Modelling of catalytic reactors with catalyst deactivation II. Model of well-mixed regions in series

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The paper deals with modelling of fixed bed catalytic reactors in which catalyst deactivation due to irreversible chemisorption of catalyst poison takes place. A pseudohomogeneous reactor model consisting of well-mixed equal volume regions in series has been chosen. Theoretical results are compared with experimental as well as theoretical under plug-flow assumption ones.

В работе рассматривается моделирование реакторов с неподвижным слоем катализатора, в которых происходит дезактивация катализатора вследствие необратимой хемосорбции каталитического яда. Избрана модель псевдогомогенного реактора, представляющая собой ряды областей хорошо смешанных равных объемов. Проводится сравнение теоретических результатов с экспериментальными, а также с теоретическими, полученными в предположении идеального вытеснения.

Due to deactivation caused by irreversible chemisorption of catalyst poison the concentration and temperature profiles move downstream through the fixed bed catalytic reactor with time. After total deactivation of the catalyst the profiles vanish and the inlet and outlet concentrations are equal. To determine suitable operation conditions it is necessary to have a mathematical model of the reactor together with the models of the deactivation mechanism and the chemical reaction.

In our previous paper [1] a pseudohomogeneous plug-flow model of a fixed bed catalytic reactor under the quasi-steady state assumption has been described. The model provides for a good qualitative description of concentration and temperature waves movement through the reactor, but the accuracy is limited. To extend the model by an axial dispersion term leads to a more complicated solution algorithm and larger consumption of computing time. This is why as an alternative model a pseudohomogeneous model of well-mixed equal volume regions in series and the same deactivation mechanism is considered.

The aim of the present study is to introduce the model equations, to work out a numerical algorithm for their solution and to compare the theoretical and experimental results.

Pseudohomogeneous model of well-mixed equal volume regions in series

Assuming that in the reactor only one catalytic reaction and catalyst deactivation caused by irreversible chemisorption of catalyst poison takes place, the well-mixed regions in series model consist of the following equations:

— mass balance of the key component

$$\dot{V}_{i-1}c_{Bi-1} + W_i v_B \dot{\xi}_w = \dot{V}_i c_{Bi} + V_i \frac{dc_{Bi}}{dt}; \quad i = 1, ..., N \tag{1}$$

— mass balance of the poison

$$\dot{V}_{i-1}c_{Ti-1} - W_i \frac{da_{Ti}}{dt} = \dot{V}_i c_{Ti} + V_i \frac{dc_{Ti}}{dt}; \quad i = 1, ..., N \tag{2}$$

— enthalpy balance

$$\dot{V}_{i-1}\varrho_g c_{pg} T_{i-1} + hA_i(T_c - T_i) + W_i(-\Delta H)\dot{\xi}_w =$$
$$= \dot{V}_i \varrho_g c_{pg} T_i + V_i \overline{\varrho c_p} \frac{dT_i}{dt}; \quad i = 1, ..., N \tag{3}$$

— rate equation of the catalytic reaction

$$\dot{\xi}_w = f_r(c_A, c_B, ..., a_T, T) \tag{4}$$

— rate equation of the poison chemisorption

$$\dot{a}_T = \frac{da_T}{dt} = f_d(c_A, c_B, ..., c_T, a_T, T) \tag{5}$$

— initial conditions, *i.e.* the solution of eqns (1) and (3) under steady state assumption and fresh catalyst

$$t = 0; \quad a_{Ti} = 0; \quad \dot{V}_{i-1}c_{Bi-1} + W_i v_B \dot{\xi}_w = \dot{V}_i c_{Bi}$$

$$\dot{V}_{i-1}\varrho_g c_{pg} T_{i-1} + hA_i(T_c - T_i) + W_i(-\Delta H)\dot{\xi}_w = \dot{V}_i \varrho_g c_{pg} T_i; \quad i = 1, ..., N \tag{6}$$

— *boundary conditions*

$$t > 0; \quad i = 1; \quad c_{Bi-1} = c_{B0}; \quad c_{Ti-1} = c_{T0}; \quad T_{i-1} = T_0 \tag{7}$$

The system of model equations is valid under the assumption that the heat exchange between catalyst and gas is perfect, so the temperature of both of them is the same and the heat released by the chemisorption of the poison is negligible with respect to reaction heat. The second assumption results from the fact that the poison is present only in small amounts and its concentration is considerably lower than the concentration of the key component. Further assumptions are constant reaction mixture density and that the reaction heat and specific heats are temperature independent.

If the reaction rate equation is separable and catalyst activity depends linearly on the adsorbed amount of the poison, eqns (4) and (5) become

$$\dot{\xi}_w = \Phi f_r(c_A, c_B, \ldots, T) \tag{8}$$

$$\dot{a}_T = -a_T^* \frac{d\Phi}{dt} = f_d(\Phi, c_T, T) \tag{9}$$

If the rate of deactivation is considerably smaller than the rate of catalytic reaction, the derivatives of concentrations and temperature with respect to time may be neglected, which means that a quasi-steady state is assumed.

Introducing the dimensionless variables

$$Y_A = \frac{c_A}{c_{A0}}; \ Y_B = \frac{c_B}{c_{B0}}; \ Y_T = \frac{c_T}{c_{T0}};$$

$$\Theta = \frac{T - T_0}{\Delta T_{ad}}; \ \tau = \frac{t}{t^o}; \ \dot{\Xi} = \frac{\dot{\xi}_w}{\dot{\xi}_w^o} \tag{10a}$$

and dimensionless parameters

$$G_i = \frac{a_T^* W}{\dot{V}_0 c_{T0} t^o N}; \ Z_{Ri} = \frac{\dot{\xi}_w^o W(-\nu_B)}{c_{B0} \dot{V}_0 N}$$

$$F_i = \frac{h2\pi RL}{\dot{V}_0 \varrho_g c_{pg} N}; \ \Delta T_{ad} = \frac{(-\Delta H)c_{B0}}{\varrho_g c_{pg}(-\nu_B)} \tag{10b}$$

we obtain the model equations in dimensionless form

$$Y_{Bi-1} - Z_{Ri}\dot{\Xi}_i = Y_{Bi} \tag{11}$$

$$Y_{Ti-1} + G_i\dot{\Phi}_i = Y_{Ti} \tag{12}$$

$$\Theta_{i-1} + F_i(\Theta_c - \Theta_i) + Z_{Ri}\dot{\Xi}_i = \Theta_i \tag{13}$$

where $\dot{V}_i = \dot{V}_{i-1} = \dot{V}_0$. The rate equations of catalytic reaction and deactivation become

$$\dot{\Xi}_i = \Phi_i f_r(Y_{Ai}, Y_{Bi}, \ldots, \Theta_i) \tag{14}$$

$$\dot{\Phi}_i = f_{\mathrm{d}}(\Phi_i, Y_{\mathrm{T}i}, \Theta_i) \tag{15}$$

The initial conditions are given by the solution of eqns (11) and (13) for unit activity and the boundary condition (7) transforms into

$$\tau > 0; \quad Y_{\mathrm{B}i-1} = Y_{\mathrm{T}i-1} = 1; \quad \Theta_{i-1} = 0 \tag{16}$$

Experimental

The scheme of the laboratory fixed bed tubular reactor is in Fig. 1. The temperature profile has been measured by movable thermocouple placed in an axial thermowell. The length of the reactor is 0.9 m, reactor internal diameter is 0.0164 m and the thermowell external diameter 0.0041 m. The reactor has been heated by silicon oil, flowing through the external tube. Its volumetric flow rate has been kept sufficiently high in order to secure equality of the inlet and outlet temperatures. The catalyst bed has been placed between the glass beds of the same mesh size as the catalyst, so the reacting gas entered into the catalyst bed by a steady flow rate and preheated to the reaction temperature. During the measurement, the composition of the outlet stream has been analyzed by a gas chromatograph. The temperature measured at the reactor axis has been averaged under the assumption of parabolic radial temperature profile [2].
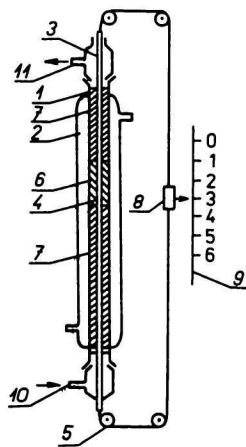

Fig. 1. Laboratory tubular reactor.
1. Internal tube
2. external tube
3. thermowell
4. thermocouple
5. pulley
6. catalyst bed
7. glass beds
8. thermocouple axial position indicator
9. scale
10. inlet of reacting gas
11. gas exit

As a model system the hydrogenation of benzene on a Ni catalyst (Ni/alumina, 58 % Ni) and thiophene as a poison has been chosen. The catalyst has been activated directly in the reactor for 8 h at the temperature of 180 °C and the hydrogen flow of 80 cm³ min⁻¹. After finishing the activation, the reactor has

been cooled to working temperature and a stream of benzene and hydrogen has been introduced into the reactor. After stabilizing the conditions, the entering stream has been switched to the thiophene-containing stream. The working conditions of the presented measurement are:

Mesh size of catalyst: 1.25—1.40 mm
Mass of catalyst: 15.0065 g
Temperature at the inlet into the catalyst bed: 98.9 °C
Jacket temperature: 98.9 °C
Volumetric flow rate: $2.38 \times 10^{-6}\,\mathrm{m^3\,s^{-1}}$
Inlet benzene concentration: $1.88\,\mathrm{mol\,m^{-3}}$
Inlet thiophene concentration: $6.17 \times 10^{-2}\,\mathrm{mol\,m^{-3}}$

The rate equation of the mentioned catalytic reaction is [1, 3]

$$\dot{\xi}_w = \Phi \frac{k_\infty K_\infty P_B P_H \exp\left(-(Q + E)/RT\right)}{1 + K_\infty P_B \exp\left(-Q/RT\right)} \tag{17}$$

or in the dimensionless form respectively

$$\dot{\Xi} = \Phi \frac{1 + \varkappa Y_B Y_H \exp\left((\alpha_i + \alpha_K)\beta\Theta/(1 + \beta\Theta)\right)}{1 + \varkappa Y_B \exp\left(\alpha_K \beta\Theta/(1 + \beta\Theta)\right)} \tag{18}$$

where

$$\varkappa = K_\infty P_{B0} \exp\left(-Q/RT_0\right) \qquad \beta = \Delta T_{ad}/T_0$$
$$\alpha_i = E/RT_0 \qquad\qquad \alpha_K = Q/RT_0$$

$$\dot{\xi}_w^0 = \frac{k_\infty K_\infty P_{B0} P_{H0} \exp\left(-(E + Q)/RT_0\right)}{1 + K_\infty P_{B0} \exp\left(-Q/RT_0\right)} \tag{19}$$

The rate equation of deactivation has been used in the form [1, 3]

$$\frac{d\Phi}{dt} = -k_T c_T \Phi \tag{20}$$

which in the dimensionless form is

$$\dot{\phi} = -Y_T \Phi \tag{21}$$

Then characteristic time of deactivation t^0 is given by the relation

$$t^0 = 1/(k_T c_{T0}) \tag{22}$$

The values of reaction rate equations and dimensionless parameters are listed in Table 1.

Table 1

Values of reaction rate equations and dimensionless parameters

$k_\varkappa$	=	$0.262 \, \text{mol kg}^{-1} \text{s}^{-1} \text{Pa}^{-1}$
$K_\varkappa$	=	$0.195 \, \text{Pa}^{-1}$
E	=	$45.07 \, \text{kJ mol}^{-1}$
Q	=	$-23.41 \, \text{kJ mol}^{-1}$
$\varkappa$	=	22
α_i	=	14.57
α_K	=	-7.57
β	=	0.824
$\dot{\zeta}_w^o$	=	$0.015 \, \text{mol kg}^{-1} \text{s}^{-1}$
ΔT_{ad}	=	$306.7 \, \text{K}$
Z_R	=	50.2

Numerical solution of the model equations

The model is described by a system of three nonlinear algebraic equations (*11—13*) in which reaction rate is given by eqn (*18*) and one ordinary differential equation (*21*). The system has been solved by the following iterative procedure:

The value of the first iteration of activity has been computed from eqn (*21*) by the explicit finite difference scheme

$$\Phi_i^j(\tau + \Delta\tau) = \Phi_i(\tau) + \Delta\tau \Phi_i(\tau) Y_{Ti}(\tau) \qquad (23)$$

for $i = 1, \ldots, N$. The values of $Y_B(\tau + \Delta\tau)$, $Y_T(\tau + \Delta\tau)$, $\Theta(\tau + \Delta\tau)$ for $i = 1, \ldots, N$ have been computed from eqns (*11—13*) by the Newton iterative method [4]. From these values the mean values

$$\hat{Y}_{Bi} = (Y_{Bi}(\tau) + Y_{Bi}^j(\tau + \Delta\tau))/2$$

$$\hat{Y}_{Ti} = (Y_{Ti}(\tau) + Y_{Ti}^j(\tau + \Delta\tau))/2$$

$$\hat{\Theta}_i = (\Theta_i(\tau) + \Theta_i^j(\tau + \Delta\tau))/2$$

$$\hat{\Phi}_i = (\Phi_i(\tau) + \Phi_i^j(\tau + \Delta\tau))/2 \qquad (24)$$

have been obtained. The next iteration $j + 1$ of the activity has been computed from the mean values

$$\Phi_i^{j+1}(\tau + \Delta\tau) = \Phi_i(\tau) + \Delta\tau \hat{\Phi}_i \hat{Y}_{Ti}; \quad i = 1, \ldots, N \qquad (25)$$

This iterative procedure has been repeated until satisfactory coincidence has been achieved.

Results and discussion

Figs. 2 and 3 illustrate dimensionless benzene and thiophene concentration at the outlet from reactor *vs.* time dependences for several numbers of well-mixed regions and for parameters $G = 250$, $F = 2000$. Best agreement has been obtained by the number of regions 90, which is in conformity with the rule that the length of one region has to be equal to the pellet diameter [5].

Fig. 2. Exit benzene concentration *vs.* time for various number of cascade members (parameter of curves).
$G = 250$, $F = 2000$.
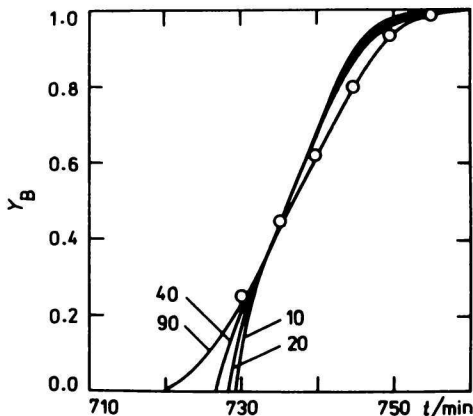
The dependence of the reactor outlet concentrations Y_B and Y_T *vs.* time is exhibited in Figs. 4 and 5 for several values of parameter G and for the number of regions 90 and $F = 2000$.
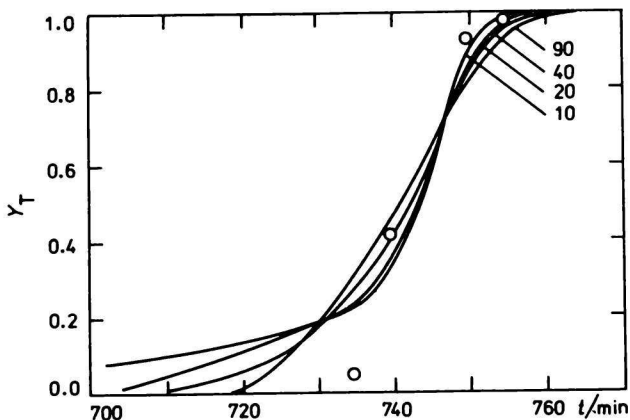

Fig. 3. Exit thiophene concentration *vs.* time for various number of cascade members (parameter of curves).
$G = 250$, $F = 2000$.

In Figs. 6 and 7 the comparison of the well-mixed regions in series model and plug-flow model both isothermal and nonisothermal is displayed. The well--mixed regions in series model provides better description of the outlet benzene concentration. This comparison for the thiophene outlet concentration is pro-blematic due to higher experimental noise low poison concentration.
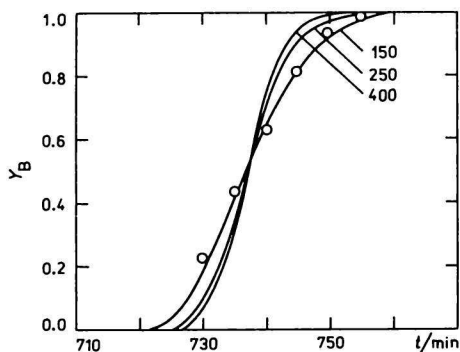

Fig. 4. Exit benzene concentration *vs.* time. Curves parametrized by G. $N = 90$, $F = 2000$.
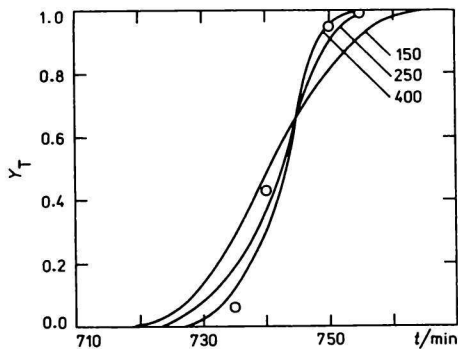

Fig. 5. Exit thiophene concentration *vs.* time. Curves parametrized by G. $N = 90$, $F = 2000$.
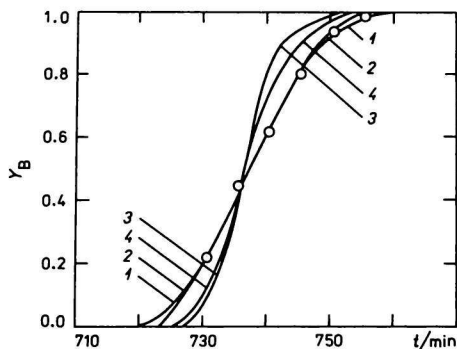

Fig. 6. Exit benzene concentration *vs.* time.
1. Nonisothermal model of well--mixed regions in series; *2.* isothermal model of well-mixed regions in series; *3.* nonisothermal plug-flow model; *4.* isothermal plug-flow model.

Fig. 7. Exit thiophene concentration *vs.* time.
1. Nonisothermal model of well--mixed regions in series; *2.* isothermal model of well-mixed regions in series; *3.* nonisothermal plug-flow model; *4.* isothermal plug-flow model.
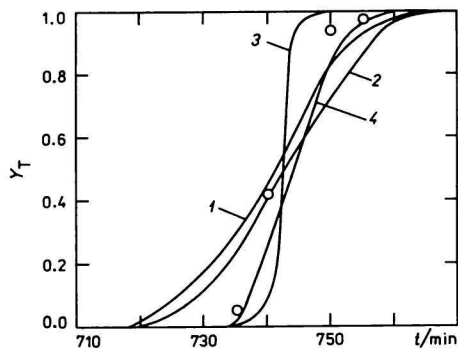
The better adequacy of the well-mixed regions in series model is caused by the fact that its mass balances take into account axial dispersion.

The movement of the temperature profile through the reactor, experimental and theoretical for several values of parameter G and $N = 90$, is shown in Fig. 8. There is a good agreement of the point of maximal temperature, its value and location. However, the experimental profiles are wider than the theoretical ones. This can be improved by the heat conduction between the individual regions.

Some of the parameters of the dimensionless equations have been estimated *a priori* from the known kinetic equations, inlet temperature, and physical properties ($\varkappa$, α_i, α_K, β, ΔT_{ad}), parameter Z_R from the experimental conditions in the tubular reactor. Parameters G and F have been estimated *a posteriori* from the comparison of the model and experimental results. Parameter F has been estimated from coincidence of the temperature profile at time $t = 0$. The influence of the parameter G is clear from Fig. 9.
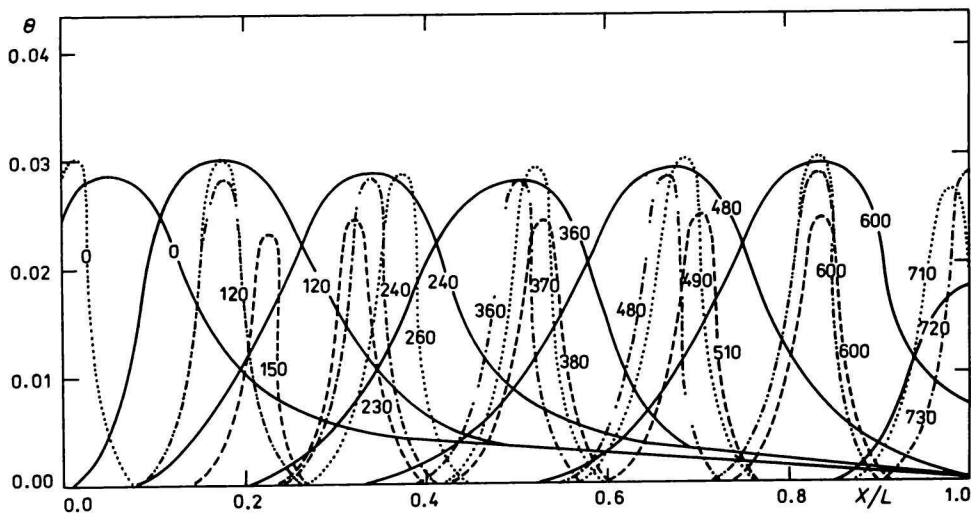

Fig. 8. Transient temperature profiles in the reactor.
$N = 90$, $F = 2000$; —experiment, $- - - G = 150$, $-\cdot-\cdot\ G = 250$, ... $G = 400$.

From presented results one concludes that the nonisothermal model of well-mixed regions in series provides for a good description of the catalytic fixed bed reactor and deactivation process. Satisfactory agreement of the outlet key component concentration and hot spot movement and good qualitative description of the temperature wave movement have been achieved. The well-mixed regions in series model yields better description than the plug-flow model under essentially shorter time of computation.
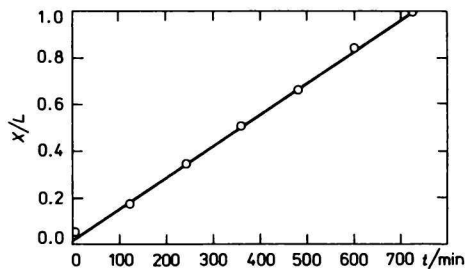
Fig. 9. Point of temperature peak *vs.* time. $N = 90$, $F = 2000$, $G = 250$; ○ experiment, — calculated.

Symbols

A_i	heat exchange surface	m^2
a_T	adsorbed amount of poison	$mol\,kg^{-1}$
a_T^*	equilibrium adsorbed amount of poison	$mol\,kg^{-1}$
$\dot{a}_T$	poison adsorption rate	$mol\,kg^{-1}\,s^{-1}$
c	concentration	$mol\,m^{-3}$
c_{pg}	heat capacity of the gas	$J\,kg^{-1}\,K^{-1}$
E	activation energy for catalytic reaction	$J\,mol^{-1}$
F	dimensionless parameter, eqn *(10)*	
G	dimensionless parameter, eqn *(10)*	
$(-\Delta H)$	heat of reaction	$J\,mol^{-1}$
h	overall heat transfer coefficient	$J\,m^{-2}\,s^{-1}\,K^{-1}$
K_∞	adsorption constant for benzene	Pa^{-1}
k_∞	frequency factor of catalytic reaction	$mol\,kg^{-1}\,s^{-1}\,Pa^{-1}$
k_T	deactivation rate constant	$m^3\,mol^{-1}\,s^{-1}$
L	catalyst bed length	m
N	number of well-mixed regions	
P	partial pressure	Pa
Q	adsorption heat of benzene	$J\,mol^{-1}$
R	reactor radius	m
T	temperature	K
t	time	s
t^o	characteristic deactivation time	s
V	volume of reactor	m^3
$\dot{V}$	volumetric flow rate	$m^3\,s^{-1}$
W	mass of catalyst in the reactor	kg
x	axial coordinate	m
Y	dimensionless concentration	
Z_R	dimensionless parameter, eqn *(10)*	
α_i	dimensionless parameter, eqn *(19)*	
α_K	dimensionless parameter, eqn *(19)*	

β	dimensionless parameter, eqn (19)	
Θ	dimensionless temperature, eqn (10)	
$\varkappa$	dimensionless parameter, eqn (19)	
ν_B	stoichiometric coefficient of key component	
$\tilde{\Xi}$	dimensionless reaction rate, eqn (10)	
ξ_w	rate of catalytic reaction	$\mathrm{mol\,s^{-1}\,kg^{-1}}$
ξ_w^0	reaction rate on the fresh catalyst inlet condition	$\mathrm{mol\,s^{-1}\,kg^{-1}}$
$\overline{\varrho c_p}$	mean heat capacity	$\mathrm{J\,K^{-1}\,m^{-3}}$
τ	dimensionless time, eqn (10)	
Φ	relative activity	
$\dot{\Phi}$	deactivation rate	

Indices

Lower:

A	component
B	key component, benzene
c	cooling medium
H	hydrogen
T	poison, thiophene
0	inlet

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