Optimization of Catalytic Activity Distributions in Series and Parallel Reaction Schemes

Optimal activity distributions within nonisothermal porous heterogeneous catalysts for series and parallel reaction networks are determined employing a numerical search procedure based on orthogonal collocation techniques. At high values of the Thiele modulus, a shell profile is found to be optimal at moderate heat of reaction parameters. In certain cases a pendulum effect, in which activity shifts from shell to core and back to shell profiles, is observed with increasing value of the heat of reaction parameters.

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Introduction

The effects of nonuniform distributions of catalytic activity on effectiveness, selectivity, or yield have been studied by many investigators. In most of these studies, single isothermal reactions with power law or Langmuir-Hinshelwood rate expressions were considered (Shadman-Yadzi and Petersen, 1972; Corbett and Luss, 1974; Wei and Becker, 1974; Villadsen, 1976; Becker and Wei, 1977a, b). Recently, studies dealing with nonisothermal catalyst particles and more complicated reaction schemes have appeared in the literature. Thus, Juang and Weng (1983) investigated nonisothermal, first-order single, consecutive, and parallel reaction networks, while the second-order parallel reaction system was analyzed by Johnson and Verykios (1984) and was applied to the ethylene oxidation scheme with Langmuir-Hinshelwood kinetics (Johnson and Verykios, 1983).

Optimization of catalytic activity distributions has mostly been performed with reference to a particular distribution function. Optimization without *a priori* restrictions on the distribution function was performed by DeLancey (1973) for infinite slab geometry and isothermal, first-order single reaction in the presence of uniform deactivation. The optimal activity distribution was found rigorously by application of Pontryagin's maximum principle and consisted of uniform impregnation of catalytic material from the pellet surface to a certain depth, dependent upon system parameters. Cukierman et al. (1983) optimized local and overall reactor yields for the isothermal van Dusse reaction scheme by obtaining proper exponential forms of activity distributions, which resulted in optimal values of the performance criterion. Dadyburjor (1982) used the calculus of variations to optimize the distribution of zeolite in a slab catalyst for hydrocracking reactions.

A novel method of optimization was developed by Morbidelli et al. (1982a, b; 1984) in which analytical solutions were found for catalysts of arbitrary geometry and single isothermal reactions following Langmuir-Hinshelwood kinetics. Optimum activity profiles were found to be Dirac delta functions whose location is dependent on system parameters. The same technique was clarified and extended by Vayenas and Pavlou (1986) to cover isothermal and nonisothermal single reactions in the presence or absence of external mass transfer resistances. A comprehensive review article by Dougherty and Verykios (1986) encompasses all aspects of catalysis with nonuniformly activated catalysts.

The purpose of the present study is to develop a general method of optimizing activity profiles for nonisothermal series and parallel reaction networks. The performance criteria employed are catalytic effectiveness, selectivity, and yield of desired product. Optimal activity profiles as a function of particle and reaction parameters are determined employing a numerical search procedure based on orthogonal collocation techniques. A quadrature formula is also derived that enables calculation of the performance index.

Results obtained in this study indicate that the magnitude of the Thiele modulus is the most important parameter in the particularization of optimal activity distributions. At high values of the Thiele modulus, regardless of reaction scheme or optimization criterion, a shell profile is usually optimal when the heat of reaction parameters are low to moderate. A pendulum effect in the shape of the optimal activity distributions is observed with

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increasing value of the heat of reaction parameters when effectiveness or yield are optimized. As values of β_i's increase, activity shifts from the pellet surface to the pellet core, and at sufficiently high values of these parameters a bimodal or shell type activity distribution becomes optimal. This phenomenon is more likely to occur and is also more pronounced at high values of the Thiele modulus.

Mathematical Description of the Systems

Series reaction scheme: $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

Assuming activity distributions of the form $u = u(r)$, reaction rate constants may be formulated as:

$$k_i(r) = k_i^* u(r) \tag{1}$$

where k_i^* refers to the volume-averaged rate constant, defined by:

$$k_i^* = \frac{1}{V} \iiint k_i(r)\, dV \tag{2}$$

In order to compare catalysts of different activity distributions, it is necessary to normalize the activity so that each distribution contains the same amount of catalytically active material. This restriction may be simplified to the form shown below, assuming k_i^* is constant.

$$\frac{3}{R^3} \int_o^R u(r) r^2\, dr = 1 \tag{3}$$

Defining Thiele moduli as:

$$\Phi_i = R \sqrt{\frac{k_{is}}{D_{ei}}} \tag{4}$$

and assuming first-order reactions, spherical geometry, and constant effective diffusivities, differential steady state mass and energy balance equations can be written in terms of the usual dimensionless variables as:

$$\nabla^2 x_1 = \Phi_1^2 u x_1 \exp\left[\gamma_1(1 - 1/\Theta)\right] \tag{5a}$$

$$\nabla^2 x_2 = \Phi_2^2 u x_2 \exp\left[\gamma_2(1 - 1/\Theta)\right] - \psi \Phi_1^2 u x_1 \exp\left[\gamma_1(1 - 1/\Theta)\right] \tag{5b}$$

$$\nabla^2 \Theta = -\beta_1 \Phi_1^2 u x_1 \exp\left[\gamma_1(1 - 1/\Theta)\right] - \beta_2 \Phi_2^2 u x_2 \exp\left[\gamma_2(1 - 1/\Theta)\right] \tag{5c}$$

External mass transfer effects are assumed negligible; therefore, boundary conditions are of the Dirichlet form:

$$\text{at} \quad z = 1, \quad x_1 = x_2 = \Theta = 1 \tag{6a}$$

$$\text{at} \quad z = 0, \quad \frac{dx_1}{dz} = \frac{dx_2}{dz} = \frac{d\Theta}{dz} = 0 \tag{6b}$$

The expressions for effectiveness factor, selectivity, and productivity or yield may be derived from their defining relationships. In terms of dimensionless variables,

$$\eta = \frac{3}{1 + \alpha^*} \int_o^1 \{x_1 \exp\left[\gamma_1(1 - 1/\Theta)\right] + \alpha^* x_2 \exp\left[\gamma_2(1 - 1/\Theta)\right]\} u z^2\, dz \tag{7}$$

$$S = \frac{3}{\eta(1 + \alpha^*)} \int_o^1 x_1 \exp\left[\gamma_1(1 - 1/\Theta)\right] u z^2\, dz \tag{8}$$

$$P = \eta s = \frac{3}{1 + \alpha^*} \int_o^1 x_1 \exp\left[\gamma_1(1 - 1/\Theta)\right] u z^2\, dz \tag{9}$$

The system may be reduced to two state equations by applying a univariant of the form:

$$\Theta(x_1, x_2) = 1 + \beta_2(1 - x_2) + (\beta_1 + \psi\beta_2)(1 - x_1) \tag{10}$$

Parallel reaction scheme: $A \xrightarrow{k_1} B; A \xrightarrow{k_2} C$

Two state equations are necessary to describe this system, a mass balance on the reactant and an energy balance. These steady state balances, in dimensionless form are:

$$\nabla^2 x_1 = \Phi_1^2 u x_1 \{\exp\left[\gamma_1(1 - 1/\Theta)\right] + \kappa \exp\left[\gamma_2(1 - 1/\Theta)\right]\} \tag{11a}$$

$$\nabla^2 \Theta = -\Phi_1^2 u x_1 \{\beta_1 \exp\left[\gamma_1(1 - 1/\Theta)\right] + \beta_2 \kappa \exp\left[\gamma_2(1 - 1/\Theta)\right]\} \tag{11b}$$

with boundary and symmetry conditions identical to those described by Eq. 6. Expressions for the effectiveness factor, selectivity, and yield of desired product are given by:

$$\eta = \frac{3}{1 + \kappa} \int_o^1 x_1 u z^2 \{\exp\left[\gamma_1(1 - 1/\Theta)\right] + \kappa \exp\left[\gamma_2(1 - 1/\Theta)\right]\}\, dz \tag{12}$$

$$S = \frac{3}{\eta(1 + \kappa)} \int_o^1 x_1 u z^2 \exp\left[\gamma_1(1 - 1/\Theta)\right] dz \tag{13}$$

$$P = \frac{3}{1 + \kappa} \int_o^1 x_1 u z^2 \exp\left[\gamma_1(1 - 1/\Theta)\right] dz \tag{14}$$

Numerical Techniques

Since the state equations describing the consecutive and parallel reaction networks are nonlinear and the performance criteria are complex, a computer analysis is necessary. Integration of the state equations was done by orthogonal collocation and a grid search was used to locate the discrete activity values, at each collocation point, yielding the best values of the performance index.

In terms of accuracy, flexibility, and computer time concerns, five internal collocation points were found to be optimal. No changes in integration accuracy were observed when more collocation points were used, while the optimal activity distributions retained their quantitative nature. The restriction of a constant amount of catalytically active material in each profile allows expression of the activity at the exterior collocation point in terms of the internal discrete activities by the standard quadrature formula:

$$u_6 = \frac{1}{w_6}\left(\frac{1}{3} - \sum_{j=1}^{6} w_j u_j\right) \tag{15}$$

For this quadrature formula to be accurate, the activity distribution function, u, must be of the polynomial form, $u = u(z^2)$, in addition to being positive semidefinite over $z \in [0, 1]$. Accordingly, the activity profile was assumed to be a standard expansion of Jacobian polynomials

$$u(z^2) = u_6 + (1 - z^2)\sum_{j=1}^{5} a_j \overline{P}_{j-1}(z^2) \tag{16}$$

Results and Discussion

Series reaction scheme

The shape of the optimal activity profile for a first-order series reaction network is primarily influenced by the values of the Thiele moduli, Φ_1 and Φ_2, the absolute values of the Arrhenius parameters, and of the heat of reaction parameters. The relative values of γ_1 and γ_2 have minor effects on the optimal activity distribution, regardless of the performance criterion. Since it is not practically possible to consider all permutations of these variables, Φ_2 was assumed equal to unity in all cases studied. Φ_1 was considered the most salient variable since it defines reactant concentration profiles that exert a significant influence on optimal activity distributions. Thus, the effects of Φ_1 on all three performance criteria were analyzed in detail while the effects of other reaction parameters were only considered on yield.

The effects of Φ_1 on the optimal activity profile for maximum pellet effectiveness are shown in Figure 1 for a case in which γ_1 is less than γ_2. At low to moderate values of Φ_1 a core profile is optimum, while at higher values of Φ_1 the activity shifts toward the pellet surface. At low values of Φ_1, concentration gradients are small; temperature effects dominate and dictate optimal activity distribution. A core profile maximizes temperature gradients that result in higher effectiveness factors. At higher values of the Thiele modulus, concentration gradients become stiffer and assume greater importance in the particularization of the optimal activity profile. Hence the shift toward a shell-type profile that minimizes concentration gradients. Competitive interactions between concentration and temperature effects were found to be present in most of the cases studied. A shell profile minimizes both temperature and concentration gradients and is most beneficial when concentration effects are limiting. When temperature effects dominate, a core profile tends to be optimal as far as effectiveness is concerned. Because of the complex dependence of reaction rates on concentration and temperature, it is not always possible to predetermine which effect would dominate in a particular situation.

If values of the Arrhenius parameters of the case presented in Figure 1 are reversed so that $\gamma_1 > \gamma_2$, a similar shift from core to shell profile is obtained with increasing value of Φ_1. In this case the shift is more rapid because concentration effects are more dominant. Although the first reaction is more temperature-sensitive than the second one, the low value of β_1 results in mild intraparticle temperature gradients. Then, concentration gradients dominate, shifting catalytic activity toward the periphery of the particle.

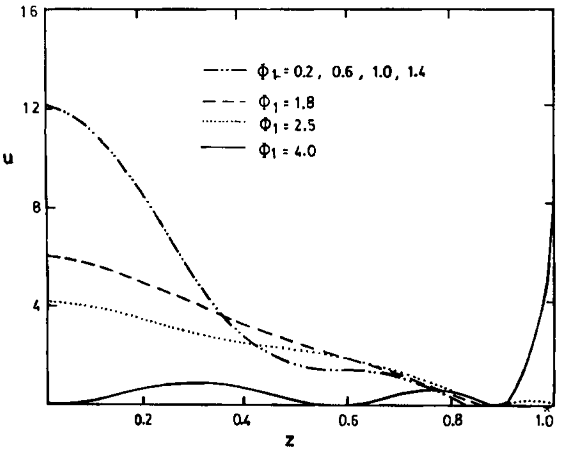

Figure 1. Effects of Φ_1 on effectiveness factor optimization for series reaction schemes.
$\Phi_2 = 1.0$; $\beta_1 = 0.05$; $\beta_2 = 0.10$; $\gamma_1 = 10$; $\gamma_2 = 15$; $\psi = 0.5$.

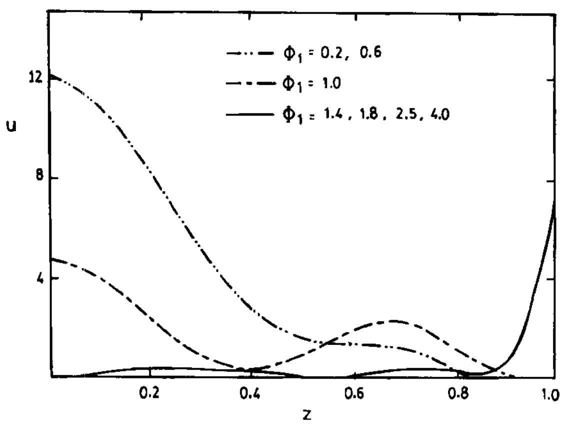

Figure 2. Effects of Φ_1 on selectivity optimization for series reaction schemes.
$\Phi_1 = 1.0$; $\beta_1 = 0.05$; $\beta_2 = 0.10$; $\gamma_1 = 15$; $\gamma_2 = 10$; $\psi = 0.5$.

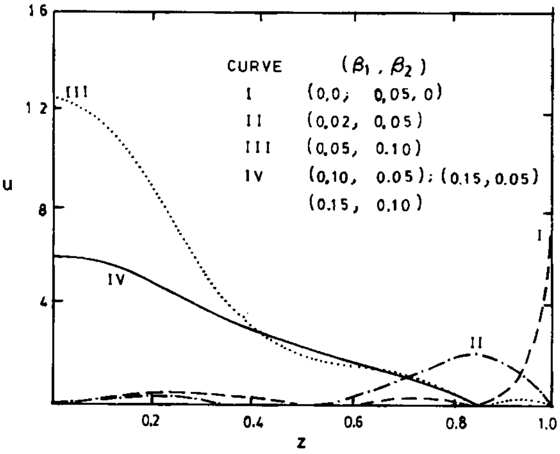

Figure 3. Heat effects on selectivity optimization for series reaction schemes.
$\Phi_1 = 1.0$; $\Phi_2 = 1.0$; $\gamma_1 = 10$; $\gamma_2 = 15$; $\psi = 0.5$.

Table 1. Series Reaction System Results

Variable	Conditions	Effects on optimal profile for η	Effects on optimal profile for S	Effects on optimal profile for Yield
$\phi_1 \uparrow$	Moderate heat effects $\gamma_1 = 10, \gamma_2 = 15$	Core → Shell $(\phi_1 < 1.8) \rightarrow (\phi_1 > 4.0)$	Core → Shell Dramatic shift at ~0.7	Core → Shell $(\phi_1 < 1.0) \rightarrow (\phi_1 > 1.8)$
	Moderate heat effects $\gamma_1 = 15, \gamma_2 = 10$	Core → Shell $(\phi_1 < 1.8) \rightarrow (\phi_1 > 4.0)$	Core → Shell $(\phi_1 < 0.6) \rightarrow (\phi_1 > 1.4)$	Core → Shell $(\phi_1 < 1.0) \rightarrow (\phi_1 > 2.5)$
$(\beta_1, \beta_2) \uparrow$	$\phi_1 = 1$ $\gamma_1 = 10$ $\gamma_2 = 15$	—	—	Shell: $\beta_1 + \beta_2 < 0.1$ Core: $\beta_1 + \beta_2 > 0.15$
	$\phi_1 = 2$ $\gamma_1 = 10$ $\gamma_2 = 15$	—	—	Shell → Uniform/core → Shell
	$\phi_1 = 1$ $\gamma_1 = 15$ $\gamma_2 = 10$	—	—	Shell → Core → Shell

Optimal activity distributions maximizing selectivity to the intermediate product are shown in Figure 2 for various values of Φ_1. A gradual shift from a core to a shell profile occurs with increasing Φ_1. At values of Φ_1 significantly lower than those of Φ_2, the dimensionless concentration of A is larger than that of B. The difference is larger when a core catalyst is employed. Intraparticle temperatures are also higher in core-profile catalysts. Higher concentrations of A relative to those of B and higher temperatures result in increased selectivity since $\gamma_1 > \gamma_2$. As Φ_1 increases, the intraparticle concentration of A decreases and begins to offset the beneficial effects of temperature on selectivity. As a result, to maximize the rate of the first reaction relative to that of the second, activity shifts toward the periphery of the catalyst where the difference between the concentrations of A and B is minimum. If values of the Arrhenius parameters of this case are reversed so that $\gamma_1 < \gamma_2$, intraparticle temperature gradients are detrimental to selectivity. In this case, the transition from a core to a shell profile was found to occur at significantly lower values of Φ_1.

The effects of the heat of reaction parameters on optimal activity distributions maximizing productivity or yield are shown in Figure 3. It can be shown theoretically that in isothermal pellets, shell activity distributions are optimal for both effectiveness and selectivity. This is demonstrated in Figure 3, which shows that for low values of β_1 and β_2, a shell profile is the optimum one. As the heat of reaction parameters increase, significant intraparticle temperature gradients develop and activity shifts toward the pellet center to make best use of higher temperatures in that part of the catalyst (curves II and III). At even higher values of the heat of reaction parameters a pendulum effect occurs and the activity shifts from a core profile to one that decreases almost linearly from the pellet center to the pellet surface (curve IV). Because of the high heats of reactions, the catalyst in this case operates under severe temperature gradients. As a result, the reactant is mostly consumed near the periphery of the pellet where selectivity is higher because of lower temperatures. Thus, a compromise is achieved between high effectiveness, which requires activity in the center of the pellet, and high selectivity, which requires activity closer to the outer periphery. An activity profile, as shown in Figure 3 (curve IV), represents such a compromise, yielding optimal productivity.

The results of the optimization study of the consecutive reaction network are presented on Table 1.

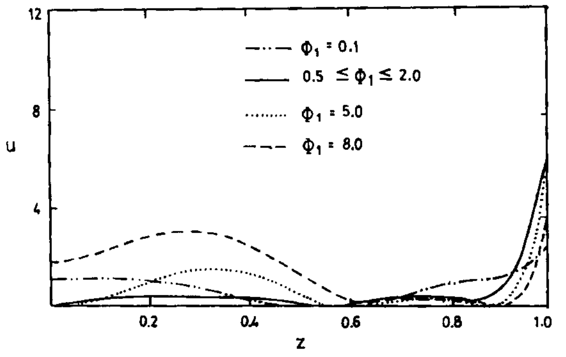

Figure 4. Effects of Φ_1 on selectivity optimization for parallel reaction schemes.

$\beta_1 = 0.05; \beta_2 = 0.10; \gamma_1 = 10; \gamma_2 = 15; \kappa = 0.5.$

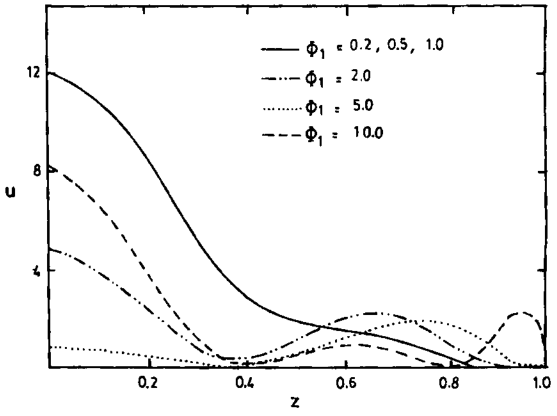

Figure 5. Effects of Φ_1 on selectivity optimization for parallel reaction schemes.

$\beta_1 = 0.05; \beta_2 = 0.10; \gamma_1 = 15; \gamma_2 = 10; \kappa = 0.5.$

Table 2. Parallel Reaction System Results

Variable	Conditions	Effects on optimal profile for η	S	Yield
$\phi_1 \uparrow$	Moderate heat effects $\gamma_1 = 10$ $\gamma_2 = 15$ $\kappa = 0.5$	Shell catalyst for all ϕ_1	Shell → Bimodal for $\phi_1 > 5$	Shell catalyst for all ϕ_1
	Moderate heat effects $\gamma_1 = 15$ $\gamma_2 = 10$ $\kappa = 0.5$	Shell catalyst for all ϕ_1	Shell → Bimodal with increasing activity toward pellet periphery	Shell catalyst for all ϕ_1
$(\beta_1, \beta_2) \uparrow$	$\phi_1 = 1$ $\gamma_1 = 10$ $\gamma_2 = 15$ $= 0.5$	—	—	Shell → Uniform
	$\phi_1 = 1$ $\gamma_1 = 15$ $\gamma_2 = 10$ $= 0.5$	—	—	Shell → Uniform/ core
$\kappa \uparrow$	$\phi_1 = 1$ Moderate heat effects $\gamma_1 = 10$ $\gamma_2 = 15$	—	—	Shell catalyst for all ϕ_1
	$\phi_1 = 1$ Moderate heat effects $\gamma_1 = 15$ $\gamma_2 = 10$	—	—	Shell → Egg white
	$\phi_1 = 1$ High heat effects $\gamma_1 = 15$ $\gamma_2 = 10$	—	—	Shell → Bimodal → Egg white

Parallel reaction scheme

Since the parallel reaction network does not contain the independent heat source of the second reaction of the series network, concentration effects dominate in the specification of optimal activity profiles when effectiveness factors or yields are used as performance criteria. However, temperature is an important concern if selectivity is the optimization criterion. Our study has shown that identical optimal activity distributions are obtained when activity or yield is used as the optimization criterion.

As in the case of the series reaction system, Φ_1 is an important parameter since it defines the intraparticle concentration gradient of the reactant. The heat of reaction parameters and the absolute values of the Arrhenius parameters are important since they control temperature effects. The relative values of γ_1 and γ_2 are very important in the determination of optimal activity distributions when selectivity is optimized.

In nearly isothermal catalyst particles (low values of heat of reaction parameters) effectiveness and yield are maximized when a shell-type activity distribution is employed. However, at very low values of the Thiele modulus ($\Phi_1 < 0.3$), yield of desired product is essentially independent of the activity profile due to negligible concentration and temperature gradients. At higher values of heat of reaction parameters, intraparticle temperature is an important factor when selectivity is optimized. Results obtained for the case in which the activation energy of the desired reaction is lower than that of the undesired reaction ($\gamma_1 < \gamma_2$) are shown in Figure 4. Since temperature gradients benefit the undesired reaction path, it is imperative that these gradients be minimized. Hence, a shell profile proves optimal. At high values of Φ_1, a bimodal activity distribution appears to be optimal. This profile is not significant for the activity present near the pellet center but is significant for the reduced surface activity. The lower values of surface activity serve to reduce reaction rates and subsequently reduce temperature excursions. The bimodal profiles observed at high values of Φ_1 are then an artifact of the requirement that all catalysts contain the same amount of active material.

If the activation energy of the desired reaction is higher than that of the undesired reaction ($\gamma_1 < \gamma_2$), the opposite effects are expected since, in this case, higher intraparticle temperatures favor selectivity. Indeed, as shown in Figure 5, at low values of Φ_1 ($\Phi_1 < 1.0$) a core profile offers the most favorable conditions for maximizing selectivity since little diffusional resistance is encountered by the reactant while high temperatures are utilized. Nevertheless, at higher values of the Thiele modulus, as mass diffusional resistances increase an interplay between concentration and temperature gradients forces activity toward the pellet surface. Thus a bimodal distribution becomes optimal and activity shifts closer to the catalyst surface with increasing value of the Thiele modulus.

Other parameters investigated in the parallel reaction scheme include heats of reaction and ratio of surface rate constant of undesired reaction to that of the desired reaction, κ. As expected, when yield is optimized, as the heat of reactions increase activity shifts toward the pellet center. However, in this reaction scheme heat effects are not strong enough to produce a pendulum effect such as was observed in the series reaction system. The influence that κ exerts on the shape of the optimal activity profile depends primarily on the value of β_2. In yield optimization, at moderate values of β_2 and low values of κ, concentration gradients dominate and force catalytic activity toward the catalyst surface. As κ is increased, enough additional heat is produced to force the activity toward the pellet core. At higher values of β_2 a pendulum effect was again observed in which catalytic activity moves from the pellet surface to the pellet core and back to the pellet surface with increasing value of κ. These results are shown on Table 2 along with a summary of other results of the parallel reaction scheme.

Notation

a_j = coefficients of activity profile expansion, Eq. 16
C = concentration
D_e = effective diffusivity
k = reaction rate constant
k^* = volume-averaged rate constant
P = yield of desired product
$\overline{P}_j(z^2)$ = Jacobi polynomial
R = catalyst radius
r = radial coordinate
S = overall selectivity
T = absolute temperature
u = activity distribution function
V = volume
w_j = weighting function used for quadrature purposes
x_i = dimensionless concentration of species $i = Ci/Ci_s$
z = dimensionless spatial coordinate $= r/R$

Greek letters

α = parameter defined by $k_{2s}C_{Bs}/k_{1s}C_{As}$
β = heat of reaction parameter $= (-\Delta H)\ CD_e/k_eT_s$
γ = Arrhenius parameter $= E/R_gT_s$
η = effectiveness factor
Θ = temperature $= T/T_s$
κ = parameter defined by k_{2s}/k_{1s}
Φ = Thiele modulus
ψ = parameter defined by $D_{eA}C_{As}/D_{eB}C_{Bs}$

Subscripts

s = surface conditions
1,2 = desired and undesired reaction routes, respectively

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