Theoretical and Experimental Investigations of Substantiating Technologies for Carbon Materials Production from Natural Gas

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Abstract

The results of theoretical and experimental investigations on methane pyrolysis with infiltration through a heated porous matrix generated from various carbon materials are presented. The features of mathematical models, kinetic relationships of process are discussed. The mathematical model of process shares on external problem (a flow of particles in an external stream) and internal problem (reaction in particle porous). The heat and mass transfer for the average (over the reactor cross section) parameters, ignoring the heat transfer in gas by thermal conductivity, is described by unsteady-state one-dimensional differential equations in partial derivatives. For the mathematical description of process kinetics of methane decomposition the approach is used by which the soot formation is treated as a chain radical process. The porous media is represented by a system of large enough particles. In its turn, every macroparticle consists of finer particles, which are also composed of microparticles, etc. Calculating programs were used for modeling and efficiency analysis of technological installations for technical carbon production in a regenerative heater, filled by a ceramic nozzle and for similar purposes concerning carbon (oven soot) in autothermal torch process of partial gas oxidation by air at a surplus factor of oxidizer in relation to stoichiometry 0.4-0.5 at pressure close to atmospheric on Sosnogorsk Gas-Processing Plant. Experiment descriptions and techniques for experimental realization are given. These results are used as fundamentals for new technologies considering pyrocarbon materials production in the continuous operation reactor.

Introduction

The reaction of thermal destruction of methane into carbon and hydrogen is the basis of physico-chemical processes of carbon production from natural gas. Two modifications of carbon are produced in the reaction of methane pyrolysis: dispersible carbon (black carbon) – in volume reactions, and pyrocarbon - deposition of solid carbon – in surface reactions. The quantitative ratio between modifications of carbon formed depends on process temperature, ratio of surface and volume in reaction space and properties of material on which surface pyrocarbon is deposited.

It is possible to distinguish two classes of industrial carbon production: technologies of black carbon production and technologies of pyrocarbon deposition.

In spite of the fact that the need for pure carbon materials is significant, the applications of dispersible carbon prepared by thermal destruction of natural gas are limited. It is used mainly in production of rubber, graphite materials (contacts of electrical machines, galvanic batteries, etc), and dyestuff. The iron and steel industry could become one of the large volume consumers of black carbon, however the usage is limited because of unsatisfactory mechanical properties required for that application (dispersibility, density, strength).

The technologies of pyrocarbon production as a high-temperature covering of surfaces as well as some special technologies for production of complicated configuration pyrocarbon parts are well known.

The new technologies of pure carbon materials production are being attractive by the reason, that natural gas is used not as a raw material, but as a final product. Another reason is the salvaging of organic waste (in particular, the waste of wood-processing industry). These materials can be produced by thermal pyrolysis of natural gas in porous structures, formed by various carbon materials, such as

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granulated black carbon, charcoal, etc.

The technologies for granulated pyrocarbon production in a flowing type reactor [1,2] and carbon materials production by simultaneous thermal processing of natural gas and wood waste are experimentally and theoretically [3] substantiated in a series of joint works proceeded at the Institute for High Temperatures RAS with Sosnogorsk Gas-Processing Plant of "SEVERGAZPROM".

The results of theoretical and experimental investigations of methane pyrolysis with infiltration through the porous carbon matrix generated from various carbon materials are discussed in this paper. The features of mathematical models, kinetic relationships of process are discussed. Experiment descriptions and techniques for experimental realization are given. Some examples of obtained theoretical and experimental results used for optimization of black carbon production technologies at the Sosnogorsk Gas-Processing Plant are shown.

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Mathematical model

The mathematical model of process of methane filtration through the heated up porous skeleton in a vertical cylindrical reactor shares on external problem (a flow of gas around particles) and internal problem (reaction in particle porous).

External problem

The heat and mass transfer for the average (over the reactor cross section) parameters, ignoring the heat transfer in gas by thermal conductivity, is described by unsteady-state one-dimensional differential equations in partial derivatives [1]:
the equation of continuity for i-th component of gas

$$f \frac{\partial \rho_g m_i}{\partial t} = -\frac{1}{F} \frac{\partial G_g m_i}{\partial x} + q_i \qquad (1)$$

the equation of motion for the gas phase

$$-\frac{\partial P}{\partial x} + \frac{v_g G_g}{kF} = 0 \qquad (2)$$

the energy equation for the gas phase

$$f \frac{\partial \rho_g c_p T_g}{\partial t} = -\frac{1}{F} \frac{\partial G_g c_p T_g}{\partial x} + \frac{\alpha l_{eff}}{S}(T_C - T_g) \quad (3)$$

the equation of continuity for the solid phase

$$(1-f)\frac{\partial \rho_c}{\partial t} = q_T \qquad (4)$$

the energy equation for the solid phase

$$(1-f)\frac{\partial \rho_c c_c T_c}{\partial t} = \frac{\partial}{\partial x}\left(\lambda_e \frac{\partial T_c}{\partial x}\right) -$$
$$- \frac{\alpha l_{eff}}{S}(T_C - T_g) + Q_T \qquad (5)$$

In Eqs. (1)-(5), ρ_g, c_p, P and T_g denote the density, heat capacity, pressure, and temperature of the gas mixture, respectively; G_g is the mass flow rate of gas; F is the effective cross-sectional area of the reactor; S is the area of the surface of heat transfer between gas and porous medium; α is the coefficient of heat transfer from porous medium to gas; λ_{eff} is the effective length; f is the porosity; m_i denotes the mass fractions of the i-th components of the gas mixture; ρ_g, c_c, T_c and λ_{eff} denote the density, heat capacity, temperature, and effective thermal conductivity of the material of the porous structure, respectively; q_i denotes the source terms in the continuity equations for i-components of the gas mixture; and Q_T is the source term in the energy equation.

The set of equations is supplemented with the equation of state for the gas mixture, relations for the thermophysical properties of gas and skeleton material, and the boundary and initial conditions.

Process kinetics

For the mathematical description of process kinetics of methane decomposition the approach is used by which the soot formation is treated as a chain radical process. The chain process of soot formation involves the formation of carbon radical nuclei (nC). The equation for the rate of formation of radical nuclei W_n may be written by modifying Semenov's equation for a branched chain process with quadratic terminations.

The basic assumptions of kinetic model [4]:
1. The porous medium is formed by chaotically located spherical particles of the same radius.
2. Each particle has internal porosity.
3. The decomposition of methane proceeds along two channels, namely,
    1) in the gas phase, with the formation of soot particles from radical nuclei (nC) by the chain radical mechanism. The overall reaction has the

form $CH_4 + nC = (n + 1)C + 2H_2$.

2) on the overall (external plus internal) surface of particles which form a layer of carbon material, as a result of active collisions between methane molecules and this surface to produce pyrocarbon. The overall reaction is $CH_4 = C + 2H_2$.

4. The source term in Eq. (1) for $i = CH_4$ is the sum of the amount of methane decomposed via two channels: $q_{CH_4} = W_V + W_S$, where W_V is the rate of methane consumption via the first channel, and W_S is the rate of methane consumption via the second channel.

Internal problem

The porous media is represented by a system of large enough particles in radius r_0 (macroparticles). In its turn, every macroparticle consists of finer particles, which are also composed of microparticles, etc. (Fig. 1).
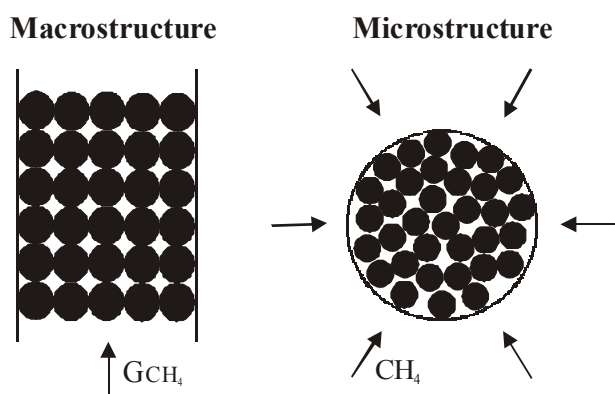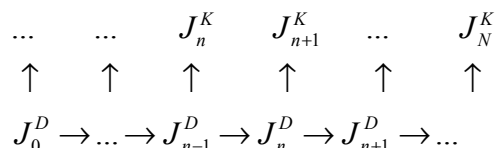
Macrostructure   **Microstructure**

Fig. 1. Structure of the porous media.

Let the number of recursions is N, then each particle will be characterized by radius r_n. We shall consider heterogeneous reaction in porous of n-th particle resulting in porosity of a particle being changed. The speed of heterogeneous reaction on a reactionary surface of porous n-th particle depends on its temperature and concentration of a gas reagent on a surface. These parameters are defined from the solving of an outer problem. The supply of a reagent to porous n-th particle is carried out through external diffusive layer outside of the particle. The part of the reagent enters the reaction on an external surface of particles; the other part diffuses inside the particle. Streams of a reagent through system of the enclosed particles can be presented as a chart:

$$\begin{array}{cccccc} ... & ... & J_n^K & J_{n+1}^K & ... & J_N^K \\ \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \end{array}$$
$$J_0^D \rightarrow ... \rightarrow J_{n-1}^D \rightarrow J_n^D \rightarrow J_{n+1}^D \rightarrow ...$$

Streams of reagents can be written as

$$J_n^D = \frac{s_n D_n (C_n - C_{n+1})}{r_n} \tag{6}$$

$$J_n^K = k_s C_n s_n \tag{7}$$

$$J_{n-1}^D = \frac{s_{n-1} D_{n-1} (C_{n-1} - C_n)}{r_{n-1}} \tag{8}$$

$$J_N^K = k_s C_N V s_N \tag{9}$$

$$J_N^D = 0 \tag{10}$$

In Eqs. (6)-(10) C_0 – volumetric concentration of a gas component outside of a particle; C_n – concentration of a gas component on a surface of n-th particles; r_n – radius of macropartical; k_D – coefficient of external masstransfer; s_n – a specific surface of particles with radius r_n; J_n^K – kinetic stream (chemical reaction) on a surface of n-th particles; D_n – coefficient of diffusion of a gaseous reagent in n-th particle pores.

The circuit of reaction may be submitted by the following system of the equations

$$\begin{aligned} J_0^D &= J_1^D + J_1^K \\ J_n^D &= J_{n+1}^D + J_{n+1}^K \\ J_{N-1}^D &= J_N^K \end{aligned} \tag{11}$$

After appropriate substitutions we receive

$$C_2 = C_1 \left(1 + \frac{k_s s_0 r_1}{s_1 D_1} + \frac{k_D s_0 r_1}{s_1 D_1} \right) - C_0 \frac{k_D s_0 r_1}{s_1 D_1}$$

$$C_{n+1} = C_n \left(1 + \frac{k_s r_n}{D_n} + \frac{s_{n-1} D_{n-1} r_n}{s_n D_n r_{n-1}} \right) -$$

$$- C_{n-1} \frac{s_{n-1} D_{n-1} r_n}{s_n D_n r_{n-1}}$$

$$0 = C_N \left(1 + \frac{k_s r_{N-1}}{D_{N-1}} \right) - C_{N-1} \tag{12}$$

The system of equations (12) may be solved by a TDMA method.

For definition of the coefficients describing porous structure of a separate particle, we shall take

advantage of model of chaotically located spheres with identical diameter [5]. Let the porosity of n-th particles is equal m_n. Then the change of an internal surface is calculated according to [4]

$$S_n = S_n^0 \frac{m_n}{m_n^0}(1 - \theta_n^0 \ln \frac{m_n}{m_n^0})^{2/3} \qquad (13)$$

where S_n – the specific surface of a particle referred to volume of n-th particle, θ_n^0 – structural parameter for n-th particles. The values m_n^0 are set proceeding from the chosen model of porous structure. The association of m_n^0 with initial porosity of real particle M_0 is determined by iterative process:

$$m_n^0 = \frac{M_n^0}{\prod\limits_{j=2}^{n-1}(1-m_j^0)}; \quad m_1^0 = M_1^0;$$

$$M_n^0 = \frac{\prod\limits_{j=1}^{n-1}(1-m_j^0)}{\sum\limits_{i=2}^{N}\left[\prod\limits_{j=1}^{n-1}(1-m_j^0)\right]} \qquad (14)$$

The coefficient of diffusion and radius of a particle are defined from ratio [2]

$$D_n = D_{n-1}m_n^2$$

$$r_n = r_n^0(1 - \theta_n^0 \ln \frac{m_n}{m_n^0})^{1/3} \qquad (15)$$

Total speed of an expenditure of a gas reagent (methane) will be written as

$$q_{CH_4} = -k_S \sum_{n=1}^{N} C_n s_n = -\sum_{n=1}^{N} q_n \qquad (16)$$

The change of porosity of n-th particles equalls

$$m_1 = M_1^0 - \frac{\rho_1}{\rho_c^0}$$

$$m_n = M_n^0 - \frac{\rho_n}{\rho_c^0 \prod\limits_{i=1}^{n-1}(1-m_i^0)}$$

$$m_N = M_N^0 - \frac{\rho_N - \rho_0}{\rho_c^0 \prod\limits_{i=1}^{N-1}(1-m_i^0)} \qquad (17)$$

where ρ_0 – initial density of a particle; ρ_c^0 – density

of carbon; ρ_n results from solution of the differential equations of type (4).

Values r_n^0 are associated with the size of internal surface S_0 by ratio

$$S_0 = \sum_{n=1}^{N} S_n^0 M_n^0 = \sum_{n=1}^{N} \frac{3(1-m_n^0)}{r_n^0 \theta_n^0} M_n^0 \qquad (18)$$

The initial data for an internal problem are: porosity M_0, internal surface S_0, initial density ρ_0, quantity of recursions N, modeling porosity m_n^0 for $n = 1...N$

The differential equations in partial derivatives were transformed to a system of the ordinary differential equations on time by the method of control volume. The derived set of ordinary differential equations was solved by the linear multistep method with automatic step selection realized in the DIFSUB algorithm [6].

Dimensionless criteria

The obtained results may be described within a unified approach, while treating heterogeneous reactions of different types such as addition (for example, the above-described process of methane pyrolysis) and decomposition (gasification) [7].

We will use the methods of the similarity theory and introduce the dimensionless variables $F = s/s_0$ (relative internal surface), $X = 1 - \dfrac{f}{f_0}$ (degree of filling of the pores) for addition reactions or $X = 1 - \dfrac{1-f}{1-f_0}$ (degree of destruction of solid skeleton) for decomposition reactions (in what follows, we will refer to the parameter X as the degree of metamorphism of porous skeleton); $\theta_0 = \dfrac{3f_0}{r_0 s_0}$ (dimensionless structure parameter), $\theta = \dfrac{3f}{rs}$ (current structure parameter); and r_0 and r (the initial and current radius of a microparticle, respectively).

After introducing the dimensionless time $\tau = t/Q$ where $Q = \dfrac{f_0 \rho_c}{C_0^n k s_0}$ is the characteristic time of metamorphism of a macroparticle (the ratio of the mass of

macroparticle pores, if they were filled, to the rate of metamorphism of the particle), the equation of chemical kinetics will be written as

$$\frac{dX}{d\tau} = \frac{F}{\left(1 + \dfrac{kC_S^{n-1}R_p Fs_0}{3k_D} + \dfrac{kC_S^{n-1}\delta}{D_{in}}\right)^n} \quad (18)$$

where C_0 is the volume concentration of the gas component of the reaction outside of the macroparticle; C_S is the mass concentration of reagent on the surface; k_D is the coefficient of external mass transfer; δ is the thickness of the layer of gaseous reaction products; R_p is the macroparticle radius; k is the reaction rate constant, and n is the reaction order. Solutions of Eq. (18) in the coordinates of dimensionless time–degree of metamorphism of porous particle for the order of reaction $n = 1$ are given in Fig. 2.

One can use these nomograms, given the value of the initial dimensionless structure parameter (all of the quantities entering the dimensionless complex may be determined experimentally, or they are calculated by the selected model of porous medium), to determine the dimensionless time during which the porous skeleton reaches the preassigned degree of metamorphism (in the case of methane pyrolysis, the degree of filling of the pores). The chemical reaction kinetics is proper defined by the quantity Q.

Experimental

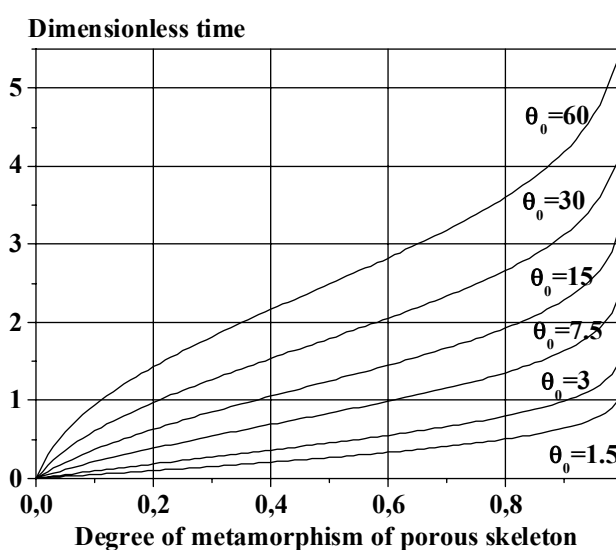In order to study methane pyrolysis process dur-

Dimensionless time

Fig. 2. Solutions of Eq. (9) in the coordinates of dimensionless time–degree of metamorphism of porous particle for reaction order $n = 1$.

ing it's filtering through a porous medium generated from granules of commercial-grade carbon and carbonized wood, two series of experiments on laboratory installation were carried out.

Figure 3 gives a schematic view of the experimental facility. The experimental section was represented by a quartz tube with an inside diameter of 43 mm and length of 500 mm. A section of the tube 400 mm long was heated by a heater made of Nichrome. The quartz tube was insulated with chamotte brick. A lock formed by two ball cocks was provided for charging commercial-grade carbon and for sealing the working volume of the experimental section. The receiving hopper was made as a cylinder 80 mm in diameter with a moving piston which enables one to shift the charge column to a preassigned distance for monitoring the mobility of the carbon layer and taking samples for weighing, those samples corresponding to the preassigned cross sections of the reactor. The gas was delivered from underneath the layer of testing material, and the gaseous reaction products were removed from the upper chamber and burnt in the flame. It was at this point that a gas sample was taken to analyze the composition of the gaseous products of pyrolysis. The temperature of the heater surface was monitored by two Chromel-Alumel thermocouples, and a thermocouple probe moving along the tube axis measured the temperature of carbon in the experimental section.

In first experimental series grade T-900 granular carbon sieved on sieves with meshes of 1 and 1.25 mm was used. Process was carried out cyclically. Portions of a carbon material, past all cycle, were weighed on analytical weights for definition of change of density for one cycle. After that the material was loaded into a reactor again another cycle being repeated.

In the second series of experiments the crushed dried up wood was used as a carbon skeleton. Due to high temperature of gaseous products of reaction of thermal decomposition of methane in the top part of a reactor occurred carbonization of wood and in a high-temperature zone of a reactor samples acted as charcoal.

The porous medium was formed, at the first, of the samples cut from beechen wood in a kind of spheres with diameter about 7 mm. The zone of maximal temperature of a wall of a skilled site was about 120 mm. The samples were heated preliminary up to temperature 400°C with simultaneous argon pumping through the reactor for 1 h. Thus there was a dry-
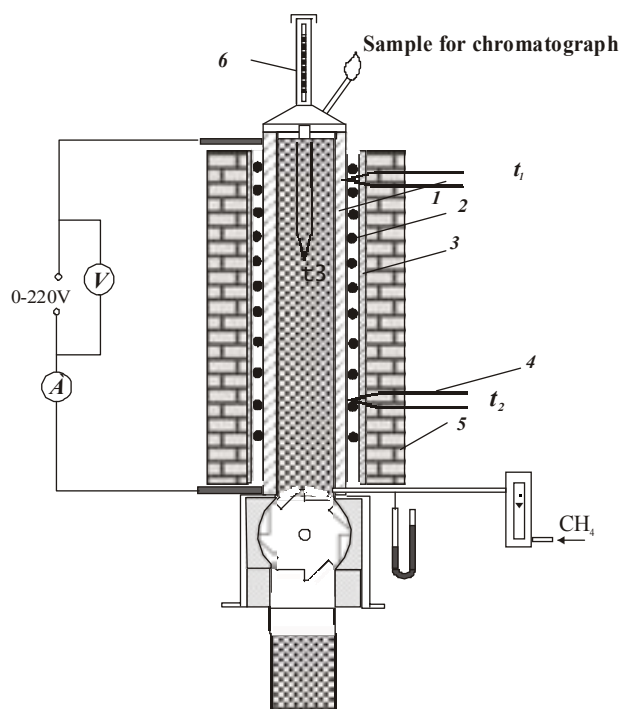
Fig. 3. Experimental section: (1) quartz tube, (2) Nichrome heater, (3) quartz cloth, (4) thermocouples, (5) refractory brick, (6) current.

ing of wood, decontamination and removal flying and pitches. The average density of the samples obtained was 0.38 g/cm³. Then the samples were maintained at temperature 1000°C for 1-2 h with pumping of natural gas through the reactor. Then the plant was cooled, the samples were unloaded from a zone of the maximal temperature and weighed for definition of density change for the period of exposure. After measuring a cycle of heating was repeated. In total six cycles were performed with a total time of heating 8.25 h. The cubic samples with the party of 4 mm were located in working volume of the reactor later on. The distribution of density of samples on height of the channel was defined at various time of exposure at temperature 900°C.

Results and Discussion

Granulated pyrocarbon

The experimental results and prediction curves for three modes with different durations of pyrolysis process are shown in Fig. 4. The maximal density of pyrocarbon granules is ranged from 1.812 to 2.0 g/cm³. In case of regular packing of spheres with the coordination number six, at which the prediction results describe adequately the experimental data, the

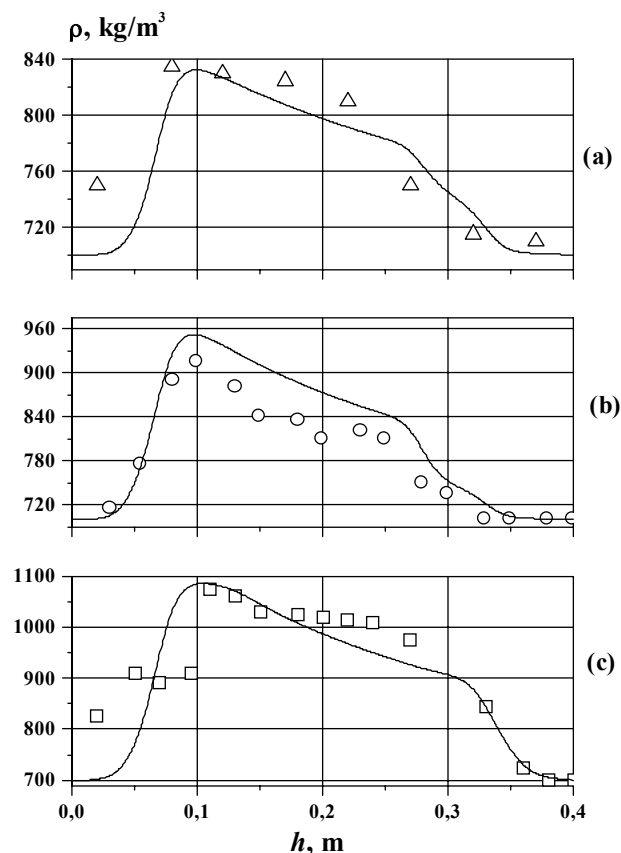maximal value of bulk density was 1.1 g/cm³.

Fig. 4. Comparison of the experimentally obtained (points) and predicted (curves) distributions of the bulk density of granular pyrocarbon over the reactor height: (a) methane flow rate, 0.056 nm³/h; temperature in the central zone of the reactor, 950°C; duration of the process of pyrolysis, 4 h; (b) methane flow rate, 0.06 nm³/h; temperature in the central zone of the reactor, 1050°C; duration of the process of pyrolysis, 6 h; (c) methane flow rate, 0.08 nm³/h; temperature in the central zone of the reactor, 1070°C; duration of the process of pyrolysis, 8 h.

The density of pyrocarbon granules is defined by the reaction rate of methane, which depends on the coefficient of reaction gas exchange. Coefficient of reaction gas exchange is a composite function of both the chemical reaction rate and the internal structure and particle size of the porous medium. Numerical estimates give the value of the penetration depth of the reaction 0.01 m at the beginning of the process. With a fairly large internal surface, the mode of bulk reaction predominates, when the rate of variation of particle mass is proportional to the volume rather than to the external surface of a particle.

The results of analysis of the correlations obtained demonstrate that two modes are possible at the ini-

tial stage of the process, namely, the bulk mode and the kinetic mode with reaction on the external and internal surfaces of the granule. As the process develops, the internal surface decreases and the process changes to a purely kinetic mode.

The suggested model of chaotically arranged spheres ignores the fact that a part of the pores may become isolated as a result of pyrocarbon formation, *i.e.*, the volume of a granule becomes unequally accessible to the gas reagent, *i.e.*, methane. In this case, one should actually observe a sharper variation of the reaction surface. In mode (c) (see Fig. 4c), the reaction in the lower part of the experimental section proceeds in a purely kinetic mode, because, during the time of the process (8 h), the granules pores are almost filled with pyrocarbon, and the reaction proceeds only on the external surface of granules. When all pores are filled, the granule radius starts increasing, and this, in turn, brings about a decrease in the macropore size and in the porosity factor. As the reaction rate in the lower part of the experimental section decreases, the rate in the upper part increases because of increase in concentration of methane. The marked kink of the curves in the coordinate region corresponding to the upper part of the reactor is attributed to the experimental temperature profile and strong temperature dependence of the rate of pyrocarbon formation, which were used for calculation.

It is obvious that the process of pyrolysis is unsteady and its efficiency varies at different stages of pyrolysis. The predicted dynamics of variation of pyrocarbon density in the most effective reactor zone ($x = 0.1$ m) and of the degree of methane at the outlet from the facility are shown in Fig. 5. The predicted composition of the gaseous reaction products differs from that measured with the help of a chromatograph (mass fraction of methane is about 70%) by no more than 5%.

Methane pyrolysis in carbonized wood porouses

Calculations were carried out for maximal number of recursions N=10. Finer splitting is not meaningful because of rather small time of pyrolysis (up to 10 h), since the filling of micropores will not be practically observed.

The best concurrence of calculation to experiment is observed at N=10 (Fig.6). In an initial part of a reactor the satisfactory results are given with model with number of recursions N=8 as the external stream
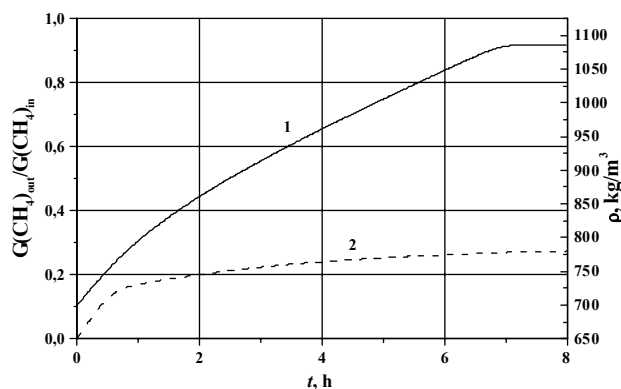

Fig. 5. The dynamics of variation of the density of pyrocarbon and efficiency of methane decomposition: (1) variation of density in the cross section of maximum efficiency (x = 0.1 m) (right-hand ordinate), (2) the ratio between the flow rate of methane at the outlet to that at the inlet (left-hand ordinate).

in this zone is enriched by methane and reaction actively goes in larger particles pores which are filled and do not give to become more active to internal areas due to reduction of coefficient of diffusion. In second half of reactor the stream of gas is less enriched by methane and speeds of reaction at various levels of recursions are small and commensurable. Accordingly at N=8 the share of speed of each reaction is more, than at N=10, therefore the results at N=8 turn out overestimated. At big times of endurance the results have only qualitative character.

Numerical calculations have shown, that during pyrolysis the samples with a various degree of porous pofilling turn out: with filling microporous (a deep level), and also with isolation microporous. Samples with identical density may have various internal structure on an arrangement in a reactor.
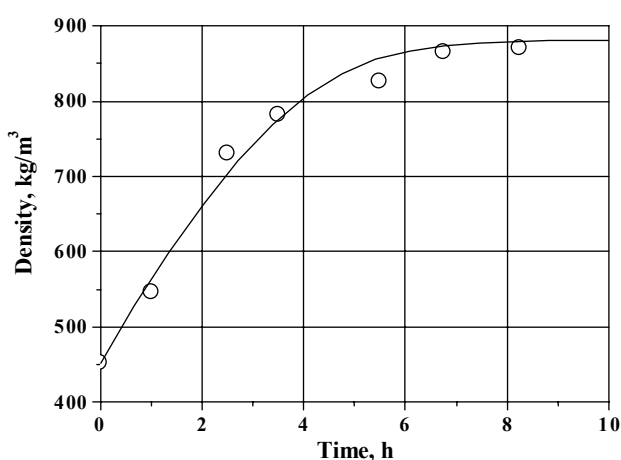

Fig. 6. The experimentally obtained (points) and predicted (curves) distributions of density of samples on height of a reactor at time of endurance.

Chemical reaction depends on an internal surface of particles, and also from conditions in an external stream. Reaction in deep layers has two strongly pronounced maxima and a minimum in the central part that is connected to active reaction in areas where a level of an recursion is less than 8. The change in relative internal surface on time of endurance has in the beginning a maximum in the field of microparticles, which then is shifted in area of macroporous particles, and there is the inaccessible internal surface formed by microparticles, and its share in due course is increased.

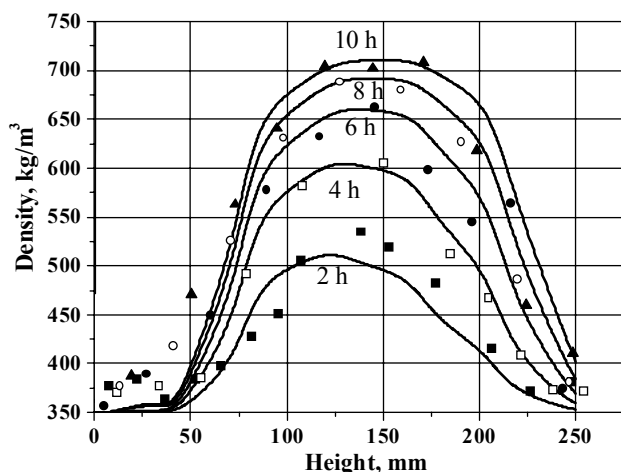Change of density of a material of samples in time is shown on Fig. 7.

Fig. 7. Change in density of samples material in time: curves - calculations, points - experiment.

Conclusion

The investigations are allowed construction of an universal enough mathematical model for methane pyrolysis and simulation for mechanism of porosity evolution in the porous skeleton, taking into account the basic physical and chemical features of the process.

Numerical models are simply adapted for calculation of wide range of similar processes and technologies. The created laboratory installation allows carrying out improvement of technologies of for preparation of carbon materials by pyrolysis of methane in various porous environments.

The studies form a basis for development of a "know-how" – granulated pyrocarbon, the material having prospect of wide industrial applications, including industrial technology for pyrocarbon material production from wood waste products.

Calculating programs were used for modeling and efficiency analysis of technological installations for technical carbon of grade T-900 production in a regenerative heater, filled by a ceramic nozzle [8]. These programs were also used for similar purposes concerning carbon of grade P-701 (oven soot) in autothermal torch process of partial gas oxidation by air at a surplus factor of oxidizer in relation to stoichiometry 0.4-0.5 at pressure close to atmospheric [4] on Sosnogorsk Gas-Processing Plant.

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