ESTIMATION OF THE CATALYST PELLET ACTIVITY DISTRIBUTION FROM ZERO ORDER KINETIC DATA

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In this paper a method of simultaneous estimation of the catalyst pellet activity distribution, the mean reaction rate constant, and the diffusion coefficient from kinetic data is described. As kinetic data measurements of outlet concentration from laboratory continuous stirred tank reactor *vs* feed rate for zero order reaction is used. The estimation technique is verified on simulated data. The mean reaction rate constant is estimated from the region of investigated dependence in which reactant penetrates into the whole catalyst pellet. The value of the effective diffusion coefficient and the activity distribution are estimated from the regime in which the reactant penetrates into the part of the pellet only.

In our previous paper[1] an estimation technique of catalyst pellet activity distribution from measurements of concentrations in the outlet stream of a laboratory continuous stirred tank reactor *vs* volumetric flow rate under constant inlet concentrations has been described. The method has been verified on simulated data for a second order reaction. The results lead to the conclusion that for reliable activity distribution estimation it is necessary to determine the values of mean reaction rate constant and diffusion coefficient by an independent method. If these independent measurements are not available, the obtained activity distribution is not reliable. As an estimation method the gradient type one has been employed and the gradient has been computed with the help of the adjoint equation[1-3].

In this paper the application of the method is presented using zero order reaction which indicates to be very advantageous for activity distribution estimation from kinetic data. Zero order reactions are quite common in catalysis. Independence of the reaction rate on the reactant concentration is explained by strong adsorption of the reactant on the catalyst surface. Due to strong adsorption the catalyst surface is covered completely by the reactant, independently on its concentration. To apply the method to more reactants reactions *e.g.* to hydrogenation of a hydrogenated component by hydrogen, one has to evaluate which of the components is present in the composition with smallest concentration with respect to stoichiometry. This component limits diffusion into the pellet. For the method application the component the order of which is zero must be present in the smallest stoichiometric amount.

THEORETICAL

For the zero order reaction the dependence of outlet concentration *vs* feed rate parameter Z_R is different according to whether the reactant penetrates into the whole pellet or not. In the first case this dependence is linear and independent on the activity distribution and the value of the Thiele modulus. This regime can be utlized for the mean reaction rate constant estimation which corresponds to the rate constant from the measurements on the crushed pellet[1]. If the reactant does not penetrate into the whole pellet the outlet concentration *vs* feed rate parameter Z_R dependence is not linear and is strongly dependent on the activity distribution and value of the Thiele modulus.

Mathematical Model of the Pellet and Reactor

Let us consider the catalyst pellet in a continuous stirred tank reactor in which zero order reaction takes place. Let us assume isothermal conditions and negligible influence of external diffusion. Then the model dimensionless equations consists of the mass balance of the pellet

$$\nabla^2 Y_A = Th_A^2 R \qquad (1)$$

with boundary conditions

$$\varphi \leqq \varphi_k : Y_A = 0$$

$$\varphi = 1 \ : Y_A = Y_A(1), \qquad (2)$$

mass balance of the reactor

$$1 - Y_A(1) = Z_R \bar{R}, \qquad (3)$$

reaction rate equation

$$R = \Phi. \qquad (4)$$

For the mean reaction rate it follows

$$\bar{R} = (n + 1) \int_{\varphi_k}^{1} \varphi^n \Phi \, d\varphi. \qquad (5)$$

The activity is defined as the ratio of the local rate constant $k(\varphi)$ and its volume averaged value k_m (ref.[4])

$$\Phi = \frac{k(\varphi)}{k_m}, \qquad (6)$$

where

$$k_m = (n + 1) \int_0^1 k(\varphi)\, \varphi^n\, d\varphi \tag{7}$$

so

$$(n + 1) \int_0^1 \Phi \varphi^n\, d\varphi = 1 . \tag{8}$$

If the reactant penetrates into the whole pellet (*i.e.* $\varphi_k = 0$) for any activity distribution it follows

$$\bar{R} = 1 \tag{9}$$

and from the reactor balance

$$Y_A(1) = 1 - Z_R = 1 - Z_{RO} k_m \tag{10}$$

and

$$k_m = \frac{1 - Y_A(1)}{Z_{RO}} . \tag{11}$$

If the reactant does not penetrate into the whole pellet ($\varphi_k > 0$) the $Y_A(1)$ *vs* Z_R dependence is obtained by the solution of the model equations.

Solution of the Model Equations

For better understanding of the pellet behaviour in which zero order reaction takes place two simple examples shall be presented for which the solution of the model equation can be carried out analytically.

Uniform activity distribution. The mean reaction rate is given by

$$\bar{R} = 1 - \varphi_k^2 \tag{12}$$

and the pellet surface concentration follows from

$$Y_A(1) = \frac{Th_A^2 [\ln \varphi_k (1 - Z_R) + Z_R(\varphi_k^2 - 1)/2]}{Th_A^2 \ln \varphi_k - 2Z_R} \tag{13}$$

and, simultaneously,

$$Y_A(1) = 1 - Z_R(1 - \varphi_k^2) . \tag{14}$$

By solving Eqs *(13)* and *(14)* we obtain the concentration $Y_A(1)$ and the space co-ordinate φ_k. This coordinate determines the part of the pellet not penetrated by the reactant. For the feed rate for which the $Y_A(1)$ *vs* Z_R dependence ceases to be linear (Fig. 1, point **A**) the relation

$$Y_A(1) = 1 - Th_A^2/4 \qquad (15)$$

holds. From this equation the value of the Thiele modulus (diffusion coefficient) can be computed.

Catalyst activity concentrated in a narrow layer. This model realizes the second limit case when the activity is concentrated in a narrow layer the distance of which is φ_1 from the pellet center. This model is suitable for testing the reactor response sensitivity on the change of the activity distribution[1].

The pellet external surface concentration is

$$Y_A(1) = \frac{Th_A^2 \ln \varphi_1}{Th_A^2 \ln \varphi_1 - 2Z_R} \qquad (16)$$

and the border of the linear and nonlinear regions (point **A** in Fig. 1) is given by the condition

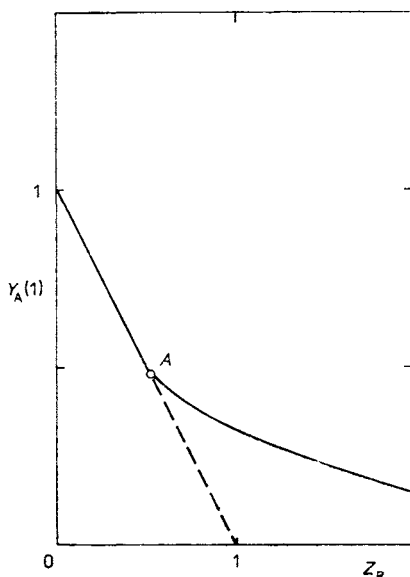$$\varphi \lneqq \varphi_1 : Y_A = 0 . \qquad (17)$$

FIG. 1

Reactor concentration *vs* feed rate parameter Z_R dependence for zero order reaction

For the limit feed rate it follows

$$Y_A(1) = (-Th_A^2 \ln \varphi_1)/2 . \tag{18}$$

With increasing diffusional resistance, *i.e.* with increasing value of the Thiele modulus, the point *A* is moving towards lower values of Z_R (larger reactant concentration in the reactor). This situation is exhibited in Fig. 2. For the method application it is necessary that the point *A* is inside the investigated feed rate interval.

Arbitrary activity distribution. Since the numerical solution of the pellet mass balance Eq. (*1*) for zero order reaction is involved the known solution for constant activity (*i.e.* the solution of equation $\nabla^2 Y_A = $ const.) has been utilized. The pellet activity profile has been divided into *I* constant activity regions (Fig. 3)

$$\Phi(\varphi) = \text{const.} = \Phi_i \quad \text{for} \quad \varphi \in (\varphi_i, \varphi_{i+1}) , \quad i = 1, ..., I - 1 . \tag{19}$$

Then for the mean reaction rate one has

$$\bar{R} = (n + 1) \int_{\varphi_k}^{1} \Phi \varphi^n \, d\varphi \tag{20}$$

and, for $n = 1$ (cylindrical pellet),

$$\bar{R} = \Phi_p(\Phi_{p+1}^2 - \varphi_k^2) + \sum_{i=p+1}^{I-1} \Phi_i(\varphi_{i+1}^2 - \varphi_i^2) . \tag{21}$$

The reactant concentration Y_A is obtained by solving the mass balance Eq. (*1*)

$$Y_{A,I-1} = Y_{A,I} + \left(Y'_{A,I} - \frac{Th_A^2 \Phi_{I-1}}{2}\right) \ln \varphi_{I-1} + \frac{Th_A^2 \Phi_{I-1}}{4}(\varphi_{I-1}^2 - 1) \tag{22}$$

$$Y'_{A,I} = \bar{R} \frac{Th_A^2}{2} \tag{23}$$

$$Y_{A,i-1} = Y_{A,i} + \left(\varphi_i Y'_{A,i} - \frac{Th_A^2 \Phi_{i-1}}{2} \varphi_i^2\right) \ln \frac{\varphi_{i-1}}{\varphi_i} + \frac{Th_A^2 \Phi_{i-1}}{4}(\varphi_{i-1}^2 - \varphi_i^2) \tag{24}$$

$$Y'_{A,i} = \left(Y'_{A,i+1} - \varphi_{i+1}\frac{Th_A^2 \Phi_i}{2}\right) \frac{\varphi_{i+1}}{\varphi_i} + \frac{Th_A^2 \Phi_i}{2} \varphi_i . \tag{25}$$

For arbitrary unknown activity distribution it is not possible to develop a simple relation for Thiele modulus estimation as in the case of uniform activity or activity in a narrow layer.
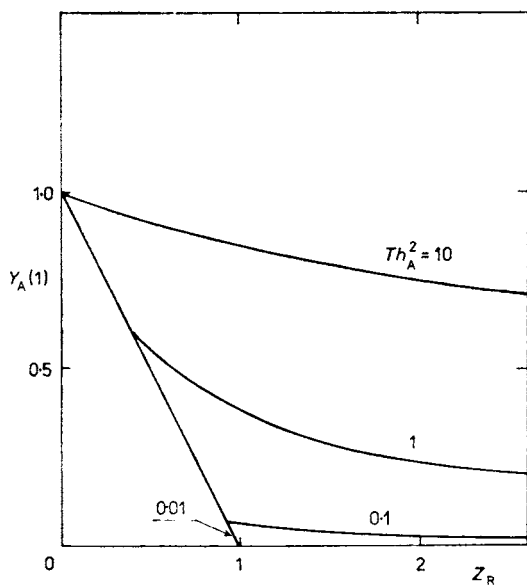
FIG. 2

Reactor concentration *vs* feed rate parameter Z_R dependence for zero order reaction and different Thiele moduli. Catalyst activity concentrated in a narrow layer at point $\varphi_1 = 0.3$
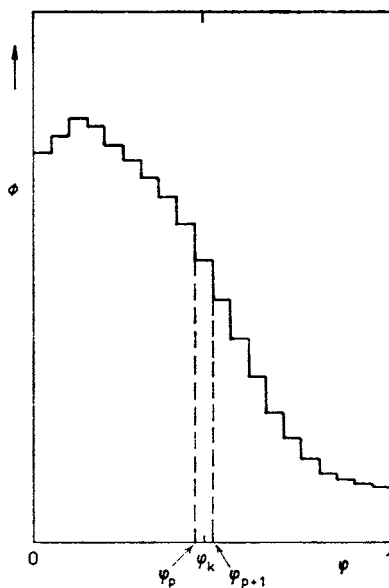

FIG. 3

Discretisation scheme for numerical solution

Numerical solution. The model equations have been solved by the following iteration scheme: Choose φ_k, compute the external surface concentration from the reactor mass balance (3) and relation for the mean reaction rate (21). Then compute the concentration towards the pellet center until it becomes negative (*i.e.* we are at the point φ_p in Fig. 3). Determine the precise value of φ_k in the interval $(\varphi_p, \varphi_{p+1})$ by the Newton procedure. If the choice of φ_k was correct, satisfactory coincidence of the chosen and computed φ_k is achieved.

Estimation of Activity Distribution and Diffusion Coefficient

The goal of the method is to estimate the activity distribution in the catalyst pellet and the value of the diffusion coefficient minimizing the objective function

$$F(D_A, \Phi(\varphi)) = \sum_{j=1}^{J} (Y_{A,I,j} - Y_{As,j})^2 , \qquad (26)$$

where $Y_{A,I}$ is the computed and Y_{As} the measured reactor concentration. The minimizing procedure has two levels. By a one parameter optimization procedure we find the minimum of the function

$$F_1(D_A) = \sum_{j=1}^{J} (Y_{A,I,j}(\hat{\Phi}(\varphi)) - Y_{As,j})^2 , \qquad (27)$$

where $\hat{\Phi}(\varphi)$ is obtained by minimizing

$$F_2(\Phi(\varphi)) = \sum_{j=1}^{J} (Y_{A,I,j} - Y_{As,j})^2 \qquad (28)$$

for a given value of the diffusion coefficient. To find the minimum of the function F_2 a gradient type method has been employed. For gradient derivation the relation for mean reaction rate (21) and reactor mass balance (3) have been applied leading to

$$Y_{A,I} = 1 - Z_R(\Phi_p(\varphi_{p+1}^2 - \varphi_k^2) + \sum_{i=p+1}^{I-1} \Phi_i(\varphi_{i+1}^2 - \varphi_i^2)) . \qquad (29)$$

After substituing into the objective function (28) and differentiation we obtain

$$\frac{\partial F_2}{\partial \Phi_i} = 2 \sum_{j=1}^{J} (Y_{A,I,j} - Y_{As,j})(-Z_R h) , \qquad (30)$$

where

$$h = \begin{cases} 0 & \text{for} \quad \varphi_i < \varphi_k \\ \varphi_{p+1}^2 - \varphi_k^2 & \varphi_i \in (\varphi_k, \varphi_{p+1}) . \\ \varphi_{i+1}^2 - \varphi_i^2 & \varphi_i \geqq \varphi_{p+1} \end{cases} \qquad (31)$$

Due to the constraint (8) and the nonnegativity of Φ_l the projected gradients method has been used similarly as in the paper[1].

RESULTS AND DISCUSSION

To test the method the examples of partially deactivated cylindrical pellet have been used. The dependences of the outlet reactor concentration Y_{As} vs feed rate have been simulated for three values of the Thiele modulus 1, 2, and 5. At the value 5 the reactant does not penetrate into the whole pellet in the entire investigated feed rate interval so the method cannot be applied because it is not possible to estimate the mean raction rate constant. For the mean reaction rate constant it is advantageous when interval of concentrations for which the reactant penetrates into the whole pellet is wide (Fig. 4). This requirement is satisfied by data computed for $Th_A^2 = 1$ for which the $Y_{As} = f(Z_R)$ dependence is linear in the interval $(0.5; 1)$.
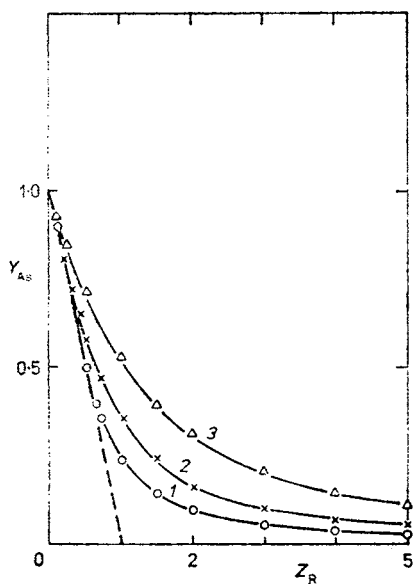
FIG. 4

Simulated data for partially deactivated cylindrical pellet. *1* $Th_A^2 = 1$; *2* $Th_A^2 = 2$; *3* $Th_A^2 = 5$
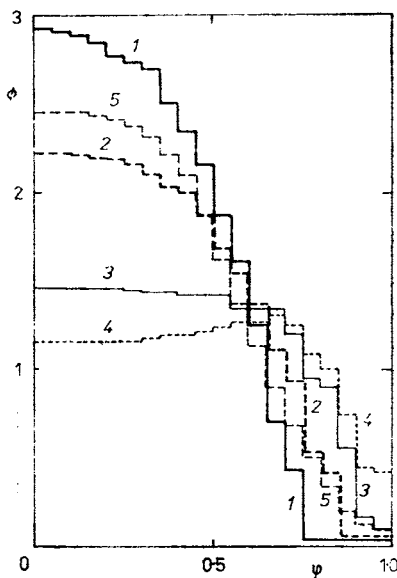
FIG. 5

Activity distribution in catalyst pellet estimated by gradient method from simulated data for $Th_A^2 = 2$, *1* $D_A/Th_{AO}^2 = 1$; *2* $D_A/Th_{AO}^2 = 0.5$; *3* $D_A/Th_{AO}^2 = 0.33$; *4* $D_A/Th_{AO}^2 = 0.25$; *5* chosen activity distribution

On the other hand, to estimate the diffusion coefficient and the activity distribution, it is necessary to move the border of the penetrated and the unpenetrated part of the pellet towards the external surface by the experimental conditions. The minimal concentration in the reactor is constrained by the practical aspects, as well as the accuracy of the analytical method and injection accuracy. The maximal concentration cannot exceed the inlet one.

For the verification of the activity distribution and the diffusion coefficient estimation method simulated data for Thiele modulus 1 and 2 have been employed. The resulting activity distribution for four chosen values of the diffusion coefficient, *i.e.* for four values of the Thiele modulus, are exhibited in Fig. 5 (simulated data for $Th_A^2 = 2$). With the increase of the diffusion coefficient the estimated activity profile is moving towards the pellet center. From the comparison of the minimal value of the objective function for different values of the diffusion coefficient it is evident, that the method leads to the correct value of the diffusion coefficient $D_A/Th_{AO}^2 = 0.5$. In Fig. 6 the deviations of the computed and correct values of the concentrations
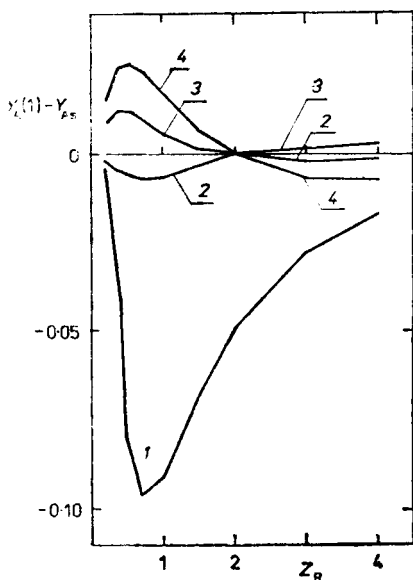

FIG. 6

The difference between computed and simulated concentrations (numbering as in Fig. 5). Values of objective function: *1* 0·03400; *2* 0·00019; *3* 0·00061; *4* 0·00290
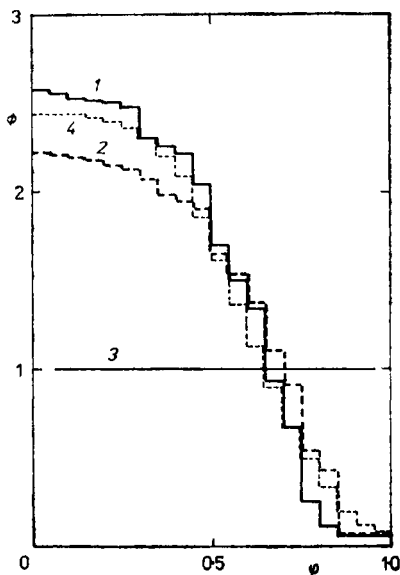
FIG. 7

Activity distribution in catalyst pellet estimated by gradient method from simulated data for $Th_A^2 = 1$. *1* $D_A/Th_{AO}^2 = 2$; *2* $D_A/Th_{AO}^2 = 1$; *3* $D_A/Th_{AO}^2 = 0.5$; *4* chosen activity distribution
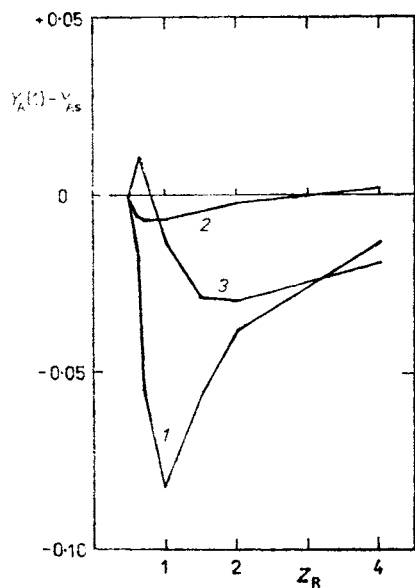
Fig. 8

Fig. 8

The difference between computed and simu-
lated concentrations (numbering as in Fig. 7).
Values of objective function: *1* 0·01470; *2*
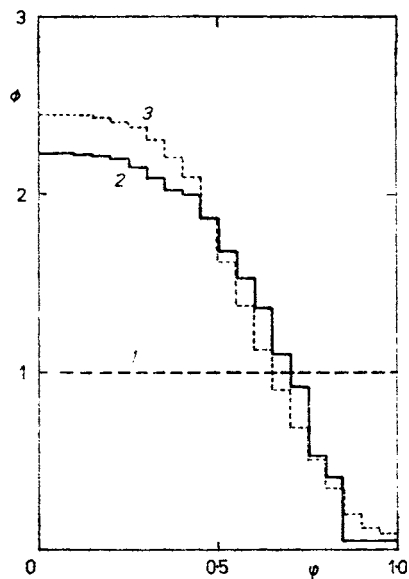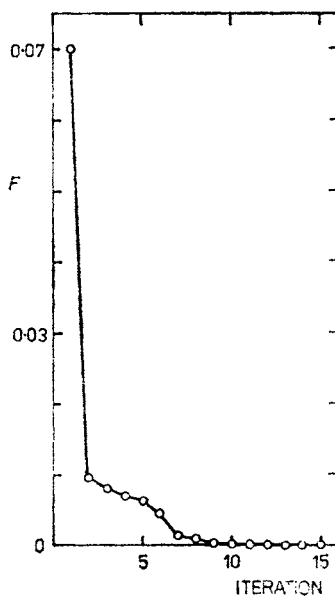0·00017; *3* 0·00249

Fig. 9

Resulting activity distribution in the pellet.
Data simulated for $Th_A^2 = 2$. *1* first iteration;
2 last iteration; *3* chosen distribution

Fig. 10

Decrease of the objective function by the
gradient method

are compared. Worst agreement has been achieved for $D_A/Th_{AO}^2 = 1$. It is due to the fact, that by any activity distribution it is not possible to fit the border of both regimes (location of point A).

The same conclusion has been made also by processing simulated data for $Th_A^2 = 1$. The first estimation enabled us to determine a narrow interval for the diffusion coefficient value. For a high value of the diffusion coefficient it was not possible to locate correctly the border of the two regime regions (point A), for a low value of the diffusion coefficient (curve 3) the best fitting has been obtained by the uniform activity distribution which is not correct (the location of the region border does not correspond to the uniform distribution). Minimal deviation of the computed and „measured" data and minimum of the objective function corresponds to the correct value $D_A/Th_{AO}^2 = 1$ (Figs 7 and 8).

Fig. 9 illustrates the comparison of the computed activity distribution (last iteration) with the chosen one (*i.e.* "experimental") for $Th_A^2 = 2$ and Fig. 10 shows the decrease of the objective function by the gradient method. In all cases as the first iteration the uniform activity distribution has been chosen.

The results demonstrate that the zero order reaction has suitable properties for simultaneous estimation of the activity distribution in the catalyst pellet and the mean reaction rate constant and diffusion coefficient (Thiele modulus). A condition for the method application is the possibility to reach the kinetic region, *i.e.* region in which reactant penetrates into the whole catalyst pellet. The interval of concentrations corresponding to the kinetic region has to be sufficiently wide in order to allow reliable estimation of the border between the kinetic and diffusion reaction regime. The movement of the regime into the diffusion one, which is the condition for reliable estimation of the activity distribution, can be obtained by decreasing reactor concentration which can be achieved by decreasing the feed rate.

LIST OF SYMBOLS

a	characteristic dimension of catalyst pellet
C_A	concentration of component A
$C_{A,ref}$	reference inlet concentration
D	effective diffusion coefficient
F, F_1, F_2	objective functions
I	number of mesh points
J	number of analysed components
k	reaction rate constant
k_m	volume averaged reaction rate constant
n	integer characteristics of pellet geometry
r	space coordinate
R	dimensionless reaction rate
Th_A	Thiele modulus, $Th_A^2 = Th_{AO}^2/D_A = a^2 k_m/(C_{A,ref} D_A)$
$\dot{V}$	volumetric flow ate

W	mass of pellet
Y_A	dimensionless concentration, $Y_A = C_A/C_{A,ref}$
Y_{As}	experimental reactor concentration
Z_R	dimensionless parameter, $Z_R = Z_{RO}k_m = k_m W/(C_{A,ref}\varrho\dot{V})$
ϱ	pellet density
φ	dimensionless space coordinate, $\varphi = r/a$
φ_k	location of the border between penetrated and unpenetrated part of pellet
φ_1	location of active layer
Φ	activity

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