

## OPTIMAL CATALYST ACTIVITY DISTRIBUTION IN FIXED-BED REACTOR WITH CATALYST DEACTIVATION

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In this paper the influence of the active catalyst location in a pellet on fixed-bed catalytic reactor performance is described. The optimal activity distribution as a function of an economic parameter (ratio of product and catalyst costs), Thiele modulus and Damkohler number is estimated.

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By nonuniform active catalyst distribution within a porous pellet we can enhance its effectiveness factor and, as a consequence, the reactor outlet conversion. The optimal catalyst activity distribution maximizing the effectiveness factor for CO oxidation has been determined by Morbidelli et al.<sup>1-3</sup>. These results have been extended to arbitrary reaction rate equation by Vayenas and Pavlou<sup>4</sup>. For any reaction kinetics the optimal activity distribution is given by a Dirac delta function the location of which depends on the kinetic equation and the value of Thiele modulus, which is defined for pellet surface conditions.

Due to the change of the bulk flow conditions along the reactor (concentrations of all components, temperature) in a fixed-bed catalytic reactor the optimal activity distribution is a function of the pellet position in the reactor. The problem of estimation the active catalyst location maximizing fixed-bed reactor outlet conversion for bimolecular Langmuir-Hinshelwood reactions has been solved in literature<sup>5-7</sup>.

The solution of the problem of maximizing reactor outlet conversion is different if we consider the reactor performance in a long time interval during which the decrease of the catalyst activity due to the deactivation process is significant. The active catalyst location affects not only the effectiveness factor, but also the course of deactivation, i.e. the decrease of the reactor performance. If the active catalyst is inside the pellet, the resistance against deactivation is increased. On the other hand, for positive order reactions this leads to decrease of the effectiveness factor. This is why we address the question of how the location of the active catalyst affects the reactor performance in a long time period in which deactivation cannot be neglected.

## THEORETICAL

*Optimization Problem*

As in the recent papers<sup>5-7</sup> we consider activity in a narrow region (Dirac delta function) at a point  $\varphi_1$ . As the objective function we choose

$$\frac{\text{profit}}{\text{time}} = \frac{\left[ \begin{array}{l} \text{Cost of products} \\ \text{per operating time} \end{array} \right] - \left[ \begin{array}{l} \text{Cost of raw materials and} \\ \text{catalyst per operating time} \end{array} \right]}{\text{operating time}}$$

It is a function of the active catalyst location  $\varphi_1$  and the operating time  $\tau^*$  (length of one cycle), because we are not able to estimate this time beforehand. Mathematically

$$\frac{\text{profit}}{\text{time}} = \frac{\alpha_1 \int_0^{\tau^*} X_B d\tau - \alpha_2 \int_0^{\tau^*} X_B d\tau - \alpha_3}{\tau^*} \quad (1)$$

Dividing by  $\alpha_3$  we obtain the objective function in the form

$$F(\varphi_1, \tau^*) = (v \int_0^{\tau^*} X_B d\tau - 1)/\tau^*, \quad (2)$$

where  $v = (\alpha_1 - \alpha_2)/\alpha_3$  is proportional to the cost of products less the cost of raw materials divided by the cost of catalyst. High value of the parameter  $v$  represents expensive product and cheap catalyst, a low value represents expensive catalyst and cheap product.

*Mathematical Model*

Let us consider a nonisothermal heterogeneous plug-flow reactor packed with catalyst pellets with activity concentrated in a narrow layer. Let us assume a first order catalytic reaction, perfect gas-to-solid heat and mass transfer, constant gas density and temperature independent heat of reaction, heat capacity and overall heat transfer coefficient. As deactivation we consider independent irreversible chemisorption of the catalyst poison. Let us neglect the heat released by the chemisorption of the poison (the poison concentration is considerably lower than the reactant concentrations) and assume that the deactivation rate is much lower than the rate of catalytic reaction. In other words we adopt the quasi-steady state assumption.

With these assumptions the dimensionless model equations are:

fluid-phase mass balance of the key component

$$\frac{dY_{B,f}}{dz} = -Da_B \langle \Xi \rangle = -Da_B (n + 1) \int_0^1 \Xi \varphi^n d\varphi; \quad (3)$$

catalyst pellet mass balance of the key component

$$\nabla^2 Y_B = Th_B^2 \Xi ; \quad (4)$$

fluid-phase enthalpy balance

$$\frac{d\Theta_f}{dz} = Da_T \langle \Xi \rangle - F(\Theta_f - \Theta_c) ; \quad (5)$$

catalyst pellet enthalpy balance

$$\nabla^2 \Theta = Th_B^2 \beta \Xi ; \quad (6)$$

fluid-phase mass balance of the poison

$$\frac{dY_{J,f}}{dz} = Da_J(n+1) \int_0^1 \dot{\Phi} \varphi^n d\varphi ; \quad (7)$$

catalyst pellet mass balance of the poison

$$\nabla^2 Y_J = -Th_J^2 \dot{\Phi} ; \quad (8)$$

catalyst reaction rate equation

$$\Xi = Y_B \Phi \exp(\alpha_c \varrho) , \quad (9)$$

where

$$\varrho = (\Theta - 1)/\Theta \quad (10)$$

and the mean reaction rate expression is

$$\langle \Xi \rangle = (n+1) \int_0^1 Y_B \Phi \exp(\alpha_c \varrho) \varphi^n d\varphi ; \quad (11)$$

deactivation rate equation

$$\dot{\Phi} = \frac{d\Phi}{d\tau} = -Y_J \Phi \exp(\alpha_D \varrho) \quad (12)$$

and the mean rate of deactivation

$$\langle \dot{\Phi} \rangle = -(n+1) \int_0^1 Y_J \Phi \exp(\alpha_D \varrho) \varphi^n d\varphi ; \quad (13)$$

initial conditions (constant amount of active catalyst at point  $\varphi_1$ )<sup>1</sup>

$$\tau = 0 : z \in \langle 0, 1 \rangle : \Phi(z, \varphi, \tau) = \Phi(z, \varphi, 0) \quad (14)$$

$$\Phi(z, \varphi, 0) = \frac{\delta(\varphi - \varphi_1)}{(n+1) \varphi_1^n} \quad (15)$$

$$(n + 1) \int_0^1 \Phi(z, \varphi, 0) \varphi^n d\varphi = 1 ; \quad (16)$$

boundary conditions

$$\tau \geq 0 ; \quad z = 0 : Y_{B,f} = Y_{J,f} = \Theta_f = 1 \quad (17)$$

$$z \in \langle 0, 1 \rangle ; \quad \varphi = 0 : dY_B/d\varphi = dY_J/d\varphi = d\Theta/d\varphi = 0 \quad (18)$$

$$\varphi = 1 : Y_B = Y_{B,f}, Y_J = Y_{J,f}, \Theta = \Theta_f . \quad (19)$$

The activity is defined as a ratio of the local reaction rate constant and the initial volume averaged value and at any time  $\tau$  can be expressed as a product of the initial activity and a time dependent dimensionless parameter  $\mu$  (relative activity)

$$\Phi(z, \varphi, \tau) = \Phi(z, \varphi, 0) \mu(z, \tau) , \quad (20)$$

where

$$\mu(z, 0) = 1 \quad \text{for } z \in \langle 0, 1 \rangle . \quad (21)$$

From Eqs (12) and (20) it follows

$$\frac{d\Phi}{d\tau} = \Phi(z, \varphi, 0) \frac{d\mu}{d\tau} . \quad (22)$$

#### *Solution of Model Equations*

From the catalyst pellet balances (4) and (6) and boundary conditions (18) and (19) it follows that at any time instant the sum ( $\beta Y_B + \Theta$ ) is constant throughout the pellet and equal to its surface value

$$\beta Y_B + \Theta = \beta Y_{B,f} + \Theta_f . \quad (23)$$

Substituting relation (23) into (10) we obtain

$$\varrho = \frac{\Theta_f + \beta(Y_{B,f} - Y_B) - 1}{\Theta_f + \beta(Y_{B,f} - Y_B)} . \quad (24)$$

Because the catalytic reaction as well as the catalyst deactivation takes place only in a narrow layer at the point  $\varphi_1$  the catalyst pellet mass balances can be solved analytically. We obtain

$$\varphi \in \langle 0, \varphi_1 \rangle : Y_B = Y_{B1}, Y_J = Y_{J1} \quad (25)$$

$$\varphi \in \langle \varphi_1, 1 \rangle : Y_B = Y_{B,f} - (Y_{B,f} - Y_{B1}) \Psi_n(\varphi) / \Psi_n(\varphi_1) \quad (26)$$

$$Y_J = Y_{J,f} - (Y_{J,f} - Y_{J1}) \Psi_n(\varphi) / \Psi_n(\varphi_1) \quad (27)$$

$$\varphi \in \langle 0, 1 \rangle : \Theta = \Theta_f + \beta(Y_{B,f} - Y_B). \quad (28)$$

$Y_{B1}$  and  $Y_{J1}$  are concentrations in the active layer and  $\Psi_n(\varphi)$  is a function of the pellet geometry

$$\begin{aligned} \Psi_n(\varphi) &= \varphi - 1 && \text{for } n = 0 \text{ (infinite slab),} \\ &= \ln \varphi && \text{for } n = 1 \text{ (infinite cylinder),} \\ &= 1 - 1/\varphi && \text{for } n = 2 \text{ (sphere).} \end{aligned} \quad (29)$$

The mean rates of reaction and deactivation can be expressed by the following formulas

$$\langle \mathcal{E} \rangle = Y_{B1} \mu \exp(\alpha_c \varrho_1) \quad (30)$$

$$\langle \mathcal{F} \rangle = -Y_{J1} \mu \exp(\alpha_D \varrho_1), \quad (31)$$

where

$$\varrho_1 = (\Theta_1 - 1) / \Theta_1. \quad (32)$$

Simultaneously, for the mean rate of reaction and deactivation we can write

$$\langle \mathcal{E} \rangle = - \frac{(n+1) \varphi_1^n}{Th_B^2 \Psi_n(\varphi_1)} (Y_{B,f} - Y_{B1}) \left[ \frac{d\Psi_n(\varphi)}{d\varphi} \right]_{\varphi=\varphi_1} \quad (33)$$

$$\langle \mathcal{F} \rangle = \frac{(n+1) \varphi_1^n}{Th_J^2 \Psi_n(\varphi_1)} (Y_{J,f} - Y_{J1}) \left[ \frac{d\Psi_n(\varphi)}{d\varphi} \right]_{\varphi=\varphi_1}. \quad (34)$$

From Eqs (30), (33) and Eqs (31), (34) we obtain

$$Y_{B1} = \frac{(n+1) Y_{B,f}}{n+1 - x \mu \exp(\alpha_c \varrho_1)} \quad (35)$$

$$Y_{J1} = \frac{(n+1) Y_{J,f}}{n+1 - Ax \mu \exp(\alpha_D \varrho_1)}, \quad (36)$$

where

$$x = Th_B^2 \Psi_n(\varphi_1) \quad (37)$$

$$A = Th_J^2 / Th_B^2. \quad (38)$$

Substituting Eqs (30) and (31) into fluid-phase balances we obtain

$$\frac{dY_{B,f}}{dz} = -Da_B Y_{B1} \mu \exp(\alpha_c \varrho_1) \quad (39)$$

$$\frac{dY_{J,f}}{dz} = -Da_J Y_{J1} \mu \exp(\alpha_D \varrho_1) \quad (40)$$

$$\frac{d\Theta_f}{dz} = Da_T Y_{B1} \mu \exp(\alpha_c \varrho_1) - F(\Theta_f - \Theta_c) \quad (41)$$

and, from Eqs (12) and (22),

$$\frac{d\mu}{d\tau} = -\mu Y_{J1} \exp(\alpha_D \varrho_1). \quad (42)$$

In this way the system of the model Eqs (3)–(22) is reduced to the system of ordinary differential equations (39)–(42) and two nonlinear algebraic equations (35) and (36). The initial and boundary conditions are

$$\tau = 0; \quad z \in \langle 0, 1 \rangle : \mu = 1 \quad (43)$$

$$\tau > 0; \quad z = 0 \quad : Y_{B,f} = Y_{J,f} = \Theta_f = 1. \quad (44)$$

The system of the model equations has been solved by the predictor–corrector method.

The maximum of the objective function (2) has been estimated by the following procedure: By a one-parameter estimation method the active point  $\varphi_1$  has been estimated. For each value of  $\varphi_1$  the time dependences of concentrations, activity and temperature along the reactor and the objective function have been computed by the solution of the model equations. The time has been increased until the objective function reached its maximum.

## RESULTS AND DISCUSSION

The behaviour of an isothermal fixed-bed catalytic reactor packed by catalyst pellets with narrow region activity distribution and bimolecular Langmuir–Hinshelwood reaction has been investigated in literature<sup>5–7</sup>. Due to different reaction rate equations we can hardly compare their results with ours. The nonisothermal problem, in which one catalyst pellet has been studied, is described in detail in ref.<sup>3</sup>. In this paper it has been proved that for positive order reactions the optimal active catalyst location can be inside the pellet solely in the presence of an intrapellet temperature

gradient. In accord with<sup>3</sup> in our numerical investigation of steady state reactor behaviour for chosen  $\alpha_c$  and  $\beta$  the optimal active catalyst location appears at the external surface.

This is shown in Figs 1 and 2. In Fig. 1 the reactor outlet concentration as a function of active catalyst location for different values of Thiele moduli is shown. In Fig. 2 the same dependence for different values of Damkohler numbers is exhibited.

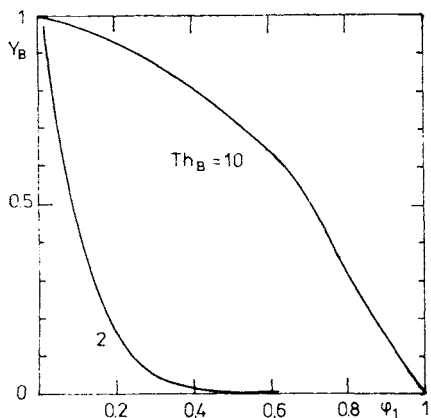


FIG. 1

Reactor outlet steady state concentration vs active catalyst location  $\varphi_1$  for different values of  $Th_B$ .  $Da_B = 10$ ,  $\beta = 1$ ,  $\alpha_c = 11$

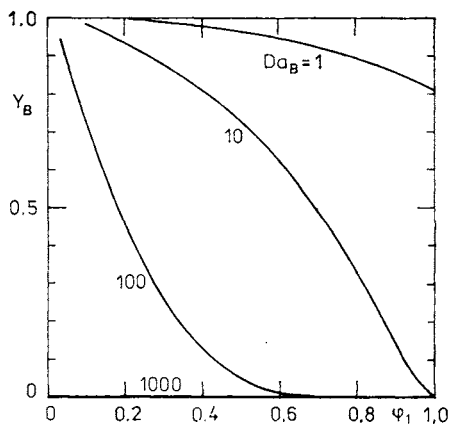


FIG. 2

Reactor outlet steady state concentration vs active catalyst location  $\varphi_1$  for different values of  $Da_B$ .  $Th_B = 10$ ,  $\beta = 1$ ,  $\alpha_c = 11$

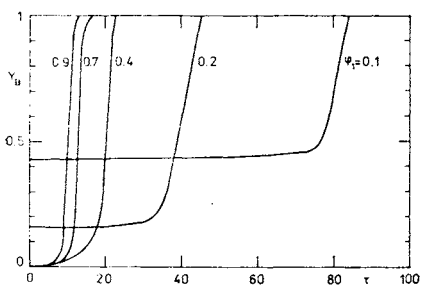


FIG. 3

Comparison of the reactor outlet concentration time dependences for different active catalyst location  $\varphi_1$ .  $Th_j = 5$ ,  $Da_j = 10$ ,  $\beta = 1$

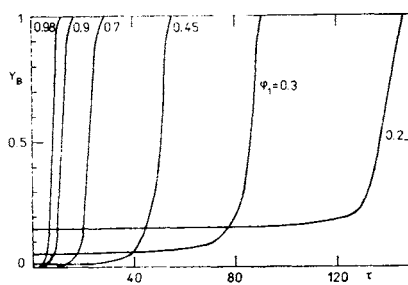


FIG. 4

Comparison of the reactor outlet concentration time dependences for different active catalyst location  $\varphi_1$ .  $Th_j = 10$ ,  $Da_j = 10$ ,  $\beta = 1$

The deactivation process (the reactor outlet concentration vs time) for different active catalyst location and two values of poison Thiele moduli is illustrated in Figs 3 and 4. From these figures it is evident that moving the active catalyst location toward the pellet center causes an increase of the reactor outlet concentration (i.e. decrease of the steady state reactor performance) and, in addition, increases the operating time significantly. This means an improvement of long time reactor performance. From these figures two different tendencies can be seen.

- a) To maximize steady state reactor outlet conversion it is advantageous to locate all active catalyst near the external surface.
- b) To maximize the duration of operation period the location in the pellet center should be given preference.

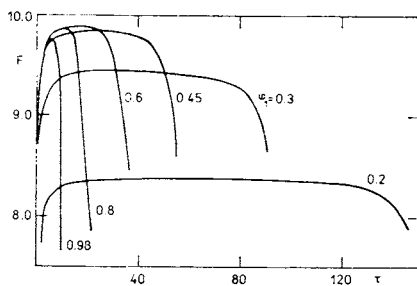


FIG. 5

The objective function time dependences for different values of the active catalyst location  $\phi_1$ .  $Th_j = 10$ ,  $Da_j = 10$ ,  $\nu = 10$

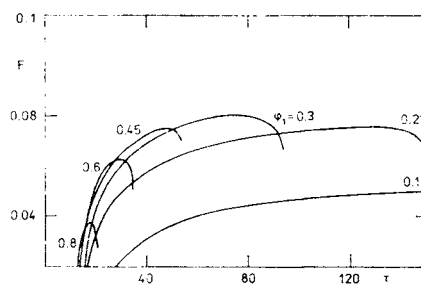
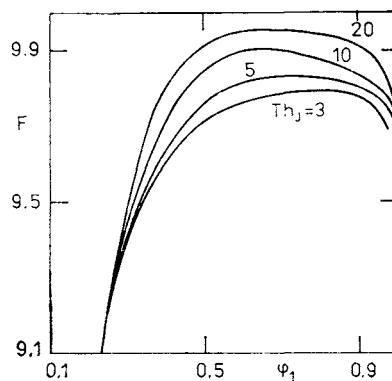
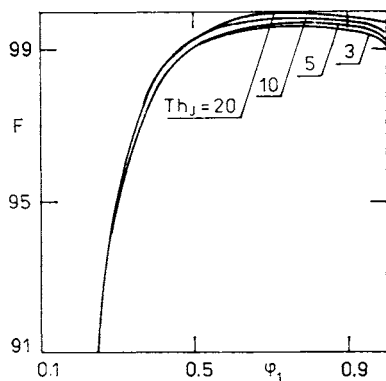


FIG. 6

The objective function time dependences for different values of the active catalyst location  $\phi_1$ .  $Th_j = 10$ ,  $Da_j = 10$ ,  $\nu = 0.1$





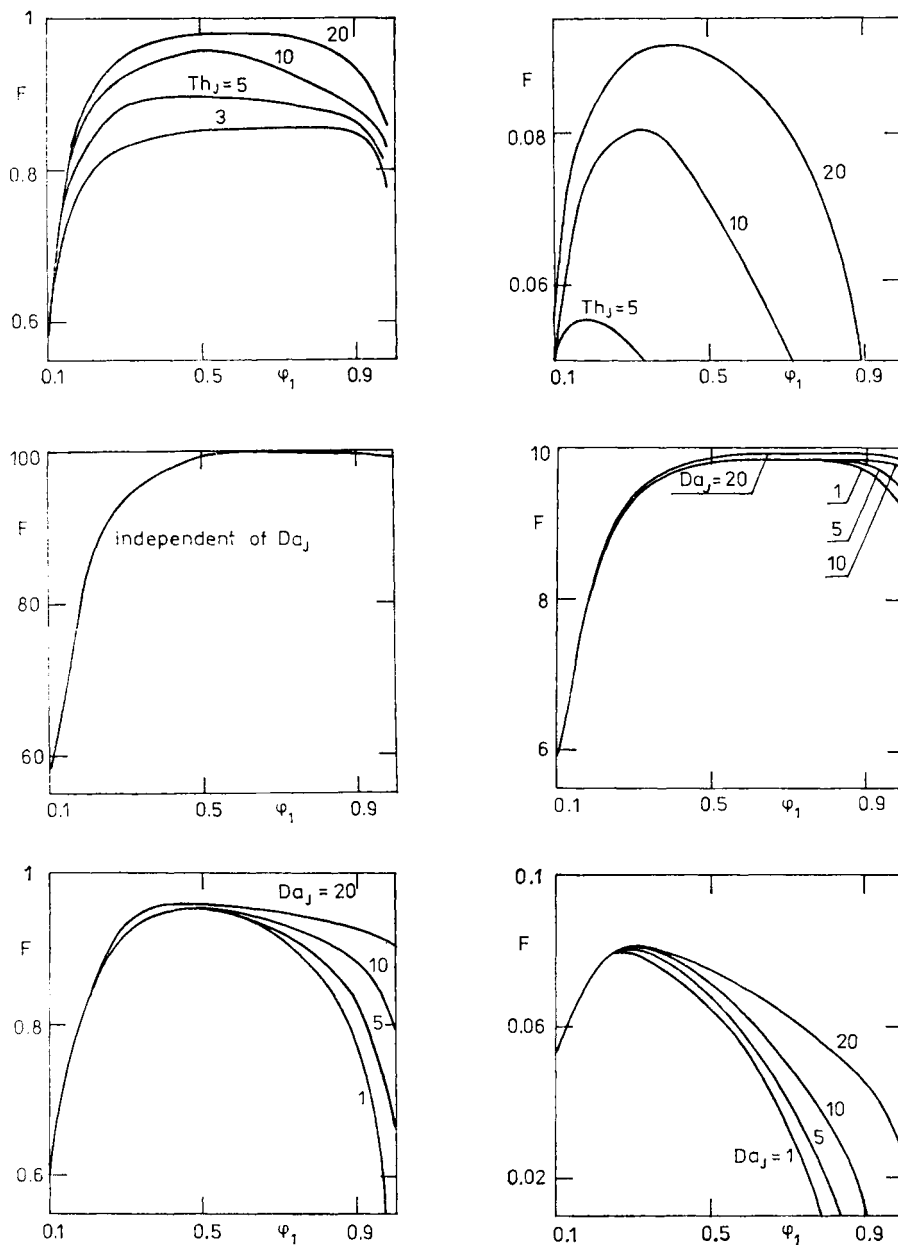


FIG. 7

Comparison of the objective function vs active catalyst location for different values of  $Th_j$  and  $Da_j$  ( $\beta = 1$ ). a  $Da_j = 10$ ,  $\nu = 100$ ; b  $\nu = 10$ ; c  $\nu = 1$ ; d  $\nu = 0.1$ ; e  $Th_j = 10$ ,  $\nu = 100$ ; f  $\nu = 10$ ; g  $\nu = 1$ ; h  $\nu = 0.1$

The dependence of the objective function  $F$  on operating time  $\tau^*$  for different active catalyst location is illustrated in Figs 5 and 6 for two values of the parameter  $\nu$ . The value  $\nu = 10$  (Fig. 5) corresponds to cheap catalyst and expensive product and the maximal value of the objective function is obtained for active catalyst location  $\phi_1 = 0.6$ . The value  $\nu = 0.1$  (Fig. 6) illustrates the opposite situation cor-

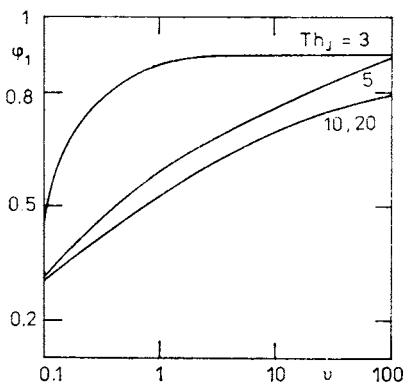


FIG. 8

Optimal active catalyst location as the function of parameter  $\nu$  for different values of  $Th_j$ .  $Da_j = 10$ ,  $\beta = 1$

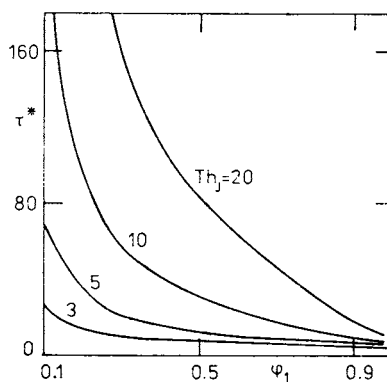


FIG. 9

Operating time  $\tau^*$  as the function of active catalyst location  $\phi_1$  for different values of  $Th_j$ .  $Da_j = 10$ ,  $\beta = 1$ ,  $\nu = 1$

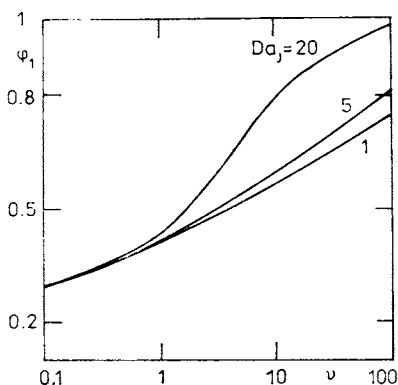


FIG. 10

Optimal active catalyst location vs parameter  $\nu$  for different values of  $Da_j$ .  $Th_j = 10$ ,  $\beta = 1$

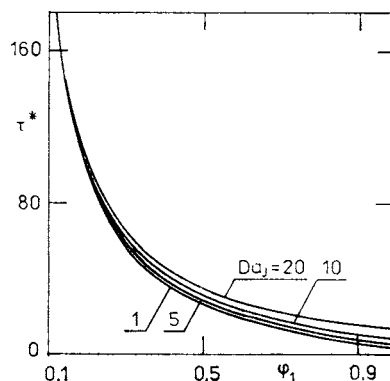


FIG. 11

Operating time vs active catalyst locations  $\phi_1$  for different values of  $Da_j$ .  $Th_j = 10$ ,  $\nu = 1$

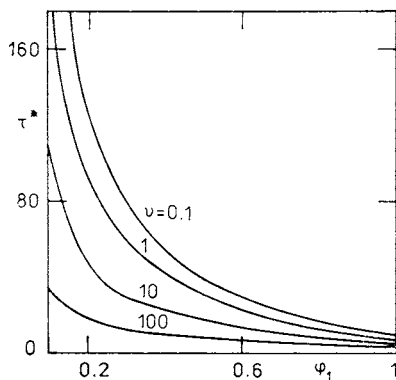


FIG. 12

Operating time vs active catalyst location  $\varphi_1$  for different values of  $\nu$ .  $Da_j = 10$ ,  $Th_j = 10$ ,  $\beta = 1$

responding to expensive catalyst and cheap product and leads to an activity location closer to the pellet center ( $\varphi_1 = 0.3$ ). The operating dimensionless time for  $\nu = 10$  is  $\tau^* = 14$  and for  $\nu = 0.1$  is  $\tau^* = 75$ . The influence of the parameters  $\nu$  and the poison Thiele modulus is evident from Fig. 7. With the decrease of  $\nu$  the optimal active catalyst location is moving towards the pellet center and the objective function is more sensitive on this location. This influence is summarized in Fig. 8. In Fig. 9 the dependence  $\tau^* vs \varphi_1$  for  $\nu = 1$  is exhibited. For high values of the poison Thiele moduli the optimal location  $\varphi_1$  is strongly dependent on the parameter  $\nu$  and simultaneously the operating time  $\tau^*$  is increasing. Similarly the influence of the parameters  $\nu$  and Damkohler number  $Da_j$  on the objective function vs  $\varphi_1$  dependence is exhibited in Fig. 7. In Fig. 10 the influence of the parameter  $\nu$  on the active catalyst location for different values of  $Da_j$  is summarized. The operating time  $\tau^* vs$  location  $\varphi_1$  dependence for several values of  $Da_j$  is illustrated in Fig. 11 and the same dependence for several values of the parameter  $\nu$  is illustrated in Fig. 12.

From all the presented results it is evident that the optimal active catalyst location strongly depends on the economic parameter  $\nu$ . Expensive catalyst (small value of  $\nu$ ) requires activity to be located inside the pellet. By this improvement the operating time can be increased significantly.

## LIST OF SYMBOLS

$a_j^*$	equilibrium amount of adsorbed poison, mol kg <sup>-1</sup>
$C$	concentration, mol m <sup>-3</sup>
$c_{p,g}$	gas heat capacity, J kg <sup>-1</sup> K <sup>-1</sup>
$D_e$	diffusion coefficient, m <sup>2</sup> s <sup>-1</sup>
$Da_B$	$= (1 - \epsilon) k_v^0 L / v$ Damkohler number for key component
$Da_T$	$= (1 - \epsilon) (-\Delta H) k_v^0 C_{B,f}^0 L / v \rho_g c_{p,g} T_f^0$ dimensionless parameter
$Da_j$	$= (1 - \epsilon) \rho_b a_j^* k_j^0 L / v$ Damkohler number for catalyst poison
$d_t$	reactor diameter, m

$E$	activation energy of catalytic reaction, $\text{J mol}^{-1}$
$E_j$	activation energy of deactivation reaction, $\text{J mol}^{-1}$
$F$	$= 4hL/d_v \rho_g c_{p,g}$ dimensionless overall heat transfer coefficient
$F$	objective function
$h$	overall heat transfer coefficient, $\text{J m}^{-2} \text{s}^{-1} \text{K}^{-1}$
$(-\Delta H)$	heat of reaction, $\text{J mol}^{-1}_r$
$k_j$	deactivation rate constant, $\text{m}^3 \text{kg}^{-1} \text{s}^{-1}$
$k_v$	catalytic reaction rate constant, $\text{s}^{-1}$
$L$	reactor length, m
$n$	integer characteristic of pellet geometry
$R$	gas constant, $\text{J mol}^{-1} \text{K}^{-1}$
$R_p$	catalyst pellet radius, m
$r$	pellet radial coordinate, m
$Th_B^2$	$= R_p^2 k_v^0 / D_{eB}$ Thiele modulus for key component
$Th_j^2$	$= R_p^2 a_j^* \rho_s / (D_{eJ} C_{j,t}^0)$ Thiele modulus for poison
$T$	temperature, K
$T_c$	cooling medium temperature, K
$t$	time, s
$t^0$	$= 1/(C_{j,t}^0 k_j^0)$ characteristic deactivation time, s
$V_f$	volumetric flow rate, $\text{m}^3 \text{s}^{-1}$
$v$	external fluid phase velocity, $\text{m s}^{-1}$
$x$	$= Th_B^2 \Psi_n(\varphi_1)$ dimensionless parameter
$X_B$	conversion of key component
$y$	axial coordinate, m
$Y$	$= C/C_f^0$ dimensionless concentration
$z$	$= y/L$ dimensionless axial coordinate
$A$	$= Th_j^2 / Th_B^2$ dimensionless parameter
$\alpha_c$	$= E/(RT_f^0)$ dimensionless activation energy
$\alpha_D$	$= E_D/(RT_f^0)$ dimensionless activation energy of deactivation
$\alpha_1$	$= (V_f C_{B,t}^0) \cdot (\text{cost of product})$ , $\text{K}\check{\text{c}}\text{s}^{-1}$
$\alpha_2$	$= (V_f C_{B,t}^0) \cdot (\text{cost of raw materials})$ , $\text{K}\check{\text{c}}\text{s}^{-1}$
$\alpha_3$	$= (\text{cost of catalyst})/t^0$ , $\text{K}\check{\text{c}}\text{s}^{-1}$
$\beta$	$= D_{eB}(-\Delta H) C_{B,t}^0 / (T_f^0 \lambda_e)$ dimensionless heat generation parameter
$\delta$	Dirac delta function
$\varepsilon$	bed void fraction
$\Theta$	$= T/T_f^0$ dimensionless temperature
$\Theta_c$	$= T_c/T_f^0$ dimensionless cooling medium temperature
$\lambda_e$	catalyst effective thermal conductivity, $\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$
$\mu$	relative activity
$\nu$	$= (\alpha_1 - \alpha_2)/\alpha_3$ dimensionless parameter
$\rho$	$= (\Theta - 1)/\Theta$ dimensionless parameter
$\rho_g$	gas density, $\text{kg m}^{-3}$
$\rho_s$	catalyst density, $\text{kg m}^{-3}$
$\rho_b$	bed density, $\text{kg m}^{-3}$
$\tau$	$= t/t^0$ dimensionless time
$\tau^*$	dimensionless operating time
$\Xi$	$= \xi_v/\xi_v^0$ dimensionless reaction rate
$\zeta_v$	reaction rate, $\text{mol m}^{-3} \text{s}^{-1}$
$\phi$	catalyst activity

$\phi$	dimensionless deactivation rate
$\varphi$	$= r/R_p$ dimensionless radial pellet coordinate
$\varphi_1$	dimensionless active catalyst location

## Subscripts

B	key component
J	catalyst poison
f	fluid phase

## Superscripts

o	inlet stream
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