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**MODELLING OF FIXED BED CATALYTIC REACTORS WITH CATALYST DEACTIVATION UNDER "CONSTANT-PATTERN TRAVELLING WAVE" ASSUMPTION**

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The models of fixed bed catalytic reactors in which catalyst deactivation takes place can be significantly simplified by introducing quasi-steady state and constant-pattern travelling wave assumptions. This results in faster algorithms. In the present paper the plug-flow, radial dispersion, and well-mixed regions in the series pseudohomogeneous models under the above assumptions are discussed. The obtained results are compared with experimental ones in the case of hydrogenation of benzene on a nickel catalyst with thiophene as a poison (irreversible deactivation).

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Fixed bed catalytic reactors, in which catalyst deactivation takes place, operate in unsteady state conditions. Due to decrease of the catalyst activity the temperature and the concentration profiles move downstream through the reactor during operation. If the catalyst activity decreases slowly with time, i.e. the contact time of a fluid element in the reactor is small compared to the time of deactivation of the catalyst bed, the model is described by a system of stiff equations the solution of which is involved. This is why we introduce so-called quasi-steady state approximation. It means, that all time derivatives except activity are neglected. This simplification in the model equations results in faster algorithms. Further simplification is to introduce the assumption of "constant-pattern travelling wave".

In our previous papers<sup>1-4</sup> the models of fixed bed catalytic reactors with catalyst poisoning under quasi-steady state assumption have been discussed. Pseudohomogeneous models have been also studied<sup>1-3</sup>. As a flow pattern the plug-flow<sup>1</sup>, well-mixed regions in series<sup>2</sup>, and axial dispersion model<sup>3</sup> have been chosen. Heterogeneous models of well-mixed region in series have been described in the preceding paper<sup>4</sup>. From the comparison of theoretical and experimental results (for the system of hydrogenation of benzene on a nickel catalyst with thiophene as the poison) the following conclusions can be made: (i) after some period the temperature and concentration profiles have constant pattern and move by constant speed downstream through the bed, (ii) the maximal temperature is constant, (iii) the deactivation rate is temperature independent.

This fact enables us to introduce the constant-pattern travelling wave assumption,

where the constant speed of movement of adsorption zone is given by the formula<sup>5</sup>

$$v = \frac{w \cdot c_{J_0}}{\varepsilon c_{J_0} + \rho_b a_J^*} \quad (1)$$

In this paper pseudohomogeneous models described in the preceding papers<sup>1,2</sup> and a model with radial dispersion under the constant-pattern travelling wave assumption are discussed.

In order to simplify theoretical analysis the following approximations have been introduced: (i) the gas density is constant, (ii) the heat exchange between catalyst and gas is perfect, so the temperature of both of them is the same, (iii) the heat released by the chemisorption of the poison is negligible, (iv) the heat of reaction, heat capacity, mass transfer, and heat transfer coefficients are temperature independent.

## THEORETICAL

### *Pseudohomogeneous Model of a Plug-Flow Reactor*

Under the above assumption the model consist of the equations mass balance of the key component

$$\delta \frac{\partial Y_B}{\partial \tau} + \frac{\partial Y_B}{\partial Z} + \dot{\Xi} = 0, \quad (2)$$

mass balance of the poison

$$\delta \frac{\partial Y_J}{\partial \tau} + \frac{\partial Y_J}{\partial Z} + G \frac{\partial A_J}{\partial \tau} = 0, \quad (3)$$

enthalpy balance

$$R_s \frac{\partial \Theta}{\partial \tau} + \frac{\partial \Theta}{\partial Z} = \dot{\Xi} - F \cdot (\Theta - \Theta_c), \quad (4)$$

boundary conditions

$$\tau > 0 \quad Z = 0 \quad Y_B = Y_J = 1, \quad \Theta = 0, \quad (5)$$

initial conditions

$$\tau = 0 \quad Z \in \langle 0, Z_R \rangle \quad A_J = 0, \quad \Phi = 1, \quad (6)$$

rate equation of the catalytic reaction

$$\dot{\Xi} = \Phi \cdot \dot{\Xi}(Y_B, \Theta), \quad (7)$$

and rate equation of the poison chemisorption

$$\frac{dA_J}{d\tau} = f(A_J, Y_J). \quad (8)$$

If the adsorption rate of the poison is equal for all nonoccupied active sites of the catalyst and one molecule of poison is adsorbed on one active site, the linear dependence between catalyst activity and adsorbed amount of catalyst poison can be developed

$$\Phi = 1 - A_J. \quad (9)$$

It yields to the rate expressions

$$\frac{dA_J}{d\tau} = Y_J(1 - A_J) \quad (10)$$

and

$$\frac{d\Phi}{d\tau} = \dot{\phi} = -Y_J\Phi. \quad (11)$$

Introducing the quasi-steady state assumption (the contact time of a fluid element in the reactor is small compared to the time of catalyst bed deactivation which results in small values of parameters  $\delta$  and  $R_S$ ) Eqs (2)–(4) become

$$\frac{dY_B}{dZ} = -\dot{\Xi} \quad (12)$$

$$\frac{dY_J}{dZ} = G\dot{\phi} \quad (13)$$

$$\frac{d\Theta}{dZ} = \dot{\Xi} - F(\Theta - \Theta_c) \quad (14)$$

and the initial and boundary conditions are given by Eqs (5) and (6).

If we assume a constant-pattern travelling wave, the transformed time variable

$$u = t - z/v \quad (15)$$

is useful. The dimensionless transformed time variable is

$$U = \tau - (G + \delta) Z \quad (16)$$

which can be further simplified assuming quasi-steady state approximation

$$U = \tau - G \cdot Z. \quad (17)$$

The balance equations (11) and (13) transformed into

$$\frac{dY_j}{dU} = - \frac{d\Phi}{dU} \quad (18)$$

$$\frac{d\Phi}{dU} = - Y_j \Phi \quad (19)$$

with boundary conditions

$$U = -\infty \quad Y_j = 0 \quad (20)$$

$$U = \infty \quad Y_j = 1.$$

From the Eqs (18) and (19) poison concentration, activity, and variable  $U$  can be expressed

$$Y_j = 1 - \Phi \quad (21)$$

$$\Phi = 1/(1 + \exp(U)) \quad (22)$$

$$U = \ln((1 - \Phi)/\Phi). \quad (23)$$

Eqs (17) and (23) allow us to compute the activity profile at any time in the catalyst bed, or on the other hand, to find the point of given activity in the reactor at a certain time.

To compute the system of model equations for a given time the following algorithm has been employed: To obtain the activity profile in the reactor choose activity from the interval  $\langle 0, 1 \rangle$ , then compute variable  $U$  from Eq. (23) and the axial coordinate from Eq. (17). To obtain the key component concentration and temperature profiles in the reactor solve Eqs (12) and (14) by the Runge-Kutta 4th order method. Once we compute the point with maximal temperature at a given time  $\tau$ , the movement of this point we obtain easily using Eq. (17). This equation helps us also to compute reactor outlet concentrations.

#### *Pseudohomogeneous Model with Radial Dispersion*

Under quasi-steady state assumption the pseudohomogeneous model of fixed bed catalytic reactor including radial dispersion term consists from the following system of model equations<sup>6</sup>:

mass balance of the key component

$$\frac{\partial Y_B}{\partial Z} - D_{BR} \left( \frac{\partial^2 Y_B}{\partial \varphi^2} + \frac{1}{\varphi} \frac{\partial Y_B}{\partial \varphi} \right) + \dot{\varepsilon} = 0, \quad (24)$$

mass balance of the catalyst poison

$$\frac{\partial Y_J}{\partial Z} - D_{JR} \left( \frac{\partial^2 Y_J}{\partial \varphi^2} + \frac{1}{\varphi} \frac{\partial Y_J}{\partial \varphi} \right) - G \frac{\partial \Phi}{\partial \tau} = 0, \quad (25)$$

enthalpy balance

$$\frac{\partial \Theta}{\partial z} - K_{eR} \left( \frac{\partial^2 \Theta}{\partial \varphi^2} + \frac{1}{\varphi} \frac{\partial \Theta}{\partial \varphi} \right) - \dot{\varepsilon} = 0, \quad (26)$$

boundary conditions

$$\tau > 0$$

$$Z = 0 : \varphi \in \langle 0, 1 \rangle; \Theta = 0; Y_B = Y_J = 1,$$

$$Z \in \langle 0, Z_R \rangle : \varphi = 0; \quad \frac{\partial \Theta}{\partial \varphi} = \frac{\partial Y_B}{\partial \varphi} = \frac{\partial Y_J}{\partial \varphi} = 0$$

$$\varphi = 1; \quad \frac{\partial Y_B}{\partial \varphi} = \frac{\partial Y_J}{\partial \varphi} = 0 \quad (27)$$

$$-K_{eR} \frac{\partial \Theta}{\partial \varphi} = H(\Theta - \Theta_c),$$

initial condition

$$\tau = 0 : Z \in \langle 0, Z_R \rangle \quad \Phi = 1, \quad (28)$$

$$\varphi \in \langle 0, 1 \rangle$$

reaction rate (Eq. (7)), and deactivation rate (Eq. (11)).

After introducing the constant-pattern travelling wave assumption and time variable  $U$ , the equation for catalyst poison can be simplified as in the case of plug-flow reactor. The relation between the variables  $Y_J$ ,  $\Phi$ , and  $U$  is given by Eqs (21) to (23).

To compute the poison concentration and activity profiles one can proceed as in the previous case. The axial and radial temperature and key component concentration profiles have been obtained by solving numerically the system of Eqs (24), (26), (27) by the predictor-corrector method. Due to high temperature gradient near the reactor wall two different step lengths have been used (smaller near the wall than in the middle).

*Pseudohomogeneous Model of Well-Mixed Regions in Series  
with Heat Exchange Between the Members*

The model of well-mixed regions in series with heat exchange between the members is given by the following equations:

mass balance of the key component

$$Y_{B,i-1} - Z_K \dot{\Xi}_i = Y_{B,i} + \delta_K \frac{dY_{B,i}}{d\tau}, \quad i = 1, \dots, N, \quad (29)$$

mass balance of the poison

$$Y_{J,i-1} + G_K \Phi_i = Y_{J,i} + \delta_K \frac{dY_{J,i}}{d\tau}, \quad i = 1, \dots, N, \quad (30)$$

enthalpy balance

$$\Theta_{i-1} + F_w(\Theta_c - \Theta_i) + F_a(\Theta_{i-1} - 2\Theta_i + \Theta_{i+1}) + Z_K \dot{\Xi}_i = \Theta_i + R_{SK} \frac{d\Theta_i}{d\tau},$$

$$i = 1, \dots, N, \quad (31)$$

boundary conditions

$$\tau > 0 : i = 1; Y_{B,i-1} = Y_{J,i-1} = 1, \Theta_{i-1} = 0, \quad (32)$$

initial conditions

$$\tau = 0 : i = 1, \dots, N; \Phi_i = 1, \quad (33)$$

kinetic equation of catalytic reaction

$$\dot{\Xi}_i = \Phi_i \dot{\Xi}(Y_{B,i}, \Theta_i), \quad i = 1, \dots, N, \quad (34)$$

and deactivation rate equation

$$\dot{\Phi}_i = -Y_{J,i} \Phi_i, \quad i = 1, \dots, N. \quad (35)$$

After introducing a constant-pattern travelling wave, the time variable  $U$  and quasi-steady state assumption, for the poison concentration and activity we obtain

$$Y_{J,i} = 1 - \Phi_i \quad (36)$$

$$U_i = \ln((1 - \Phi_i)/\Phi_i) \quad (37)$$

$$U_i = \tau - i \cdot G_K \quad (38)$$

for  $i = 1, \dots, N$

$$U = -\infty \quad \text{for} \quad \Phi = 1 \quad (39)$$

and

$$U = \infty \quad \text{for} \quad \Phi = 0.$$

The model equations (29) and (31) reduce to algebraic equations. The algorithm of the solution of the model equations is as follows: choose time  $\tau_1$  and activity  $\Phi_1 \approx 0$ , compute  $U$  from Eq. (37) and the number of region  $i^*$  from Eq. (38). For  $i < i^*$  set  $\Phi_i = 0$ , for  $i > i^*$  compute  $U_i$  from Eq. (38) and  $\Phi_i$  from Eq. (37). Increase  $i$  until unit activity is obtained. To compute the key component concentration and temperature profiles solve the Eqs (29) and (31) numerically.

The movement of the region with maximal temperature we can compute from the relation

$$i = (\tau - U_{\max})/G_K, \quad (40)$$

where  $U_{\max}$  is value of the variable  $U$  corresponding to the number of regions with maximal temperature at time  $\tau_1$ . The inlet concentrations can be computed from Eq. (38) and from the profile at any time  $\tau_1$ .

The system of Eqs (29) and (31) is a system of  $2N$  nonlinear algebraic equations, which have been solved by the Newton-Raphson procedure. The number of regions  $N$  has been estimated by the relation<sup>7</sup>

$$N = L/d_p. \quad (41)$$

In our case the number of regions has been between 60 and 100, which leads to the system of at least 120 nonlinear equations.

## EXPERIMENTAL

For experimental verification of the described models the benzene hydrogenation on Ni catalyst as a model reaction and thiophene as a catalyst poison have been chosen. The experimental system as well as the experimental procedure has been described in literature<sup>8</sup>.

The rate equation for benzene hydrogenation is

$$\xi_w = \frac{k_{w\infty} K_{\infty} P_B \cdot P_H \cdot \exp(-(E+Q)/RT)}{1 + K_{\infty} P_B \cdot \exp(-Q/RT)} \quad (42)$$

or, in the dimensionless form

$$\xi = \frac{(1 + \kappa) \cdot Y_B Y_H \cdot \exp((\alpha_i + \alpha_K) \beta \Theta / (1 + \beta \Theta))}{1 + \kappa Y_B \cdot \exp(\alpha_K \beta \Theta / (1 + \beta \Theta))}. \quad (43)$$

In all our experiments hydrogenation took place under a large excess of hydrogen, so the hydrogen concentration through the entire catalyst bed has been constant,  $Y_H \approx 1$ . The values of the kinetic rate equation parameters have been obtained from rotating basket reactor measurements<sup>9</sup>

and their values are:  $k_{w\infty} = 0.59 \cdot 10^{-2} \text{ mol kg}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ ;  $K_{\infty} = 0.29 \cdot 10^{-5} \text{ Pa}^{-1}$ ;  $E = 12.4 \text{ kJ mol}^{-1}$ . The experimental conditions are: catalyst diameter 0.7–1.0 mm; mass of catalyst 11.64 g; length of bed 0.085 m; inlet temperature 378 K; ambient temperature 378 K; volumetric flow rate  $5.46 \cdot 10^{-6} \text{ m}^3 \text{ s}^{-1}$ ; inlet concentration of benzene  $1.89 \text{ mol m}^{-3}$ ; inlet concentration of thiophene  $2.69 \cdot 10^{-2} \text{ mol m}^{-3}$ .

## RESULTS AND DISCUSSION

The outlet benzene and thiophene concentrations and the movement of the point of temperature peak for individual models and experiment are illustrated in Fig. 1.

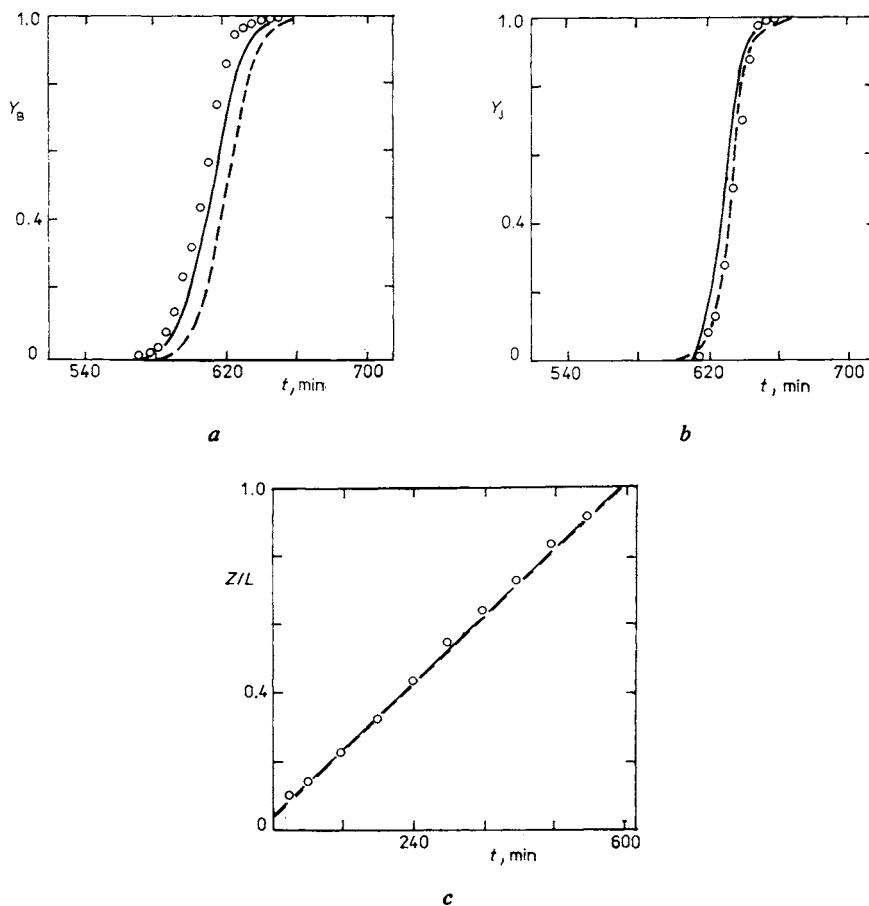


FIG. 1

Comparison of experiment and models. *a* Benzene outlet concentration vs time; *b* thiophene outlet concentration vs time; *c* point of temperature peak vs time.  $\circ$  experiment, full line — model of well-mixed regions in series; dashed line — plug-flow model and model with radial dispersion. In place of  $Z/L$  should be the expression  $z/L$



The corresponding axial mean temperature profiles at time  $t = 300$  min are displayed in Fig. 2. The mean experimental temperature is obtained from measured temperature in the reactor center assuming a parabolic radial temperature profile.

The results obtained for the plug-flow model and the model with radial dispersion are not different for parameters corresponding to our experimental system (important axial heat conduction). There is also no significant difference between experimental outlet concentrations and movement of the point of temperature peak and these dependences for all models (Fig. 1). This is not true for axial temperature profiles. The best agreement has been achieved for well-mixed regions in series model, which includes axial temperature conduction.

For given parameters the obtained results are not different whether the constant-pattern travelling wave has been assumed or not. However, introducing the assumptions of quasi-steady state and constant-pattern travelling wave simplify the model equations significantly. In the case of plug-flow and radial dispersion models the key component and enthalpy balance equations are reduced from partial to ordinary differential equations. The poison balance in all cases can be solved analytically. This simplification in mathematical model leads to faster algorithm and significant saving of computing time.

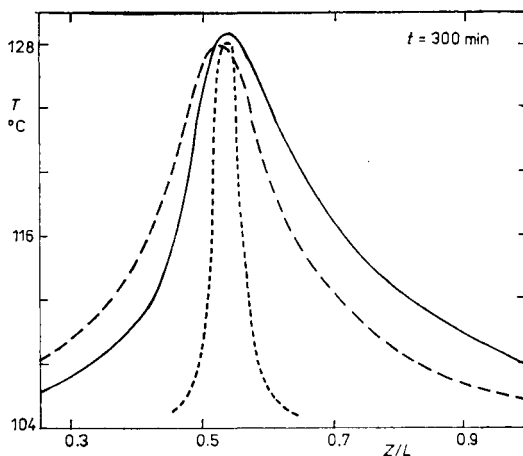


FIG. 2

Transient temperature profiles. Full line — experiment; dashed line — model of well-mixed regions in series; dotted line — plug-flow model and model with radial dispersion. In place of  $Z/L$  should be the expression  $z/L$

## LIST OF SYMBOLS

$A_J$	$= a_j/a_j^*$ dimensionless poison adsorbed amount
$a_j$	poison adsorbed amount, mol kg <sup>-1</sup>
$a_j^*$	equilibrium poison adsorbed amount, mol kg <sup>-1</sup>
$c$	concentration, mol m <sup>-3</sup>
$c_{pg}$	heat capacity of gas, J kg <sup>-1</sup> K <sup>-1</sup>
$c_{ps}$	heat capacity of solid, J kg <sup>-1</sup> K <sup>-1</sup>
$D_{BR}$	$= D_{Br}c_{Bo}/\xi_w^0 R^2 \rho_b$ dimensionless parameter, see Eq. (24)
$D_{JR}$	$= D_{Jr}c_{Bo}/\xi_w^0 R^2 \rho_b$ dimensionless parameter, see Eq. (25)
$D_r$	radial dispersion coefficient, m <sup>2</sup> s <sup>-1</sup>
$d_p$	diameter of catalyst pellet, m
$d_r$	diameter of reactor, m
$E$	activation energy, J mol <sup>-1</sup>
$F$	$= 4hc_{Bo}/d_r \rho_b \xi_w^0 \rho_g c_{pg}$ dimensionless parameter, see Eq. (4)
$F_a$	$= AS_R/\rho_g c_{pg} \dot{V}_o$ dimensionless parameter, see Eq. (31)
$F_w$	$= \pi h d_r L / N \rho_g c_{pg} \dot{V}_o$ dimensionless parameter, see Eq. (31)
$G$	$= c_{Bo} a_j^* / \xi_w^0 \rho_g c_{J_0}$ dimensionless parameter, see Eq. (3)
$G_K$	$= a_j^* W / N c_{J_0} \dot{V}_o$ dimensionless parameter, see Eq. (30)
$(-\Delta H)$	heat of reaction, J mol <sup>-1</sup>
$H$	$= c_{Bo}/\rho_g c_{pg} R$ dimensionless parameter, see Eq. (27)
$h$	overall heat transfer coefficient, J m <sup>-2</sup> s <sup>-1</sup> K <sup>-1</sup>
$K$	adsorption constant, Pa <sup>-1</sup>
$K_{eR}$	$= \lambda_{er} c_{Bo} / \rho_g c_{pg} R^2 \xi_w^0 \rho_b$ dimensionless parameter, see Eq. (26)
$k_w$	chemical reaction rate constant, mol kg <sup>-1</sup> s <sup>-1</sup> Pa <sup>-1</sup>
$k_D$	deactivation rate constant, m <sup>3</sup> kg <sup>-1</sup> s <sup>-1</sup>
$L$	length of reactor, m
$N$	number of well-mixed regions
$P$	pressure, Pa
$Q$	adsorption heat of benzene, J mol <sup>-1</sup>
$R$	radius of reactor, m
$R_S$	$= \langle \bar{q} c_p \rangle c_{Bo} / \rho_g c_{pg} \rho_b \xi_w^0 \rho_g$ dimensionless parameter, see Eq. (4)
$R_{SK}$	$= \langle \bar{q} c_p \rangle S_R L / N \rho_g c_{pg} \dot{V}_o$ dimensionless parameter, see Eq. (31)
$r$	radial coordinate, m
$S_R$	section area of reactor, m <sup>2</sup>
$T$	temperature, K
$t$	time, s
$t^0$	$= 1/k_D c_{J_0}$ characteristic deactivation time, s
$U$	$= u/t^0$ dimensionless transformed time variable
$u$	transformed time variable, s
$V$	volume, m <sup>3</sup>
$\dot{V}_o$	volumetric flow rate, m <sup>3</sup> s <sup>-1</sup>
$v$	speed of adsorption zone movement, m s <sup>-1</sup>
$W$	mass of catalyst in the reactor, kg
$w$	velocity of fluid, m s <sup>-1</sup>
$Y$	$= c/c_o$ dimensionless concentration
$Z$	$= \rho_b \xi_w^0 z / c_{Bo} w$ dimensionless axial coordinate
$Z_R$	$= \rho_b \xi_w^0 L / c_{Bo} w$ dimensionless length of reactor
$Z_K$	$= W \xi_w^0 L / c_{Bo} \dot{V}_o$ dimensionless parameter, see Eq. (29)

$z$	axial coordinate, m
$\alpha$	heat transfer coefficient from catalyst bed to reactor wall, $\text{J m}^{-2} \text{s}^{-1} \text{K}^{-1}$
$\alpha_i$	$= E/RT_0$ dimensionless parameter, see Eq. (45)
$\alpha_K$	$= Q/RT_0$ dimensionless parameter, see Eq. (45)
$\beta$	$= (-\Delta H) c_{B_0}/\rho_g c_{pg} T_0$ dimensionless parameter, see Eq. (45)
$\delta$	$= \varepsilon c_{B_0}/\rho_b t^0 \xi_w^0$ dimensionless parameter, see Eq. (2)
$\delta_K$	$= LS_R/NV_0 t^0$ dimensionless parameter, see Eqs. (29, 30)
$\varepsilon$	bed void fraction
$\Theta$	$= (T - T_0) \rho_g c_{pg}/c_{B_0}(-\Delta H)$ dimensionless temperature
$\kappa$	$= K_\infty P_{B_0} \exp(-Q/RT_0)$ dimensionless parameter, see Eq. (45)
$\lambda$	heat transfer coefficient between members of cascade, $\text{J m}^{-2} \text{s}^{-1} \text{K}^{-1}$
$\lambda_{cr}$	catalyst bed effective thermal conductivity, $\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$
$\rho_b$	bed density, $\text{kg m}^{-3}$
$\rho_g$	gass density, $\text{kg m}^{-3}$
$\rho_s$	catalyst density, $\text{kg m}^{-3}$
$\langle \bar{c}_p \rangle$	average thermal capacity of reactor, $\text{J m}^{-1} \text{K}^{-1}$
$\tau$	$= t/t^0$ dimensionless time
$\xi_w$	reaction rate, $\text{mol kg}^{-1} \text{s}^{-1}$
$\xi_w^0$	reaction rate on the fresh catalyst corresponding to the inlet conditions, $\text{mol kg}^{-1} \text{s}^{-1}$
$\bar{\xi}$	$= \xi_w/\xi_w^0$ dimensionless reaction rate
$\Phi$	catalyst activity
$\dot{\Phi}$	deactivation rate
$\varphi$	$= r/R$ dimensionless radius coordinate

## Subscripts

o	inlet stream
c	ambient stream
B, J, H	key component, poison, hydrogen

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