STUDY OF ACTIVITY DISTRIBUTION FOR CONSECUTIVE REACTIONS

Zuzana LETKOVA, Alena BRUNOVSKA and Josef MARKOS

Laboratory of Reaction Engineering,
Slovak Technical University, 812 37 Bratislava, The Slovak Republic

The optimal pellet activity distribution for a system of consecutive reactions is analyzed numerically. Two cases are studied: the case of unconstrained activity (without predescribed maximal concentration of active component) leading to a Dirac delta activity distribution and the case with upper bound for the activity distribution (concentration of active component can not exceed given maximal value) which leads to a step function profile. As the objective function global selectivity is chosen. Examples of both cases are given. The reaction kinetics is described by Langmuir–Hinshelwood type of equations.

Several previous works have shown that the performance of a catalyst pellet can be improved significantly by using nonuniform activity distribution. Most important results are summarized in the recent review of Gavrilidis et al.[1].

The first papers addressing the case of maximal selectivity of consecutive reactions have been published by Vayenas and Pavlou[2–5]. Wu et al.[6] and Ye and Yuan[7] studied nonisothermal reaction systems with arbitrary kinetics. In these papers the optimal catalyst activity distribution in a symmetric porous pellet is investigated analytically by maximizing the effectiveness factor, the global selectivity or the global yield.

In the paper by Wu et al.[6] an optimality criterion was developed using the method described in the paper of Brunovska et al.[8]. This optimality criterion allows to conclude that under quite general conditions the optimal activity distribution is of the Dirac delta type. In the paper of Ye and Yuan[7] the same result was obtained by applying the maximum principle.

The catalysts with nonuniform activity distribution (egg shell, egg white, egg yolk) are well known and have been commercially used. They are usually prepared by impregnation because of its simplicity and wide use. The desired distribution effect within the catalyst support particle depends on the chosen impregnation technique (wet or dry impregnation, coimpregnation), concentration of precursor, time of impregnation, etc. (see Prince and Varma[9]).

The aim of the present work is to estimate the optimal activity distribution in symmetric spherical porous catalyst particles for the case of consecutive reactions using the

criteria from Brunovska et al.[8]. The role of maximal active catalyst concentration (i.e. upper bound for the activity) is considered as well.

THEORETICAL

The Optimization Problem

The problem is to estimate the activity distribution $\Phi(\varphi)$ for which the maximal value of the objective function is obtained. As the objective function global selectivity is considered which represents the efficiency of the reaction system in converting the reactants into the desired product.

Let us assume that B component is the desired product originating from key component A. Global selectivity is defined as the ratio of the rate of production of the component B and the rate of consumption of the component A:

$$S = \frac{\int_0^1 \Phi \left(\sum_{j=1}^J \nu_{Bj} Th_j^2 R_j \right) \varphi^n \, d\varphi}{\int_0^1 \Phi \left(\sum_{j=1}^J \nu_{Aj} Th_j^2 R_j \right) \varphi^n \, d\varphi} \quad . \tag{1}$$

Catalyst activity is defined as the ratio of the local concentration of available catalytically active sites and its volume-average value

$$\Phi(\varphi) = \frac{\sigma(\varphi)}{\overline{\sigma}} \quad , \tag{2}$$

where

$$\overline{\sigma} = (n+1) \int_0^1 \sigma(\varphi) \, \varphi^n \, d\varphi \quad . \tag{3}$$

The activity distribution has to satisfy the following constraints

$$\Phi(\varphi) \geq 0 \quad , \qquad \Phi(\varphi) \leq K$$

$$(n+1) \int_0^1 \Phi(\varphi) \, \varphi^n \, d\varphi = 1 \quad , \tag{4}$$

where $K \in \langle 1, \infty)$ is the upper bound for the activity. Its actual value depends on the maximal admissible concentration of active component on the catalyst support.

The following optimality criterion was developed by Brunovska et al.[8] and Wu et al.[6]

$$(n + 1) \int_0^1 G\hat{\Phi}(\varphi) \, \varphi^n \, d\varphi \geq (n + 1) \int_0^1 G\Phi(\varphi) \, \varphi^n \, d\varphi \ , \tag{5}$$

where $\hat{\Phi}(\varphi)$ is the optimal activity distribution and $\Phi(\varphi)$ is any other activity distribution. Parameter G is a function the form of which depends on the reaction scheme. The optimality criterion practically excludes any activity distribution $\Phi(\varphi)$ which is not of Dirac delta type (Wu et al.[6]). If K is tending to infinity, the maximum value of the integral criterion (5) is always obtained by concentrating all active catalyst at the point $\overline{\varphi}$ where the function G has its maximum. This means that

$$\hat{\Phi}(\varphi) = \frac{\delta(\varphi - \overline{\varphi})}{(n + 1)\,\overline{\varphi}^n} \ . \tag{6}$$

If K is finite and greater than 1 and the function G is unimodal, the optimal distribution is the step function (see Fig. 1)

$$\Phi(\varphi) = 1/(\varphi_2^{n+1} - \varphi_1^{n+1}) = K \ , \quad \varphi \in \langle \varphi_1, \varphi_2 \rangle$$

$$\Phi(\varphi) = 0 \ , \qquad \varphi \in \langle 0, \varphi_1 \rangle \ \text{and} \ \varphi \in (\varphi_2, 1 \rangle \ . \tag{7}$$
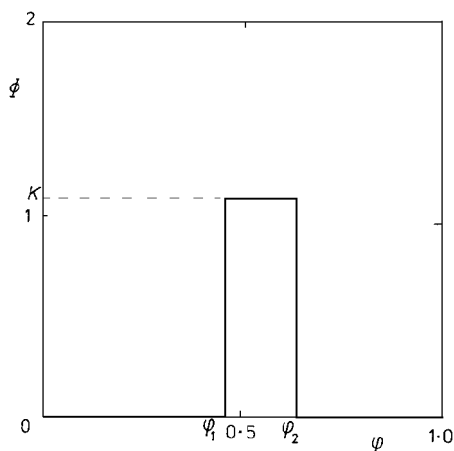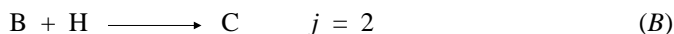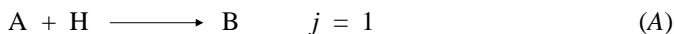

FIG. 1
Step function of activity distribution

The interval $\langle \varphi_1, \varphi_2 \rangle$ can be found from the condition (5) by maximizing the integral criterion using standard optimization technique and with the assumption that the reaction does not take place outside the interval. The limit case for $K = 1$, which leads to the uniform activity distribution

$$\Phi(\varphi) = 1 \ , \qquad \varphi \in \langle 0, 1 \rangle \ . \tag{8}$$

Application to the Case of Consecutive Reactions

Let us consider two consecutive reactions

$$\text{A} \ + \ \text{H} \ \xrightarrow{\hspace{1cm}} \ \text{B} \qquad j \ = \ 1 \tag{A}$$

$$\text{B} \ + \ \text{H} \ \xrightarrow{\hspace{1cm}} \ \text{C} \qquad j \ = \ 2 \tag{B}$$

occurring in a symmetric spherical porous catalyst pellet with negligible external mass and heat transfer. We denote A to be the key component and B to be desired product. The scheme given above corresponds i.e. to the hydrogenation reactions.

The dimensionless steady-state balances are:

– mass balances of reactants

$$\nabla^2 Y_i = \Phi \sum_{j=1}^{J} (-\nu_{ij}) \, Th_j^2 R_j \ , \ , \quad i = \text{A, B, H} \tag{9}$$

– heat balance

$$\nabla^2 \eta = -\Phi \sum_{j=1}^{J} \beta_j Th_j^2 R_j \tag{10}$$

with boundary conditions
$\varphi = 0$:

$$\frac{\mathrm{d}Y_i}{\mathrm{d}\varphi} = \frac{\mathrm{d}\eta}{\mathrm{d}\varphi} = 0 \ ,$$

$\varphi = 1$:

$$Y_i = \eta = 1 \ , \qquad\qquad i = \text{A, B, H} \ . \tag{11}$$

The expressions of Langmuir–Hinshelwood type were selected as the reaction rate concentration terms. Assuming that C is not adsorbed the reaction rates are

$$R_1 = \frac{\omega Y_A Y_H u_1}{(1 + z_A Y_A + z_B Y_B + z_H Y_H)^2} \ , \tag{12}$$

$$R_2 = \frac{\omega Y_B Y_H u_2}{(1 + z_A Y_A + z_B Y_B + z_H Y_H)^2} \ . \tag{13}$$

The objective function is the global selectivity defined by formula (*1*). The corresponding system of adjoint equations (see Appendix) is as follows

$$\nabla^2 p_i + \Phi \sum_{j=1}^{J} \frac{\partial R_j}{\partial Y_i} Th_j^2 V_j = 0 \ , \qquad\qquad i = \text{A, B, H,} \tag{14}$$

$$\nabla^2 p_\eta + \Phi \sum_{j=1}^{J} \frac{\partial R_j}{\partial \eta} Th_j^2 V_j = 0 \tag{15}$$

with boundary conditions

$\varphi = 0$:

$$\frac{\mathrm{d}\, p_i}{\mathrm{d}\, \varphi} = \frac{\mathrm{d}\, p_\eta}{\mathrm{d}\, \varphi} = 0 \ ,$$

$\varphi = 1$:

$$p_i + p_\eta = 0 \ , \qquad\qquad i = \text{A, B, H} \tag{16}$$

and the expression for the optimality criterion

$$\frac{(n+1)}{v_x^2} \int_0^1 \hat{\Phi} G \, \varphi^n \, \mathrm{d}\varphi \geq \frac{(n+1)}{v_x^2} \int_0^1 \Phi G \, \varphi^n \, \mathrm{d}\varphi \ , \tag{17}$$

where

$$G = \sum_{j=1}^{J} R_j Th_j^2 V_j \ , \quad J = 2 \tag{18}$$

and for given reaction scheme V_1, V_2, v_x and v_y are

$$V_1 = v_x - v_y - p_A + p_B - p_H + \beta_1 p_\eta \ , \tag{19}$$

$$V_2 = -v_x - p_B - p_H + \beta_2 p_\eta \ , \tag{20}$$

$$v_x = (n+1)\int_0^1 \hat{\Phi} \sum_{j=1}^{J} \nu_{Aj} Th_j^2 R_j \, \varphi^n \, \mathrm{d}\varphi \ , \tag{21}$$

$$v_y = (n+1)\int_0^1 \hat{\Phi} \sum_{j=1}^{J} \nu_{Bj} Th_j^2 R_j \, \varphi^n \, \mathrm{d}\varphi \ . \tag{22}$$

By solving the system of partial differential equations (model equations (9) – (10) and adjoint equations (14) – (15) we obtain function $G(\varphi)$ which is function of adjoint variables (in this case p_A, p_B, p_H, p_η) and its form depends on the reaction scheme and objective function. The system of mass balance equations and adjoint equations was solved by the collocation method[10].

RESULTS AND DISCUSSION

Figure 2 represents the dependence of the global selectivity (see Eq. (1)) versus the location of Dirac delta function. For given values of parameters ($\alpha_1 = \alpha_2 = 5$, $\beta_1 = \beta_2 = 0.1$, $Th_2^2/Th_1^2 = 0.67$) optimal location of activity is at $\overline{\varphi} = 0.84$ (vertical line) where the global selectivity has its maximum.

The influence of the location of Dirac delta function on the function $G(\varphi)$ is shown on the Fig. 3. Curve *1* indicates that the optimal position of the activity is more closer to the center than the proposed one ($\overline{\varphi} = 0.9$). Curves *3* and *4* indicate that the optimal position is closer to the pellet surface. The maximum of curve *2* corresponds to the optimal location ($\overline{\varphi} = 0.84$).

The case with upper bound for the activity is illustrated by Fig. 4. The optimal position for constrained activity $K = 1.7$ corresponds to a step distribution located in the region of maximal value of the function $G(\varphi)$ (hatched area) with boundaries $\varphi_1 = 0.6$ and $\varphi_2 = 0.93$ (φ_1 and φ_2 satisfy the constraint (7), i.e. $K = 1/(0.93^3 - 0.6^3) = 1.7$). Vertical line represents optimal position of the activity for $K \to \infty$. In order to maximize the optimality criterion (Eq. (17)) the values of the function $G(\varphi)$ at the points φ_1 and φ_2 must be equal.

Figure 5 represents the function $G(\varphi)$ for various positions of step activity distribution $\langle\varphi_1,\varphi_2\rangle$. In the figure it is shown that for step functions analyzed in our case the maximum of $G(\varphi)$ is always located in the vicinity of the optimal location of activity.

The influence of the ratio Th_2^2/Th_1^2 on the location of the maximum and the shape of the function $G(\varphi)$ for uniform activity distribution is shown in the Fig. 6. Maximum of $G(\varphi)$ moves towards the surface with decreasing value of this ratio. This indicates also the shift of the optimal active layer location towards the pellet surface.
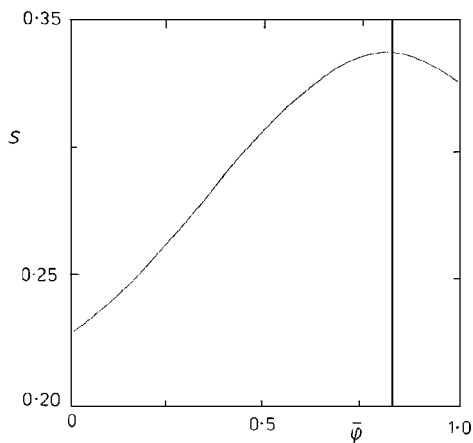

FIG. 2

Dependence of the global selectivity S for various locations of Dirac delta activity distribution $\overline{\varphi}$. Parameters: $\alpha_1 = \alpha_2 = 5$, $\beta_1 = \beta_2 = 0.1$, $Th_2^2/Th_1^2 = 0.67$
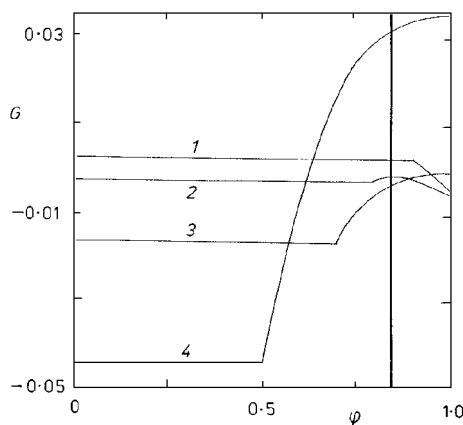

FIG. 3

Dependence of G versus φ for various positions of Dirac delta activity distribution: $1\ \overline{\varphi} = 0.9$, $2\ \overline{\varphi} = 0.8$, $3\ \overline{\varphi} = 0.7$, $4\ \overline{\varphi} = 0.5$; parameters as in Fig. 2
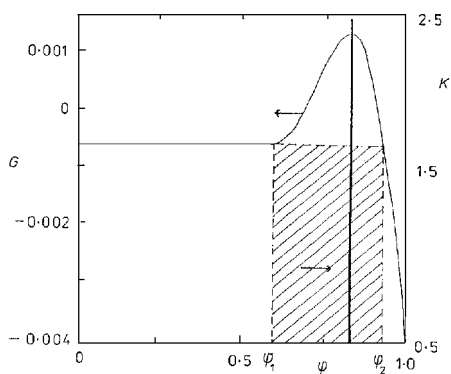

FIG. 4

Dependence of G versus φ for optimal distribution with constraint activity: $K = 1.7$, $\varphi_1 = 0.6$, $\varphi_2 = 0.93$; other parameters as in Fig. 2

CONCLUSION

The results presented concern the case of consecutive reactions with Langmuir–Hinshelwood type of kinetic equations. The optimal catalyst pellet activity distribution (maximizing the integral criterion (*5*)) for a given amount of total catalyst (i.e. constant value of integral (*3*)) depends upon the upper bound for the activity K. If there is no upper bound ($K \to \infty$) it corresponds to a Dirac delta activity distribution. For a finite value of the upper bound it yields a step function distribution, the position of which depends on actual reaction patterns, values of parameters and reaction conditions.

APPENDIX

In this Appendix we derive adjoint Eqs (*14*) – (*15*) and optimality criterion (*17*).

If we take any $\Phi(\varphi)$ satisfying Eq. (*4*), then

$$\Phi(\varphi) = \hat{\Phi}(\varphi) + \varepsilon \, [\Phi(\varphi) - \hat{\Phi}(\varphi)] \qquad (A1)$$

will satisfy Eq. (*4*) for all $0 \le \varepsilon \le 1$.

Let us denote $\delta x = \mathrm{d}x/\mathrm{d}\varepsilon$. By differentiating (*A1*), Eqs (*9*) – (*10*) with boundary conditions (*11*) and objective function (*1*) with respect to ε we obtain
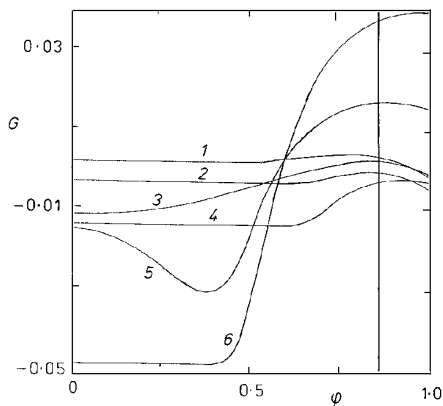

FIG. 5

Dependence of G versus φ for various positions of step activity distribution characterized by the interval $\langle \varphi_1, \varphi_2 \rangle$: *1* $\varphi_1 = 0.5$, $\varphi_2 = 1.0$; *2* $\varphi_1 = 0.6$, $\varphi_2 = 0.9$; *3* $\varphi_1 = 0.1$, $\varphi_2 = 1.0$; *4* $\varphi_1 = 0.6$, $\varphi_2 = 0.8$; *5* $\varphi_1 = 0.01$, $\varphi_2 = 0.5$; *6* $\varphi_1 = 0.4$, $\varphi_2 = 0.5$; other parameters as in Fig. 2
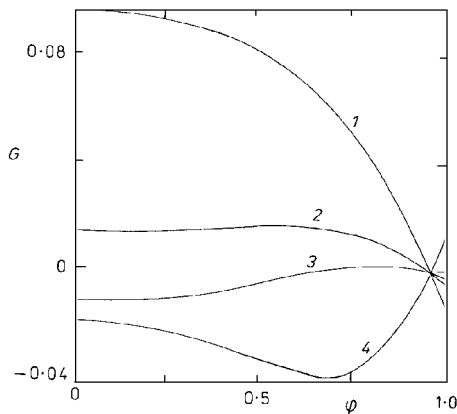

FIG. 6

Dependence of G versus φ for uniform activity distribution $\Phi(\varphi) = 1$ and for various values of Th_2^2/Th_1^2 : *1* $Th_2^2/Th_1^2 = 1$; *2* $Th_2^2/Th_1^2 = 0.7$; *3* $Th_2^2/Th_1^2 = 0.67$; *4* $Th_2^2/Th_1^2 = 0.1$; parameters: $\alpha_1 = \alpha_2 = 5$, $\beta_1 = \beta_2 = 0.1$

$$\delta\Phi(\varphi) = \Phi(\varphi) - \hat{\Phi}(\varphi) \ , \tag{A2}$$

$$\nabla^2 Y_i = \left[\sum_{j=1}^{J} (-\nu_{ij}) Th_j^2 R_j\right] \delta\Phi + \Phi\left[\sum_{j=1}^{J} (-\nu_{ij}) Th_j^2 \left(\sum_{i=1}^{I} \frac{\partial R_j}{\partial Y_i} \delta Y_i + \frac{\partial R_j}{\partial \eta} \delta\eta\right)\right] \ , \tag{A3}$$

$$\nabla^2 \delta\eta = -\left[\sum_{j=1}^{J} \beta_j Th_j^2 R_j\right] \delta\Phi - \Phi\left[\sum_{j=1}^{J} \beta_j Th_j^2 \left(\sum_{i=1}^{I} \frac{\partial R_j}{\partial Y_i} \delta Y_i + \frac{\partial R_j}{\partial \eta} \delta\eta\right)\right] \ , \tag{A4}$$

$\varphi = 0$:

$$\frac{d\delta Y_i}{d\varphi} = \frac{d\delta\eta}{d\varphi} = 0$$

$\varphi = 1$:

$$\delta Y_i = \delta\eta = 0 \tag{A5}$$

and linearized objective function

$$\delta S = \frac{(n+1)}{v_x^2}\left[v_x \int_0^1 \left(\sum_{j=1}^{J} \nu_{Bj} Th_j^2 R_j\right) \delta\Phi \, \varphi^n \, d\varphi - v_y \int_0^1 \left(\sum_{j=1}^{J} \nu_{Aj} Th_j^2 R_j\right) \delta\Phi \, \varphi^n \, d\varphi + \right.$$

$$+ v_x \int_0^1 \Phi\left\{\sum_{j=1}^{J} \nu_{Bj} Th_j^2 \left(\sum_{i=1}^{I} \frac{\partial R_j}{\partial Y_i} \delta Y_i + \frac{\partial R_j}{\partial \eta} \delta\eta\right)\right\} \varphi^n \, d\varphi -$$

$$\left. - v_y \int_0^1 \Phi\left\{\sum_{j=1}^{J} \nu_{Aj} Th_j^2 \left(\sum_{i=1}^{I} \frac{\partial R_j}{\partial Y_i} \delta Y_i + \frac{\partial R_j}{\partial \eta} \delta\eta\right)\right\} \varphi^n \, d\varphi\right] \ , \tag{A6}$$

where $i = $ A, B, H.

After multiplying (A3) and (A4) by $[(n+1)/v_x^2] \, p_i$ and integrating over $\langle 0,1 \rangle$, interchanging the sides and adding to (A6), we have

$$\delta S = \frac{(n+1)}{v_x^2}\left[v_x \int_0^1 \left(\sum_{j=1}^{J} \nu_{Bj} Th_j^2 R_j\right) \delta\Phi \, \varphi^n \, d\varphi - v_y \int_0^1 \left(\sum_{j=1}^{J} \nu_{Aj} Th_j^2 R_j\right) \delta\Phi \, \varphi^n \, d\varphi + \right.$$

$$+ v_x \int_0^1 \Phi\left\{\sum_{j=1}^{J} \nu_{Bj} Th_j^2 \left(\sum_{i=1}^{I} \frac{\partial R_j}{\partial Y_i} \delta Y_i + \frac{\partial R_j}{\partial \eta} \delta\eta\right)\right\} \varphi^n \, d\varphi -$$

$$- v_y \int_0^1 \Phi \left\{ \sum_{j=1}^J \nu_{Aj} Th_j^2 \left(\sum_{i=1}^I \frac{\partial R_j}{\partial Y_i} \delta Y_i + \frac{\partial R_j}{\partial \eta} \delta \eta \right) \right\} \varphi^n \, d\varphi \right] +$$

$$+ \frac{(n+1)}{v_x^2} \left[\int_0^1 \left(\sum_{i=1}^I p_i \nabla^2 \, \delta Y_i + p_\eta \nabla^2 \, \delta \eta \right) \varphi^n \, d\varphi + \int_0^1 \sum_{j=1}^J \left(\sum_{i=1}^I p_i \nu_{ij} Th_j^2 R_j + \right. \right.$$

$$+ p_\eta \beta_j Th_j^2 R_j \bigg) \delta \Phi \, \varphi^n \, d\varphi - \int_0^1 \Phi \sum_{i=1}^I p_i \left\{ \sum_{j=1}^J (-\nu_{ij}) Th_j^2 \left(\sum_{i=1}^I \frac{\partial R_j}{\partial Y_i} \delta Y_i + \right. \right.$$

$$+ \frac{\partial R_j}{\partial \eta} \delta \eta \bigg) \bigg) \varphi^n \, d\varphi + \int_0^1 \Phi p_\eta \left\{ \sum_{j=1}^J \beta_j Th_j^2 \left(\sum_{i=1}^I \frac{\partial R_j}{\partial Y_i} \delta Y_i + \frac{\partial R_j}{\partial \eta} \delta \eta \right) \right\} \varphi^n \, d\varphi \right] . \tag{A7}$$

Integrating by parts the expression $\int_0^1 \left(\sum_{i=1}^I p_i \nabla^2 \, \delta Y_i + p_\eta \nabla^2 \, \delta \eta \right) \varphi^n \, d\varphi$ from $(A7)$ we

obtain $\int_0^1 \left(\sum_{i=1}^I \nabla^2 p_i \, \delta Y_i + \nabla^2 p_\eta \, \delta \eta \right) \varphi^n \, d\varphi$. Then, if p_i is solution of the adjoint equations

$$\nabla^2 p_i + \Phi \sum_{j=1}^J \frac{\partial R_j}{\partial Y_i} Th_j^2 V_j = 0 \ , \qquad i = A, B, H \tag{A8}$$

$$\nabla^2 p_\eta + \Phi \sum_{j=1}^J \frac{\partial R_j}{\partial \eta} Th_j^2 V_j = 0 \tag{A9}$$

with boundary conditions

$\varphi = 0$:

$$\frac{dp_i}{d\varphi} = \frac{dp_\eta}{d\varphi} = 0$$

$\varphi = 1$:

$$p_i = p_\eta = 0 \ , \qquad i = A, B, H \tag{A10}$$

we have

$$\delta S = \frac{(n+1)}{v_x^2} \int_0^1 \left(\sum_{j=1}^J Th_j^2 R_j V_j \right) \delta \Phi \, \varphi^n \, d\varphi \ . \tag{A11}$$

Adjoint variables (in our case p_A, p_B, p_H, p_η) correspond to Lagrangian multipliers.

Applying Eq. (A2), (A11) leads to

$$\delta S = \frac{(n+1)}{v_x^2} \int_0^1 \left(\sum_{j=1}^{J} Th_j^2 R_j V_j \right) [\Phi(\varphi) - \hat{\Phi}(\varphi)] \, \varphi^n \, d\varphi \ , \tag{A12}$$

from which we obtain the general optimality condition (17).

SYMBOLS

c	concentration, mol m^{-3}
D_e	effective diffusion coefficient, m^2 s^{-1}
E	dimensionless activation energy, $E = E_a/\mathbf{R}_g T_0$
E_a	activation energy, J mol^{-1}
ΔH	heat of reaction, J mol^{-1}
K	upper bound for the activity, $K \in \langle 1, \infty \rangle$
K_0	adsorption constant, m^3 mol^{-1}
n	integer characteristic of pellet geometry (slab $n = 0$, cylinder $n = 1$, sphere $n = 2$)
p	adjoint variable
Q	adsorption heat, J mol^{-1}
r	radial pellet coordinate, m
R_j	dimensionless reaction rate
$\mathbf{R}_g$	ideal gas constant, J mol^{-1} K^{-1}
R_p	catalyst pellet radius, m
S	global selectivity
T	temperature, K
Th_j	Thiele modulus, $Th_j^2 = R_p^2 \rho \xi_{0j} / D_e c_0$
u_1	$= \exp[\varepsilon(\alpha_A + \alpha_H + E_1)]$
u_2	$= \exp[\varepsilon(\alpha_B + \alpha_H + E_2)]$
Y	dimensionless concentration, $Y = c/c_0$
z_A	$= \chi_A \exp(\alpha_A \varepsilon)$
z_B	$= \chi_B \exp(\alpha_B \varepsilon)$
z_H	$= \chi_H \exp(\alpha_H \varepsilon)$
α	dimensionless adsorption heat, $\alpha = Q/\mathbf{R}_g T_0$
β	dimensionless reaction heat, $\beta_j = (-\Delta H_j) D_e c_0 / \lambda T_0$
δ	Dirac delta function
ε	$= (\eta - 1)/\eta$
λ	thermal conductivity, J m^{-1} s^{-1} K^{-1}
Φ	activity, Eq. (2)
η	dimensionless temperature, $\eta = T/T_0$
χ	adsorption constant, $\chi = \chi_0 \exp(\alpha \varepsilon)$
χ_0	$= c_0 K_0$
v_{ij}	stoichiometric coefficient of i-th component in j-th reaction
$\overline{\sigma}$	concentration of catalytically active sites
φ	dimensionless radial coordinate, $\varphi = r/R_p$

φ_1, φ_2	boundaries of the step function activity distribution
$\overline{\varphi}$	Dirac delta function location
ρ	catalyst density, kg m^{-3}
ω	$= (1 + \chi_A + \chi_B + \chi_H)^2$
∇	Nabla operator

Subscripts

A, B, C, H	reactants
i	i-th reactant
I	number of reactants
j	j-th reaction
J	number of reactions in the system
0	reference conditions (i.e. bulk flow)

Superscript

^	optimal value

REFERENCES

1. Gavrilidis A., Varma A., Morbidelli M.: Catal. Rev. Sci. Eng. *35*, 399 (1993).
2. Vayenas C. G., Pavlou S.: Chem. Eng. Sci. *42*, 1655 (1987).
3. Vayenas C. G., Pavlou S.: Chem. Eng. Sci. *42*, 2633 (1987).
4. Vayenas C. G., Pavlou S.: Chem. Eng. Sci. *43*, 2729 (1988).
5. Vayenas C. G., Pavlou S., Pappas A. D.: Chem. Eng. Sci. *44*, 113 (1989).
6. Wu H., Brunovska A., Morbidelli M., Varma A.: Chem. Eng. Sci. *45*, 1855 (1990).
7. Ye J., Yuan Q.: Chem. Eng. Sci. *47*, 615 (1992).
8. Brunovska A., Morbidelli M., Brunovsky P.: Chem. Eng. Sci. *45*, 917 (1990).
9. Prince D. M., Varma A.: Presented at *AICHE Annual Meeting, New York 1987.*
10. Villadsen J., Michelsen M. L.: *Solution of Differential Equation Models by Polynomial Approximation.* Prentice-Hall, Englewood Cliffs 1978.