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Part II. Effect of Diffusional and Mass Transfer Resistances

The effects of diffusional and mass transfer resistances on the optimal distribution of a bifunctional catalyst were studied for the case where each catalyst is supported on a separate carrier in the packed bed of a plug flow, tubular reactor. The width of the segment requiring a catalyst mixture is reduced by the presence of transport resistance due to shifts of both switching points away from the ends of the reactor. The extent of the change in each of the two switching point locations depends upon the relative magnitudes of the effectiveness factors for the two reactions, as does also the change of packing policy in the singular segment. As observed in Part I, the first switching location is again independent of the dimensionless residence time; in the presence of the transport resistance, however, the first switching location increases by the multiplier of the respective inverse effectiveness factors. The results from previous numerical studies were shown to be particular cases of these general analytic results, and one specific reaction scheme with first-order kinetics was studied in detail for illustration.

SCOPE

Processes involving chemical reactions using multiple catalysts may be optimized by choosing a best catalyst distribution along a tubular reactor. This problem is most conveniently handled by the application of optimization theory. In this paper, results are reported on the effect of transport resistance on the optimal distribution of bifunctional catalysts in a plug flow, tubular reactor. Corresponding parameter comparisons are used to gain insight into the problem at hand, based upon results of a simpler standard problem. The general results are applied to a particular case with first-order reaction kinetics.

CONCLUSIONS AND SIGNIFICANCE

The absolute and relative magnitudes of effectiveness factors are both significant in determining optimal policies in systems that include mass transfer resistance. In the presence of transport resistance, the width of the singular segment decreases. This shrinkage can occur from either side, depending on the particular reaction to be favored in the bordering segments of bang-bang policy. The choice of catalyst mix in the singular policy segment

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is similarly affected, as is illustrated in detail for a particular case of first-order kinetics. A technique that uses corresponding parameters for comparisons with a standard problem provides a straightforward and relatively simple way to handle the complexities arising from the transport contributions.

The first part of this series (Choi and Perlmutter, 1977) addressed itself to the affects of reaction kinetics on optimal singular policies in a dual catalyst, plug flow reactor. It is the purpose of this part to examine the effect of transport resistance for the case where each of the two catalysts is supported on a separate carrier. The need for separate carriers may arise where there are differences in the deactivation rates and/or the treatment procedures for the two catalysts.

The results have specific relevance to the numerical works of Al-Samadi et al. (1974) and Chang and Reilly (1976) who also examined transport resistance, but here the results are given in a more general and analytic context which includes the prior results as particular cases.

SYSTEM EQUATIONS

The mass conservation equations developed in Part I of this set for reactions free of transport or diffusional limitations may equally well be applied to the problems under consideration here, provided that the reaction functions are interpreted to include appropriate modifications. If, for example, η_1 and η_2 are the effectiveness factors for the first and the second reactions, respectively, and f_1 and f_2 are the intrinsic reaction rate expressions based upon the bulk phase concentrations, we get

$$f_1' = \eta_1 f_1 \tag{1}$$

and

$$f_2' = \eta_2 f_2 \tag{2}$$

If one assumes that η_1 and η_2 are independent of conversion, Equation (17) of Part 1 is again applicable with the slight modification

$$\alpha = \frac{\eta_1 f_1^2}{\eta_2 f_2^2} \frac{\dfrac{\partial f_2}{\partial \xi_1}}{\dfrac{\partial f_1}{\partial \xi_2}} \tag{3}$$

and the problem in the presence of transport resistance becomes the same as the original one in the absence of transport resistance with only the simple substitutions of

$$P' = P\eta_1 \tag{4}$$

and

$$\alpha' = \alpha\eta_2/\eta_1 \tag{5}$$

Since the effective dimensionless residence time P' appears as a simple multiplicative factor in the Equations (10) and (11) of Part I, the first switching location will be independent of residence time. The extent variables at the first switching point will differ from those for the case of no transport resistance owing to the modification of α by a factor of (η_2/η_1). Because this multiplier is a ratio of effectiveness factors, it may have only a negligible effect on α', in some cases even when the individual $\eta << 1$. In other circumstances, this ratio may not be constant but could change appreciably with conversion. To compare a reactor with significant transport resistance to a similar reactor with negligible transport resistance, the first switching point locations are first related according to

$$\tau_1' = \tau_1/\eta_1 \tag{6}$$

if the first segment policy is $u = 1$, or according to

$$\tau_1' = \tau_1/\eta_2 \tag{7}$$

if the first segment policy is $u = 0$. When $\eta < 1$, as is usually the case, Equation (6) indicates that the first switching point τ_1 has moved toward the reactor effluent end in the presence of diffusional resistance. This result implies also that while $P\tau_1$ is independent of residence time, its magnitude does increase in the presence of the intraparticle resistance.

Similar arguments can be used to examine the changes in the second switching point location caused by mass transfer and diffusional resistances. For this purpose, the ratio of the adjoint variables assumes a role similar to the one played by the parameter α and the extent variable in the determination of the first switching point location. For convenience, the comparison is based on the reaction scheme I of Part I for which the control policies of $u = 1$ and $u = 0$ have already been found for the first and last segments, respectively.

The ratio (λ_1/λ_2) at the reactor exit is fixed by the boundary conditions on these variables obtained by differentiating the objective function with respect to the extent variables. The effect of transport resistance will, according to Equation (5), depend upon the magnitudes of η_2/η_1 and f_2/f_1 at the second switching point. This (λ_1/λ_2) value at the second switching point may decrease under diffusional resistance, even when η_1 and η_2 are assumed constant, because f_1 is likely to increase while f_2 remains about constant as diffusional resistance reduces overall bulk phase conversion.

For the case where $u = 0$ in the final segment

$$\frac{d(\lambda_1/\lambda_2)}{d(P\tau)} = \eta_2\alpha \left[-\frac{\partial f_2}{\partial \xi_1} + \frac{\lambda_1}{\lambda_2} \frac{\partial f_2}{\partial \xi_2} \right] \tag{8}$$

with $(\lambda_1/\lambda_2) = 0$ at the reactor exit. For first-order kinetics and for the reaction scheme I of Part I

$$f_2 = \xi_1 - \xi_2 \tag{9}$$

$$\frac{\partial f_2}{\partial \xi_1} = 1 \tag{10}$$

$$\frac{\partial f_2}{\partial \xi_2} = -1 \tag{11}$$

and

$$\frac{d(\lambda_1/\lambda_2)}{d(P\tau)} = \eta_2\alpha \left[-1 - \frac{\lambda_1}{\lambda_2} \right] \tag{12}$$

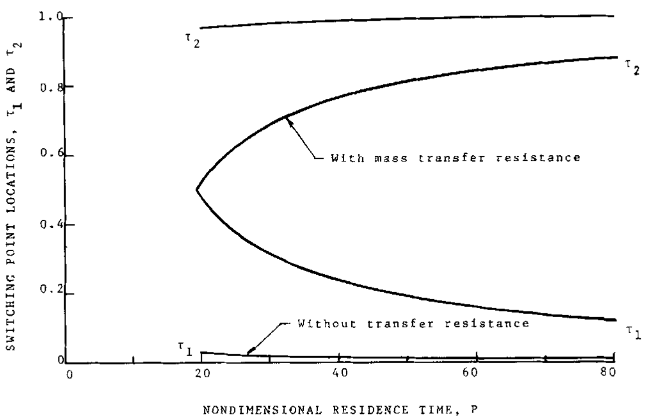

Fig. 1. Effect of mass transfer resistance on optimal switching point locations for $\alpha = \beta = \zeta = 1, w = 0.1$.

If $\eta_2 < 1$, Equation (12) shows that the second switching point will move closer to the feed side of the reactor. Similar reasoning may be extended to cases where the policy $u = 1$ is optimal for the final segment. These findings indicate, in agreement with the numerical results of Chang and Reilly (1976), that the width of the singular segment decreases in the presence of transport resistance, the exact extent depending on which of the extreme policies is chosen for the first and last segments. The corresponding changes in singular segment policy can be inferred from Equation (56) of Part I, the specific effects depending on changes in the product $(\nu\eta_2 f_2/\eta_1 f_1)$.

MASS TRANSFER LIMITATIONS

If we follow the details of the reaction scheme I of Part I for first-order kinetics, steady state mass conservation over a boundary layer surrounding a particle of the first catalyst gives

$$k_A(C_A - C_{AS}) = k_1 C_{AS} - k_{-1} C_{BS} \qquad (13a)$$

and

$$k_B(C_{BS} - C_B) = k_1 C_{AS} - k_{-1} C_{BS} \qquad (13b)$$

for the two species A and B. Simultaneous solution for the surface values gives

$$C_{BS} = \frac{k_1 k_A C_A + (k_1 + k_A) k_B C_B}{k_{-1} k_A + k_B (k_1 + k_A)} \qquad (14)$$

$$C_{AS} = \frac{[k_{-1}k_1 + k_{-1}k_A + k_B(k_1 + k_A)]k_A C_A + k_{-1}(k_1 + k_A)k_B C_B}{(k_1 + k_A)[k_{-1}k_A + k_B(k_1 + k_A)]} \qquad (15)$$

Similar derivation for a particle of the second catalyst provides

$$C_{BS} = \frac{k_B}{k_2 + k_B} C_B \qquad (16)$$

The same relationships can also be put in dimensionless variables in the form of

$$X_{BS} = \frac{X_A + (1 + w)\zeta X_B}{\beta + \zeta(1 + w)} \qquad (17)$$

$$X_{AS} = \frac{[\beta + \beta w + w\zeta(1 + w)]X_A + \beta(1 + w)\zeta X_B}{(1 + w)[\beta + \zeta(1 + w)]} \qquad (18)$$

for the first catalyst, and

$$X_{BS} = \frac{w\zeta}{\alpha + w\zeta} X_B \qquad (19)$$

for the second catalyst

If we use Equations (17) to (19), the reactor Equations (10) and (11) of Part I can also be put in terms of the bulk phase extent variables by denoting

$$f_1' = \frac{X_A - \beta X_B}{1 + (\beta + \zeta)/w\zeta} = \eta_1(X_A - \beta X_B) = \eta_1 f_1 \qquad (20)$$

and

$$f_2' = \frac{X_B}{1 + (\alpha/w\zeta)} = \eta_2 X_B = \eta_2 f_2 \qquad (21)$$

Equations (20) and (21) correspond in form to those applicable in the absence of transport resistance except for the appearance of the two effectiveness factors η_1 and η_2 as linear multiplicative factors; thus

$$\frac{\eta_2}{\eta_1} = \frac{\beta + \zeta + w\zeta}{\alpha + w\zeta} \qquad (22)$$

from which it may be noted that the ratio $(\eta_2/\eta_1) \gtrless 1$ when $(\beta + \zeta) \gtrless \alpha$. This observation facilitates comparisons with prior results, since any parameter changes may be associated with a modified effective α' by means of Equations (5) and (22). Using, for example, the listing of Table 1 in Part I, one finds that the singular control policy u_m will call for a greater fraction of the first catalyst when $(\beta + \zeta) > \alpha$, a result consistent with the numerical study of Chang and Reilly (1976) on Langmuirian reaction kinetics.

The effect of mass transfer resistance on the switching point locations is to be found in Equations (21) and (22) of Part I, modified by substitution of the effective residence time and the (η_2/η_1) ratio of Equation (22). A typical numerical comparison is shown as Figure 1 for a choice of parameters in the range of $\alpha < (\beta + \zeta)$. In general, the effect of transport resistance is to reduce the width of the singular policy segment, the shrinkage occurring as both switching points move away from the respective ends of the reactor. Similar calculations in the range of $\alpha > (\beta + \zeta)$ gave the same results with small deviations of no numerical significance.

MASS TRANSFER AND DIFFUSION INTO CATALYST PARTICLES

The effects of external mass transfer combined with diffusional resistance in flat slab catalyst particles can be studied via the balance equations

$$\frac{d^2 x_A}{dZ^2} = \frac{a^2}{D_A}(k_1 x_A - k_{-1} x_B) = Q(x_A - \beta x_B) \qquad (23)$$

and

$$\frac{d^2 x_B}{dZ^2} = \frac{a^2}{D_B} k_2 x_B = Q\alpha\psi x_B \qquad (24)$$

with the boundary conditions

$$\frac{dx_A}{dZ} = \frac{dx_B}{dZ} = 0; \quad Z = 0 \qquad (25)$$

and

$$\left.\begin{aligned} \frac{dx_A}{dZ} &= \frac{k_A a\delta}{D_A}(X_A - x_A) = \phi(X_A - x_A) \\ \frac{dx_B}{dZ} &= \frac{k_B a\delta}{D_B}(X_B - x_B) = \phi\psi(X_B - x_B) \end{aligned}\right\} Z = 1 \qquad (26)$$

Solving these equations and comparing with the PFTR Equations (10) and (11) of Part I, we get

$$f_1 = \frac{\zeta\kappa n \sinh n(\beta X_B - X_A)}{n(\beta + \zeta)\sinh n + \zeta\phi(\beta\psi + 1)\cosh n} \tag{27}$$

and

$$f_2 = \frac{p\zeta\kappa X_B}{\phi\alpha(p \sinh p + \zeta\phi\psi \cosh p)} \tag{28}$$

A parallel derivation for spherical particle geometry gives

$$f_1 = \frac{\zeta\kappa(n \cosh n - \sinh n)(\beta X_B - X_A)}{[\zeta(\phi - 1) - \beta(1 - \phi\psi\zeta)] \sinh n + n(\beta + \zeta)\cosh n} \tag{29}$$

and

$$f_2 = \frac{\zeta\kappa(p \cosh p - \sinh p)X_B}{\phi\alpha[p \cosh p + (\zeta\phi\psi - 1)\sinh p]} \tag{30}$$

Consider the particular case where $\psi = \zeta = 1$ and the kinetic rate constant k_1 is much larger than both $(D_A/\alpha a^2)$ and $[D_A/(1 + \beta)a^2]$, such that

$$Q\alpha >> 1 \tag{31}$$

and

$$Q(1 + \beta) >> 1 \tag{32}$$

If at the same time mass transfer is much faster than kinetics and intraparticle diffusion, $\delta k_A >> \sqrt{k_1 D_A \alpha}$, $\delta k_A >> \sqrt{k_1 D_A(1 + \beta)}$

$$\phi >> p \tag{33}$$

$$\phi >> n \tag{34}$$

and Equations (29) and (30) for the slab shape reduce to

$$f_1 = \frac{1}{\sqrt{Q(1 + \beta)}}(X_A - \beta X_B) \tag{35}$$

and

$$f_2 = \frac{1}{\sqrt{Q\alpha}} X_B \tag{36}$$

In the opposite case

$$\phi << p \tag{37}$$

$$\phi << n \tag{38}$$

$$f_1 = \frac{\kappa}{1 + \beta}(X_A - \beta X_B) \tag{39}$$

and

$$f_2 = \frac{\kappa}{\alpha} X_B \tag{40}$$

For the case of Equations (35) and (36)

$$\alpha' = \alpha\frac{\eta_2}{\eta_1} = \alpha\left[\frac{1 + \beta}{\alpha}\right]^{1/2} \tag{41}$$

whereas for the case of the Equations (39) and (40)

$$\alpha' = \alpha\frac{\eta_2}{\eta_1} = (1 + \beta) \tag{42}$$

This last result is the same as that for the nonporous case, as expected for a system controlled by external mass transfer. For the result (41), the dependence of the singular policy on the relative magnitudes of $(1 + \beta)$ and α is similar to that found for the nonporous case; however, the degree of dependence is much weaker in this case by the square root factor. When the external mass transfer resistance is negligible, the reaction rate is distributed along the catalyst half thickness.

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NOTATION

a = half thickness or radius
C_i = concentration of species i
C_{is} = concentration of species i at the surface of the catalyst particle
D_i = intraparticle diffusion coefficient of species i
f_1', f_2' = the normalized intrinsic rate expressions based on bulk phase concentrations
f_1, f_2 = normalized rate expressions for the first and second reactions with transport resistance included
k_A, k_B = mass transfer coefficients for species A and B, s^{-1}
k_1, k_{-1}, k_2 = reaction rate constants for forward, reverse and second reaction, s^{-1}
L = reactor length
n = $\sqrt{Q(1 + \beta\psi)}$
p = $\sqrt{Q\alpha\psi}$
P = dimensionless residence time = $k_1 L/v$
Q = $a^2 k_1/D_A$, dimensionless
u = policy variable, fraction of first catalyst
u_m = policy variable in the singular segment
v = superficial linear velocity, cm/s
w = k_A/k_1
x_i = normalized concentration of species i inside the porous catalyst particle
X_i = normalized bulk phase concentration of species i
X_{is} = normalized concentration of species on the surface
z = reactor length coordinate
Z = fractional distance through the particle

Greek Letters

α = k_2/k_1
β = (k_{-1}/k_1)
δ = volume of packing per unit transfer surface, cm
ζ = k_B/k_A
η_1, η_2 = effectiveness factors for the first and second reactions
κ = $k_A\delta/ak_1$
λ_1, λ_2 = adjoint variables
ν = $(d\xi_1/d\xi_2)$ = the slope of the switching curve
ξ_1, ξ_2 = reaction extent variables for the first and second reactions
τ = dimensionless reactor coordinate = (z/L)
ϕ = $k_A a\delta/D_A$ dimensionless
ψ = D_A/D_B

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