on the direction of the flow. This "asymmetry" of the reactor has important implications on the design and operation of a RFBR.

The purpose of this study is to determine the influence of changes in the flow direction on the conversion in an isothermal, cylindrical or spherical RFBR in which a single reaction occurs, accompanied by radial dispersion of material and change of volume, and to develop a better understanding of the factors responsible for this effect. To this end analytical criteria are derived predicting the magnitude of the difference in the conversion between inward and outward flow for reactions which do not involve any change in volume. Numerical simulations are used to assess the difference in the conversion for reactions involving a change in volume. Qualitative information about the nature of the governing equations is utilized to isolate special kinetic expressions for which a change in the flow direction does not affect the conversion. In addition, a simple criterion is derived for predicting the conditions under which radial dispersion of material has a negligible impact on the conversion in a RFBR.

DEVELOPMENT OF A MATHEMATICAL MODEL

We describe the RFBR by a pseudo-homogeneous model assuming that the pressure drop across the bed is small and that the flow distribution is uniform. We assume that a single, isothermal reaction

$$A \rightarrow (\nu + 1)B$$

occurs, that the gaseous reaction mixture behaves as an ideal gas, and that the feed consists of pure A.

The steady-state material balance for an outward RFBR is:

$$\frac{d}{dr}\left(-Dr^s \frac{dC_A}{dr}\right) + \frac{d}{dr}(ur^s C_A) + r^s g(C_A) = 0 \qquad (1)$$

where

$$s = \begin{Bmatrix} 1 & \text{for a cylindrical RFBR} \\ 2 & \text{for a spherical RFBR} \end{Bmatrix} \qquad (2)$$

and $g(C_A)$ is the rate of consumption of A.

The corresponding inlet and outlet boundary conditions are:

$$u(C_{Af} - C_A) = -D\frac{dC_A}{dr} \qquad r = R_1 \qquad (3)$$

$$\frac{dC_A}{dr} = 0 \qquad r = R_2 \qquad (4)$$

To solve Eq. 1 we need to determine the dependence of the molar average velocity u on the radial position r. A material balance for species A from the inlet to radial position r gives:

$$N(R_1) - G = N(r)y + a\left(-D\frac{dC_A}{dr}\right) \qquad (5)$$

where N is the total molar flow rate, G the number of moles of consumed reactant and y the mole fraction of A. Overall material balance (assuming that the dispersion coefficients of A and B are the same) gives:

$$N(R_1) + G\nu = N(r) \qquad (6)$$

The molar average velocity u is defined as:

$$u = \frac{N(r)}{aC_{Af}} \qquad (7)$$

It follows from Eqs. 5 to 7 that

$$u = \frac{N(R_1)\,(1 + \nu) + \nu a D C'_A}{a(C_{Af} + \nu C_A)} \qquad (8)$$

where the prime denotes differentiation.

When the Reynolds number is larger than unity, the Bodenstein number:

$$N_{Bo} = \frac{ud_p}{D} \qquad (9)$$

is a constant equal to about two (Himmelblau and Bischoff, 1968, p. 319). (Note that in some texts the Bodenstein number is defined as the Peclet number based on particle diameter.)

Substitution of Eq. 9 into 8 gives:

$$ur^s = \frac{u_1 R_1^s C_{Af}(1 + \nu)}{C_{Af} + \nu C_A - \nu d_p C'_A/N_{Bo}} \qquad (10)$$

Substitution of Eq. 10 into Eq. 1 and simplification yields:

$$u_1 R_1^s C_{Af}^2(1 + \nu)(d_p C''_A/N_{Bo} - C'_A) - r^s g(C_A)(C_{Af} + \nu C_A - \nu d_p C'_A/N_{Bo})^2 = 0 \qquad (11)$$

Defining the dimensionless variables:

$$N_{Da} = \frac{R_2^{s+1} g(C_{Af})}{u_1 R_1^s C_{Af}} \qquad N_{Pe} = \frac{u_2 R_2}{D_2}$$

$$y = C_A/C_{Af} \qquad f(y) = g(yC_{Af})/g(C_{Af}) \qquad (12)$$

$$\xi = r/R_2 \qquad \xi_1 = R_1/R_2$$

Eq. 11 and the corresponding boundary conditions become:

$$\frac{1}{N_{Pe}} y'' - y' - \frac{N_{Da}\xi^s}{(1 + \nu)} f(y)\,(1 + \nu y - \nu y'/N_{Pe})^2 = 0 \qquad (13)$$

(For comments on Eq. 13, see Appendix.)

$$y'/N_{Pe} = y - 1 \qquad \xi = \xi_1 \tag{14}$$

$$y' = 0 \qquad \xi = 1 \tag{15}$$

A similar derivation of the material balance for the inward RFBR gives:

$$w''/N_{Pe} + w' - \frac{N^*_{Da}\xi^s}{(1 + \nu)} f(w)\,(1 + \nu w + \nu w'/N_{Pe})^2 = 0 \tag{16}$$

where w denotes the dimensionless reactant concentration for the inward RFBR and

$$N^*_{Da} = \frac{R_2^{s+1}g(C_{Af})}{u_2R_2^sC_{Af}} = \frac{R_2g(C_{Af})}{u_2C_{Af}} = \frac{u_1\xi_1^sN_{Da}}{u_2} \tag{17}$$

The corresponding boundary conditions are:

$$w' = 0 \qquad \xi = \xi_1 \tag{18}$$

$$w'/N_{Pe} = 1 - w \qquad \xi = 1 \tag{19}$$

When the performance of an outward RFBR and an inward RFBR is compared at the same gas feed rate, N^*_{Da} is equal to N_{Da}. Hereafter we examine such cases.

For Reynolds numbers smaller than unity the axial dispersion coefficient is a constant independent of the velocity (Himmelblau and Bischoff, 1968). In this case,

$$ur^s = \frac{u_1R_1^sC_{Af}(1 + \nu) + \nu Dr^sC'_A}{C_{Af} + \nu C_A} \tag{20}$$

and the material balance for the outward RFBR becomes

$$[(1 + \nu y)\,(\xi^sy')' - \nu\xi^sy'^2]/N^*_{Pe} - (1 + \nu)y' - N_{Da}\xi^sf(y)\,(1 + \nu y)^2 = 0 \tag{21}$$

where $N^*_{Pe} = u_1R_1^s/(DR_2^{s-1})$

subject to boundary condition (Eq. 15) and

$$\xi_1^sy'/N^*_{Pe} = y - 1 \qquad \xi = \xi_1 \tag{22}$$

Similarly, the material balance for the inward flow RFBR is

$$[(1 + \nu w)\,(\xi^sw')' - \nu\xi^sw'^2]/N_{Pe} + (1 + \nu)w' - N_{Da}\xi^sf(w)\,(1 + \nu w)^2 = 0 \tag{23}$$

subject to boundary conditions (18 and 19). Once again we note that, when the performance of the outward and inward RFBR is compared for the same gas feed rate, N_{Pe} is equal to N^*_{Pe}.

QUALITATIVE ANALYSIS OF SPECIAL CASES

We analyze now the qualitative behavior of several special cases in order to develop a better understanding of the processes which may cause the conversion to depend on the flow direction.

Plug Flow With No Dispersion of Material ($N_{Pe} \to \infty$)

In the limiting case of no radial dispersion, the material balance for the outward RFBR reduces to:

$$(1 + \nu)y' + N_{Da}\xi^sf(y)\,(1 + \nu y)^2 = 0 \tag{24}$$

$$y = 1 \qquad \text{at } \xi = \xi_1 \tag{25}$$

while that for the inward RFBR becomes:

$$(1 + \nu)w' - N_{Da}\xi^sf(w)\,(1 + \nu w)^2 = 0 \tag{26}$$

$$w = 1 \qquad \text{at } \xi = 1 \tag{27}$$

Integration of Eqs. 24 and 26 gives:

$$\int_1^{y(1)} \frac{dy}{f(y)\,(1 + \nu y)^2} = \frac{-N_{Da}}{(1 + \nu)}\int_{\xi_1}^1 \xi^sd\xi = \int_1^{w(\xi_1)} \frac{dw}{f(w)\,(1 + \nu w)^2} \tag{28}$$

It follows from Eq. 28 that

$$y(1) = w(\xi_1) \tag{29}$$

We conclude that in the absence of radial dispersion of material, the conversion in an isothermal RFBR is independent of the flow direction.

Zeroth-Order Kinetics

Consider a zeroth-order reaction occurring in a RFBR with a constant Bodenstein number and such that $y(1)w(\xi_1) > 0$. Here, steady-state Eqs. 13 and 16 may be rewritten as:

$$\frac{y''/N_{Pe} - y'}{(1 + \nu y - \nu y'/N_{Pe})^2} = \frac{N_{Da}\xi^sH(y)}{(1 + \nu)} \tag{30}$$

$$\frac{w''/N_{Pe} + w'}{(1 + \nu w + \nu w'/N_{Pe})^2} = \frac{N_{Da}\xi^sH(w)}{(1 + \nu)} \tag{31}$$

where H is the Heavyside's function.
Subtracting Eq. 31 from Eq. 30 and integration between ξ_1 and 1 gives:

$$\left.\frac{1}{1/\nu + y - y'/N_{Pe}}\right|_{\xi_1}^{1} = \left.\frac{1}{1/\nu + w + w'/N_{Pe}}\right|_{1}^{\xi_1} \tag{32}$$

Using boundary conditions (Eqs. 14, 15, 18 and 19) Eq. 32 gives:

$$y(1) = w(\xi_1) \tag{33}$$

One may prove by contradiction that it is impossible for either $y(1)$ or $w(\xi_1)$ to vanish unless Eq. 33 holds.

For the constant dispersion coefficient case equations Eqs. 21 and 23 may be rewritten as:

$$\frac{1}{N_{Pe}}\left(\frac{\xi^sy'}{1 + \nu y}\right)' + \left(\frac{1 + \nu}{\nu(1 + \nu y)}\right)' = N_{Da}\xi^sH(y) \tag{34}$$

$$\frac{1}{N_{Pe}}\left(\frac{\xi^sw'}{1 + \nu w}\right)' - \left(\frac{1 + \nu}{\nu(1 + \nu w)}\right)' = N_{Da}\xi^sH(w) \tag{35}$$

and the same technique may be used to prove that Eq. 33 is valid also in this case. We conclude that for a zeroth-order reaction the conversion is independent of the flow direction. In fact, it can be shown that:

$$w(\xi_1) = y(1) = \frac{[1 - N_{Da}(1 - \xi_1^{s+1})/(s + 1)]}{[1 + \nu N_{Da}(1 - \xi_1^{s+1})/(s + 1)]}\,H\left[1 - \frac{N_{Da}(1 - \xi_1^{s+1})}{(s + 1)}\right] \tag{36}$$

First-Order Reaction With No Change in Number of Moles

Analytical solutions of the steady-state equations describing a first-order reaction occurring in a RFBR without any change in the number of moles ($\nu = 0$) are attainable except for a spherical RFBR with a constant dispersion coefficient. These solutions consist of rather cumbersome expressions and will not be reported here. However, the influence of flow reversal may be determined in these cases without obtaining these complex solutions.

Consider first the constant dispersion coefficient case. Steady-state Eqs. 21 and 23 reduce to:

$$(\xi^sy')'/N_{Pe} - y' = N_{Da}\xi^sy \tag{37}$$

$$(\xi^sw')'/N_{Pe} + w' = N_{Da}\xi^sw \tag{38}$$

Multiplying Eq. 37 by w and Eq. 38 by y, subtracting the second equation from the first and integration between ξ_1 to 1 gives:

$$\int_{\xi_1}^{1} \{[w(\xi^s y')' - y(\xi^s w')']/N_{Pe} - (yw)'\}d\xi = 0 \tag{39}$$

Integration of Eq. 39 and use of boundary conditions (Eqs. 15, 18, 22 and 19) gives:

$$w(\xi_1) = y(1) \tag{40}$$

The same result may be proved similarly for the constant Bodenstein number case. We conclude that for a first-order reaction, not involving a change in the number of moles, the conversion in the RFBR is independent of the flow direction.

INFLUENCE OF FLOW DIRECTION ON CONVERSION ($\nu = 0$)

Analytical solutions of Eqs. 13, 16, 21, and 23 for $\nu = 0$ are not attainable except for zero and first-order reactions. However, approximate solutions may be attained for either small or large N_{Pe} by the method of singular perturbations (Burghardt and Zaleski, 1971).

The axial dispersion model is best suited for describing small deviations from plug flow. Thus, we treat here only the practical case of large Peclet numbers. Using the method of matched asymptotic expansions (Nayfeh, 1973, p. 110; Van Dyke, 1964, p. 77), the following one-term approximate solution of Eq. 13 to Eq. 15 is attained for large N_{Pe}:

$$y(\xi) = y_p(\xi) + \frac{N_{Da}f[y_p(\xi)]}{N_{Pe}}\left\{-\xi^s - \int_{\xi_1}^{\xi} x^s d\ln f[y_p(x)]\right\} + \frac{N_{Da}f[y_p(1)]}{N_{pe}}\exp[N_{Pe}(\xi - 1)] \tag{41}$$

where $y_p(\xi)$ is the plug flow solution for a RFBR in which no dispersion exists. The solution is valid only if $f[y_p(x)]$ does not vanish in $\xi_1 < x < 1$. Such an exceptional case may happen for a reaction with an order less than unity and a large Damköhler number. However, this mathematical restriction does not pose any constraint in applications, as it is well known that an n-th order rate expression with $n < 1$ is not valid for very small concentrations.

The concentration of the effluent is:

$$y(1) = y_p(1) - \frac{N_{Da}f[y_p(1)]}{N_{Pe}}\int_{\xi_1}^{1} x^s d\ln f[y_p(x)] \tag{42}$$

Similarly, for the inward RFBR

$$w(\xi_1) = y_p(1) + \frac{N_{Da}f[y_p(1)]}{N_{Pe}}\int_{\xi_1}^{1} x^s d\ln f[w_p(x)] \tag{43}$$

To evaluate the preferred flow direction, we subtract Eq. 43 from Eq. 42 to obtain after integration by parts:

$$y(1) - w(\xi_1) = \frac{N_{Da}f[y_p(1)]}{N_{Pe}}\left\{\int_{\xi_1}^{1} sx^{s-1}F_1(x)dx - (1 - \xi_1^s)\ln[f(1)f(y_p(1))]\right\} \tag{44}$$

where

$$F_1(x) = \ln\{f[y_p(x)]f[w_p(x)]\} \tag{45}$$

It is shown in the Appendix that if $f(y)$ is a convex twice differentiable function, i.e.,

$$f''(y) > 0 \qquad \text{for} \quad 0 < y < 1 \tag{46}$$

then

$$F_1(x) < \ln\{f(1)f[y_p(1)]\} \text{ for } 0 < x < 1 \tag{47}$$

Thus,

$$\int_{\xi_1}^{1} sx^{s-1}F_1(x)dx < (1 - \xi_1^s)\ln\{f(1)f[y_p(1)]\}. \tag{48}$$

Substitution of Eq. 48 into Eq. 44 gives:

$$y(1) < w(\xi_1) \tag{49}$$

and the outward flow gives a higher conversion. Similarly, it can be proved that if $f(y)$ is a twice differentiable concave function, i.e.,

$$f''(y) < 0 \qquad \text{for } 0 < y < 1 \tag{50}$$

then

$$y(1) > w(\xi_1) \tag{51}$$

and the inward flow gives a higher conversion.

When the dispersion coefficient is independent of the velocity, a one term expansion gives:

$$y(1) = y_p(1) - \frac{N_{Da}f[y_p(1)]}{N_{Pe}}\int_{\xi_1}^{1} x^{2s} d\ln f[y_p(x)] \tag{52}$$

$$w(\xi_1) = y_p(1) + \frac{N_{Da}f[y_p(1)]}{N_{Pe}}\int_{\xi_1}^{1} x^{2s} d\ln f[w_p(x)] \tag{53}$$

Subtracting Eq. 53 from Eq. 52 and integration by parts gives:

$$y(1) - w(\xi_1) = \frac{N_{Da}f[y_p(1)]}{N_{Pe}}\left\{\int_{\xi_1}^{1} 2sx^{2s-1}F_1(x)dx - (1 - \xi_1^{2s})\ln[f(1)f[y_p(1)]]\right\} \tag{54}$$

It can be shown that also in this case Eq. 49 holds for any kinetic expression satisfying Eq. 46, while Eq. 51 holds whenever Eq. 50 is satisfied.

In the above analysis we assumed that Eqs. 13 and 16 have a unique solution. This will be the case if the rate expression $f(y)$ is either strictly convex or concave for all y in (0, 1) (Luss, 1968).

For an n-th order reaction ($n \neq 1$), Eqs. 44 and 54 become:

$$y(1) - w(\xi_1) = \frac{nN_{Da}^2}{N_{Pe}}\left[1 + \frac{(n - 1)N_{Da}(1 - \xi_1^{s+1})}{s + 1}\right]^{\frac{n}{1-n}} \times \int_{\xi_1}^{1}\left\{\frac{\xi^{2s}}{1 + \frac{(n - 1)N_{Da}}{s + 1}(\xi^{s+1} - \xi_1^{s+1})} - \frac{\xi^{2s}}{1 + \frac{(n - 1)N_{Da}}{(s + 1)}(1 - \xi^{s+1})}\right\}d\xi \tag{55}$$

$$y(1) - w(\xi_1) = \frac{nN_{Da}^2}{N_{Pe}}\left[1 + \frac{(n - 1)N_{Da}(1 - \xi_1^{s+1})}{s + 1}\right]^{\frac{n}{1-n}} \times \int_{\xi_1}^{1}\left\{\frac{\xi^{3s}}{1 + \frac{(n - 1)N_{Da}}{s + 1}(\xi^{s+1} - \xi_1^{s+1})} - \frac{\xi^{3s}}{1 + \frac{(n - 1)N_{Da}(1 - \xi^{s+1})}{(s + 1)}}\right\}d\xi \tag{56}$$

We conclude that the conversion in an outward RFBR with high Peclet number exceeds that for the inward flow for all convex kinetic rate expressions, i.e., those satisfying Eq. 46. An important case for which this result applies is an n-th order reaction with $n > 1$. On the other hand, for all concave rate expressions which satisfy Eq. 50 the inward RFBR gives a higher conversion than the outward RFBR. An important case for which this result applies is an n-th order reaction with $0 < n < 1$, for which the reactant concentration does not vanish in the reactor.

Numerical simulations indicate that the accuracy of the one-term expansion is improved with increasing Peclet numbers and

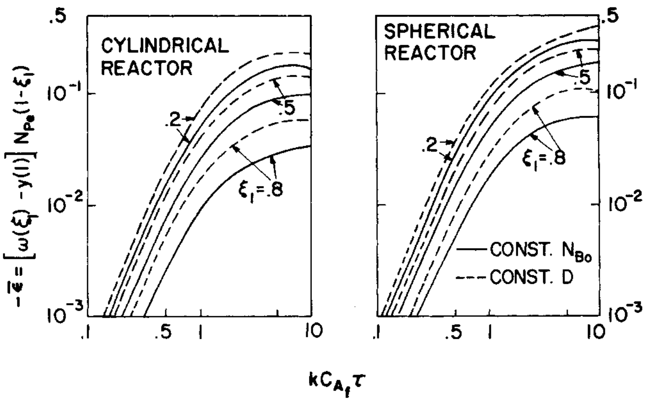

Figure 1. Difference in conversion between the two flow directions for a second-order reaction for large Peclet numbers according to Eqs. 55 and 56.

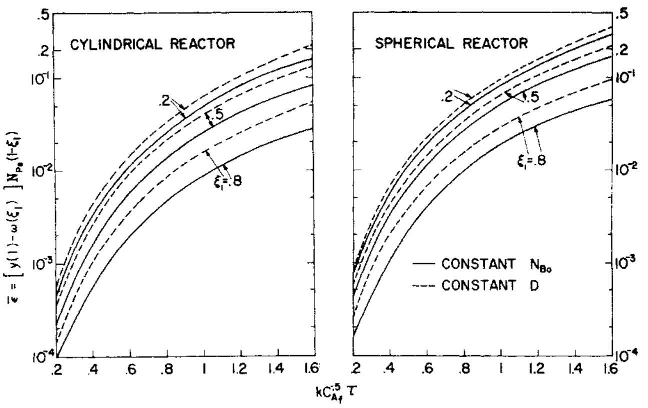

Figure 2. Difference in conversion between the two flow directions for a half-order reaction for large Peclet numbers according to Eqs. 55 and 56.

decreasing values of $kC_{A_f}^{n-1}\tau = N_{Da}(1 - \xi_1^{s+1})/(s + 1)$. Calculations for a second order reaction indicate that for any $N_{Pe} > 20$ and $kC_{A_f}\tau < 1$ the difference between the exact value of either $y(1)$ or $w(\xi_1)$ and the approximate value is less than 1%. However, the percentage error in $\epsilon = y(1) - w(\xi_1)$ is much larger. For example, for $kC_{A_f}\tau = 1$ and N_{Pe} of 20, 100, 500 the percentage error in ϵ is 125, 21 and 1.6, respectively. The calculations indicate that the value of ϵ as calculated by Eqs. 44 and 54 for n-th order reactions always exceeds the exact value, suggesting that the above equation gives a conservative estimate.

The one-term solutions (Eqs. 55 and 56) predict that for an n-th order reaction the value of $[y(1) - w(\xi_1)]N_{Pe}$ depends only on $kC_{A_f}^{n-1}\tau = N_{Da}(1 - \xi_1^{s+1})/(s + 1)$ and on ξ_1. The Peclet number is defined with R_2 being the characteristic length. However, it is customary to use the actual length of the bed, $R_2(1 - \xi_1)$, as the characteristic length in the definition of the Peclet number. Thus, we describe in Figure 1, the dependence of:

$$\bar{\epsilon} = [y(1) - w(\xi_1)]N_{Pe}(1 - \xi_1) \tag{57}$$

on $kC_{A_f}^{n-1}\tau$ and ξ_1 for a second order reaction, carried out in a cylindrical and spherical RFBR. The graphs indicate that $\bar{\epsilon}$ increases monotonically with increasing values of $kC_{A_f}^{n-1}\tau$ and with decreasing values of ξ_1. In all these cases, the conversion in the outward flow is higher than that for inward flow, i.e., $w(\xi_1) > y(1)$, as predicted by Eq. 49.

Figure 2 is a similar graph for a reaction of half order. The trends are similar to those found for the second order reaction. However, in this case the conversion in the inward RFBR is higher than that in the outward RFBR, i.e., $y(1) > w(\xi_1)$, as predicted by Eq. 51.

Figures 1 and 2 indicate that the maximal absolute value of $\bar{\epsilon}$ is less than $1/N_{Pe}(1 - \xi_1)$ and this approximation is good only for large Peclet numbers. These graphs should be useful for a rapid estimation of the influence of flow direction on the conversion in a RFBR. Exact numerically computed values of $w(\xi_1) - y(1)$ will be presented later.

INFLUENCE OF CHANGE IN VOLUME ($\nu \neq 0$)

When the reaction involves a change in the number of moles ($\nu \neq 0$) the complex interaction among the dispersion, change in gas volume and change in flow cross-section affect the conversion in a much more intricate fashion than in the $\nu = 0$ case. Here, the conversion depends on the flow direction for all kinetic rate expressions except for the zeroth-order case.

To illustrate the new features introduced by the change in volume we consider the case of a first-order reaction, for which the conversion is independent of flow direction if the reaction does not involve a change in the number of moles. For the outward RFBR with a constant N_{Bo} matched asymptotic expansion solution of Eq. 13 subject to boundary conditions Eqs. 14 and 15 gives:

$$\begin{aligned} y(\xi) &= y_p(\xi) \\ &\quad + \frac{N_{Da}}{(1 + \nu)N_{Pe}} \Big\{ y_p(\xi)[1 + y_p(\xi)]^2 \Big[-\xi^s \\ &\quad - \int_{\xi_1}^{\xi} t^s d\ln y_p(t) \Big] \\ &\quad + y_p(1)[1 + \nu y_p(1)]^2 \exp[(\xi - 1)N_{Pe}] \Big\} \end{aligned} \tag{58}$$

Similarly, for the inward RFBR one gets:

$$\begin{aligned} w(\xi) &= w_p(\xi) \\ &\quad + \frac{N_{Da}}{(1 + \nu)N_{Pe}} \Big\{ w_p(\xi)[1 + \nu w_p(\xi)]^2 \Big[-\xi^s \\ &\quad - \int_{1}^{\xi} t^s d\ln w_p(t) \Big] \\ &\quad + w_p(\xi_1)[1 + \nu w_p(\xi_1)]^2 \xi_1^s \exp[N_{Pe}(\xi_1 - \xi)] \end{aligned} \tag{59}$$

Using the fact that:

$$w_p(\xi_1) = y_p(1) \tag{60}$$

Eqs. 58 and 59 give

$$w(\xi_1) - y(1) = \frac{N_{Da}}{(1 + \nu)N_{Pe}} y_p(1)[1 + \nu y_p(1)]^2 I \tag{61}$$

where

$$\begin{aligned} I &= \int_{\xi_1}^{1} \xi^s (d\ln w_p + d\ln y_p) \\ &= (1 - \xi_1^s)\ln y_p(1) + s \int_{\xi_1}^{1} \xi^{s-1} F_2(\xi) d\xi \end{aligned} \tag{62}$$

and

$$F_2(\xi) = -\ln[y_p(\xi)w_p(\xi)] \tag{63}$$

It is proved in the Appendix that when $\nu > 0$

$$w(\xi_1) > y(1) \tag{64}$$

and the outward flow direction is the preferred one. When $\nu < 0$

$$w(\xi_1) < y(1) \tag{65}$$

and the inward flow gives the higher conversion. It is proved in the Appendix that Eqs. 64 and 65 hold also when D is a constant independent of the gas velocity.

A similar analysis is not possible for a general kinetic rate expression. However, the results for the $\nu = 0$ case and the first-order reaction with $\nu \neq 0$ lead one to expect that the outward flow direction will give a higher conversion for reactions with a convex rate expression and $\nu > 0$. Similarly, the inward flow direction is expected to be the preferred one for

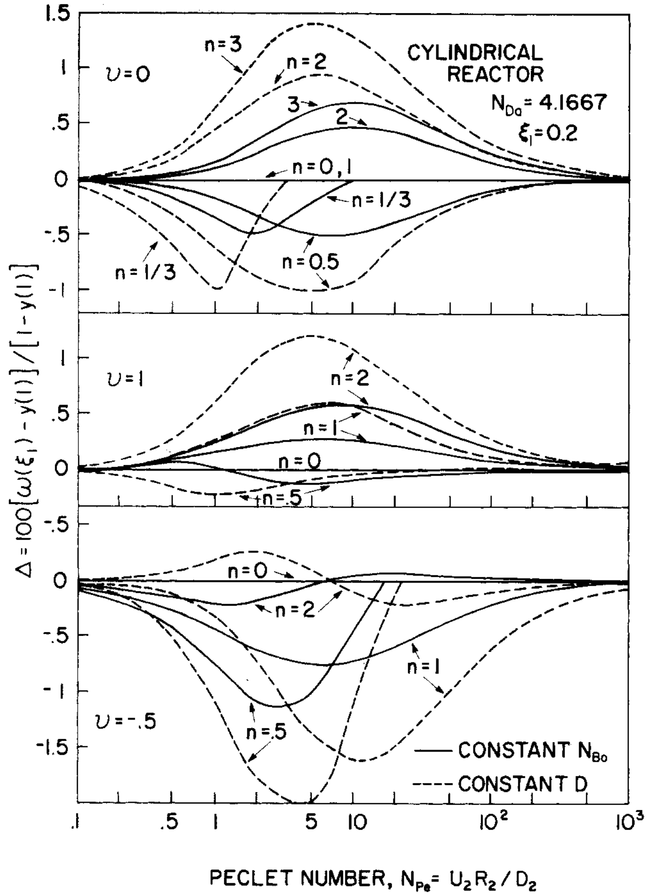

Figure 3. Difference in conversion between the two flow directions in a cylindrical RFBR as a function of the Peclet number, reaction order and change in moles.

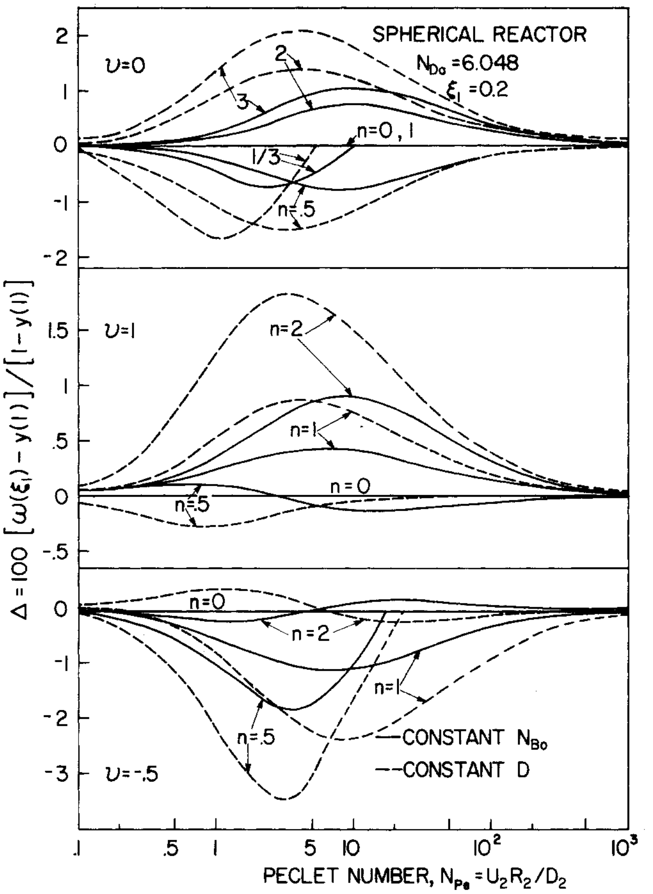

Figure 4. Difference in conversion between the two flow directions in a spherical RFBR as a function of the Peclet number, reaction order and change in moles.

reaction with a concave rate expression and $\nu < 0$. In all other cases we can not predict *a priori* the preferred flow direction.

NUMERICAL RESULTS AND DISCUSSION

Analytical solutions of the steady-state Eqs. 13, 16, 21 and 23 are not obtainable when the reaction is accompanied by a change in the number of moles ($\nu \neq 0$). Only in the special case of a zeroth-order reaction it is still possible to derive an expression predicting the outlet concentration (Eq. 36). Numerical solutions of the steady-state equations were carried out using the orthogonal collocation method (Villadsen and Michelsen, 1978). A six and ten decimal point accuracy was found using 10 and 15 collocation points, respectively.

Figures 3 and 4 describe the dependence of:

$$\Delta = \frac{w(\xi_1) - y(1)}{[1 - y(1)]} 100 \tag{67}$$

on the Peclet number in cylindrical and spherical RFBR for various values of ν and reaction orders.

The computations indicate that Δ is usually rather small, i.e., the change in the conversion following a reversal in the flow direction in an isothermal RFBR is at most a few percent. This additional conversion is obtained without any additional construction or operational expense and should be exploited whenever it is possible.

The numerical calculations confirm the predictions of the singular perturbation analysis that when the reaction does not cause any volume change ($\nu = 0$), the conversion is higher for the outward flow for reactions with a convex kinetic rate expression, and for the inward flow when the kinetic rate expression is concave.

The graphs show that for reactions with a fractional order ($n < 1$), Δ vanishes in certain cases for large Peclet numbers. In these special cases complete conversion is obtained for both inward and outward RFBR.

The computations verify the prediction that for a reaction with convex kinetics and $\nu > 0$, the outward flow direction is always preferable, i.e., $w(\xi_1) > y(1)$, while for a reaction with a concave rate expression and $\nu < 0$ the inward flow direction is to be preferred. The cases of $n = 2$, $\nu = 1$ and $n = 0.5$, $\nu = -0.5$ in Figures 3 and 4 clearly illustrate this behavior. On the other hand, when the kinetic expression is convex and $\nu < 0$, or when the kinetic expression is concave and $\nu > 0$, the sign of Δ depends on the Peclet number. This behavior is illustrated in Figures 3 and 4 by the cases of $n = 2$, $\nu = -0.5$ and $n = 0.5$, $\nu = 1$.

We propose now a heuristic explanation of the influence of the flow reversal on the conversion when $\nu = 0$, i.e., the residence time is independent of the flow direction. When N_{Bo} or the dispersion coefficient D are constant, the dispersion term at each point is proportional to ξ^s/N_{Pe} and increases monotonically with ξ. Thus, in the outward flow the mixing occurs later than in the inward flow, and it is well known (Zweitering, 1959) that for a reaction with a convex rate expression, a delay in the mixing improves the conversion.

Numerical simulations as well as the perturbation analysis indicate that the influence of flow direction on the conversion for the constant dispersion coefficient case is usually larger than that for the constant N_{Bo} case. This comparison is somewhat misleading since the radial Peclet number, (uR_2/D) is independent of the radial position when N_{Bo} is constant, while it is a monotonic increasing function of the radial position when D is constant. The Peclet numbers in the figures and in Eqs. 13, 16, 21 and 23 are based on the condition at the inlet to the reactor. Thus, for the same Peclet number, the average radial Peclet number in the reactor for the constant D case differs from that for the constant N_{Bo} case.

CRITERIA PREDICTING NEGLIGIBLE IMPACT OF RADIAL DISPERSION

The analysis has shown that radial dispersion affects the performance of RFBR and is responsible for the influence of flow direction on the conversion. We present here criteria predicting the conditions under which the radial dispersion has a negligible influence on the conversion in a RFBR for a reaction which does not involve any change in volume, using a technique developed by Mears (1971).

Consider first an outward RFBR in which an isothermal n-th order reaction occurs with no change in volume at a space time τ and a constant N_{Bo}. A one-term perturbation solution gives:

$$\frac{y(1)}{y_p(1)} = 1 + \frac{n(s+1)^2(C_{Af}^{n-1}k\tau)^2 I_o}{(1-\xi_1^{s+1})^2[1+(n-1)C_{Af}^{n-1}k\tau]N_{Pe}} \tag{68}$$

where

$$I_o = \int_{\xi_1}^{1} \frac{\xi^{2s}d\xi}{1 + \dfrac{(n-1)C_{Af}^{n-1}k\tau(\xi^{s+1}-\xi_1^{s+1})}{(1-\xi_1^{s+1})}} \tag{69}$$

The corresponding exit concentration from a plug flow reactor is:

$$y_p(1) = [1+(n-1)C_{Af}^{n-1}k\tau]^{\frac{1}{1-n}} H[1+(n-1)C_{Af}^{n-1}k\tau] \tag{70}$$

If the same reaction is carried out in an identical RFBR in which no axial dispersion exists, the same conversion is obtained for a space time τ_p, such that

$$\tau_p = \tau(1-\delta) \tag{71}$$

We define the influence of the axial dispersion to be negligible whenever

$$\delta < 0.05 \tag{72}$$

Noting that by definition

$$y_p(1, \tau_p) = y(1,\tau) \tag{73}$$

it follows from Eqs. 68, 70 and the relation

$$(1+x)^p \approx 1 + px \qquad x \ll 1 \tag{74}$$

that Eq. 72 is satisfied if

$$N_{Pe} \triangleq \frac{N_{Bo}R_2}{d_p} > \frac{20nC_{Af}^{n-1}k\tau(s+1)^2}{(1-\xi_1^{s+1})^2} I_o \tag{75}$$

A similar analysis indicates that criterion (Eq. 75) is valid also for the inward RFBR after replacing I_o with I_i, where

$$I_i = \int_{\xi_1}^{1} \frac{\xi^{2s}d\xi}{1 + \dfrac{(n-1)C_{Af}^{n-1}k\tau(1-\xi^{s+1})}{(1-\xi_1^{s+1})}} \tag{76}$$

For a first-order reaction $I_o = I_i$ and Eq. 75 becomes

$$N_{Pe} > \frac{20k\tau(s+1)^2(1-\xi_1^{s+1})}{(2s+1)(1-\xi_1^{s+1})^2} \tag{77}$$

When the radial dispersion coefficient is independent of velocity (Eq. 72) is satisfied if

$$N_{Pe} > \frac{20nC_{Af}^{n-1}k\tau(s+1)^2 J_o}{(1-\xi_1^{s+1})^2} \tag{78}$$

where

$$J_o = \int_{\xi_1}^{1} \frac{\xi^{3s}d\xi}{1 + \dfrac{(n-1)C_{Af}^{n-1}k\tau(\xi^{s+1}-\xi_1^{s+1})}{1-\xi_1^{s+1}}} \tag{79}$$

Condition (Eq. 78) holds also for the inward RFBR upon replacement of J_o by J_i, where

$$J_i = \int_{\xi_1}^{1} \frac{\xi^{3s}d\xi}{1 + \dfrac{(n-1)C_{Af}^{n-1}k\tau(1-\xi_1^{s+1})}{(1-\xi^{s+1})}} \tag{80}$$

For the special case of a first-order reaction $J_o = J_i$ and Eq. 78 reduces to

$$N_{Pe} > \frac{20k\tau(s+1)^2(1-\xi_1^{3s+1})}{(3s+1)(1-\xi_1^{s+1})^2} \tag{81}$$

The asymptotic expansion technique can be used also to derive criteria for general kinetic rate expressions. However, the resulting criteria have a cumbersome form and are not presented here.

CONCLUDING REMARKS

The conversion in an isothermal RFBR depends in general on the flow direction. While the impact of flow direction on the conversion is usually rather small, this additional conversion may be obtained at no additional construction or operational expense and should be exploited whenever possible. When the reaction network consists of several simultaneous reactions, the influence of flow direction on the yield of a desired product is expected to be larger than the change in conversion.

The model presented assumes ideal radial fluid distribution. In certain applications the need to avoid flow maldistribution [Chang and Calo, 1978; Ponzi and Kaye, 1979] may dictate the use of a certain flow direction even though a higher conversion may be obtained with the other flow direction in an ideal RFBR. The influence of the gas flow direction on channeling and flow stability is expected to be especially important in moving bed radial flow reactors, which are used in several commercial processes, such as catalytic reforming (Trambouze, 1978).

The analysis presented here for the isothermal case may be extended directly for the non-isothermal case if the effective thermal diffusivity and the radial dispersion coefficient depend in a similar fashion on the velocity. In such cases the steady-state temperature may be expressed as a linear function of the limiting reactant's concentration and a single differential equation, with the concentration being the dependent variable can describe the steady-state behavior. General statements about the preferred flow direction can still be made as long as the rate expression is either convex or concave in the region of interest ($0 \le y \le 1$).

ACKNOWLEDGEMENT

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APPENDIX

Proof of Eq. 47

Differentiation of Eq. 45 gives

$$F_1'(\xi) = N_{Da}\xi^s\left\{\frac{df}{dw_p}[w_p(\xi)] - \frac{df}{dy_p}[y_p(\xi)]\right\} \tag{A1}$$

Note that y_p and w_p satisfy:

$$y_p' + \xi^s N_{Da} f(y_p) = 0 \tag{A2}$$

$$w_p' - \xi^s N_{Da} f(w_p) = 0 \tag{A3}$$

Subject to the boundary conditions:

$$y_p(\xi_1) = w_p(1) = 1 \tag{A4}$$

Moreover, according to Eq. 29

$$y_p(1) = w_p(\xi_1) \tag{A5}$$

Since y_p is a monotonic decreasing function of ξ and w_p is a monotonic increasing function of ξ, y_p and w_p intersect only once in $(\xi_1, 1)$, say at ξ_o.

Suppose now that Eq. 46 holds so that $f'(y)$ is a monotonic increasing function of y. In $\xi_1 < \xi < \xi_o$

$$y_p(\xi) > w_p(\xi) \tag{A6}$$

and hence

$$F'_1(\xi) < 0 \tag{A7}$$

Similarly, in $\xi_o < \xi < 1$

$$y_p(\xi) < w_p(\xi) \tag{A8}$$

and consequently

$$F'_1(\xi) > 0 \tag{A9}$$

It follows that $F_1(\xi)$ has a unique minimum at ξ_o and its largest value in $(\xi_1, 1)$ has to occur either at ξ_1 or at 1. Substitution of Eqs. A4 and A5 into Eq. 45 yields Eq. 47.

Proof of Eqs. 64 and 65 for Constant N_{Bo} Case

Differentiation of Eq. 63 gives

$$F'_2(\xi) = \frac{N_{Da}}{(1+\nu)}\xi^s[[1+\nu y_p(\xi)]^2 - [1+\nu w_p(\xi)]^2] \tag{A10}$$

Thus, $F'_2(\xi)$ vanishes only at the point ξ_o at which the profiles w_p and y_p intersect. Moreover, if $\nu > 0$

$$F'_2(\xi_1) = \frac{N_{Da}\xi_1^s}{(1+\nu)}[(1+\nu)^2 - [1+\nu y_p(1)]^2] > 0 \tag{A11}$$

$$F'_2(1) = \frac{N_{Da}\xi_1^s}{(1+\nu)}[[1+\nu y_p(1)]^2 - (1+\nu)^2] < 0 \tag{A12}$$

and

$$F_2(1) = F_2(\xi_1) = -\ln[y_p(1)] \tag{A13}$$

It follows that $F_2(\xi)$ has a unique maximum in $(\xi_1, 1)$ and its minimal value in this interval is given by Eq. A13. Now

$$s\int_{\xi_1}^{1} \xi^{s-1}F_2(\xi)d\xi > \int_{\xi_1}^{1} s\xi^{s-1}F_2(1)d\xi = (1-\xi_1^s)\ln[y_p(1)] \tag{A14}$$

Substitution of Eq. A14 in Eq. 62 gives

$$I > 0 \tag{A15}$$

Substitution of Eq. A15 in Eq. 61 yields Eq. 64. Similarly, it can be shown that for $\nu < 0$, $I < 0$, which implies Eq. 65.

Proof of Eqs. 64 and 65 for Constant D Case

Consider a first-order isothermal reaction occurring in a RFBR in which the dispersion coefficient is constant. A singular perturbation solution of Eq. 21 subject to boundary conditions Eqs. 15 and 22 gives:

$$y(\xi) = y_p(\xi) + \frac{N_{Da}y_p(\xi)[1+\nu y_p(\xi)]^2}{(1+\nu)^2N_{Pe}}\left\{-\xi^{2s}[1+\nu y_p(\xi)] - \int_{\xi_1}^{\xi} x^{2s}\left(\frac{1}{y_p}+\nu\right)dy_p(x)\right\} + \frac{N_{Da}y_p(1)[1+\nu y_p(1)]^3}{N_{Pe}(1+\nu)^2} \times \exp[N_{Pe}(\xi-1)(1+\nu)/(1+\nu y_p(1))] \tag{A16}$$

Similarly, solution of Eq. 23 subject to boundary conditions Eqs. 18 and 19 gives

$$w(\xi) = w_p(\xi) + \frac{N_{Da}w_p(\xi)[1+\nu w_p(\xi)]^2}{N_{Pe}(1+\nu)^2}\left\{-\xi^{2s}(1+\nu w_p) + \int_{\xi}^{1} x^{2s}\left(\frac{1}{w_p}+\nu\right)dw_p(x)\right\} + \frac{N_{Da}w_p(\xi_1)[1+\nu w_p(\xi_1)]^3}{(1+\nu)^2N_{Pe}} \times \exp\{N_{Pe}(1+\nu)(\xi_1-\xi)/[1+\nu w_p(\xi_1)]\} \tag{A17}$$

Using Eq. 60, Eqs. A16 and A17 we obtain

$$w(\xi_1) - y(1) = \frac{N_{Da}y_p(1)[1+\nu y_p(1)]^2}{N_{Pe}(1+\nu)^2} I_1 \tag{A18}$$

where

$$I_1 = \int_{\xi_1}^{1}\left[\frac{w'_p}{w_p} + \frac{y'_p}{y_p} + \nu(w'_p + y'_p)\right]\xi^{2s}d\xi = (1-\xi_1^{2s})[\ln y_p(1) + \nu + \nu y_p(1)] - 2s\int_{\xi_1}^{1}\xi^{2s-1}F(\xi)d\xi, \tag{A19}$$

and

$$F(\xi) = \ln[y_p(\xi)w_p(\xi)] + \nu[y_p(\xi) + w_p(\xi)] \tag{A20}$$

Note that

$$F(\xi_1) = F(1) = \ln[y_p(1)] + \nu + \nu y_p(1) \tag{A21}$$

Differentiation of Eq. A20 gives

$$F'(\xi) = \frac{y'_p}{y_p} + \frac{w'_p}{w_p} + \nu(w'_p + y'_p) = \frac{N_{Da}\xi^s}{(1+\nu)}[(1+\nu w_p)^3 - (1+\nu y_p)^3] \tag{A22}$$

Thus, $F'(\xi)$ vanishes only at the point ξ_o at which the profiles w_p and y_p intersect. When $\nu > 0$ it can be shown that $F'(\xi)$ has a unique minimum in $(\xi_1, 1)$ and its maximal value in this interval is given by Eq. A21. Thus,

$$2s\int_{\xi_1}^{1}\xi^{2s-1}F(\xi)d\xi < 2s\int_{\xi_1}^{1}\xi^{2s-1}F(1)d\xi = (1-\xi_1^{2s})[\ln y_p(1) + \nu + \nu y_p(1)] \tag{A23}$$

Substitution of Eq. A23 into Eq. A21 gives

$$I > 0 \tag{A24}$$

which upon substitution into Eq. A18 gives Eq. 64. Similarly, when $\nu < 0$ it can be shown that $I < 0$ which gives Eq. 65.

Comments about Eqs. 13 and 21

Previous models on the influence of axial dispersion and volume change on the conversion in a tubular reactor are based on the approximation that the volume of the reacting mixture varies linearly with conversion. This leads to the following relationship between the conversion x and the mole fraction y (Levenspiel, 1972, p. 72).

$$x = (1-y)/(1+\nu y) \tag{A25}$$

An analysis of Eqs. 6-10 describing the outward flow for the constant N_{Bo} case indicates that

$$x = \left(1 - y - \frac{\nu y'}{N_{Pe}}\right)/(1 + \nu y - \nu y'/N_{Pe}) \tag{A26}$$

For the constant dispersion case the following holds

$$x = (1 - y - \nu y y'\xi^s/N_{Pe})/(1+\nu y) \tag{A27}$$

The expressions for the inward flow are obtained by changing the sign of the terms containing N_{Pe} in Eqs. A26 and A27. The above relations hold for a tubular reactor and indicate that Eq. A25 is exact only if either $N_{Pe} \to \infty$, or at the outlet of the reactor where $y' = 0$. Setting $s = 0$ in Eq. 13 or 21 we obtain the proper model for the tubular reactor.

The corresponding inlet boundary condition states that the mass (or molar) flux of A is continuous across the inlet. Note that it does not contain the volume change parameter ν explicitly.

NOTATION

a = area normal to flow direction
C_A = molar concentration of species A
d_p = diameter of catalyst particle
D = dispersion coefficient
f = kinetic function defined by Eq. 12
$g(C_A)$ = rate of consumption of reactant A

G = number of moles of A reacted
H = Heavyside's function
I = integral defined by Eq. 62
I_o = integral defined by Eq. 69
I_i = integral defined by Eq. 76
J_o = integral defined by Eq. 79
J_i = integral defined by Eq. 80
k = reaction rate constant
n = reaction order
$N(r)$ = molar flow rate of reaction mixture
N_{Bo} = Bodenstein number, ud_p/D
N_{Da} = Damköhler number, defined by Eq. 12
N^*_{Da} = Damköhler number defined by Eq. 17
N_{Pe} = Peclet number, u_2R_2/D_2
N^*_{Pe} = $u_1R_1^s/DR_2^{s-1}$
r = radial distance
s = geometry exponent, defined by Eq. 2
u = molar velocity of reaction mixture
$w(\xi)$ = mole fraction of species A for inward flow
$y(\xi)$ = mole fraction of species A for outward flow

Greek Letters

δ = quantity defined by Eq. 71
Δ = quantity defined by Eq. 67
ϵ = $y(1) - w(\xi_1)$
$\bar{\epsilon}$ = quantity defined by Eq. 57
τ = space time (volume of reactor/feed flow rate)
ξ = dimensionless radial distance, r/R_2
ν = stoichiometric coefficient describing change in total mole number

Subscripts

f = feed conditions
i = inward flow
o = outward flow
p = plug flow
1 = interior surface of the reactor
2 = exterior surface of the reactor

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Minimum Reflux Conditions

Part I: Theory*

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This paper presents a new formulation of the infinite plate or minimum reflux limit of a multicomponent distillation column. Based on this model, two new calculation methods are developed. The first is a short-cut method which extends Underwood's classic minimum reflux treatment to variable molar overflow situations. The second is a rigorous method which is similar to a multicomponent flash calculation and represents a significant computational advance over other rigorous methods.

SCOPE

Accurate plate-by-plate simulations of multistage, multicomponent distillation columns require substantial computational effort. Consequently, simpler, limiting descriptions are useful to guide process synthesis decisions and optimum column design. This investigation focuses on the infinite plate or minimum reflux limit.

The calculation of minimum reflux conditions for a specified separation has often been the subject of theoretical study. Underwood (1946, 1948), Shiras et al. (1950), Bachelor (1957), McDonough and Holland (1962), Erbar and Maddox (1962), Lee (1974), Chien (1978), and Tavana and Hanson (1979) have all considered this problem. These authors approximate the infinite stage column by increasingly larger finite columns. Except in the case where relative volatilities and molar over-

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