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NUMERICAL SIMULATION OF PROCESSES OF THERMOCHEMICAL TRANSFORMATION OF SINGLE COAL PARTICLES AT ELEVATED PRESSURES

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Mathematical models, algorithms, programs, and results of calculations of processes of thermochemical processing of single high-ash coal particles at elevated pressures corresponding to functioning conditions of installations with a circulating fluidized bed are considered.

Thermochemical processing (pyrolysis, burning, and gasification) of high-ash coals under pressure in installations with a circulating fluidized bed (CFB) is one of most promising ways of involving these fuels in the fuel and energy balance of the CIS countries, overcoming the energy crisis, and solving environmental problems connected with tightening the requirements on the volume of harmful atmospheric waste of nitrogen oxides, sulfur, and other components [1].

Development of mathematical models and methods of calculation that reflect the behavior of single coal particles within a wide range of regime conditions and physicochemical and structural parameters of the fuel is one of most important stages of modeling the processes of thermochemical processing of high-ash coals in CFB under pressure. This is necessary for determination of fuel–gas reaction limits and evaluation of macrokinetic parameters, conditions of inflammation, burn-out, gasification, thermal destruction, and interaction of particles, and the characteristic times of the main stages of the process.

Earlier [2], we carried out numerical investigations on mathematical modeling of thermochemical processing of single particles of high-reaction brown coals under atmospheric pressure with consideration of the effect of the physical stages (effective diffusion, thermal conductivity, filtration, yield of moisture and volatiles) and the intrapore reactions. The results obtained demonstrated substantial participation of the above-mentioned factors in thermochemical transformation of the fuels under investigation and made it possible to develop mathematical models, algorithms, and programs for calculation that made it possible to achieve reasonable agreement with experimental data in our calculations.

The objective of the present work is to extend approaches proposed in [2] to the region of elevated pressures that are characteristic for functioning conditions of experimental and pilot-scale production installations with a CFB [1].

As applied to the air gasification process of high-ash GSSh grade coal in the installation of [1], we model the three main cases of particle transformation: 1) combustion: gasification of coke-ash fuel residue in dry air; 2) thermochemical transformation of real moist coal in a multicomponent gasified medium in the absence of an intermediate condensed phase in the particle pores; 3) thermocontact pyrolysis of fuel in the presence of a liquid phase containing condensed and dissolved gases, liquid resins, and hydrocarbons in the pores. The first and second cases are characteristic for conditions of processing high-ash coals in the gasifying reactor of the installation of [1], and the last one in a pyrolyzer.

The mathematical description of the combustion–gasification process of single particles of the coke-ash residue of GSSh coal in dry air accounts for the effective diffusion, thermal conductivity, and heterogeneous

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chemical reactions of interaction of coke with CO_2 and O_2 in the pores within the framework of a quasihomogeneous model of the porous fuel structure. The macrokinetics of gasification reactions of coke with CO_2 is modeled by an expression analogous to the Langmuir–Hinshelwood equation, and the reaction with O_2 is described by a power-law kinetic equation with a variable observable order of the reaction. The model includes a mass transfer equation and a continuity equation for flows in the gaseous and soplid phases and an energy transfer equation [3]:

$$\frac{\partial}{\partial t}[\alpha_1\rho_1 c_{1j}] = \frac{D^{e}_{1j}}{r^2}\frac{\partial}{\partial r}\left[\alpha_1\rho_1 r^2\frac{\partial c_{1j}}{\partial r}\right] \pm \nu_{sj} w_s \alpha_2 F_{\text{spec}} \quad (j = \overline{1, m_g};\ s = \overline{1, n_s}); \tag{1}$$

$$\frac{\partial}{\partial t}[\alpha_1\rho_1] = -\frac{\partial}{\partial t}[\alpha_2\rho_2] = \nu_{sc} w_s \alpha_2 F_{\text{spec}}; \tag{2}$$

$$\frac{\partial}{\partial t}[\alpha_2\rho_2 c_{2j}] = \nu_{sj} w_s \alpha_2 F_{\text{spec}} \quad (j = \overline{1, m_s}); \tag{3}$$

$$\frac{\partial}{\partial t}[T_p C^{e}_{p}] = \frac{\lambda^{e}_{p}}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial T_p}{\partial r}\right] + \sum_{s=1}^{n_s} w_s Q_s \alpha_2 F_{\text{spec}}; \tag{4}$$

$$\sum_{j=1}^{m_g} c_{1j} = \sum_{j=1}^{m_s} c_{2j} = 1; \quad \alpha_1 + \alpha_2 = 1; \tag{5}$$

$$\rho_2 \approx \text{const}; \quad P_1 = RT_p\rho_1\sum_{j=1}^{m_g}\frac{c_{1j}}{M_j}; \tag{6}$$

$$r = 0:\ \frac{\partial c_{1j}}{\partial r} = \frac{\partial T_p}{\partial r} = 0; \tag{7}$$

$$r = r_p(t):\ \lambda^{e}_{p}\frac{\partial T_p}{\partial r} + \sum_{s=1}^{n_s} w_s Q_s + C_{p1}T_p\sum_{j=1}^{m_g} D^{e}_{1j}\alpha_1\rho_1\frac{\partial c_{1j}}{\partial r} = H^{*}_{\text{con}}(T_p - T^{*}_{\text{in}}) + {}$$

$$+ \varepsilon^{*}_{c}\sigma_0\left[\left(\frac{T_p}{100}\right)^4 - \left(\frac{T^{*}_{\text{in}}}{100}\right)^4\right]; \tag{8}$$

$$D^{e}_{1j}\alpha_1\rho_1\frac{\partial c_{1j}}{\partial r} \pm \nu_{sj} w_s = \beta^{*}_{\text{con}}(\rho_{1j} - \rho^{0}_{1j}) \quad (j = \overline{1, m_g};\ s = \overline{1, n_s}); \tag{9}$$

$$t = 0:\ T_p = T^{0}_{p};\ c_{1j} = c^{0}_{1j};\ c_{21} = C^{w};\ c_{22} = A^{w};\ \alpha_1 = \varepsilon;\ \alpha_2 = 1 - \varepsilon; \tag{10}$$

$$w_s = \beta k^{0}_{s}\exp\left[\frac{E_s}{R}\left(\frac{1}{T_0} - \frac{1}{T_p}\right)\right]\rho^{n}_{O_2} \quad (s = \overline{1, 2}); \tag{11}$$

$$w_3 = \frac{\bar{k}_3\rho_{CO_2}}{1 + \bar{k}_4\rho_{CO_2} + \bar{k}_5\rho_{CO}}; \quad \bar{k}_s = k^{0}_{s}\exp\left[\frac{E_s}{R}\left(\frac{1}{T_0} - \frac{1}{T_p}\right)\right]\rho \quad (s = \overline{3, 5});$$

$$C^{e}_{p} = \sum_{i=1}^{2}\alpha_i\rho_i C_{pi}; \quad \lambda^{e}_{p} = \sum_{i=1}^{2}\alpha_i\lambda_i.$$

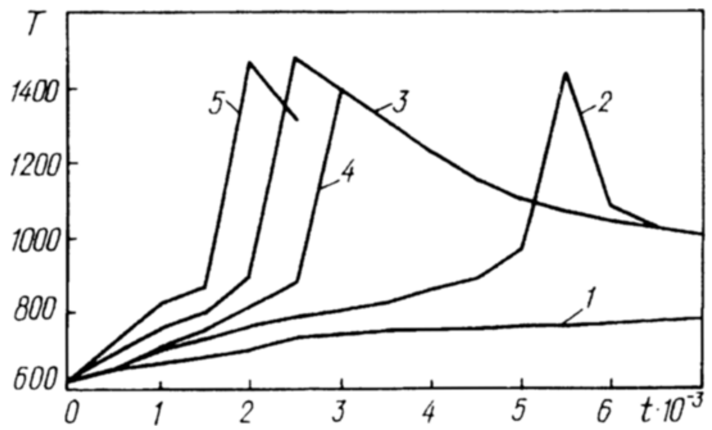

Fig. 1. Effect of the temperature of the surrounding gas on temperature at the center of a coke-ash residue particle of GSSh coal: 1) $T_g^0 = 773$ K, 2) 873, 3) 973, 4) 1073, 5) 1173 K. T, K; t, sec.

The mathematical description of thermochemical processing of a real moist GSSh coal particle in a multicomponent gasification medium is based on the theory of interpenetrating continua and a quasihomogeneous model of the porous structure of the fuel. It takes into account the stages of yield of moisture and volatiles, effective diffusion, thermal conductivity, and filtration of gaseous components, and heterogeneous reactions of interaction of the fuel carbon with O_2, CO_2, and H_2O. In addition, it includes equations of mass transfer and continuity of flows in gaseous and solid phases and energy transfer [2]. The macrokinetics of the stages of yield of moisture and volatiles is modeled by power-law kinetic expressions, and the stage of the convective filtration process is modeled by the Darcy law.

A specific feature of the mathematical model of thermocontact pyrolysis of a GSSh coal particle is consideration of component transfer in the condensed phase due to effective diffusion, filtration, capillary forces, and phase transitions (evaporation–condensation), in addition to the above-mentioned physical stages. The model includes equations of mass transfer and continuity of flows in gaseous and condensed phases and energy transfer [3]. The composition of the resins and hydrocarbons produced in pyrolysis is modeled by seven key components that comprise a set reflecting the main structures entering the coal composition: benzene, toluene, dimethylnaphthalene, methylethyltetralene, undecane, phenanthrene, and phenol [4]. The model also takes into account secondary heterogeneous reactions of interaction of the coke-ash fuel residue with pyrolysis products (H_2, CO_2, and H_2O) whose macrokinetics is modeled by expressions similar to the Langmuir–Hinshelwood equation.

Algorithms for solving the systems of equations of the three mathematical models are analogous to the Seidel method. Procedures for automatic choice of the time step based on Richardson's extrapolation are used. A specific feature of the algorithm for simulation of thermocontact pyrolysis of coal particles is the additional assumption of the presence of thermodynamic equilibrium between the concentrations of the components in the gaseous and condensed phases that is imposed on the system, which makes it possible to compose an overdetermined system of equations of the model and use some of them for iterative estimation of phase transition rates of condensed components within a particle.

Programs for calculation of parameters of particle behavior were coded in Turbo Basic 1.0 (Borland International) and Microsoft FORTRAN Version 5.0 (Microsoft Corporation).

A numerical analysis of the effect of the functioning conditions of the TsKS-1.0 pilot-scale production installation [1] being developed at the Scientific and Technical Center for Coal Electric Technologies of the National Academy of Sciences and the Energy and Electrification Ministry of Ukraine on the behavior of GSSh coal particles at elevated pressures, was carried out on an IBM PC/AT-386-compatible personal computer.

It was shown that the algorithms and programs developed are robust and make it possible to achieve effective times of thermochemical transformation of the fuel that are comparable with those observed in CFB installations under pressure.

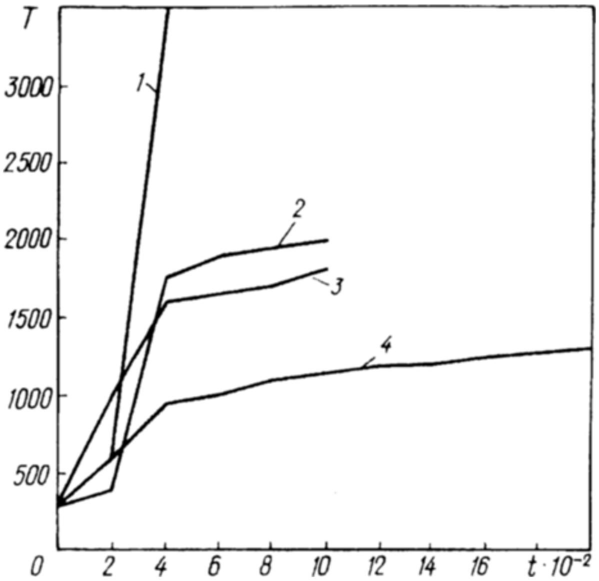

Fig. 2. Dynamics of temperature variations at the center of a particle for various CO_2:O_2 ratios in the environment: 1) CO_2:O_2 = 0.25:0.75, 2) 0.5:0.5, 3) 0.75:0.25, 4) 0.99:0.01.

In our investigations of the process of combustion-gasification of single particles of GSSh coke-ash residue in dry air we substantiated qualititavely conclusions of preceding experimental investigations that gasification reactions for the given type of fuel proceed within the intrakinetic region, and combustion reactions take place in the transitional region between the intrakinetic and intradiffusional regions. The applicability in principle of the assumptions of the mathematical model proposed for the analysis of conditions of thermal breakup, burn-out, gasification, and inflammation of particles is substantiated, which is evidenced by results of calculations of the effect of the temperature of the surrounding gas on the temperature at the center of a particle under a pressure P_0 = 0.8 MPa (Fig. 1).

The possibility was noted of the appearance of temperatures close to the slagging point of the fuel under investigation upon inflammation of coke-ash GSSh particles, and of phenomena of thermal instability of the burn-out process, especially at diameters $d_p^0 \geq 4.0 \cdot 10^{-3}$ m. The effects specified can be favorable for the occurrence of accidents during operation of CFB installations. This circumstance should be taken into account in designing technological recommendations on optimum conditions for carrying out burn-out processes of coke-ash residues of high-ash coals in a CFB under pressure. The reason for the thermal instability consists in disruption of the heat balance between heat release during the chemical transformation and convective radiative heat exchange with the environment accompanied by a sharp decrease in the fraction of the reactive surface in pores and gradual passage of the process into the internal and external diffusion regions.

In a numerical analysis of the mathematical model of the process of thermochemical transformation of a GSSh particle in the multicomponent gasification medium we obtained data on the dynamics of the yield of moisture and volatiles, thermal stresses, compositions of reacting substances, particle dimensions, degrees of conversion, particle temperatures, pressures in pores, observed rates of thermochemical transformation of the fuel, and other characteristics within the range of parameters of the TsKS-1.0 pilot-scale production installation being designed [1] that can be used in engineering technological practice when developing recommendations on combustion–gasification of high-ash coals in a CFB under pressure.

It was shown that for the GSSh coal particles 0.8–1.3 mm in diameter being utilized in the installation of [1] thermal decomposition is highly probable both at the drying–pyrolysis stage and at the stage of burn-out of the coke-ash residue of the fuel. At the initial stage this results from concentration of steam in the pores due to intense moisture evaporation and emergence of pressure gradients along the particle radius, and at the stage of burn-out this takes place due to substantial temperature gradients along the particle radius that are connected with

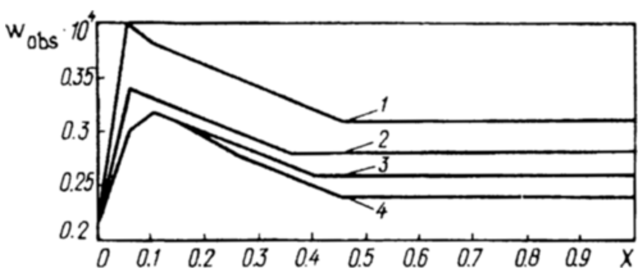

Fig. 3. Effect of the pressure on the observed rate of gasification of coke-ash residue of GSSh coal: 1) P_0 = 0.868 MPa, 2) 0.55, 3) 0.25, 4) 0.108; $\bar{r}_p^0$ = 0.5·10 m; $T_p^0 = T_g^0$ = 693 K.

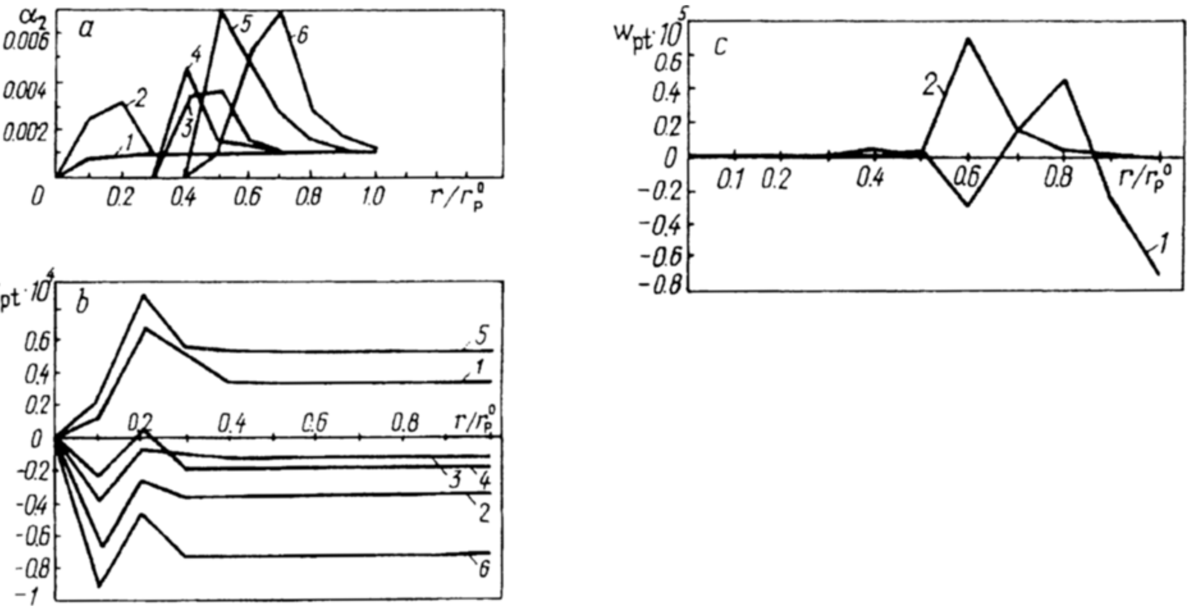

Fig. 4. Profiles of volume fractions of the condensed phase (a) and the total phase transition rate (b, c) along the particle radius at various instants: a: 1) t = 0.5 sec; 2) 0.8, 3) 1.0, 4) 1.7, 5) 0.0095, 6) 0.02 sec; b: 1) t = $0.115 \cdot 10^{-2}$ sec, 2) $0.18 \cdot 10^{-2}$, 3) $0.31 \cdot 10^{-2}$, 4) $0.5 \cdot 10^{-2}$, 5) $0.95 \cdot 10^{-2}$, 6) $0.2 \cdot 10^{-2}$ sec; c: 1) t = 1.0 sec, 2) 1.66.

gradual passage of the process into the internal and external diffusion regions, as well as intense gasification reactions in the pores. It should be noted that for particles 0.8 mm in diameter their maximum temperature in the calculations was close to the slagging point of GSSh coal, and for particles 1.3 mm in diameter the temperature exceeded the slagging point. Therefore the dimensions presented can be recommended as limiting for combustion in a circulating fluidized bed without preliminary thermal treatment. Combustion of larger particles seems to be unreasonable due to possible slagging of the bed in nonstationary transient regimes of the process and occurrence of accidents. An increase in the external pressure and temperature of the surrounding gas in the calculations led to similar effects. An increase in the CO_2 concentration in the CO_2:O_2 ratio was favorable for stabilization of the temperature regime and prevention of temperatures close to the slagging point of the GSSh coal, which is evidenced by the results of the calculations presented in Fig. 2.

Calculations have also demonstrated the possibility in principle of describing the extremum behavior of the observed rates of gasification of coke-ash residues of GSSh coal at elevated pressures, which is evidenced by the dependences of this parameter on the degree of fuel conversion presented in Fig. 3 which agree qualitatively with experimental data.

The extremum character of the curves in this case is explained by blockage of pores by ash and gaseous reaction products.

Calculations of the process of thermocontact pyrolysis of a single GSSh coal particle in the presence of an intermediate condensed phase in the pores have shown that the proposed model, algorithm, and program for calculation make it possible to analyze the fields of concentration of gaseous and condensed components, temperatures, pressures, filtration rates, phase and chemical transformations, thermal stresses, yields of volatiles, and other characteristics of the process at various instants, which opens up in the future new possibilities for its application in engineering-technological practice when evaluating and optimizing times of yield of volatiles in pyrolysis apparatuses and when developing optimum methods of fuel feeding for gasification in a CFB. Examples of profiles of volume fractions of the condensed phase and total rates of the phase transition under a pressure $P_0 = 0.8$ MPa and for a particle dimension $d^0_p = 1.3 \cdot 10^{-3}$ m are presented in Fig. 4.

NOTATION

t, time; α_1, volume fraction of the gas phase in the pores; ρ_1, density of the gaseous mixture in the pores; c_{1j}, weight fraction of the j-th component in the gaseous phase; D^e_{1j}, effective diffusion coefficient of the j-th gaseous component in the pores; r, coordinate of the particle radius; ν_{sj}, stoichiometric coefficient of the j-th gaseous component in the s-th reaction; ω_s, rate of the s-th heterogeneous reaction; F_{spec}, total specific surface of a particle; j, number of a gaseous component: 1) CO_2, 2) CO, 3) O_2, 4) N_2; n_s, total number of heterogeneous reactions; m_g, total number of gaseous components; α_2, volume fraction of coke-ash residue (carbon); ρ_2, density of coke-ash residue; c_{2j}, weight fractions of coke-ash residue components: $j = 1$, carbon; $j = 2$, ash; m_s, total number of components in the solid phase; T_p, temperature of a particle; C^e_p, λ^e_p, effective specific heat and thermal conductivity of a particle; Q_s, thermal yields of heterogeneous chemical reactions; P_1, pressure in the gaseous phase; R, gas constant; M_j, molecular weight of the j-th gaseous component; r_p, running radius of a particle; C_{p1}, specific heat of the gaseous phase in the pores; H^*_{con}, effective coefficient of convective heat exchange of a particle with its environment; T^*_{in}, mean integral temperature of the inert ash particles surrounding a fuel particle in the fluidized bed; ε^*_c, effective degree of blackness of coke-ash residue; σ_0, coefficient of black-body radiation; β^*_{con} (β^e_{con}), effective coefficient of convective mass transfer between particles and their environment; ρ_{1j}, ρ^0_{1j}, volume concentrations of gaseous components ($\rho_{1j} = \rho_1 c_{1j}$, $\rho^0_{1j} = \rho_1 c^0_{1j}$) on the surface and in the bulk of the surrounding medium; T^0_p, initial temperature of a particle; c^0_{1j}, weight fractions of gaseous components in the bulk of the environment; C^w, A^w, weight fractions of carbon and ash in the fuel per working weight; ε, porosity of a particle; β, empirical stoichiometric coefficient reflecting the degree of completion of reactions of combustion of coke-ash residue to CO_2 and CO (in the calculations it was taken to be 0.465); k^0_s, observed pre-exponential multipliers of heterogeneous reactions; E_s, observed activation energies of heterogeneous reactions; T_0, basic temperature that was taken to be equal to the temperature averaged over the particle radius at the given instant; n, observed order of the reaction; ρ_{O_2}, ρ_{CO_2}, ρ_{CO}, volume concentrations of gaseous components; k_3, k_4, k_5, observed constants of gasification reactions; λ_i, coefficient of thermal conductivity of a phase (1, gas; 2, solid phase); T^0_g, P^0_g, initial temperature and pressure of the gas; X, degree of fuel conversion; $\overline{w}_{pt}$, phase transition rate.

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