CONCLUSION

In addition to providing an accurate representation of the fully developed velocity, our representation has other significant features. The first and most important feature is that it proves extremely useful in the analysis of the entrance region problem. Secondly, with this representation it is possible to obtain a closed-form expression for the average fully developed velocity. Finally, all of the constants in this representation can be written in terms of the duct input parameters: r_1, r_2, and e. Thus, the effect of the input parameters on the fully developed velocity can be analyzed.

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NOTATION

a_n, b_{mn} = Fourier coefficients defined by Equation (4)

$A_i = \dfrac{c_i}{r_i} - \sqrt{\left(\dfrac{c_i}{r_i}\right)^2 - 1} \qquad (i = 1, 2)$

$B, \overline{B}$ = plane of symmetry of duct

$B_i = 1 - 1 \Big/ \sqrt{1 - \left(\dfrac{r_i}{c_i}\right)^2} \qquad (i = 1, 2)$

c_1, c_2 = duct centers defined by Figure 1

$C, \overline{C}$ = duct walls

$e\ (= c_2 - c_1)$ = eccentricity

$h = \sqrt{c_i^2 - r_i^2} \qquad (i = 1, 2)$

$k_i = \ln\left\{\dfrac{\sqrt{c_i + r_i} + \sqrt{c_i - r_i}}{\sqrt{c_i + r_i} - \sqrt{c_i - r_i}}\right\} \qquad (i = 1, 2);$

$k_3 = k_1 - k_2$

p = pressure

r_1, r_2 = duct radii

u = fully developed velocity (v = dimensionless fully developed velocity)

V = average (dimensionless) fully developed velocity

x, y, z = Cartesian coordinates

ξ, η = transformed coordinates for x and y, respectively

μ = viscosity

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Recycle Effects on the Distribution of ATP Regeneration Catalysts

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Although ATP is one of the more important cofactors in biochemistry (Kalckar, 1969; Mahler and Cordes, 1971), its high cost has prevented common use in biosynthetic reactions and has stimulated interest in regeneration from its lower phosphorylated counterparts such as ADP, AMP, and adenosine. Among the possible means for the regeneration of ATP, the extracellular bi-enzymatic processes were proposed as most economic (Langer et al., 1976, 1977; Yang et al., 1976; Pace et al., 1976), and these prospects became more attractive with the advent of immobilized enzyme systems (Zaborsky, 1973). One particular path suggested by Langer et al. (1976) uses the phosphotransferases, that is, adenylate kinase and acetate kinase, to catalyze the reactions

$$\text{AMP} + \text{MgATP} \xrightleftharpoons{\text{Adenylate Kinase}} \text{ADP} + \text{MgADP} \tag{1}$$

$$\text{AcP} + \text{MgADP} \xrightarrow{\text{Acetate Kinase}} \text{Ac} + \text{MgATP} \tag{2}$$

The immobilized forms of these two enzyme catalysts are suited to use in a packed-bed tubular reactor system where they may be distributed along the reactor to achieve the optimal yield for ATP. Such optimization problems have been studied by King et al. (1972) and Choi and Perlmutter (1977); however, the net forward rate of the adenylate kinase reaction will be very small even with the optimal catalyst distribution policy, because the adenylate kinase reaction is readily reversible and the initial feed to the system will usually contain a very small fraction of ATP left over from a prior biosynthetic reaction. Depending on the initial concentrations of the system chemical species, this reaction may even proceed in the reverse direction when less than optimal catalyst distributions are used. In view of such difficulties, it is of interest to examine the effect of recycle on the objective of obtaining maximum yields of ATP. The following reports such a study for a representative set of initial concentrations and system parameters.

SYSTEM EQUATIONS

The plug flow tubular reactor (PFTR) equations can be written in terms of normalized extent variables as

$$\frac{d\xi_1}{d\tau} = Puf_1 \qquad (3)$$

$$\frac{d\xi_2}{d\tau} = P(1 - u)\alpha f_2 \qquad (4)$$

where u represents the fraction of the first immobilized catalyst and $(1 - u)$ that of the second catalyst. The specific form of the catalyst is irrelevant so long as diffusional resistances are negligible and each catalyst acts independently of the other. The absolute concentration of the catalyst is incorporated in the dimensionless residence time and does not occur explicitly.

With boundary conditions at reactor inlet

$$\xi_i = \xi_{iF} \qquad (5)$$

the recycle relationship between inlet and effluent is

$$\xi_{iF} = \frac{r}{1 + r}\,\xi_{iE} \qquad (6)$$

The objective is to maximize ATP concentration at the reactor exit by establishing the optimal catalyst distribution subject to the constraint on fractional catalyst composition:

$$0 \leq u \leq 1 \qquad (7)$$

The normalized rate expressions f_1 and f_2 refer to the adenylate kinase reaction and the acetate kinase reaction, respectively. These can be derived from Langer (1974) and expressed in terms of the totals of both free and complexed forms for each of the adenosine compounds as

$$f_1 = \frac{\zeta X_M X_T - \beta\eta X_D^2}{\begin{aligned}&[(1 + S_1X_M + S_2X_D + S_3)\\ &+ T_1X_M(1 + S_4 + S_{17}X_M)\\ &+ T_2X_T(1 + S_5 + S_{18}X_T)\\ &+ T_3X_TX_M + T_4X_D(1 + S_6X_M)\\ &\qquad + T_5X_D(1 + S_7X_D) + T_6X_D^2]\end{aligned}} \qquad (8)$$

and

$$f_2 = \frac{\lambda X_D X_B - \gamma\mu X_T X_A}{\begin{aligned}&[(1 + S_8X_D + S_9) + T_7X_D(1 + S_{10}X_T\\ &+ S_{11}X_A + S_{12}) + T_8X_B(1 + S_{13}X_M + S_{14}X_D\\ &+ S_{15}X_T) + T_9X_BX_D(1 + S_{16})\\ &+ T_{10}X_A + T_{11}X_T + T_{12}X_TX_A]\end{aligned}} \qquad (9)$$

where the normalized concentrations are related to the normalized extent variables by

$$X_M = X_{Mo} - \xi_1 \qquad (10)$$

$$X_D = X_{Do} + 2\xi_1 - 2\xi_2 \qquad (11)$$

$$X_T = X_{To} - \xi_1 + 2\xi_2 \qquad (12)$$

$$X_B = X_{Bo} - 2\xi_2 \qquad (13)$$

$$X_A = X_{Ao} + 2\xi_2 \qquad (14)$$

NUMERICAL STUDY

Specific calculations were carried out to determine optimal policies and their results. The procedures were modified forms of those used previously by King et al. (1972) and Choi and Perlmutter (1977) on PFTR systems without recycle and involved combinations of bang-bang and singular policies. Specific parameter values were set by following Langer (1974) for total metal concentration of 10 to 100 mM and total concentration of adenosine compounds of 100 mM. At these concentration levels, most of the ATP exists in complexed form, and AMP exists in free form:

$\alpha = 0.3$
$\beta = 3.6$
$\gamma = 0.0025$
$\zeta = 0.554$
$\eta = 0.064$
$\lambda = 0.554$
$\mu = 0.064$

The parameters T_i and S_i are not available in the reference cited, but this lack need not interfere with the comparison to be provided here. If we note that these parameters are in essence measures of the relative degree of kinetic inhibition attributable to each species, and with the expectation that ATP is more inhibitory than the other components, it is a conservative estimate to use $T_i = S_i = 1$ in the computations. The actual effect of recycle will produce smaller yields of ATP than obtained here but with similar qualitative dependence. The initial concentrations were set at

$X_{Mo} = 0.8$
$X_{Do} = 0.19$
$X_{To} = 0.01$
$X_{Bo} = 2.7$
$X_{Ao} = 0$

To estimate the overall effects for any selected recycle ratio, optimal conversions were first calculated for an arbitrary set of values of ξ_{iF} for several values of the residence time. These conversion values were stored as a data pool for later use. A typical set of such results is shown in Figure 1 for specified feed levels. Such stored intermediate results were used to obtain corresponding feed and effluent conversions for given reactor residence times and recycle ratios. In this procedure, it was necessary to use an effective residence time

$$P' = \frac{P}{1 + r} \qquad (15)$$

Finally, the set of values ξ_{iE} and ξ_{iF} were obtained as those that simultaneously satisfied the foregoing and also the recycle condition (6).

RESULTS AND DISCUSSION

The results shown in Figure 2 were obtained for various recycle ratios at a residence time of $P = 160$. The optimal effluent concentration of ATP showed a variation less than 5% over the range of recycle ratio from $0 < r < 3$. Beyond the recycle ratio of $r = 3$, the ATP yield decreased slowly to the limit found by direct search on the optimal catalyst composition for the CSTR with the same residence time. A similar trend may be expected for other values of residence time because the maximum conversions obtainable will change in the same direction as the residence time. The recycle does not give a higher yield, possibly because of the dilution of the coreactants (AMP, ADP, and AcP) that accompanies the increase in ATP content at the reactor inlet, as well as the stronger inhibitory effect of ATP (Langer, 1974). Perhaps the recycle stream should be concentrated with ATP by means of a separator step.

The reactor position at which a policy change is made with respect to catalyst use is commonly called a switch-

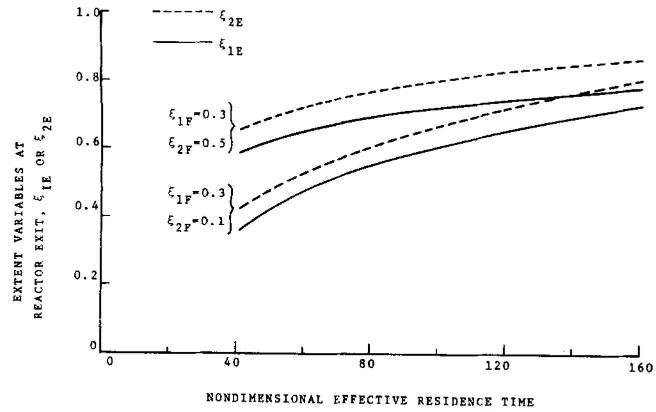

Fig. 1. Effect of residence time on conversion for several levels of feed concentration.

ing point. The switching point locations for each recycle ratio are presented in Figure 3. The width of the singular segment increases with recycle and then decreases toward the optimal catalyst composition for the CSTR limit found through direct search, suggesting that the overall catalyst composition approaches that limit through the shrinkage of the singular segment rather than through the expansion of the singular segment and the approach of the singular control to the optimal CSTR catalyst composition. This has a practical significance, indicating that the bang-bang suboptimal policy can in certain cases be at least as good a substitute for the optimal policy as the fixed composition suboptimal policy. The bang-bang policy may give better yields than the fixed composition policy and may also have advantages in ease of catalyst handling.

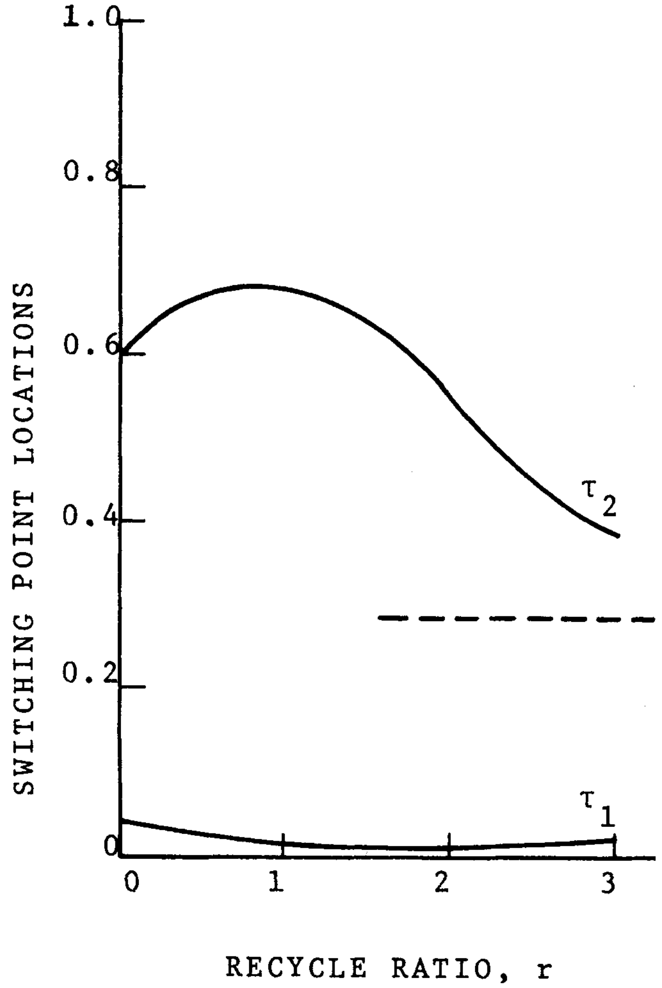

Fig. 3. Effect of recycle on switching point locations for $P = 160$. The dashed line is the equivalent catalyst mix for the corresponding CSTR.

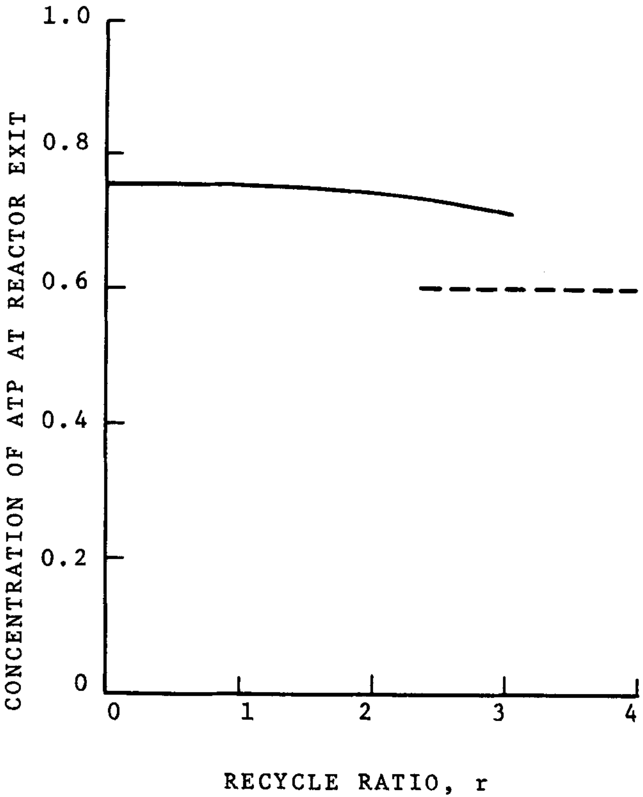

Fig. 2. Effect of recycle on optimal yield of ATP. The dashed line is the optimal yield for the corresponding CSTR.

The control profiles for several cases are shown in Figure 4. These become slightly flatter as one increases the recycle ratio and the change in the width of the singular segment is rather substantial, but the change in the magnitude of the singular policy is hardly noticeable over the range $0 < r < 3$.

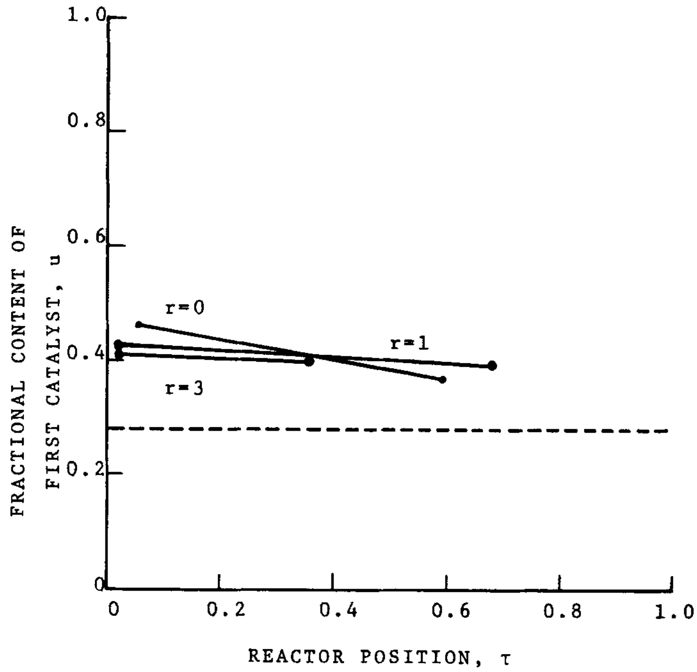

Fig. 4. Singular optimal policies for several recycle ratios at $P = 160$. The dashed line is the optimal level for the corresponding CSTR. In each case the policy is $u = 0$ for the final reactor segment. The policy is also $u = 0$ for the first segment for $r = 0$, but is $u = 1$ for $r \geq 1$.

ACKNOWLEDGMENT

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NOTATION

X_i = normalized concentration of species i
P = Lk/v
f_i = normalized rate expression for the i^{th} reaction
r = recycle ratio
u = fraction of total catalyst concentration devoted to first catalyst
$u_m(\tau)$ = policy in singular segment
T_i, S_i = parameters in rate expressions
k = rate constant for the first forward reaction
v = linear superficial velocity
Z = reactor coordinate
L = reactor length

Greek Letters

α, β, γ = ratios of rate constants
$\zeta, \eta, \lambda, \mu$ = parameters in rate expressions
ξ_1 = normalized extent variable for i^{th} reaction
ξ_{1F} = ξ_1 at reactor inlet
ξ_{1E} = ξ_1 at reactor exit
τ = normalized reactor coordinate = (Z/L)
τ_1, τ_2 = first and second switching points

Subscripts

M = mono
D = di
T = tri
A = acetate
B = acetyl phosphate

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Magma Density and Dominant Size for Size Dependent Crystal Growth

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The design or control of mixed-suspension mixed-product removal (MSMPR) crystallizers using population balance techniques is dependent on an accurate representation of the crystal size distribution (CSD). As illustrated by Moyers and Randolph (1973), CSD is important not only as a characterization of the output from a crystallization operation, but also in determining the nucleation and growth characteristics within the crystallizer.

Suspension density is a primary variable in correlating nucleation rates, and dominant crystal size is an important characteristic of the crystalline product. The calculation of these quantities when the crystal growth rate is size dependent can be quite difficult. The Abegg-Stevens-Larson (ASL) model (1968) has been used successfully to correlate growth rate with crystal size; a method is herein described for the determination of suspension density and dominant crystal size when the ASL model can be used to describe crystal growth rate.

SIZE INDEPENDENT GROWTH

For an MSMPR crystallizer operating at steady state, Randolph and Larson (1971) show that the general population balance equation reduces to

$$\frac{\partial(nG)}{\partial L} = -\frac{n}{\tau} \tag{1}$$

For size independent growth ($\partial G/\partial L = 0$) Equation (1) may be integrated to give

$$n = n^\circ \exp\left[-L/G\tau\right] \tag{2}$$

where n° is $\lim\limits_{L\to 0} n$, the nuclei population density.

The mass of crystals in a size range dL is

$$dM = \rho k_v L^3 n dL \tag{3}$$

so the suspension density can be calculated as

$$M_T = \rho k_v \int_0^\infty nL^3 dL = 6\rho k_v n^\circ \,(G\tau)^4 \tag{4}$$

and the mass distribution is given by

$$m(L) = \frac{dM}{dL} = \rho k_v L^3 n^\circ \exp\left[-L/G\tau\right] \tag{5}$$

The maximum of the mass distribution, called the dominant size of the CSD, L_D, can be found by maximizing $m(L)$ from Equation (5), yielding

$$L_D = 3G\tau \tag{6}$$
