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MATHEMATICAL MODELING OF THERMAL PROCESSING OF INDIVIDUAL SOLID-FUEL PARTICLES

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A mathematical model, an algorithm, and a program for calculating the thermal processing of individual solid-fuel particles are developed with account for moisture evaporation, escape of volatiles, and burn-out of the carbon residue. Numerical calculations of the influence of regime conditions on the gasification-combustion of individual particles of Chelyabinsk brown coal are performed. A comparison with experiment is made.

Introduction. Combustion and gasification in a low-temperature fluidized bed is one of the progressive means for thermal processing of low-grade power-generating fuels, including high-ash ones [1, 2]. To develop reliable and correct calculation and design methods for furnaces and apparatuses with a fluidized bed, mathematical models and calculation procedures for analyzing the behavior of fuel particles are needed that permit estimation, to an accuracy acceptable for engineering practice, of effective burn-out times of the fuel in the bed, regions of heterogeneous reactions of the fuel with gases, characteristic times of different stages of the process of thermochemical conversion of the fuel, different macrokinetic characteristics of it, the conditions for particle ignition, and the number and character of nonstationary and stationary regimes occurring in conversion of the fuel and permit the study of such collective effects as collisions, agglomeration, crushing, wearability, thermal disintegration, and removal of the fuel [3–8].

The current mathematical models and calculation procedures for the processes in thermal processing of individual solid-fuel particles, which are devoted predominantly to analyzing the stage of carbon residue burn-out, take practically no account of the influence of the stages of moisture evaporation and escape of volatiles and phenomena of intrapore reaction [1, 2, 5, 9, 10]. In this case either some effective depth of penetration of the oxidant into the porous structure that takes no account of its characteristics is introduced [5, 11] or the macrokinetics of decidedly surface reactions of the fuel with gases is analyzed. However, as recent theoretical [2, 12, 13] and experimental investigations [14, 15] have shown, due to a significant content of moisture and volatiles in a number of highly reactive power-generating fuels (near-Moscow and Irsha-Borodinsk brown coals, the commercial product gas-flame seed culm (GSC), etc.) and their complex and branched porous structure the influence of the stages of drying and pyrolysis of the fuel and intrapore reaction phenomena on thermochemical conversions of fuel particles can be very substantial in a fluidized bed. Ignoring the influence of these stages can lead to significant errors in estimating the effective characteristics of fuel burn-out, macrokinetic parameters, and coefficients of heat transfer of the fuel particles with a gas flow. Therefore to solve practical engineering problems, it is essential and expedient to develop mathematical models and procedures in calculating the processes of thermochemical processing (pyrolysis, combustion, and gasification) of individual coal particles that enable us to take into account the influence of physical stages (transfer, filtration, and phase transitions) and intrapore reaction on their course.

Applying the well-known "contractile nucleus" model [1, 2, 9, 10] for the above purposes appears problematic to us. In view of the absence to date of substantiated physicochemical models of the porous structure of real power-generating fuels a quasihomogeneous model of a pore space, or a "progressive conversion" model [2,

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8], is more acceptable for the solution of problems of accounting for the influence of physical stages and intrapore reaction on transformations of solid particles in a fluidized bed. This model interprets the porous structure of solids as a unified continuous medium that is characterized by some effective transfer (diffusion, thermal conductivity, filtration) coefficients that depend on both the physicochemical properties of the gases in the pores and a number of empirical parameters that characterize the structure of the solid: porosity, specific surface, roughness, sinuosity, etc. In particular, the authors of [13, 15] constructed a mathematical model using this model and developed an algorithm for calculating the process of drying and pyrolysis of an individual brown coal particle in a disperse flow and obtained certain numerical results that reflect the behavior of the particle in the above stages. In particular, they showed that it is in moisture evaporation and escape of volatiles from a fuel that substantial pressure gradients develop inside the porous structure of the fuel particles, which can be a possible reason for their thermal disintegration in gasification of coal dust in a flow. However, the authors of [13, 15] did not deal with the stage of burn-out of carbon-ash residue of the fuel or the influence of chemical reactions inside the porous structure of the particles on their thermal conversions. Meanwhile in the combustion of highly reactive coals in a fluidized bed when the temperature is about 785–950°C in the apparatus [16], in the particle pores along with the escape of moisture and volatiles there can be heterogeneous reactions of oxygen, water vapor released in moisture evaporation, and volatiles with the ash residue of the fuel. Therefore in studying models of thermal processing of fuel particles in a fluidized bed the model of [13, 15] naturally requires modification and development.

Physical Statement of the Problem. We deal with an individual porous particle of a coal fuel in a high-temperature gaseous medium. We assume that inside the pore space of the particle two mutually penetrating continua are concentrated proportionally to the volume fractions of the phases α_i: a gas and a solid; the solid phase consists of coke, moisture, volatiles, and ash; the stages in which the moisture and volatiles reach the gaseous phase inside the pores are rapid [13, 15, 17]; material and energy transfer inside the pores is by effective diffusion and heat condition and by convective-filtration flows due to the presence of pressure gradients along the particle radius that occur in the stage of moisture escape (drying) and persist in the entire period of the process, including the stage of carbon residue burn-out; along with the stages of escape of moisture and volatiles there are heterogeneous reactions of the fuel carbon-ash residue with O_2, CO_2, and H_2O; the gas, coke, and ash temperatures are equal inside the particle; the ash is a solid product of chemical transformations [18]. Furthermore, in constructing a mathematical description we will take into account generally accepted assumptions of multiphase hydrodynamics [19, 20]: the shape of the particle is spherical, each phase is homogeneous and continuous, averagings of the parameters are possible over volume elements.

Mathematical Statement of the Problem. According to the above assumptions, the system of equations for the mathematical model of thermal processing of an individual coal particle will appear as [4]:

a) mass transfer and continuity of the flows in the gaseous phase

$$\frac{\partial}{\partial t}[\alpha_1 \rho_1 c_{1j}] = \frac{D_{1j}^{(\mathrm{ef})}}{r^2} \frac{\partial}{\partial r}\left[\alpha_1 r^2 \rho_1 \frac{\partial c_{1j}}{\partial r}\right] - \frac{\partial}{\partial r}[u_1 \alpha_1 \rho_1 c_{1j}] \pm \nu_{sj} W_s \alpha_2 F_{\mathrm{sp}} +$$

$$+ q_w \alpha_1 \rho_1 c_{\mathrm{H_2O}} + q_{\mathrm{v}} \alpha_1 \rho_1 \overset{*}{c}_{1j}, \quad j = \overline{1, m_g}; \tag{1}$$

$$\frac{\partial}{\partial t}[\alpha_1 \rho_1] = -\frac{\partial}{\partial r}[u_1 \alpha_1 \rho_1] + \sum_{s=1}^{n_s} \nu_{sc} W_s \alpha_2 F_{\mathrm{sp}} + q_{\mathrm{v}} \alpha_1 \rho_1 \overset{*}{c}_{\mathrm{v}} + q_w \alpha_1 \rho_1 c_{\mathrm{H_2O}}; \tag{2}$$

b) mass transfer and continuity of the flows in the solid phase

$$\frac{\partial}{\partial t}[\alpha_2 \rho_2 c_{21}] = -\sum_{s=1}^{n_s} \nu_{sc} W_s \alpha_2 F_{\mathrm{sp}}; \tag{3}$$

$$\frac{\partial}{\partial t}\,[\alpha_2 \rho_2 c_{22}] = \sum_{s=1}^{n_s} \nu_{sa} W_s \alpha_2 F_{\mathrm{sp}}\,; \tag{4}$$

$$\frac{\partial}{\partial t}\,[\alpha_2 \rho_2 c_{23}] = -\, q_w \alpha_1 \rho_1 c_{\mathrm{H_2O}}\,; \tag{5}$$

$$\frac{\partial}{\partial t}\,[\alpha_2 \rho_2 c_{24}] = q_{\mathrm{v}} \alpha_1 \rho_1 c_{\mathrm{v}}^{*}\,; \tag{6}$$

$$\frac{\partial}{\partial t}\,[\alpha_2 \rho_2] = \sum_{s=1}^{n_s} (\nu_{sa} - \nu_{sc})\, W_s \alpha_2 F_{\mathrm{sp}} + q_{\mathrm{v}} \alpha_1 \rho_1 c_{\mathrm{v}}^{*} - q_w \alpha_1 \rho_1 c_{\mathrm{H_2O}}\,; \tag{7}$$

c) energy transfer

$$\frac{\partial}{\partial t}\,[c_p^{(\mathrm{ef})} T_p] = \frac{\lambda_p^{(\mathrm{ef})}}{r^2}\,\frac{\partial}{\partial r}\left[r^2 \frac{\partial T_p}{\partial r^2} \right] - \frac{\partial}{\partial r}\,[u_1 \alpha_1 \rho_1 c_{p1} T_p] +$$

$$+ \sum_{s=1}^{n_s} W_s Q_s \alpha_2 F_{\mathrm{sp}} - q_w \alpha_1 \rho_1 c_{\mathrm{H_2O}} h_w\,; \tag{8}$$

d) normalization conditions and the equations of state for the phases

$$\sum_{j=1}^{m_g} c_{1j} = 1\,; \quad \sum_{j=1}^{m_s} c_{2j} = 1\,; \quad \sum_{i=1}^{2} \alpha_i = 1\,; \tag{9}$$

$$P_1 = R T_p \rho_1 \sum_{j=1}^{m_g} \frac{c_{1j}}{M_{1j}}\,; \quad \rho_2 \approx \mathrm{const}\,; \tag{10}$$

e) initial and boundary conditions

$$t = 0:\ \alpha_1 = \varepsilon\,; \quad c_{1j} = \overset{\mathrm{o}}{c}_{1j}\,; \quad T_p = T_p^{\mathrm{o}}\,; \quad c_{21} = C^{\mathrm{w}}\,; \quad c_{22} = A^{\mathrm{w}}\,; \quad c_{23} = W^{\mathrm{w}}\,;$$

$$c_{24} = V^{\mathrm{w}}\,; \quad P_1 = P_0\,; \tag{11}$$

$$r = r_p(t):\ D_{1j}^{(\mathrm{ef})} \alpha_1 \rho_1 \frac{\partial c_{1j}}{\partial r} = \beta_j (\rho_{1j} - \overset{\mathrm{o}}{\rho}_{1j})\,, \quad j = \overline{1\,,\, m_g}\,; \tag{12}$$

$$\lambda_p^{(\mathrm{ef})} \frac{\partial T_p}{\partial r} - u_1 \alpha_1 \rho_1 c_{p1} T_p + c_{p1} \alpha_1 \rho_1 T_p \sum_{j=1}^{m_g} D_{1j}^{(\mathrm{ef})} \frac{\partial c_{1j}}{\partial r} =$$

$$= \alpha_2 \rho_2 \left[H_{\mathrm{h}}^{\mathrm{k}} (T_p - T_p^{\mathrm{o}}) - \varepsilon_c \sigma_0 \left\{ \left(\frac{T_p}{100} \right)^4 - \left(\frac{T_p^{\mathrm{o}}}{100} \right)^4 \right\} \right], \quad P_1 = P_0\,; \tag{13}$$

$$r = 0:\ \frac{\partial T_p}{\partial r} = \frac{\partial c_{1j}}{\partial r} = \frac{\partial P_1}{\partial r} = 0\,. \tag{14}$$

The effective diffusion coefficients entering in the system of equations (1)-(14) are determined using the recommendations of [8]:

$$1/D_{1j}^{(\mathrm{ef})} = 1/D_{1j}^{(\mathrm{m})} + 1/D_{1j}^{(\mathrm{ef})}, \tag{15}$$

where $D_{1j}^{(\mathrm{m})}$ are the effective molecular diffusion coefficients:

$$D_{1j}^{(\mathrm{m})} = \Pi\, D_{1j} = \frac{\varepsilon\sigma}{\xi\tau} D_{1j}; \tag{16}$$

D_{1j} are the diffusion coefficients in the gaseous phase; $\Pi = 0.1-0.2$ is the permeability coefficient; $\sigma = 0.5-0.7$ is the shape factor; $\xi = 1.4-2.0$ is the coefficient of sinuosity; $\tau = 1.5-2.0$ is the shape factor for the pores; $D_{1j}^{(\mathrm{k})}$ is the Knudsen diffusion coefficient:

$$D_{1j}^{(\mathrm{k})} = 9700\bar{r}_{\mathrm{por}} \sqrt{\left(\frac{T_p}{M_{1j}}\right)}, \tag{17}$$

where $\bar{r}_{\mathrm{por}}$ is the statistical mean radius of the pores.

The effective heat capacity and thermal conductivity of the particle are calculated using the relations [20]:

$$\lambda_p^{(\mathrm{ef})} = \sum_{i=1}^{2} \alpha_i \lambda_i; \quad c_p^{(\mathrm{ef})} = \alpha_2 \sum_{j=1}^{m_s} c_{p2j}\, c_{2j} + \alpha_1 \sum_{j=1}^{m_g} c_{p1j}\, c_{1j}. \tag{18}$$

The rate of convective-filtration transfer inside the pores is assumed to obey the Darcy law [20]

$$u_1 = -\gamma_1 \frac{\partial P_1}{\partial r}; \quad \gamma_1 = \frac{K_\mathrm{f}}{\mu_1}; \quad K_\mathrm{f} = \frac{\varepsilon^3}{5F_{\mathrm{sp}}^2}, \tag{19}$$

where K_f is the filtration coefficient.

We calculated the rates of heterogeneous reactions of combustion and gasification inside the particle by macrokinetic expressions of the first order

$$W_s = \bar{k}_s^{\mathrm{o}} \exp\left[\frac{E_s}{R}\left(\frac{1}{T_p^0} - \frac{1}{T_p}\right)\right] \rho_1\, c_{1j}, \tag{20}$$

where $\bar{k}_s^{\mathrm{o}}$ is the observed reference constant of the reaction rate related to the initial temperature of the particle T_p^0; E_s is the observed activation energy. We chose the observed kinetic parameters of the gasification reaction of $C + CO_2$ and $C + H_2O$ from the results of [21, 22]. To estimate the macrokinetic constants of the combustion reaction of $C + O_2$ and $C + 1/2\ O_2$, we performed a special experimental investigation of the kinetics of reaction of coke particles of Chelyabinsk brown coal of the 0.4–0.63 mm fraction with the oxygen of air in a gradient-free fluidized-bed pulse reactor [14, 23]. It was established that the reaction under investigation occurs in the near-intradiffusion reaction region. In mathematical processing of the experimental data on an IBM PC AT using minimization methods for functions of many variables and a specially developed procedure for estimating confidence intervals and correlation coefficients for the macrokinetic constants [21] we obtained the following weakly correlated estimates of the observed preexponential factor and activation energy for the reactions of combustion of the carbon-ash residue of Chelyabinsk brown coal inside the porous structure of the particle:

$$k_{1,2}^{0} = (4.4 \pm 0.2)\cdot 10^5 \ \ 1/{}^\circ\mathrm{C} \quad \text{and} \quad E_{1,2} = (104 \pm 4.1) \ \ \mathrm{kJ/mole} \tag{21}$$

for the correlation coefficients $\hat{\rho}_{12} = 0.07$.

A comparison of the experimental values of the observed rates of thermochemical transformation of the particle at the points of the maximum of the macrokinetic curves $\overline{W}_{\mathrm{obs}} = f(X_c)$ [14, 23] with those calculated by

Eq. (20) using the estimates (21) showed an agreement of the results obtained that is satisfactory for engineering practice. Nevertheless on the descending branches of the curves there was disagreement of the data in a number of experiments, confirming the assumption that allowance for the influence of the physical stages and intrapore reaction is necessary in processing experimental data. To calculate the rates of escape of moisture and volatiles inside the particle, we used dependences and constants obtained in [13, 17] in experimental investigations of thermal decomposition of brown coals of the Kansk-Achinsk coal field under conditions identical to those dealt with in the present work:

$$q_{\mathrm{v}} = -\frac{dV_{\mathrm{v}}}{dt} = k_{\mathrm{v}}^{0}\,\alpha_2\rho_2 \exp\,[-E_{\mathrm{v}}/RT_p]\,c_{\mathrm{v}}^{m_1}\,; \tag{22}$$

$$q_w = -\frac{dW}{dt} = k_w^{0}\,\alpha_2\rho_2 \exp\,[-E_w/RT_p]\,W^{m_2}\,. \tag{23}$$

The coefficients of heat and mass transfer between the particle and the ambient gas were determined using criterial expressions [10, 24, 25] that take into account a possible heat transfer from inert ash particles in the fluidized bed. In solving the system of equations (1)-(13) we also determined the values of radial and hoop thermal stresses developing inside the particle [6], the integral mean observed conversion rate, the current level of fuel conversion and the averaged one, the "observed" level of use of the inner surface of the particle and the true one [4]:

$$\sigma_{t,r} = \frac{2\alpha_t E_t}{1-\nu_t}\left[\frac{2}{(\overset{0}{r}_p)^3}\int\limits_0^{\overset{0}{r}_p} T_p(r)\,r^2 dr - \frac{1}{r_p^3}\int\limits_{\overset{0}{r}_p}^{r_p} T_p(r)\,r^2 dr\right]; \tag{24}$$

$$\sigma_{t,\theta} = \frac{\alpha_t E_t}{1-\nu_t}\left[\frac{2}{(\overset{0}{r}_p)^3}\int\limits_0^{\overset{0}{r}_p} T_p(r)\,r^2 dr + \frac{1}{r_p^3}\int\limits_{\overset{0}{r}_p}^{r_p} T_p(r)\,r^2 dr - T_p(r)\right]; \tag{25}$$

$$\overline{W}_{\mathrm{obs}} = \frac{1}{t^* - t_0}\,\frac{1}{\overset{0}{r}_p - r_p}\int\limits_{t_0}^{t^*}\int\limits_{\overset{0}{r}_p}^{r_p}\frac{\partial}{\partial t}\,[\alpha_2\rho_2 c_{21}]\,dt dr\,; \tag{26}$$

$$\overline{X}_c = \frac{1}{\overset{0}{m}_C C^p}\int\limits_{t_0}^{t^*}\left[\int\limits_V \overline{X}_r dV\right] dt\,; \tag{27}$$

$$\overline{\eta}_{\mathrm{obs}} = (\overline{W}_{\mathrm{obs}}F_{\mathrm{tr}})/(\overline{W}_{\mathrm{kin}}F_{\mathrm{sp}})\,;\quad \overline{\eta}_{\mathrm{tr}} = \overline{W}_{\mathrm{obs}}/\overline{W}_{\mathrm{kin}}\,. \tag{28}$$

Numerical Implementation of the Model. To solve the system of equations (1)-(23), we developed a calculation algorithm analogous to the Zeidel method [19, 26]. The equations of transfer of material (1) and energy (8) were reduced to an explicit form with respect to the gas component concentrations c_{1j} and the particle temperature T_p by substituting the continuity equations (2) into them. The latter equation in turn was reduced to an explicit form with respect to the new variable $z = P_1^2$. Once the above rearrangements had been performed, we carried out a finite-difference approximation of the newly obtained system of equations with the application of implicit difference schemes [27, 28], derivatives that contained convective terms being approximated by central differences. The equations of transfer in the solid phase (3)-(17) were also approximated using explicit (Eq. (7)) and semiimplicit difference schemes (Eqs. (3)-(6)) [27, 28]. We integrated the equations of the kinetics of escape of moisture (22) and volatiles (23) using explicit difference schemes [27]. We solved the differential equations obtained by a run method with automatic selection of the time step using Richardson's extrapolation [28], which consists in comparing maximum relative errors of the calculation of temperatures inside a particle at a full time step and two half-steps. The main stages of the calculation consisted in successive computation of the content of moisture and volatiles, chemical transformation rates, levels of use of the inner surface and fuel conversion levels, carbon and ash content, volume fractions of the solid phase and the gaseous one, pressure in the pores, gas component concentrations, particle temperature and rates of convective-filtration transfer along the particle radius at different instants, integral mean thermal stresses, and macrokinetic characteristics of the process.

The programs for calculating the thermochemical processing of a highly reactive coal fuel particle are implemented in FORTRAN-IV for an ES computer and in FORTRAN-77 for an IBM PC AT personal computer.

Results of a Numerical Analysis and Discussion. In a numerical analysis of the model (1)-(28) on an ES 1061 computer we investigated the influence of the particle size, oxygen concentration and of the temperature ambient gas, moisture content of the fuel on the ignition, burnt-out, and thermal destruction of particles of Chelyabinsk brown coal as applied to the conditions of thermochemical processing of it in a prefurnace with a low-temperature fluidized bed [16]. The behavior of both moist coal particles and dry carbon-ash residues of this fuel was analyzed.

The calculations confirmed existing ideas [1, 2, 7, 9, 10, 29] that the process under consideration is divided into the following basic stages: heating of a particle, moisture escape (drying of the particle), fuel pyrolysis (escape of volatiles), intrapore combustion-gasification of volatiles, and heating up and burn-out of the carbon residue.

In the stage of heating there was a gradual increase in the particle temperature to values corresponding to the onset of escape (evaporation) of the moisture in the fuel into the gaseous phase inside the pores.

The stage of moisture escape involved rapid accumulation of water vapor in the pores of the coal particle that displaces the remaining components to the ambient and its gradual cooling, enhanced with increasing sizes. The cooling stage is unstable on large particles (Fig. 1a). The time of moisture escape into the gaseous phase was practically independent of particle size and lay within $4.0 \cdot 10^{-3}$ and $7.0 \cdot 10^{-3}$ sec (Fig. 1b). In this stage substantial pressure gradients, growing with time and with increase in the moisture and particle size, developed inside the pores (Fig. 1c). The pressure growth inside the pores in the stage of moisture escape contributed to the most substantial change in the radial thermal stresses. The values of the thermal stresses increased as the initial size of the particles increased, and the period of their decrease "extended" in time to the stage of escape of volatiles (Fig. 1d). The values of the hoop thermal stresses were close to the radial ones in the range of varied parameters. The noted results, showing that intense accumulation of the water vapor in the gaseous phase in the stage of moisture escape is the reason for the substantial pressure growth, are in agreement with the conclusions of [13, 15]. Consequently, thermal disintegration of particles of highly reactive brown coals in a fluidized bed is the most likely in the indicated stage. For more accurate, quantitative conclusions on the probability of particle disintegration, we need to compare the calculated values of the thermal stresses with the thermal and mechanical strengths of this specific type of fuel. Unfortunately, for the moment these data on brown coals are practically nonexistent in literature. Therefore, allowing for highly approximate values of the linear expansion coefficients α_t, Young's shear modulus E_t, and the Poisson coefficient ν_t used in the calculations [30], the above conclusions on the likely disintegration of particles is of a qualitative, tentative character as yet and needs refinement in a separate special investigation.

Once the moisture ceased to escape, the volatiles in the fuel began to escape into the gaseous phase inside the particle porous structure. The time of escape of volatiles increased as the particle size increased (Fig. 2a) and depended weakly on the remaining parameters of the model. Its value was in the range of 0.3 to 10 sec and agreed with the experimental data given in the monograph of V. I. Babii and Yu. F. Kuvaev [29]. The intrapore pressure in the stage of escape of volatiles decreased with time and with a decrease in both the particle size (Fig. 2b) and other parameters of the model.

Gradual accumulation of the pyrolysis products CO_2, CO, H_2O, H_2, and O_2 in the pores contributed to intensification of the rates of heterogeneous chemical reactions of combustion and gasification inside the particle and to an increase in its temperature. Small particles were heated more rapidly in the stage of heating of the

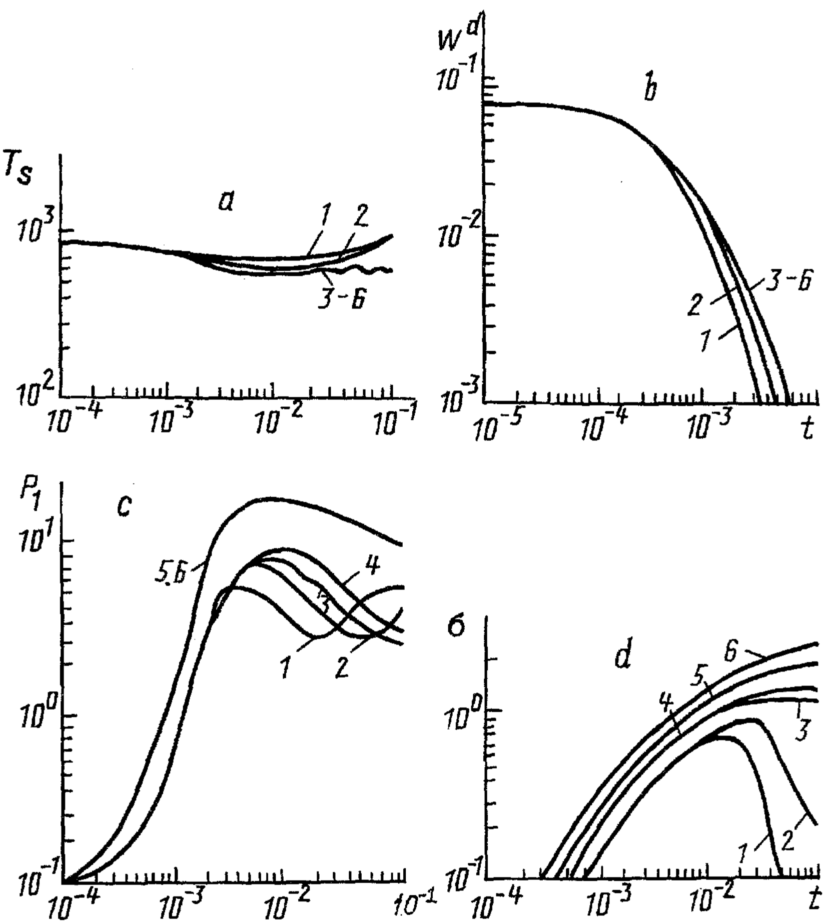

Fig. 1. Dynamics of: a) temperature change for the surface of a particle of moist Chelyabinsk brown coal in the stages of heating and drying; b) moisture escape from the coal; c) pressure change in the center of the particle in the stage of moisture escape, d) change in radial and thermal stresses inside the particle: 1) $r_p^0 = 0.05 \cdot 10^{-3}$; 2) $0.08 \cdot 10^{-3}$; 3) $0.2 \cdot 10^{-3}$; 4) $0.315 \cdot 10^{-3}$; 5) $0.8 \cdot 10^{-3}$ m. T_s, K; P_1, σ, MPa; t, sec.

carbon-ash residue of the fuel (Fig. 2c). For particles with $d_p^0 = 0.16-1.6$ mm the particle surface stabilized subsequently in the region of values close to those of the ambient temperature (Fig. 2c). We observed no substantial temperature gradients along the particle radius or high-temperature stationary regimes in the indicated size range for the remaining prescribed parameters. Maximum heating up of the particles with respect to the ambient gas did not exceed 35 K, and heterogeneous gasification and combustion reactions for the volatiles occurred in practically the entire volume of the particle, i.e., in the intrakinetic region. The reaction of vapor gasification of the carbon-ash residue of the fuel was the slowest and, thus, limiting stage of the process in this case. The characteristic times of the heating-up stage for the carbon-ash residue obtained by the model proposed are also in satisfactory agreement with experiment [29] in the 0.16–1.6 mm particle diameter range.

Growth of the integral mean porosity of a 0.5 mm diameter particle from $\varepsilon = 0.5$ to $\varepsilon = 0.8$ (with a change in $c_{O_2}^0$ from 0.1 to 0.95) and from $\varepsilon = 0.5$ to $\varepsilon = 0.65$ (with a change in T_p^0 from 1058 and 1128 K) occurred with time in the initial stage of heating up of the carbon-ash residue as the oxygen concentration and temperature of the ambient increased. These facts confirm qualitatively literarature data [3, 14, 23, 31] on the possibility of developing pores (increasing the porosity) of fuel particles in their thermal processing of them in a fluidized bed. High residual pressures of the gas components inside the particle that persisted subsequently and in the burn-out stage due to slow removal of the products of chemical transformations into the ambient and blocking of the pores with the ash, which is, within the framework of the adopted model, a solid product of chemical transformations, were the reason for a stabilized particle temperature in this size range. This kept new portions of gas reagents from

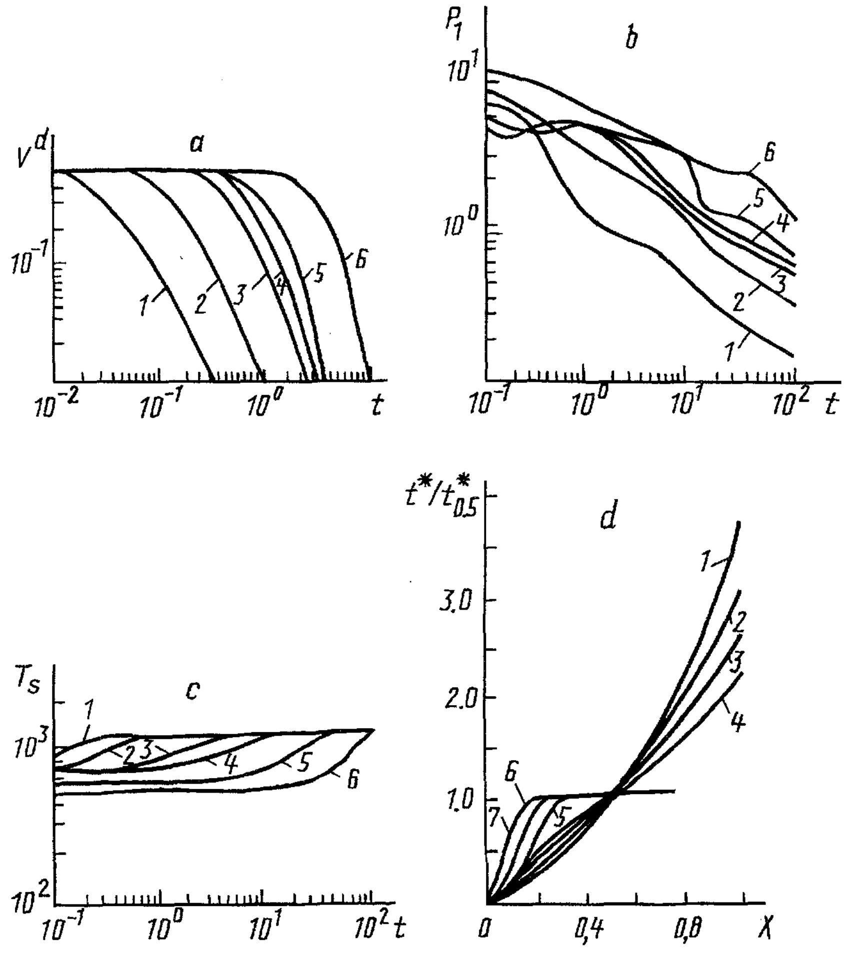

Fig. 2. Dynamics of: a) escape of volatiles from coal with varying sizes, b) pressure change in the center of a particle in the stage of fuel pyrolysis (escape of volatiles); c) temperature change of the particle surface in time with varying sizes in the stages of fuel pyrolysis, combustion-gasification of volatiles, and heating up of the carbon-ash residue [a–c) notation is the same as in Fig. 1]; d) change in the dimensionless relative effective time of thermochemical transformation (burn-out) for particles of carbon-ash residues of Chelyabinsk brown coal ($t^*_{0.5}$, time of 50% fuel conversion) vs. level of conversion and time: 1) $r_p^0 = 0.05\cdot10^{-3}$; 2) $0.08\cdot10^{-3}$; 3) $0.5\cdot10^{-3}$; 4) $0.8\cdot10^{-3}$; 5) $1.5\cdot10^{-3}$; 6) $2.0\cdot10^{-3}$; 7) $3.5\cdot10^{-3}$ m.

entering the particle and inhibited efficient heat and mass transfer with the ambient and slowed down substantially the duration of the burn-out stage.

Thermochemical transformation of the carbon-ash residue had its own special features in the 3.0–7.0 mm range of particle diameters. Here a rather rapid displacement of the combustion reactions into a narrow layer near the outer surface of the particle occurred (the transition from the intrakinetic reaction region to the intradiffusion one) that involved a drastic increase in temperature to values of 2400–2700 K, close to those of the adiabatic heatings up of the indicated reactions. As a result, the oxygen was practically depleted inside the particle and predominantly intense reactions of gasification of the carbon-ash residue with CO and H_2O occurred in the pores. Under these conditions the heating up of the center of the particle with respect to the outer surface was about 200–250 K. The reaction C + CO_2 was also displaced subsequently to the outer surface rather rapidly and switched to the intradiffusion region whereas vapor gasification persisted practically in the entire volume of the particle. A large amount of products of the chemical transformations, predominantly CO, whose rate of removal to the ambient by diffusion and filtration limited the subsequent process of thermochemical transformation of the particle,

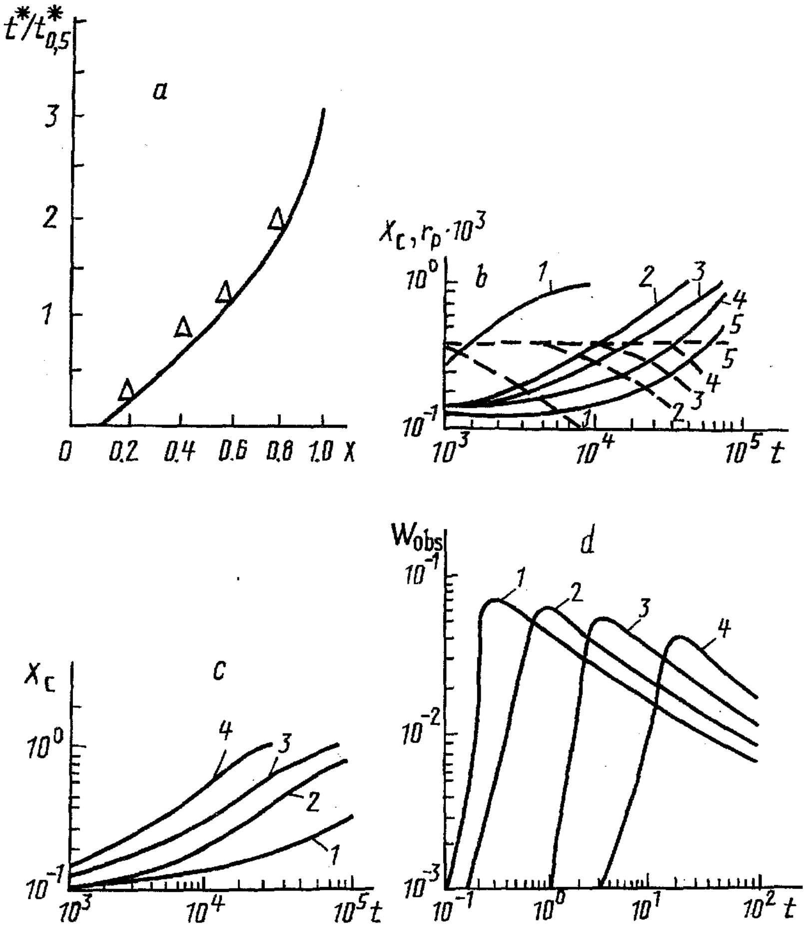

Fig. 3. Results of comparing the calculated relative effective burn-out times for particles with a $0.25 \cdot 10^{-3}$ m radius (solid line) with the experimental ones (points) estimated by the procedure of [31] (a); dynamics of the change in: b) level of conversion (solid lines) and size of a particle of the carbon-ash residue of Chelyabinsk brown coal (dashed lines) $0.5 \cdot 10^{-3}$ m in diameter vs O_2 concentration in the ambient: 1) $C^0_{O_2} = 0.5$; 2) 0.21; 3) 0.15; 4) 0.1; 5) 0.05; c) conversion level of a particle of the carbon-ash residue of Chelyabinsk brown coal $0.5 \cdot 10^{-3}$ m in diameter vs ambient gas temperature: 1) $T^0_p = 1058$; 2) 1123; 3) 1173; 4) 1223 K; d) observed thermochemical transformation rate for particles of the carbon-ash residue of Chelyabinsk brown coal with varying sizes (notation is the same as in Fig. 1). X_c, r_p, m; W_{obs}, kg/(m^3·sec).

accumulated in the pores as a result of intense gasification reactions. The rate of transformation in time slowed down substantially but the particle temperature remained stable and close to the value of the adiabatic heating up of the vapor gasification reaction (2720–2730 K).

Figure 2d presents a generalized dependence of the relative effective time for thermochemical transformation of particles of the carbon-ash residue of Chelyabinsk brown coal (without moisture or volatiles) on the level of conversion and the size. The value of $t^*_{0.5}$ here corresponds to a 50% level of fuel conversion. It is evident that for $\overline{X} \leq 0.5$ small particles burn-out more rapidly than large ones in the range of initial particle radii $r^0_p = 0.05–0.8$ mm and for $\overline{X}_c > 0.5$ vice versa. At the same time large particles with radii $r^0_p = 1.5–2.5$ mm are converted appreciably only in the initial stage of the process, but subsequently their transformation slows down substantially. A similar picture of the change in $t^*/t^*_{0.5}$ is associated with the above special features of the process of thermochemical transformation of variously sized particles. Thus, at low levels of conversion the observed transformation rate for the carbon-ash residue is determined by its temperature change and therefore small particles

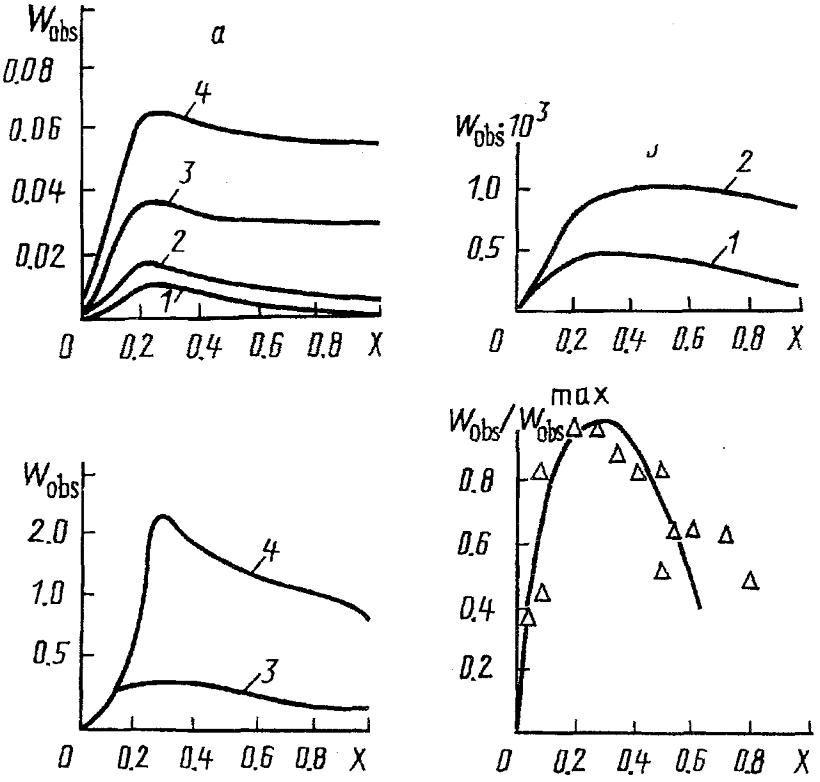

Fig. 4. Dynamics of the change in: a) observed thermochemical transformation rate for $0.5 \cdot 10^{-3}$ m diameter particles of the carbon-ash residue of Chelyabinsk brown coal vs conversion level and ambient temperature: 1) $T_p^0 = 793$; 2) 1123; 3) 1173; 4) 1223 K; b, c) observed thermochemical transformation rate for $0.5 \cdot 10^{-3}$ m diameter particles vs conversion level and O_2 concentration in the ambient: 1) $c_{O_2}^0 = 0.05$; 2) 0.1; 3) 0.21; 4) 0.5; d) results of comparing the calculated relative values of the observed thermochemical transformation rates for $0.5 \cdot 10^{-3}$ m diameter particles of the carbon-ash residue of Chelyabinsk brown coal (solid line) with the experimental ones for the same conditions (points).

are converted more rapidly. The reason for the more intense burn-out of large particles in the range of $r_p^0 = 0.05-0.08$ mm and for the decrease in $t^*/t_{0.5}^*$ with growth in size is intensification of gasification reactions inside the particle and emergence of decelerations due to convective-filtration transfer. And finally, the substantially decelerated transformations of particles in the size range of $r_p^0 = 1.5-2.5$ mm are associated with practically complete blocking of pores with gaseous and solid products of the chemical transformations. To estimate the degree of confidence of the proposed model, we compared the calculated values of $t^*/t_{0.5}^*$ with the relative effective burn-out times for coke particles of Chelyabinsk brown coal, determined independently from experimental investigations of the burn-out macrokinetics for this fuel in a gradient-free fluidized bed pulse reactor [14, 25, 31] by the procedure of [31]. Results of this comparison for particles 0.5 mm in diameter are presented in Fig. 3a. It is evident that the agreement of the data obtained is sufficiently satisfactory.

Dynamic patterns of the conversion levels for a particle of the carbon-ash residue of Chelyabinsk brown coal 0.5 mm in diameter as functions of the oxygen concentration and temperature in the ambient gas (Fig. 3b and c) point to a decrease in the thermochemical transformation time for the particle as the mentioned regime parameters increase.

Due to the blocking of pores with the gaseous components and ash the curves of the observed rate of particle transformation as a function of time and the level of fuel conversion are of a complex, extremum character, which is indicated by the calculated results in Figs. 3d and 4. It can be seen that as the particle size grows, the maximum values of the observed rate decrease and switch to the zone of larger transformation times (Fig. 3d), and the character of the change in this parameter is in agreement with the particle temperature dynamics in the stage of heating up of the carbon-ash residue in Fig. 2c. Consequently, for brown coals the growth in the observed rate of thermochemical transformation of the fuel is governed by the change in the particle temperature (heating up), and the considered process itself occurs in the intrakinetic region. At the same time the decrease in the observed rate with a further increase in the transformation time or the level of fuel conversion is associated, as has already been noted, with blocking of pores with gaseous products of the intrapore reaction of volatiles and the ash, and the decrease in this parameter as the size grows is associated with an increased time of stay of the gaseous components inside the particle and the appearance of decelerations due to convective-filtration transfer. As the oxygen concentration and temperature of the ambient increased, the maximum values of the observed rate of thermochemical transformation of dry carbon-ash residues increased but their displacement as a function of the time or the conversion level (toward smaller values of these parameters) was insignificant (Fig. 4a-c).

The extremum character of the macrokinetic dependences $\overline{W}_{\rm obs} = f(\overline{X}_c)$ or $\overline{W}_{\rm obs} = f(t)$ is not in conflict with results of experimental investigations of processes of combustion and gasification of cokes of different power-generating fuels in a gradient-free fluidized-bed pulse reactor [14, 23, 31]. To estimate the degree of qualitative agreement of the model proposed with experiment, we compared calculated relative values of the thermochemical transformation rates $\overline{W}_{\rm obs}^{\rm max}$ with data of the above-mentioned experimental investigation the macrokinetics of heterogeneous interaction of carbon residues of Chelyabinsk brown coal with the oxygen of air. For particles with a statistical mean diameter of 0.5 mm we achieved sufficiently satisfactory agreement of results of calculation with experiment for the following values of the observed kinetic combustion constants (Fig. 4d):

$$k_1^{\rm o} = 1.0 \cdot 10^6 \quad 1/^\circ{\rm C}\, ; \quad k_2^{\rm o} = 2.0 \cdot 10^6 \quad 1/^\circ{\rm C}\, ; \quad E_1 = E_2 = 95.0 \quad {\rm kJ/mole}\, . \tag{29}$$

These values, which are different from the initial constants (21) established in the calculation, point to a dependence of the observed macrokinetic parameters for the process of thermochemical transformation of a solid fuel on its structural and physicochemical characteristics, which is in agreement with results of [3, 12, 14, 25, 31] and calls for consideration of this circumstance in analyzing and processing experimental data. However, because of the tentative values of the kinetic constants for the stage of drying and pyrolysis, the characteristics of the porous structure of the fuel, and the effective transfer (diffusion, thermal conductivity, and filtration) coefficients used in the model in view of the absence of reliable data on the indicated parameters for the processes in thermochemical processing of solid fuel, the above-described results have mainly a qualitative character so far, rather than a quantitative one. Improvement and development of the proposed model and calculation procedure require further theoretical and experimental investigations of the refinement of the physicochemical and structural characteristics for the fuel under investigation and existing ideas of mechanisms of the stage of drying, pyrolysis, and chemical transformations inside the pores, the development of reliable procedures and estimates of the effective diffusion, thermal conductivity, and filtration coefficients for different power-generating fuels, analysis of the influence of convective and radiant heat transfer as well as heat and mass transfer processes and hydrodynamics in a gas envelope adjacent to the outer surface of particles on their ignition, thermal destruction, and burn-out conditions, and study of the conditions of multiplicity of stationary states and stability when the processes of thermochemical transformation of particles occur in a low-temperature fluidized bed.

Conclusions. In the work we proposed a mathematical model and a procedure for calculating the processes in thermochemical processing of individual highly reactive carbon fuel particles in a low-temperature fluidized bed. The processes of drying, pyrolysis, effective diffusion, heat conduction, filtration, and chemical transformations within the porous structure of the particle are taken into account. We developed an efficient and stable algorithm that reduces substantially the machine calculating time and enables us to obtain in calculations times of thermochemical transformation of the fuel that are comparable with those obtained in experimental and experimental-industrial technological installations. We made a numerical analysis of the influence of particle size and regime conditions on the process of thermochemical transformation of Chelyabinsk brown coal particles. It is shown that thermal disintegration of the brown coal particles in a low temperature fluidized bed is most likely to occur in the stages of escape of moisture and volatiles, and the burn-out stage can be substantially affected by filtration effects associated with the fact that high pressures, developing in the porous structure of the particle in the drying and pyrolysis stages, do not relax instantaneously. The above effects and the blocking of particle pores with ash cause the nonstationary character of the dependence of the observed thermochemical transformation rates for carbon-ash residues of the brown coals on time or the level of conversion. The vapor gasification reaction of the carbon-ash residue was the limiting stage of the indicated process. We confirmed existing ideas that in the 0.16–1.6 mm size range fuel particles remain practically isothermal in thermochemical processing of them in a fluidized bed. We noted the possibility of high-temperature stationary regimes occurring in transformations of particles whose sizes are $d_p^0 \geq 3.0$ mm. Results of the calculations agree satisfactorily with experimental data of investigation of the macrokinetics of heterogeneous interaction of carbon-ash residues of Chelyabinsk brown coal in a gradient-free fluidized-bed pulse reactor. We determined the main directions of further development of the proposed model and calculation procedure that can be used in engineering-technological practice for processing and analyzing data of macrokinetic experiments and those of prediction of the conditions of thermal destruction, ignition, and burn-out of various power-generating fuels when the process is complicated by the influence of physical stages, intrapore reaction, and nonstationary effects associated with the time variation of the characteristics of the porous structure and the reacting surface of the carbon particles.

NOTATION

A, ash content of the fuel; c, concentration, weight fractions; m_g, total number of components in the gaseous phase; α, volume fraction; t, time; ρ, density; D, diffusion coefficient; r, current radius of the particle; u, convective transfer rate; γ, permeability coefficient [20]; P, pressure; R, universal gas constant; T, temperature; M, molecular weight; c_p, heat capacity; λ_p, thermal conductivity coefficient; ε, porosity; C^{w}, V^{w}, and W^{w}, fraction of carbon, volatiles, and moisture in the fuel per working mass; β, mass transfer coefficient; H, heat transfer coefficient; σ_0, blackbody radiation coefficient; $\sigma_{t,r}$, $\sigma_{t,\theta}$, radial and hoop thermal stress; α_t, E_t, and ν_t, thermal expansion coefficient, Young's shear modulus, and the Poisson coefficient; X, conversion level; η, level of use for the inner surface; m_{C}^0, carbon particle weight; n_s, total number of heterogeneous reactions; ν, stoichiometric coefficient; W, chemical reaction rate; F, surface; q_{v}, q_w, rate of escape of volatiles and moisture [13, 15, 17]. Subscripts: i, phase number: 1, gas; 2, solid; j, component number: 1, CO_2; 2, CO; 3, H_2O; 4, H_2 (gaseous phase); $j = 1$, coke; $j = 2$, moisture; $j = 3$, volatiles; $j = 4$, ash (solid phase); p, particle; h, heat transfer; obs, observed; tr, true; kin, conditions corresponding to the concentration and temperature in the ambient; sp, specific. Superscripts: w, working mass of the fuel; ef, effective value; g, gaseous; s, solid; o, ambient and the initial value; c, convective; *, conditions of the initial escape of volatiles from the fuel.

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