MASS TRANSFER IN CATALYST PARTICLES OF NON-TRADITIONAL SHAPE

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The numerical solution of a system of partial differential equations describing the reacting component transfer in catalyst particles of non-traditional shapes, in extrudates of the starcat and starring types, facilitates the concept of concentration field in a catalyst and of the effectiveness factor of internal diffusion which determines the total reaction rate and thus the catalyst performance. The problem solution was carried out for the first-order reaction of infinite long extrudate and for the particles of star-shaped catalyst of finite length. The favourable effect was confirmed of the catalyst extrudate shaping on its performance as far as the rection takes place in the diffusion region.
Key words: Effectiveness factor; Internal diffusion; Star-shaped pellets.

A vast majority of processes in the field of petrochemistry and organic technology is based on the utilization of heterogeneous catalysts and therefore the enduring attention is paid to evaluating their behaviour under real conditions at their application under industrial conditions. In such reacting systems, transport phenomena often manifest themselves which influence the apparent rate of chemical conversion. The interaction of transport phenomena with the exothermal reaction is so far serious that, in dependence on the reaction conditions, it can lead to the existence of multiple steady states, in liquid systems in the vicinity of boiling point of reaction mixture, a partial or complete phase change of the reaction mixture may take place, and the like. The reaction may then take place with substantially higher rate, can have other mechanism or other kinetics. For exothermic reactions, such a pathological state may result not only in the catalyst destruction in the place of its local overheating, but also from the point of view of safety of the reactor operation, it represents even considerable risk. Therefore, profiled extruded catalyst supports with extremely high ratio of their external geometric surface to their volume have recently appeared on the market. In this way, a more intensive mass and heat transfer is reached between the reaction mixture and the catalyst particle. As an example serve products of Engelhard Co. (Houston, U.S.A.) called “starring” or “starcat” with cross section in the shape of a regular star with or without axial hole. The judgement of efficiency of such a catalyst for an isothermal system is a subject of this work.

To the theory of diffusion transfer of reacting components in a porous catalyst particle is devoted, e.g., monograph[1] in which the pertinent solutions can be found of diffusion equation for the basic shapes – plate, sphere, finite and infinite cylinder. The properties of catalyst particles shaped to the cross section in the form of tetralobe have been modelled for isothermal conditions and evaluated in our recent papers[2,3]. The numerical algorithms used for solving the pertinent diffusion equations are summarized in monograph[4].

In some cases the knowledge of the model behaviour is useful in dependence on the parameter which can define the catalyst particle shape, the character of concentration field in its neighbourhood and the like. Methodical text for the parametric studies is represented by monograph[5].

THEORETICAL

The concentration field of a reacting component in a catalyst particle in the shape of star is given by the solution of the pertinent diffusion equation formulated in the coordinate system depicted in Fig. 1. This partial differential equation of eliptic type has the following form for the description of the three-dimensional catalyst particle, i.e., the extrudate of the given cross section and finite length occurring in a steady state and for the first-order reaction:

$$\frac{\partial^2 C}{\partial X^2} + \frac{\partial^2 C}{\partial Y^2} + \frac{\partial^2 C}{\partial Z^2} - F^2 C = 0 \quad . \qquad (1)$$

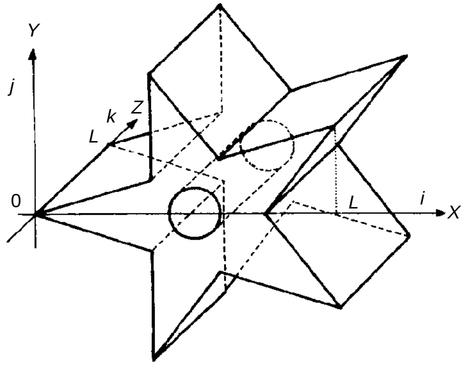

FIG. 1
Scheme of catalyst extrudate of length or thickness L with designated coordinate system

To solve this equation, it is necessary to use the following boundary conditions taking into account partly the constant concentration on the external surface of particle and partly the longitudinal, (*X*–*Z*), or transversal, (*X*–*Y*), plane of its symmetry:

$$X = X_e \qquad Y = Y_e \qquad Z = Z_e \qquad C = 1 \tag{2}$$

$$X > 0 \qquad Y = 0 \qquad L \geq Z \geq 0 \qquad \partial C/\partial Y = 0 \tag{3}$$

$$X > 0 \qquad Y > 0 \qquad Z = L/2 \qquad \partial C/\partial Z = 0 \ . \tag{4}$$

Characteristic dimension *L* in Thiele modulus *F* is considered as the length of catalyst extrudate (usually 3 to 7 mm), this dimension corresponding simultaneously to the extrudate thickness (see Fig. 1):

$$F = L(K/D_{ef})^{1/2} \ . \tag{5}$$

The ratio of volume *V* to extrudate external surface *S* depends on its length. For instance, for the types produced by Engelhard Co., whose cross section has the shape of regular five-pointed star (with the corner angle 36°) without a hole (starcat) or with an axial hole (starring, *d* = 0.251 *L*), holds

$$V/S = 0.073\, L \tag{6}$$

or

$$V/S = 0.054\, L \ . \tag{7}$$

Calculations

Diffusion equation (*1*) was solved as the Dirichlet problem with boundary conditions (*2*)–(*4*) for both the catalyst types. For the solution, the finite difference method with equidistant dividing of the network knot points was used, the extrudate edge on the cross section being replaced by a stepwise line. For the comparison of numerical results with other particle geometries, the simpler two-dimensional problem was also solved which corresponds to the infinite long extrudate.

By replacing the derivatives by differences, differential equation (*1*) was transformed to the system of linear algebraic equations of the following form:

$$C_{i,j,k} = (C_{i-1,j,k} + C_{i+1,j,k} + C_{i,j-1,k} + C_{i,j+1,k} + C_{i,j,k-1} + C_{i,j,k+1})/(6 + F^2h^2) \quad . \tag{8}$$

Counting indexes i, j, k are related to the coordinate axes X, Y, Z:

$$X_i = i \,.\, h \quad \text{for} \quad i = 0, 1, \ldots, 82 \tag{9}$$

$$Y_j = j \,.\, h \quad \text{for} \quad j = 0, 1, \ldots, 44 \tag{10}$$

$$Z_k = k \,.\, h \quad \text{for} \quad k = 0, 1, \ldots, 42 \quad . \tag{11}$$

On the assumption of an identical (dimensionless) integration step in the direction of all three spatial coordinates (h = 0.0125), the boundary conditions for a quarter of catalyst particle delimited by two mutually perpendicular planes of symmetry, are to be rewritten into the relations:

$$C_{i,j,0} = 1 \tag{12}$$

$$C_{i_e,j_e,k} = 1 \qquad k = 1, \ldots, 41 \tag{13}$$

$$C_{i,0,k} = C_{i,1,k} \tag{14}$$

$$C_{i,j,41} = C_{i,j,42} \quad , \tag{15}$$

where subscripts i_e and/or j_e correspond to the particle surface and can be determined by the methods common in analytical geometry. For instance, for the central hole of starring catalyst holds

$$i_e = 45 + [112 - (j_e - 1)^2]^{1/2} \quad . \tag{16}$$

The system of algebraic equations (*8*)–(*15*) was solved by the Gauss–Seidel method. To attain the needed accuracy of calculation, a considerable number of iterations is necessary which depends on the problem parameters, i.e., on the required accuracy of solution and above all on the value of the Thiele modulus, characterizing the effect of diffusion transfer of reacting component on the course of reaction in catalyst particle. This fact is illustrated by the data given in Fig. 2 for both the examined shapes of catalyst, viz. starcat and starring, at the required accuracy of solution of the system of equations, $e = 10^{-8}$, defined by the absolute value of relative difference of concentrations between two successive iterations fulfilled at all the network knot points. It appeared that the largest number of iterations has to be used for the values of the Thiele modulus corresponding to the transient region between the kinetic and diffusion regime.

RESULTS AND DISCUSSION

The concentration field of reacting component in catalyst particle of the starcat or starring profile can be illustrated, e.g., in the axial plane of symmetry in dependence on the distance from the particle front edge defined by the value of index *k*. The resultant concentration profiles for values of the Thiele modulus $F = 15$ are given in Figs 3 and 4, and it is possible to identify on them the difference between the starcat and starring

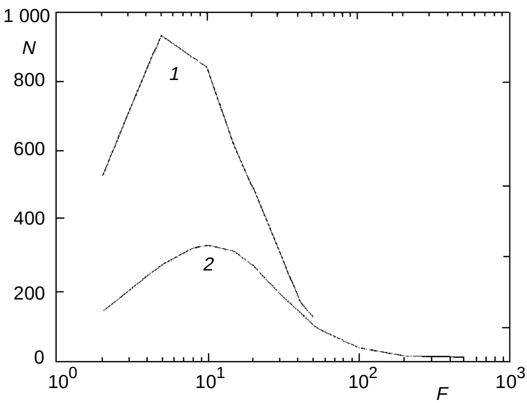

FIG. 2
Dependence of needed number of iterations N in numerical solution of system of agebraic equations on value of Thiele modulus F for $e = 10^{-8}$: *1* starcat catalyst; *2* starring catalyst

types of catalyst. It is comprehensible that the mean value of concentration in particles of the second type is considerably higher.

The concentration profiles on the straight line of intersection of the longitudinal and transversal plane of symmetry of extrudate are shown in Figs 5 and 6 for various values of the Thiele modulus for the stars without hole and with hole.

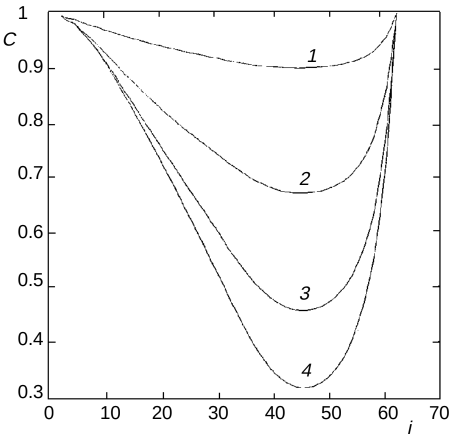

FIG. 3
Concentration profiles in axial plane of symmetry and in various distances from the face of starcat extrudate: F = 15; j = 1; *1* k = 2; *2* k = 5; *3* k = 10; *4* k = 41

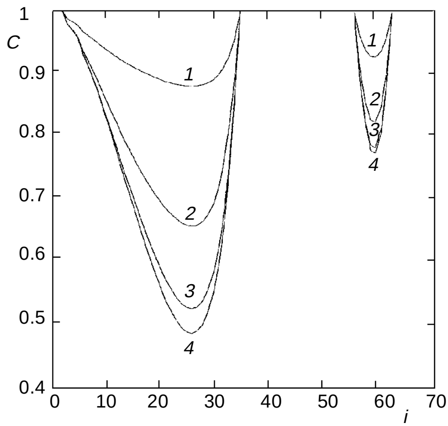

FIG. 4
Concentration profiles in axial plane of symmetry and in various distances from the face of starring extrudate: characteristics as in Fig. 3

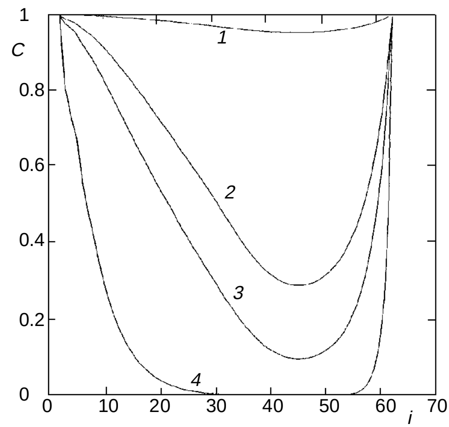

FIG. 5
Effect of value of Thiele modulus on concentration profile along locus of intersection of longitudinal and transaversal plane of symmetry of starcat extrudate: j = 1; k = 41; *1* F = 2; *2* F = 10; *3* F = 15; *4* F = 50

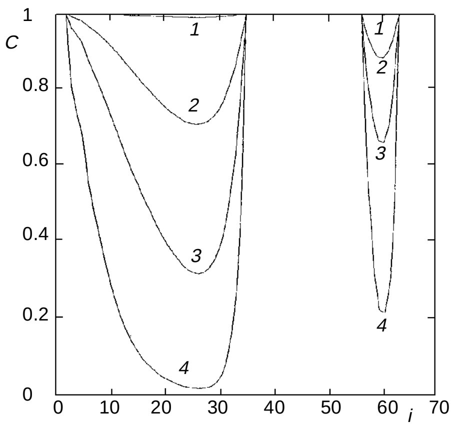

FIG. 6
Effect of value of Thiele modulus on concentration profile along locus of intersection of longitudinal and transaversal plane of symmetry of starring extrudate: characteristics as in Fig. 5

The three-dimensional axonometric illustration is of interest of concentration profiles on the cross section perpendicular to the particle axis passing through the centre of gravity made by means of the software MATLAB 4.0, The Math Works, Inc., Natick, MA, U.S.A. These profiles are depicted in Figs 7–10 for the catalyst of the starcat and starring types for the values of the Thiele modulus F = 10 and F = 50 and demonstrate the fact that the catalyst extrudate shape modifies the shape of concentration field inside its porous structure. For high values of the Thiele modulus, naturally, there exists a zone in the catalyst particle with practically zero value of concentration of reacting component.

On the basis of the calculated dimensionless concentrations in catalyst particle, it was easy to determine its mean value which corresponds, for the first-order kinetics, directly to the effectiveness factor of internal diffusion. The result of calculations for

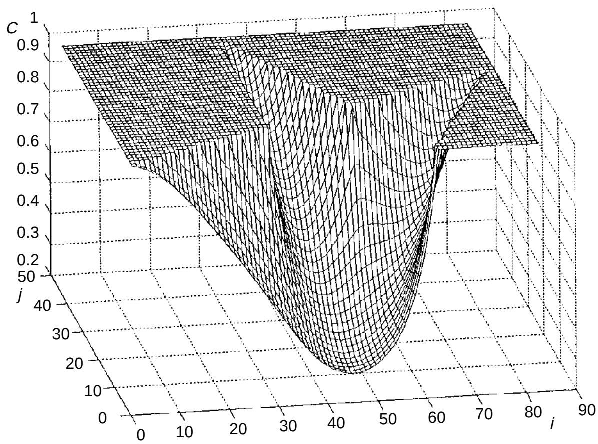

FIG. 7
Axonometric illustration of concentration field in transversal plane of symmetry in starcat extrudate: F = 10; k = 41

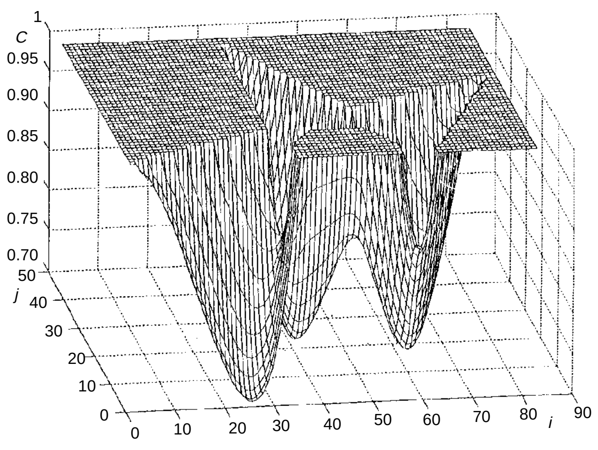

FIG. 8
Axonometric illustration of concentration field in transversal plane of symmetry in starring extrudate: characteristics as in Fig. 7

particles in the shape of stars without hole and with hole is illustrated in Fig. 11. It is apparent from the results that in the region of strong effect of internal diffusion, i.e., for high values of the Thiele modulus, it is advantageous to use just the catalyst with axial hole.

For illustration, in Fig. 12 we compare the result of calculation for two-dimensional cases, i.e., for infinitely long extrudates of different profiles in the shape of circle (cylinder), stars and tetralobe[2]. The characteristic dimension in the definition of Thiele modulus F' was in this case considered as a half of the extrudate diameter. This definition is of practical importance when comparing the activity of the catalyst extrudate occupying the given volume of reactor bed. It is evident that the suitable shaping of extrudates has a favourable influence on the reduction of the effect of internal diffusion on the efficiency of the catalyst which works in the diffusion region, i.e., such a cata-

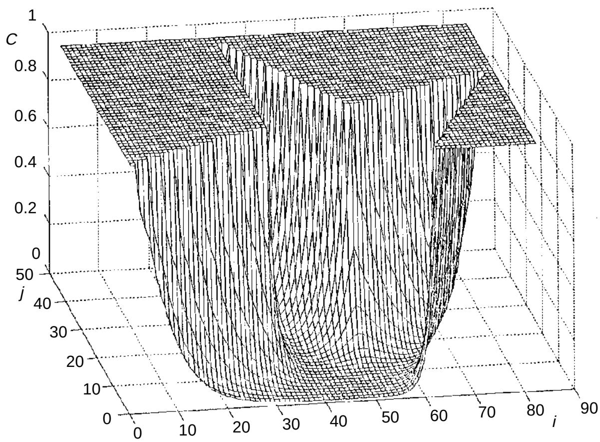

FIG. 9
Axonometric illustration of concentration field in transversal plane of symmetry in starcat extrudate: $F = 50$; $k = 41$

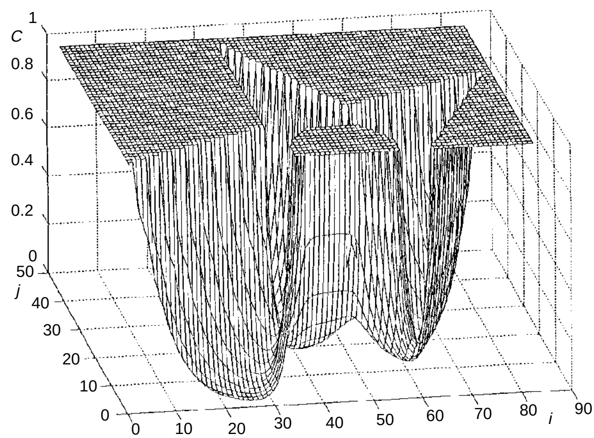

FIG. 10
Axonometric illustration of concentration field in transversal plane of symmetry in starring extrudate: characteristics as in Fig. 9

lyst which is noted for a high activity and/or which is used for the reactions taking place in the liquid phase where the reacting component has a considerably lower diffusion coefficient.

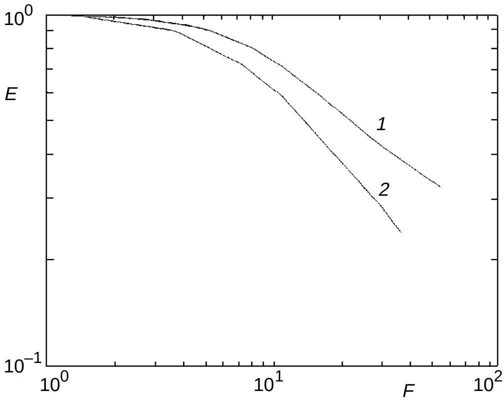

FIG. 11
Effectiveness factor of internal diffusion *E* in dependence on Thiele modulus *F*: *1* starring extrudate, *2* starcat extrudate

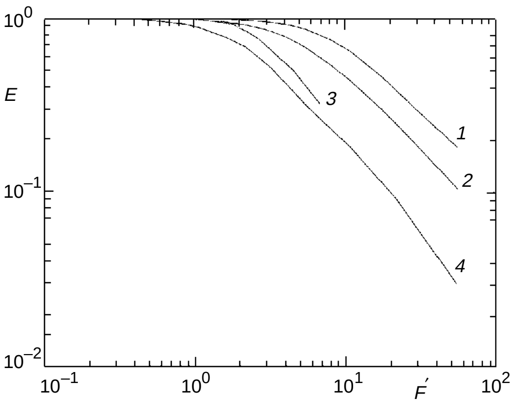

FIG. 12
Effect of shape of cross-sectional profile of infinitely long extrudate on its effectiveness factor *E* for various values of Thiele modulus *F′*: *1* starring extrudate, *2* starcat extrudate, *3* tetralobe[2], *4* circle (infinite cylinder)[1]

SYMBOLS

C	dimensionless concentration related to value on external surface of particle
d	diameter of axial hole in extrudate, m
D_{ef}	effective diffusivity of reacting component, $m^2\ s^{-1}$
e	accuracy of numerical solution
E	effectiveness factor of internal diffusion
F	Thiele modulus, see Eq. (*5*)
F'	Thiele modulus for extrudate of infinite length
h	dimensionless integration step
K	rate constant of first-order reaction, s^{-1}
L	length or thickness of extrudate, m
N	number of iterations
S	external surface of extrudate, m^2

V	volume of extrudate, m^3
X, Y, Z	dimensionless coordinates related to dimension L
Subscripts	
e	external surface of extrudate
i, j, k	counting index in direction X, Y, Z

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