
MODELLING OF INTERNAL DIFFUSION INSIDE A CATALYST PARTICLE WITH NON-UNIFORM RADIAL ACTIVITY PROFILE FOR PARALLEL REACTIONS

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Numerical solution of the system of diffusion equations which describe a system of parallel reactions under the conditions of internal diffusion in a non-isotropic spherical catalyst particle was carried out in this paper. The solution of the problem was sought for various radial activity profile corresponding to the concentration profile of active component in a particle of supported catalyst and for various values of the Thiele modulus of both parallel reactions. Further, the effect of reaction order of single reactions (zeroth or first) with respect to the effectiveness factor of the internal diffusion and to the selectivity of the main reaction was investigated. It is evident from the results that the change of the activity profile in the particle has a great effect on the selectivity and on the effectiveness factor of the internal diffusion.

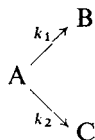
The impregnation techniques of catalyst preparation or its gradual deactivation in the course of its exploitation often cause the existence of non-uniform activity profile in the catalyst particle. Under these conditions it is impossible to use usual methods¹ for describing the effect of internal diffusion on the rate of catalytic reaction. Especially significant are the catalysts with an active component concentrated in the particle surface shell which exhibit higher reaction rate², and in case of consecutive reactions also the enhanced selectivity³.

The previous works dealing with the problem of non-uniform activity profile in an isothermal catalyst particle were summarized in survey⁴. Recently, the theoretical description of the problem has been used to seek the optimum distribution of active component inside the catalyst particle both from the point of view of the maximum selectivity of the parallel and consecutive reactions⁵⁻⁷ and also with regard to the deactivation of catalyst⁸. The opposite approach was followed in papers^{9,10} when the distribution of activity in the catalyst particle was determined on the basis of kinetic data. The practical importance of theoretical knowledge consists, e.g., in optimizing the ethylene oxidation^{6,11}, increasing the selectivity of naphthalene oxidation¹², etc.

The aim of this work has been the numerical solution of the problem of internal diffusion for isothermal reactions of the zeroth or first order. Analogously to our preceding papers^{2,3}, the collocation method was used for the solution.

THEORETICAL

The diffusion of reacting components for parallel reactions illustrated by the scheme



is described, for the spherical particle geometry, by the following system of differential equations

$$\frac{1}{R^2} \frac{d}{dR} \left(R^2 \frac{dC_A}{dR} \right) = (\varphi_1^2 C_A^n + \varphi_2^2 C_A^m) R^\alpha, \quad (1)$$

$$\frac{1}{R^2} \frac{d}{dR} \left(R^2 \frac{dC_B}{dR} \right) = -\varphi_1^2 C_A^n R^\alpha \quad (2)$$

where φ_i represents the Thiele modulus of the i -th reaction defined by the equation

$$\varphi_i^2 = d_{\text{eff},i}^2 (k_{0,i} C_0^{n-1} / D_{\text{eff}}). \quad (3)$$

The activity profile in the catalyst particle is represented by the chosen function of radial coordinate according to the relation²

$$k = k_0 R^\alpha. \quad (4)$$

These equations must be completed by the boundary conditions

$$\frac{dC_A}{dR} = \frac{dC_B}{dR} = 0, \quad R = 0 \quad (5a)$$

$$C_A = 1, \quad C_B = 0, \quad R = 1. \quad (5b)$$

Solution of Model

On the basis of spherical symmetry of the system, it is apparent that the concentration profiles of reacting components inside the particle of catalyst can be approximated by an even function. In the simplest case it is possible to use polynomials with even powers of radial coordinate to describe the concentration profiles of component A or B . The polynomials satisfy completely the system of differential equations at the collocation point chosen in advance. Unlike the procedures starting from the Jacobi

polynomials^{13,14}, the proposed method is considerably simpler and the numerical calculation more rapid.

Therefore, the solution of the system of differential equations (1), (2) will be assumed in the form of the following polynomials corresponding to the concentration profiles of component *A* or *B*, respectively, in the catalyst particle:

$$C_A(R) = A_0 + A_2R^2 + A_4R^4 + A_6R^6, \quad (6)$$

$$C_B(R) = B_0 + B_2R^2 + B_4R^4 + B_6R^6. \quad (7)$$

Let the chosen polynomials fulfil the diffusion equation at two chosen collocation points within the interval $R_i \in \langle 0, 1 \rangle$ and, further, also both boundary conditions at the points $R = 0$ and 1 , respectively. In this way it is possible to determine the unknown coefficients A_j , B_j in the chosen polynomials.

Let us consider the unity orders of both reactions ($n = m = 1$). Differential equation (1) may then be replaced by a system of linear equations which has the following form

$$-A_0[\varphi_1^2 + \varphi_2^2]R_i^\alpha + A_2[6 - R_i^{2+\alpha}(\varphi_1^2 + \varphi_2^2)] + A_4[20R_i^2 - R_i^{4+\alpha}(\varphi_1^2 + \varphi_2^2)] + A_6[42R_i^4 - R_i^{6+\alpha}(\varphi_1^2 + \varphi_2^2)] = 0; \quad i = 1; 2 \quad (8)$$

From boundary conditions (5a) and (5b) follow two more equations for the unknown coefficient of the sought polynomial $C_A(R)$

$$A_0 + A_2 + A_4 + A_6 = 1 \quad \text{for } R = 1, \quad (9)$$

$$2A_2 + 4A_4 + 6A_6 = 0 \quad \text{for } R = 0. \quad (10)$$

Thus, the solution of Eq. (1) is replaced by the solution of four linear equations (8)–(10) with respect to the sought coefficients A_j . The concentration profile of substance *B* in the catalyst particle is determined analogously by solving the following system of linear algebraic equations

$$6B_2 + 20B_4R_i^2 + 42B_6R_i^4 + \varphi_1^2R_i^\alpha C_A(R) = 0, \quad i = 1, 2 \quad (11)$$

$$B_0 + B_2 + B_4 + B_6 = 1, \quad (12)$$

$$2B_2 + 4B_4 + 6B_6 = 0. \quad (13)$$

The systems of Eqs (8)–(10) and (11)–(13) were in this work solved by the matrix inversion method for the chosen collocation points with coordinates $[R_1, R_2] = [1/3, 2/3]$ and $[0.8, 0.9]$, respectively.

The system of differential equations which describe the system of parallel reactions was solved also for the zeroth order of both reactions and for the combination of orders 0 and 1.

The solution of diffusion equations for parallel reactions each of zeroth order is much simpler. The respective equations have these forms

$$A_2[4 + 2R_i^2] + A_4[4R_i + 12R_i^4] + A_6[6R_i^3 + 30R_i^6] = [\varphi_1^2 + \varphi_2^2] R_i^\alpha, \quad (14)$$

$$6B_2 + 20B_4R_i^2 + 42B_6R_i^4 = -\varphi_1^2 R_i^\alpha, \quad i = 1; 2 \quad (15)$$

In case that the first order was considered for the first parallel reaction and the zeroth order for the second one, numerical solution leads to the following relations

$$-A_0\varphi_1^2 R_i^\alpha + A_2[6 - \varphi_1^2 R_i^{2+\alpha}] + A_4[20R_i^2 - \varphi_1^2 R_i^{4+\alpha}] + A_6[42R_i^4 - \varphi_1^2 R_i^{6+\alpha}] = \varphi_2^2 R_i^\alpha. \quad (16)$$

$$6B_2 + 20B_4R_i^2 + 42B_6R_i^4 = -\varphi_1^2 R_i^\alpha C_A(R); \quad i = 1; 2 \quad (17)$$

Determination of Effectiveness Factor and Selectivity

By finding all coefficients A_j in the chosen polynomial $C_A(R)$ and coefficients B_j in polynomial $C_B(R)$, the concentration profiles of reacting components in the catalyst particle are defined and can be used for calculating the effectiveness factor of internal diffusion according to the relation¹

$$\eta = [3 + \alpha] \int_0^1 R^{2+\alpha} [C_A^n(R)] dR. \quad (18)$$

After inserting the polynomial and integration, we get in case of the first reaction order the following form for the effectiveness factor

$$\eta = [3 + \alpha] \left[\frac{A_0}{3 + \alpha} + \frac{A_2}{5 + \alpha} + \frac{A_4}{7 + \alpha} + \frac{A_6}{9 + \alpha} \right]. \quad (19)$$

The effect of internal diffusion on the selectivity of parallel reactions* can be expressed by the selectivity parameter defined by the relation

$$S = [\varphi_1^2 + \varphi_2^2] \frac{\int_0^1 C_A^n R^{2+\alpha} dR}{\int_0^1 [\varphi_1^2 C_A^n + \varphi_2^2 C_A^m] R^{2+\alpha} dR}. \quad (20)$$

* $S(\text{diffusion}) = S \cdot S(\text{kinetic})$, where $S(\text{kinetic}) = k_{01}/(k_{01} + k_{02})$ for $n = m$

For parallel reactions of the same order, the selectivity parameter S depends neither on the activity profile in the particle nor on the Thiele moduli of both the reactions, and parameter S is equal to unity.

For the combination of the first reaction order of the first reaction and zeroth order of the second reaction, we obtain, for the selectivity parameter of the system of parallel reactions, the relation

$$S = [\varphi_1^2 + \varphi_2^2] \left[\frac{A_0}{3 + \alpha} + \frac{A_2}{5 + \alpha} + \frac{A_4}{7 + \alpha} + \frac{A_6}{9 + \alpha} \right] / \left[\frac{\varphi_1^2 A_0}{3 + \alpha} + \frac{\varphi_1^2 A_2}{5 + \alpha} + \frac{\varphi_1^2 A_4}{7 + \alpha} + \frac{\varphi_1^2 A_6}{9 + \alpha} + \frac{\varphi_2^2}{3 + \alpha} \right]. \quad (21)$$

Solvability of the System of Algebraic Equations

For the first order parallel reactions, the system of algebraic equations has a solution for the whole chosen interval of values of the Thiele modulus φ_2 ($0.1 < \varphi_2 < 50$). No other constraints occur even for various degrees of inhomogeneity α ($0.1 \div 10$) and for the ratio of the Thiele moduli of both the reactions K ($0.1 \div 10$). For the zeroth order of both the reactions, the system is solvable (i.e., the calculated concentrations of components in the particle are positive) for $\alpha < 2$ within the interval of the Thiele moduli $\varphi_2 \leq 2$, and for $\alpha \geq 2$ in the interval of $\varphi_2 \leq 5$. Further constraint occurs for the ratio of the Thiele moduli $K > 1$. For $K = 2$ and for $\alpha < 1$, it is possible to obtain usable solutions of system of algebraic equations only for low values of the Thiele modulus φ_2 (up to $\varphi_2 = 1$). For $K = 10$ and for $0.1 < \alpha < 10$, the system is solvable within the interval $\varphi_2 < 0.5$.

When solving the system of algebraic equations for the combination of different reaction orders of parallel reactions (1 or 0), when the first order was assigned to the first reaction, it is possible to obtain the solution in the whole investigated interval of values of the Thiele modulus ratio of both reactions ($0.1 \leq K \leq 10$) and degrees of inhomogeneity ($\alpha = 0.1 \div 10$). However, the usable results are obtained only for lower values of the Thiele modulus ($\varphi_2 \leq 5$).

Similarly to the preceding work², the accuracy of the numerical determination of the effectiveness factor was judged on the basis of comparison of the calculation result for an approximately isotropic spherical particle ($\alpha = 0.1$) and for the reaction of the first order with analytical solution. It has appeared that the error of numerical solution increases with increasing value of the Thiele modulus φ_2 . For $\varphi_2 = 5$, the deviation of numerical solution compared to the analytical one reaches 0.7%. For higher values of the Thiele modulus ($\varphi_2 = 10$), the numerical calculation shows already considerable deviations from the analytical solution (as much as several ten percent) in dependence on the chosen parameters. In this case it was necessary to choose greater number of collocation points to obtain a more accurate result.

Choice of Position of Collocation Points

In Table I it is lucidly shown how differ the solutions of diffusion equations for different pairs of collocation points $[1/3, 2/3]$ and $[0.8, 0.9]$. It follows from the values given in Table I that the effect of choosing the position of collocation points is the greater the higher is the value of the Thiele moduli for both reactants, therefore in the case when both the reactions take place mostly in the surface shell of the catalyst particle.

On the basis of physical view it is therefore better to locate the collocation points into the regions where the assumed solution, i.e., the dependence of concentration of reacting components on the radial coordinate has a high derivative.

RESULTS AND DISCUSSION

The numerical results presented in this work provide an insight into the dependence of the internal diffusion effectiveness factor and selectivity parameter on the properties of system, i.e., on the ratio of the Thiele moduli $K = \varphi_1/\varphi_2$, the degree of inhomogeneity of the catalyst particle α and the order of both reactions n, m .

Effectiveness Factor of Internal Diffusion

The dependence of effectiveness factor of the catalyst on the Thiele modulus φ_2 is shown in Fig. 1 for various values of inhomogeneity parameter α . The ratio of the Thiele moduli of both parallel reactions of orders $[n, m] = [1, 1]$ or $[1, 0]$ was chosen $K = 1$ in this case. It follows from the figure that the non-uniform distribution

TABLE I
Effect of the position of collocation points on the effectiveness factor

Parameters of calculation				Thiele modulus φ_2	Effectiveness factor η	
α	K	n	m		$R_i = [1/3; 2/3]$	$R_i = [0.8; 0.9]$
0.1	1	0	0	0.1	0.99895	0.99876
				0.5	0.97383	0.96921
				1.0	0.89532	0.87685
				2.0	0.58130	0.50740
10	10	1	1	5	0.90539	0.93539
				10	0.87571	0.66499
				20	0.86500	0.61143
				50	0.86080	0.59748

of active component in the catalyst particle considerably influences the relationship between the Thiele modulus and the effectiveness factor. For both the combinations of reaction orders holds that with increasing the inhomogeneity parameter, i.e., in case that the catalyst activity increases from the centre of particle to its surface, increases also the value of effectiveness factor. Further it follows from the figure that for the increasing value of both the Thiele moduli, decreases naturally the effectiveness factor. The calculated dependences give further an evidence that higher values of the effectiveness factor were attained on the assumption of the unity reaction orders of both reactions.

The character of dependences found is the same also for other reaction orders of both reactions, i.e., 0 or 1, respectively. For example, Fig. 2 was obtained for the zeroth order of both reactions.

Comparison of the effect of reaction orders of both reactions is given in Fig. 3. It illustrates the dependence of the effectiveness factor on the Thiele moduli for different values of reaction orders of parallel reactions. It follows from the figure that this dependence is especially sensitive to the values of reaction order in the region of higher values of the Thiele modulus and for the isotropic catalyst particle, therefore, in the cases of greater effect of internal diffusion on the course of both reactions.

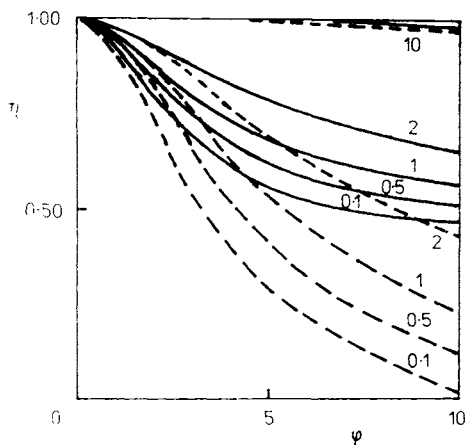


FIG. 1

Effect of the Thiele moduli ϕ and character of activity profile on the effectiveness factor η ($K = 1$); $n = 1, m = 1$ (solid line), $n = 1, m = 0$ (broken line) for the inhomogeneity parameters $\alpha = 0.1$ to 10

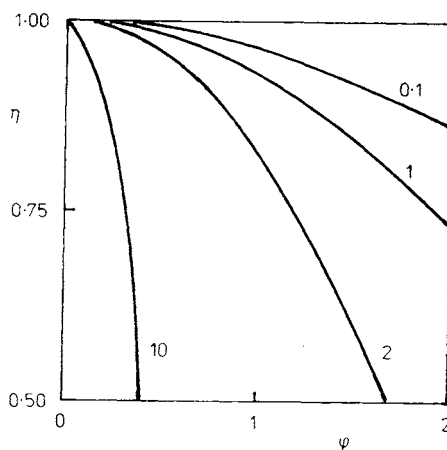


FIG. 2

Effect of the Thiele moduli ϕ on the effectiveness factor η ; $n = 0, m = 0, \alpha = 1, K = 0.1$ to 10

Selectivity of Parallel Reactions

Besides the effectiveness factor of internal diffusion of catalyst, in this work was also studied the selectivity of parallel reactions of various orders in dependence on the ratio of the Thiele moduli K and the degree of inhomogeneity α .

The selectivity parameter defined by Eq. (20) was examined only for reactions of different orders ($n = 1, m = 0$) because for the parallel reactions of the same order, the value of the selectivity parameter does not change with respect to the parameters examined and is always equal to unity.

The results of calculation are given in Fig. 4 for various values of the Thiele moduli. The low values of moduli ($\varphi_2 = 0.1$ and $K < 10$) represent the situation close to the kinetic region whereas the data determined for $\varphi_2 > 1$ and $K > 1$ illustrate the situation of a greater effect of internal diffusion on the course of parallel reactions. In this figure, the effect of the inhomogeneity degree of the catalyst particle on the value of the selectivity parameter is as well shown. It has appeared that the dependence is considerably sensitive to the value of inhomogeneity degree α , with its increasing value increases also the value of the selectivity parameter. This statement leads to the conclusion that the particles of catalysts which have inside steeper activity profile yield higher selectivity of parallel reactions.

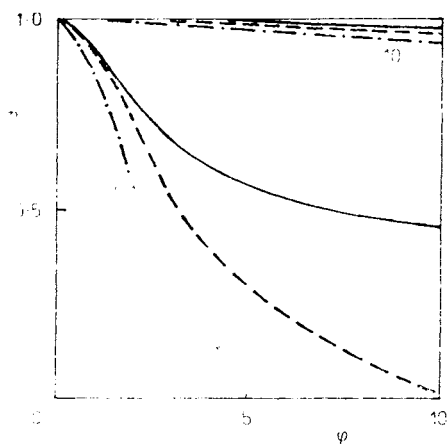


FIG. 3

Effect of reaction orders of reactions n, m on the dependence of effectiveness factor η on the Thiele moduli φ for $K = 1$; $n = 1, m = 1$, (solid line), $n = 1, m = 0$ (broken line), and $n = 0, m = 0$ (dash and dot line)

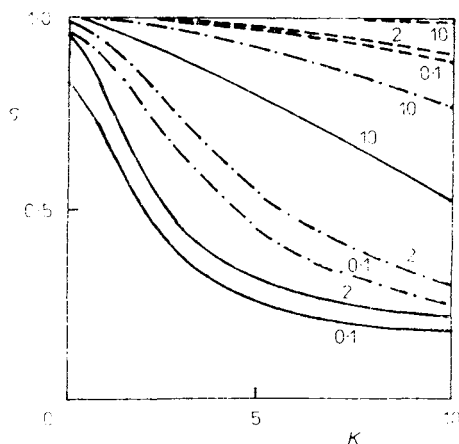


FIG. 4

Effect of ratio of the Thiele moduli K and activity profile on the selectivity S of reactions of different order ($n = 1, m = 0$); $\alpha = 0.1$ to 10 for $\varphi_2 = 2$ (solid line), $\varphi_2 = 1$ (dash and dot line), and $\varphi_2 = 0.1$ (broken line)

Conclusion

The main aim of this work has been the numerical solution of mathematical model of anisotropic catalyst particle for a system of parallel reactions influenced by internal diffusion.

To solve the system of diffusion equations, the collocation method using 2 collocation points was chosen. It has appeared that the collocation points are better to be located to the place where the assumed solution, i.e., the function of concentration of reacting component on radial coordinate, has a high derivative.

The numerical solution was obtained for a limited range of parameters. More precise results, especially in the region of strong influence of internal diffusion, would be possible to reach by solving the problem with more collocation points.

The effect was investigated of the catalyst particle inhomogeneity, of the ratio of the Thiele moduli of both reactions and of reaction orders on the internal diffusion effectiveness factor and on the selectivity parameter of parallel reactions.

It has followed from the results that the catalysts with a higher value of the inhomogeneity degree (i.e., such where the concentration of active component increases from the centre of particle towards its outer surface) yield both higher values of the internal diffusion effectiveness factors and also higher selectivity of parallel reactions of different order.

LIST OF SYMBOLS

A_j	coefficient of polynomial
B_j	coefficient of polynomial
C	dimensionless concentration of reacting component
C_0	concentration outside particle, mol l^{-1}
d_{ekv}	equivalent diameter of grain, m
D_{ef}	effective diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
k_0	rate constant for $R = 1$
K	ratio of Thiele moduli of parallel reactions
m	reaction order
n	reaction order
R	radial coordinate
S	selectivity parameter
α	inhomogeneity parameter
η	internal diffusion effectiveness factor
φ	Thiele modulus

Subscripts

A	reaction component A
B	reaction component B
i	designation of collocation point
j	designation of coefficient of polynomial
1, 2	designation of reactions

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