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Mathematical model of chemical reactions in polydisperse porous media

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Abstract

The recursive mathematical model of the porous media is developed, in which the structure of a porous macroparticle is represented as a system of finer porous particles (microparticles), each of which in turn also consists of a next level system of porous microparticles, etc. The porous structure of microparticles of each level is described by a model of chaotically located spheres. This recursive model is used for developing a mathematical model of chemical reaction in the porous media describing speeds of reagent supply to a reactionary surface as a function of internal structure of a particle, diffusion resistance of microparticles of various levels being accounted. Calculations of a high-temperature pyrolysis process of methane in the porous carbonized samples of wood are carried out. Satisfactory agreement with experimental data is received.

Keywords: Polydisperse porous media; Chemical reactions; Mathematical model

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1. Introduction

The real porous medium consists of the particles of various forms and sizes, i.e. it is polydisperse. Owing to chaotic arrangement of pores and particles the structure of the porous media is irregular and stochastic. This circumstance practically excludes the opportunity of local supervision over concrete particles and physical and chemical processes occurring in individual pores. In contrary to homogeneous mixes diffusion transfer of a gas reagent in porous media proceeds by numerous channels and in comparison with free diffusion is less intensive. The rate of reaction in a porous material depends on rates on various sites of a surface, each being characterized by unique availability for diffusion flow. In many numerical models of chemical reactions, diffusion of a gaseous reagent in particle pores is described by some effective diffusion coefficient [1,2]. The account of polydispersiveness of radii distribution of particles forming a skeleton of the porous media, assumes that pores in the particle structure strongly differ by size and diffusion coefficient. Besides, changes of a porous skeleton structure in time due to chemical reactions have the result that a part of pores becomes isolated or, on the contrary, open. Correct description of chemical reaction in the porous media assumes the solving equation for probability density function (PDF) of particles (or pores) distribution by radii, which is a special mathematical and numerical problem.

The aim of the present work is to develop a mathematical model of chemical reactions in porous media with the correct description of a reagent supply speed to a reactionary surface as a function of the particle internal structure.

2. Recursive model of the porous medium

Let us consider a single porous macroparticle with a heterogeneous reaction $A_G = P_S + L_G$, proceeding on it's surfaces (external and internal).

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Nomenclature

A_G	initial gaseous component
C_0	volumetric concentration of a gas component outside a particle
C_i	concentration of a gas component on a surface of a particle of a level *i*
D_i	effective diffusion coefficient for gaseous reagent in pores of a level *i*
F_i	specific surface of a particle related to a volume of a particle of a level $i-1$
i	level
J_i^{D}	diffusion flow through a surface of a level *i*
J_i^{K}	mass flow due to chemical reaction on particle surfaces of a level *i*
k_{D}	coefficient of external mass transfer
L_G	gaseous products of reaction
m_i	porosity of a particle of a level *i*
M_{part}	mass of a macroparticle
M_i^0	skeleton porosity considering level *i*
N	number of the levels
P_S	solid products of reaction
r	radius of a microparticle of a level *i*
R_{p}	radius of a macroparticle
s_i	specific particle surface of a level *i*
V_{p}	volume of a macroparticle

Greek symbols

ρ_C	density of a macroparticle
ρ_0	initial density of a macroparticle
ρ_i	particle density of a level *i*
ρ_C^0	true density of a material
θ_i^0	structural parameter for particle of a level *i*

Subscript

i	level

Let the volume of macroparticle be V_0. We shall allocate elementary volume $V_{N-1} \ll V_0$ which is small enough but anyhow consists of a large number of particles of radius r_N distributed in random manner.

The structure of elementary volume V_{N-1} may be described as a model of monodisperse medium [3]. Let the effective diffusion coefficient of this volume be equal D_{N-1}. Further, we shall allocate volume V_{N-2} ($V_{N-2} \gg V_{N-1}$), consisting of a large number of particles of radius r_{N-1}, located chaotically. The allocated volume is characterized by effective radius r_{N-2} and effective diffusion coefficient D_{N-2}. The structure of volume V_{N-2} also can be described by means of a model of the monodisperse medium. Thus, it is possible to make a chain satisfying conditions $V_0 \gg V_1 \gg \cdots V_{N-1} \gg V_N$. This means that the porous macroparticle can be represented as a system of finer particles (microparticles), each of which in turn will also consist of finer particles, etc. (Fig. 1). Each microparticle of a level i is a macroparticle in relation to a level $i+1$. Each macroparticle of a level i is a microparticle in relation to a level $i-1$.

Each system of microparticles (by the order of smallness) can be formally characterized by a level i, which is defined by the size of the microparticles effective radius $r_i(r_{i+1} \ll r_i \ll r_{i-1})$. The number of levels is limited $(i = 1, \ldots, N)$. In such a system, microparticles on each level (except for level N where porosity is equal to zero) are characterized by the porosity m_i and an internal surface s_i. Physically such approach corresponds to a structure consisting pores of different sizes, characterized by their own effective diffusion coefficients.

Let us consider heterogeneous reaction in pores of a level i microparticle the result of which is a change of particle porosity. The rate of the heterogeneous reaction on surface of a microparticle depends on its temperature and gas reagent concentration on its surface. The supply of reagent to a particle of a level i is proceeded through external diffusion layer outside the particle. As a first approximation, we shall not take into account resistance of reaction products in a layer. A part of reagent reacts on an external surface of a particle, the other diffuses inside. Schematically flow of a reagent are submitted in Fig. 2.

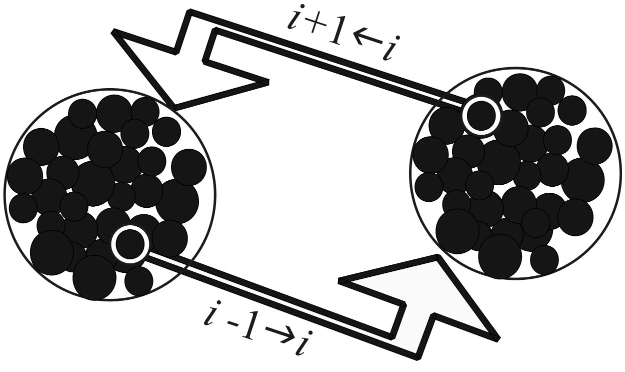

Fig. 1. The structure of a porous medium.

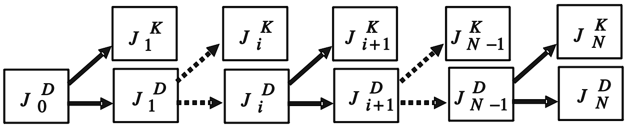

Fig. 2. The scheme of reaction.

Flows can be written down as

$$J_0^{\mathrm{D}} = 4\pi R_{\mathrm{p}}^2 k_{\mathrm{D}}(C_0 - C_1), \tag{1}$$

$$J_i^{\mathrm{D}} = \frac{s_i D_i (C_i - C_{i+1})}{r_i} V_{\mathrm{p}}, \tag{2}$$

$$J_i^{\mathrm{K}} = k_{\mathrm{s}} C_i s_i V_{\mathrm{p}}, \tag{3}$$

$$J_N^{\mathrm{K}} = k_{\mathrm{s}} C_N s_N V_{\mathrm{p}}, \tag{4}$$

$$J_N^{\mathrm{D}} = 0. \tag{5}$$

The scheme of reaction can be submitted by the following system of equations

$$\begin{aligned} &J_0^{\mathrm{D}} = J_1^{\mathrm{D}} + J_1^{\mathrm{K}},\\ &J_i^{\mathrm{D}} = J_{i+1}^{\mathrm{D}} + J_{i+1}^{\mathrm{K}},\\ &J_{N-1}^{\mathrm{D}} = J_N^{\mathrm{K}}. \end{aligned} \tag{6}$$

Or in view of dependences (1)–(5)

$$\begin{aligned} &C_0 \frac{3k_{\mathrm{D}}}{R_{\mathrm{p}}} - C_1\left(\frac{3k_{\mathrm{D}}}{R_{\mathrm{p}}} + \frac{D_1 s_1}{r_1} + k_{\mathrm{S}} s_1\right) + C_2 \frac{D_1 s_1}{r_1} = 0,\\ &C_{i-1}\frac{D_{i-1}s_{i-1}}{r_{i-1}} - C_i\left(\frac{D_{i-1}s_{i-1}}{r_{i-1}} + \frac{D_i s_i}{r_i} + k_{\mathrm{S}} s_i\right) + C_{i+1}\frac{D_i s_i}{r_i} = 0,\\ &C_{N-1}\frac{D_{N-1}s_{N-1}}{r_{N-1}} - C_N\left(\frac{D_{N-1}s_{N-1}}{r_{N-1}} + k_{\mathrm{S}} s_N\right) = 0. \end{aligned} \tag{7}$$

In the system of Eqs. (7) there are N unknown variables C_i ($i = 1, \ldots, N$) and N equations. The matrix of system (7) has a three-diagonal kind and if the factors are known the problem may be solved using the TDMA method.

Let us determine the coefficients of system of equations (7). Let porosity of a particle of a level i be equal m_i. Then according to [3] variation of an internal surface is calculated as

$$F_i = F_i^0 \frac{m_i}{m_i^0}\left(1 - \theta_i^0 \ln\frac{m_i}{m_i^0}\right)^{2/3}. \tag{8}$$

The values m_i^0 are set, proceeding from the chosen model of porous structure.

Relationship between F_i and s_i is expressed as

$$s_i = F_i \prod_{j=1}^{i-1}(1 - m_i). \tag{9}$$

The effective diffusion factor and radius of particle of a level i are defined from equations

$$\begin{aligned} &D_i = D_{i-1} m_i^2,\\ &r_i = r_i^0\left(1 - \theta_i^0 \ln\frac{m_i}{m_i^0}\right)^{1/3}. \end{aligned} \tag{10}$$

Total consumption rate of a gas reagent is

$$q = -k_{\mathrm{S}} \sum_{i=1}^{N} C_i s_i = -\sum_{i=1}^{N} q_i. \tag{11}$$

The change of particle porosity for a level i is

$$\begin{aligned} &m_1 = M_1^0 - \frac{\rho_1}{\rho_{\mathrm{C}}^0},\\ &m_i = M_i^0 - \frac{\rho_i}{\rho_{\mathrm{C}}^0 \prod_{j=1}^{i-1}(1 - m_j^0)},\\ &m_N = M_N^0 - \frac{\rho_N - \rho_0}{\rho_{\mathrm{C}}^0 \prod_{j=1}^{N-1}(1 - m_j^0)}. \end{aligned} \tag{12}$$

For every ρ_i using equations

$$\begin{aligned} &\frac{\mathrm{d}M_{\mathrm{part}}}{\mathrm{d}t} = q,\\ &\rho_{\mathrm{C}} = \sum_{i=1}^{N} \rho_i, \end{aligned} \tag{13}$$

it is possible to receive algebraic system

$$\rho_i(t + \Delta t) = \rho_i(t) + \frac{q_i}{\sum_{i=1}^{N} q_i}(\rho_{\mathrm{C}}(t + \Delta t) - \rho_{\mathrm{C}}(t)). \tag{14}$$

Completing the statement of the problem it is necessary to associate the modeling internal surface with a real internal surface of a macroparticle F_0. For this purpose, it is possible to use the probability density distribution function of an internal surface on the sizes of particles or pores (PDF), considering equation

$$F_0 = \sum_{i=1}^{N} s_i^0(r_i^0). \tag{15}$$

Thus, using Eq. (15) the sequence of modeling radii r_i can be chosen, and, generally, N may be unlimited. Going over to continuous PDF it is possible not to use the condition ($r_{i+1} \ll r_i \ll r_{i-1}$), having replaced it with ($r_i - \mathrm{d}r_i < r_i < r_i + \mathrm{d}r_i$), where $\mathrm{d}r_i$ is a small value.

For the further calculations, it is necessary to associate m_i^0 with initial porosity M_0 of a real particle. It can be made using the following numerical procedure:

1. Let values m_i^0 be set.
2. Calculating values M_i^0 using expressions:

$$\begin{aligned} &M_1^0 = m_1,\\ &M_i^0 = m_i \prod_{j=1}^{i-1}(1 - m_j^0),\ i > 1. \end{aligned} \tag{16}$$

3. Carry out normalizing

$$M_i^0 = \frac{M_i^0}{\sum_{j=1}^{N} M_j^0}. \tag{17}$$

4. Associate with macroparticle porosity M_0

$$M_i^0 = M_i^0 M_0. \tag{18}$$

5. Calculating new values m_i^0

$$\begin{aligned} &m_1^0 = M_1^0,\\ &m_i^0 = \frac{M_i^0}{\prod_{j=1}^{i-1}(1 - m_j^0)},\ i > 1. \end{aligned} \tag{19}$$

3. Mathematical model of methane pyrolysis

The model of the porous medium submitted above was used for modeling high-temperature methane pyrolysis in carbon skeleton made up by particles of carbonized wood.

The mathematical model of methane filtration process through a heated up porous skeleton in a vertical cylindrical reactor is composed of two parts. External part considers the behaviour of particles in an external stream whereas internal part deals with reaction in particle pores.

Following are the main features of an external model.

The heat and mass transfer for the average (over reactor cross-section) parameters, neglecting heat transfer in gas by thermal conductivity, is described with a set of non-stationary one-dimensional differential equations in partial derivatives [4].

The system of the equations is supplemented with a equation of state for a gas mixture, relations for thermophysic properties of gas and the porous skeleton material, so as with boundary and initial conditions.

The basic assumption for model kinetics consists in the idea that decomposition of methane occurs along two channels [5]:

(a) in a gas phase with formation of particles of soot from radicals-nuclei (nC) by the radical-chain mechanism. Overall reaction looks like $CH_4 + nC = (n+1)C + 2H_2$;

(b) on full (external plus internal) surface of particles as a result of active impacts of methane molecules with this surface pyrocarbon being generated. Overall reaction is $CH_4 = C + 2H_2$.

Experimental installation and conditions of experiment are submitted in work [6].

4. Results and discussion

Calculations were carried out using recursive model of the porous medium.

Calculated and experimental [6] dependences for carbon samples density by time of pyrolysis on various distances from reactor input are submitted in Fig. 3. As shown in figure, the best conformity of calculation results with experiment is observed at $N = 10$. For an entrance part of reactor (distance—100 mm from entrance) satisfactory results are received with $N = 8$ because on initial part of reactor external flow is rich with methane and reaction actively goes on large microparticles belonging to levels with small i their pores being filled up. Hence, internal areas with large values of i are not activated (effective diffusion coefficient decreases).

On the contrary, at the top part of reactor the stream of gas is less rich with methane and reaction rates in particle pores at various levels are small and commensurable. At $N = 8$ the contribution of each reaction increases in comparison with $N = 10$ and calculated results for the top part of the reactor turn out to be overestimated. Similarly, the overestimated results turn out at long durations of pyrolysis. At $N = 6$ results have only qualitative character.

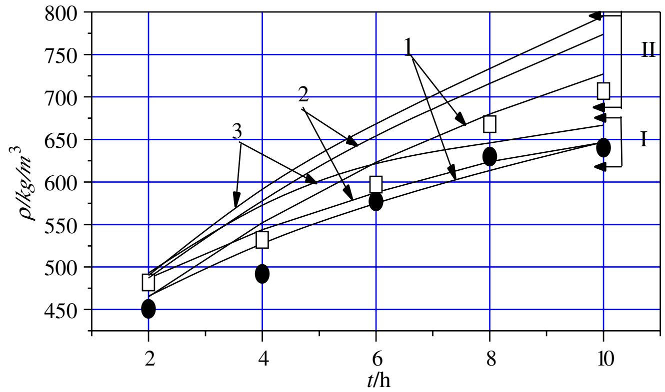

Fig. 3. Calculated and experimental distribution of density of samples depending on time of pyrolysis for various distances from the input of the reactor: I—100 mm, II—175 mm. The curves are calculation results, points are experimental data (1—$N = 10$, 2—$N = 8$ and 3—$N = 6$).

The following figures give representation about process of reaction.

Calculated dynamics of relative internal surface alterations depending on time of pyrolysis for distance 75 mm from the reactor entrance are submitted in Fig. 4. During the initial moment, the main part of the surface is determined by microparticles with radiuses of 10^{-7}–10^{-8} m.

While the time of pyrolysis is increased the maximum of the reaction surface is shifted to microparticles with radiuses $\sim 7 \times 10^{-6}$ m (curve 1). Cross-section of 75 mm corresponds to the beginning of active reactions. Temperature at the cross-section is not so high; therefore, rates of reaction at all levels are comparable. While pyrolysis duration increases the maximum of the reactionary surface is gradually moving towards microparticles with larger radius (the main reaction occurs in pores of particle with small i). This results in isolation of microparticle pores with large i. The curve 6 shows, that at rather long time of pyrolysis real reactionary ability is concentrated on levels with $i = 3$–4 (radius of microparticles 10^{-5} m). The internal surface

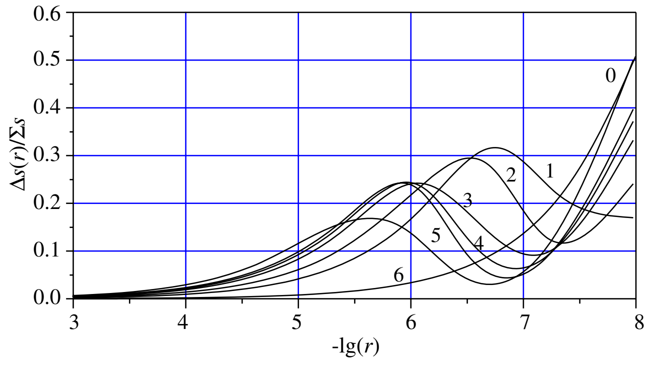

Fig. 4. A relative internal reactionary surface: 0—initial distribution, 1—2 h, 2—4 h, 3—6 h, 4– 8 h, 5—10 h and 6—20 h.

formed by microparticles of higher level, is practically inaccessible. In other cross-sections of the reactor the nature of internal reactionary surface alterations will be slightly different due to conditions in an external flow.

Figs. 5 and 6 demonstrate the nature of reactions in various zones of the reactor. Distributions of density growth of carbon samples at various levels i are submitted in Fig. 5. Basic distinction of the reaction mechanism at the deepest levels is shown in Fig. 5a. At entrance and output parts of a reactor external conditions, first of all temperature and concentration of methane, essentially differ from conditions at the central part of the reactor. Rate of the reaction in particle pores reaches two strongly pronounced maxima at these zones and a minimum at the central part where, due to more intensive reactions, a pore filling in microparticles of low levels exists and pores of microparticles of higher levels are not accessible to gas reagent.

Distributions of density increases for microparticles of low levels are submitted in Fig. 5b. The maximum of density is observed for microparticles, which pores were not filled yet ($i = 1, 2, 3, 4$), for $i = 6, 7$ the density nearly does not change (reaction has practically ended) and an intermediate variant ($i = 5$).

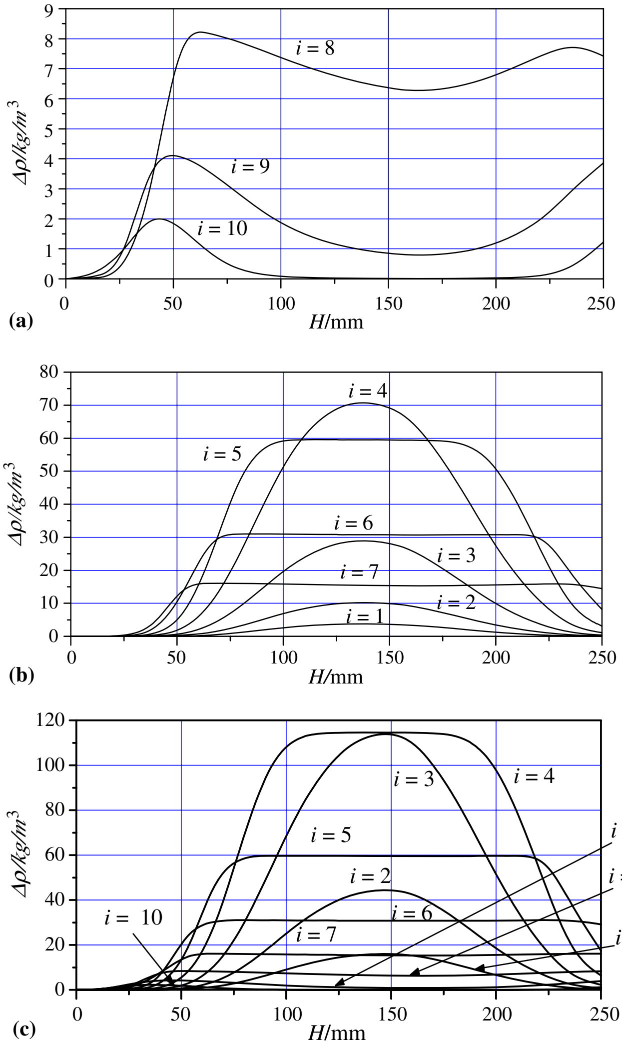

Fig. 5. Calculated distribution of density increase for samples along the reactor. Time of pyrolysis: a—2 h; b—4 h and c—10 h.

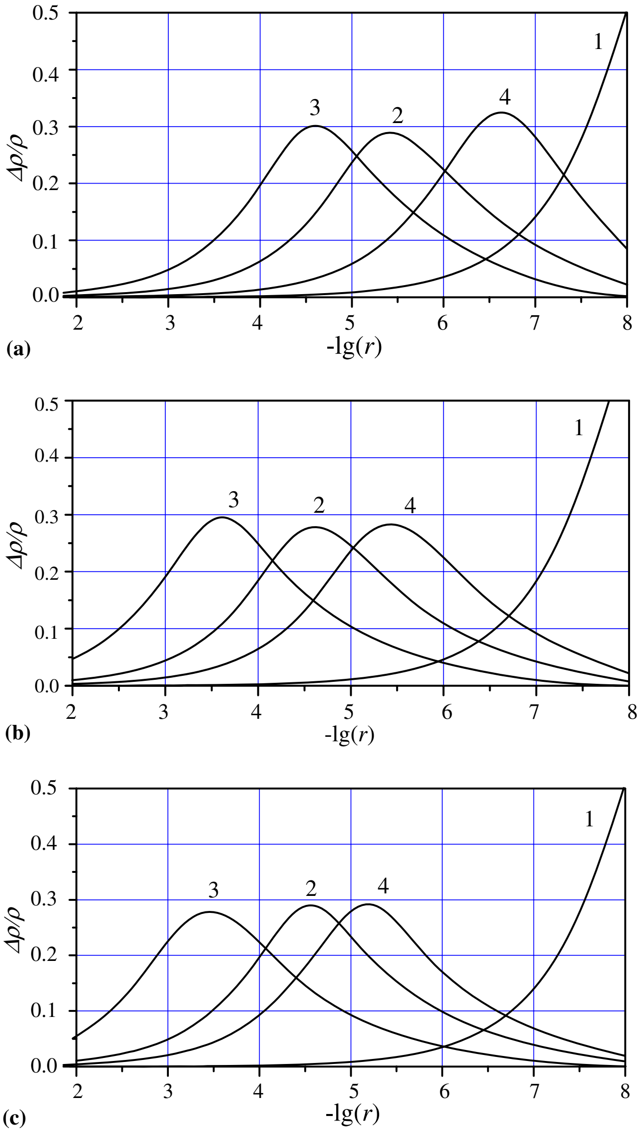

Fig. 6. Distribution of relative density increase of samples for various distances from the entrance of the reactor (1—50 mm, 2—100 mm, 3—150 mm and 4—220 mm). Time of pyrolysis: a—2 h; b—6 h and c—10 h.

Distributions of density increase for microparticles of all levels for 10 h duration of pyrolysis are submitted in Fig. 5c.

Relative distributions of density for carbon samples at various distances from the entrance of the reactor are shown in Fig. 6.

As could be seen from figures active reactions at various parts of the reactor take place in pores of particles of different levels. At the entrance part of the reactor, where the rate of reaction is small because of low temperature, reactions go in microparticle pores of all levels, but more intensive pore filling exists for finer particles belonging to levels with large i (curve 1). Along the altitude of the reactor

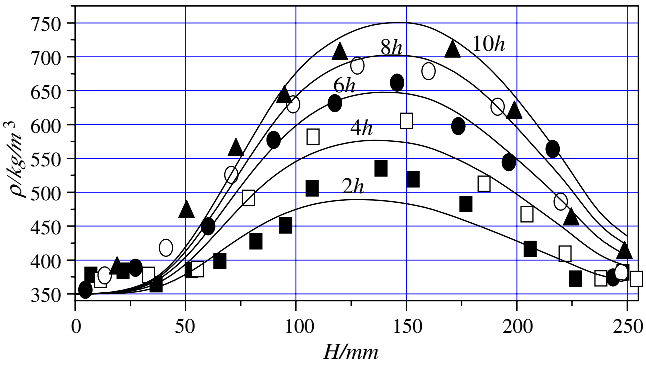

Fig. 7. Calculated and experimental density distribution of samples along the altitude of the reactor by the time of endurance 2, 4, 6, 8, 10 h. Curves—calculated, points—experimental.

reactions take place mainly in pores of microparticles which level i is low (rather large microparticles). The pores of finer microparticles are isolated (curves 2 and 3).

At the top part of the reactor conditions of the reaction are similar to those existing at its entrance part by the reason of that methane concentration and temperature are decreasing. With increase of pyrolysis duration the maximum density increase is shifted towards larger microparticles. Using similar graphs, it is possible to determine the mode of the system at present moment.

Thus, carbon samples can have identical density, but vary by internal structures due to various degrees of microparticles pore filling on different levels.

Calculated and experimental [6] distributions of sample density along the reactor for various times of pyrolysis are submitted in Fig. 7.

The greatest mismatch between calculated and experimental data is observed for short durations of pyrolysis. It could be explained by complex dependence of reactions rate from internal structure of porous particles. As it has been shown above, internal surfaces of microparticles of all levels vary while process goes on and this circumstance in turn determines the process rate.

Understating or overestimating of the real process rate at it's starting can take place if the number of calculated levels N will be reduced. The reason is that the reaction rate will be determined by a large initial internal surface, which is being split by different levels in accordance with the chosen discrete distribution function of pores by radii.

During the process the microparticle pores of high levels become practically isolated and their influence will be insignificant so as an uncertainty of setting the size of an internal surface (as has been shown above, the pores of microparticles of levels $i = 8$–10 become practically inaccessible to reagent after 6 h from the process start).

5. Conclusions

A mathematical model of reaction in the porous medium has been developed using recursive model of the porous medium in which the skeleton of a porous macroparticle is composed of a system of finer porous particles (microparticles), each of which in turn also consists of a system of porous microparticles of the following level (the level of recursion), etc. The porous structure of microparticles of each level is described by a model of randomly located spheres.

Comparison of calculation results and experimental data for a process of high-temperature pyrolysis of methane filtration through the porous media generated by samples of carbonized wood has been made, demonstrating adequacy of the developed model. The model correctly describes as an initial stage of process (fast pore filling), so as the final stage (slow rates of reaction due to increase of diffusion resistance). It is shown, that the best conformity of calculation results with experiment is observed at number of recursion levels $N = 10$. Reduction of their number leads to non-correct description of real process rate associated with more accessible internal surface. On the other hand, though the increase in number of levels also raises accuracy of results, the demand for computing resources is larger. In practical calculations recursion levels higher than 10 actually do not influence on final results and are not used.

The developed model can be used to solve similar problems, especially, for polydisperse structures with large dispersion.

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