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# MODELING OF THE PYROLYSIS PROCESS OF COAL PARTICLES

**G. Ya. Gerasimov**

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*A mathematical model of pyrolysis of coal particles is developed that takes into account the heat transfer of a particle with the surrounding medium, the kinetics of release of volatile components, the secondary reactions of cracking, and the depositions of tar in its motion in the particle pores. Calculated results are compared to available experimental data.*

The first chemical stage of coal conversion in various high-temperature processes (combustion, gasification, coke formation, etc.) is the process of thermal destruction (pyrolysis) of its organic mass with escape of volatile components. Therefore the construction of a mathematical model of pyrolysis is the first step toward the development of mathematical models of the more general processes.

At present no sufficiently rigorous theory is available to describe the kinetics of the release of volatile components for coals of different classes. In the majority of cases the pyrolysis of each particular coal is studied experimentally to elucidate the influence of the process parameters on the composition of its products. Then on the basis of theory, the results obtained are interpreted qualitatively and a more or less adequate model of the process is constructed [1].

In recent years investigations have been reported in which attempts were made to develop the general principles of construction of coal pyrolysis models (see, for instance, [2]). In the models suggested numerous chemical characteristics are used for reproduction of the structure of the organic mass of coal. The chemical changes occurring during pyrolysis are described by a set of elementary reactions obtained in experiments with model substances. However, despite the fact that these models are based on a more comprehensive representation of the structure of the organic mass of coal and the processes involved in thermal destruction, they are inapplicable for engineering solutions.

The basic stage in the creation of a mathematical model of coal pyrolysis is the description of the behavior of a single particle of coal placed in a high-temperature region. Changing the boundary conditions on the particle surface allows one to use such a model to design different power facilities: combustion chambers, reactors-gasifiers, reactors-pyrolyzers, etc.

Construction of mathematical models of pyrolysis of coal particles with account for their internal structure is a matter of concern of voluminous literature (see, for instance, [3-5]). As a rule, these models are cumbersome and difficult to implement numerically. We have developed a rather simple model of pyrolysis of a single coal particle that is convenient for practical calculations and, on the basis of the elemental composition of coal, allows representation of the process and determination of the composition of the products formed.

1. Experimental investigations carried out for different classes of coal at different heating rates, particle diameters, and pressures show that for small particles (with a size of less than 500 $\mu$m) and heating rates of about $10^3-10^4$ K/sec neither the distribution of the pyrolysis products nor the rate of their release depends strongly on the diameter of the particles [6]. Larger particles are not heated instantaneously, and considerable temperature gradients develop inside them. The pyrolysis products formed in particles migrate outward. This is accompanied by various secondary reactions, mainly, cracking and condensation and polymerization of tar with deposition of a certain amount of carbon [7].

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In considering the mass transfer in coal particles, various models are used that are closely related to the plasticity of the coal. For "plastic" coals, which under heating become softened, sinter, and swell, the particles can be represented in the form of liquid drops inside which bubbles are formed [1]. Particles that do not pass to the plastic state upon heating, are usually described as a bimodal structure (micropores and macropores), wherein the volatile components escape outward via macropores, the diameter of which is several microns. Below, consideration is given to rather coarse coal particles whose plastic properties remain unchanged upon heating.

The continuity equation describing the behavior of the $i$-th component of the volatile compounds inside a porous particle can be written in a spherical coordinate system as [4, 8]

$$\partial (\rho \varepsilon y_i)/\partial t + r^{-2}\, \partial (r^2 N_i)/\partial r = R_i\,, \quad N_i = y_i N\,, \tag{1}$$

$$R_i = G_i(r, t)\, \rho_s (1 - \varepsilon_0)(1 - A^c/100) + A_{sec} \exp(- E_{sec}/T)\, \rho \varepsilon y_{tar}\, \xi_i\,.$$

For the kinetic parameters of the secondary reactions the following values can be taken: $A_{sec} = 10^{13}$ sec$^{-1}$, $E_{sec} =$ 32,700 K [3]. Evaluations show that the mass-mean velocity of the gas in a particle $v_0 \doteq N/\rho\varepsilon$ is considerably lower than the velocity of sound. Therefore in considering the gas flow in particle pores one can restrict considerations to the quasisteady regime and neglect the first term in Eq. (1).

The mass flows $N_i$ entering Eq. (1) depend on the gradients of the concentrations $y_i$ and the pressure $p$ [4]. We will neglect the effect of diffusion on $N_i$. This assumption is, generally speaking, incorrect for gasification and combustion of solid fuel since diffusion processes play a decisive role there. In the case of pyrolysis the diffusion of the gas components relative to each other is insignificant, and here the main contribution is made by the mass flow of the pyrolysis products in the pore space of a particle that occurs due to the pressure drop [9]. In this case, the equation for determination of $p(r, t)$ inside a particle is as follows:

$$N = - \rho \varepsilon\, (a^2/8\eta)\, \partial p/\partial r\,, \tag{2}$$

$$\rho = p \sum_i y_i/\mu_i/(RT)\,. \tag{3}$$

The boundary conditions for Eqs. (1) and (2) with account for the assumptions adopted can be written as

$$N_i(r, t)\,|_{r=0} = 0\,, \quad p(r, t)\,|_{r=r_0} = p_a\,.$$

The total release $V_i(T)$ of component $i$ into the surrounding medium in time $t$ is determined by the formula

$$V_i(t) = \int_0^t 3N_i(r_0, t)\, (\rho_s r_0)^{-1}\, dt\,.$$

In considering the solid substance of a particle we will neglect the thermal effect of pyrolysis reactions, the convective heat transfer by the gas components, and the influence of a change in the particle mass on temperature-field formation [7]. In this case, the equations of material and energy balance are

$$\partial\, [\rho_s (1 - \varepsilon)]/\partial t = - \sum_i R_i\,, \tag{4}$$

$$\rho_s c_s\, \partial T/\partial t = \lambda_s r^{-2}\, \partial (r^2 \partial T/\partial r)/\partial r\,. \tag{5}$$

Note that in the simplified system of equations (1)-(5) for the yield of volatile components, heat-conduction equation (5) is not related to the other relations and can be solved separately. In [10], results of numerical solution of (5) with the boundary conditions

$$-\lambda_s\,\partial T(r,t)/\partial r\,|_{r=r_0} = (\mathrm{Nu}\,\lambda_a/2r_0)\,[T(r_0,t) - T_a]\,,$$

$$\partial T(r,t)/\partial r\,|_{r=0} = 0$$

and the initial temperature $T(r, 0) = T_0$ are reported. Below, these results are approximated by analytical formulas that make it possible to obtain easily and rather exactly the temperature field inside a particle:

$$T(r,t) - T_a = \sin(\beta r/r_0)\,(\beta r/r_0)^{-1}\,[1 + 0.1\,\mathrm{Bi}\,(r/r_0)^{10}]^{-1}\,[T(0,t) - T_a]\,, \tag{6}$$

$$T(0,t) - T_a = \exp(-\beta^2 a t/r_0^2)\,(T_0 - T_a)\,;$$

$$\beta = \pi/2 + \arctan(1.67\log\mathrm{Bi})\,;\quad \mathrm{Bi} = \mathrm{Nu}\,\lambda_a/2\lambda_s\,;$$

$$a = \lambda_s/\rho_s c_s\,;\quad \mathrm{Nu} = 2 + 0.6\,\mathrm{Re}^{0.5}\,\mathrm{Pr}^{0.333}\,.$$

2. Modern models of pyrolysis consider the organic mass of coal to be an ensemble of condensed aromatic, hydroaromatic, and heterocyclic structures (clusters) bearing different functional groups as substituents. Upon rapid heating of coal particles the bonds attaching the functional groups to the circular clusters break, and volatile gaseous components ($CO$, $CO_2$, $H_2O$, $H_2$, $CH_4$, $HCN$, $H_2S$, aliphatic hydrocarbons) are formed [11]. It is considered that the functional groups are released independently of each other, and the kinetics of this process is independent of the grade of coal [1]. Simultaneously with the release of the light gas components the bridged structure of coal undergoes splitting to form large molecular fragments, i.e., tar. At the temperatures typical of the pyrolysis of coal particles the tar is in the gaseous state and is considered to be one of the gaseous components whose concentration is described by Eq. (1).

We will consider a porous spherical coal particle with a constant radius $r_0$ located in a high-temperature region. The kinetics of release of the functional groups from the particle to the gaseous phase during thermal destruction of its organic mass is described by the following system of differential equations [12]:

$$dY_i(r,t)/dt = -G_i(r,t)\,,\quad Y_i(r,0) = Y_{i0}\,, \tag{7}$$

$$G_i(r,t) = Y_{i0}\int_0^{\infty} A_i \exp\left\{-E/T(r,t) - A_i\int_0^{t}\exp[-E/T(r,t)]\,dt\right\} f_i(E)\,dE\,,$$

$$f_i(E) = [\sigma_i(2\pi)^{1/2}]^{-1}\exp[-(E - E_i)^2/2\sigma_i^2]\,.$$

The kinetic parameters of release of different functional groups from the organic mass of coal are given in Table 1.

In determining the initial concentrations $Y_{i0}$ it is assumed that the entire oxygen in the organic mass of coal is in the COOH, CO, and OH groups. The content of carbon $C^{daf}$ in the dry ash-free (daf) mass of coal is adopted as the main parameter determining the degree of coal metamorphism. The distribution of oxygen over the groups for different classes of coal as a function of $C^{daf}$ is based on experimental data [13, 14] and can be approximated by the following expressions (daf%):

$$O^{daf} = (38.0z^2 + 132.0)^{0.5} - 10.0\,,$$

$$z = -0.2\,C^{daf} + 19.0\,,\quad 65 \le C^{daf} \le 95\,;$$

TABLE 1. Kinetic Parameters of Release of the Functional Groups from Coal under High-Speed Coal Pyrolysis Conditions

| Functional group | Mass coefficient | $\log(A_i, \text{sec}^{-1})$ | $E_i$, K | $\sigma_i$, K | Reference |
|---|---|---|---|---|---|
| $CO_2$ | 1.0 | 13.22 | 27,200 | 6300 | [12] |
| CO | 0.3 | 11.22 | 26,000 | 2500 | [1, 2] |
| | 0.7 | 13.00 | 36,100 | 6000 | |
| $H_2O$ | 1.0 | 14.32 | 30,000 | 1500 | [1] |
| $CH_x$ | 1.0 | 13.22 | 30,000 | 2400 | [12] |
| $H_2$ | 1.0 | 13.22 | 37,300 | 4300 | [12] |
| HCN | 0.3 | 12.23 | 30,300 | 1500 | [1] |
| | 0.7 | 14.00 | 47,500 | 4700 | |
| Tar | 1.0 | 13.65 | 26,400 | 1500 | [1] |

$$O^{COOH} = \begin{cases} O^{daf} - 3.75z + 0.5, & z \geq 2.1744, \\ 0, & z < 2.1744; \end{cases}$$

$$O^{CO} = \begin{cases} 1.53z + 0.79, & z \geq 2.1744, \\ 0.5379\, O^{daf}, & z < 2.1744; \end{cases}$$

$$O^{OH} = \begin{cases} 2.22z - 1.29, & z \geq 2.1744, \\ 0.4621\, O^{daf}, & z < 2.1744. \end{cases}$$

In the process of coal pyrolysis aromatic hydrogen $H^{ar}$ passes to the gaseous phase in the form of $H_2$, and aliphatic hydrogen $H^{al}$, in the form of $CH_x$. Data on the composition of the functional groups for different coals [1] show that the content of $H^{ar}$ in coal is practically independent of the coal grade and is, on average, 1.5 daf%. The content of aliphatic hydrogen can be calculated by the formula

$$H^{al} = H^{daf} - H^{ar} - 0.125\, O^{OH} - 0.0714\, N^{daf} - 0.0625\, S^{daf}.$$

Here it is assumed that nitrogen of the fuel passes to the gaseous phase in the form of HCN, and organic sulfur, in the form of $H_2S$. The distribution of the maximum yield of aliphatic hydrocarbons over the components can be determined using the data of [12].

Tar consists of minimally disrupted fragments of the initial coal. Therefore it can be considered that the ratio of the functional groups in tar is approximately the same as in the initial coal [1]. In this case, for the mass fraction $\xi_i$ of component $i$ in the products of thermal destruction of tar we have $\xi_i = Y_{i0}/(1 - \text{Tar})$, $\xi_{tar} = -1$. The initial concentrations of the functional groups $Y_{i0}$ (mass fractions, daf) are determined by the relations

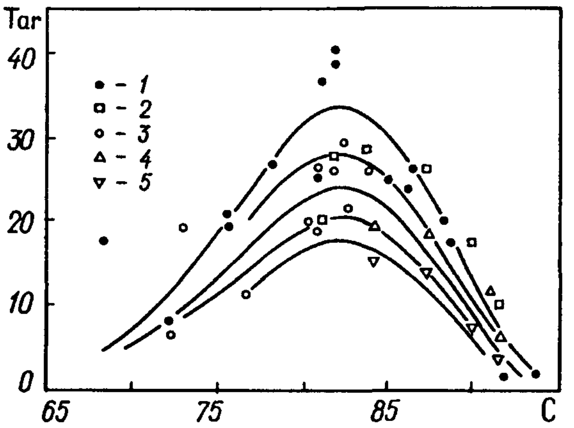
$$CO_2\colon\ Y_0 = 0.01375\,(1 - \text{Tar})\, O^{COOH},$$

$$CO\colon\ Y_0 = 0.01750\,(1 - \text{Tar})\, O^{CO},$$

$$H_2O\colon\ Y_0 = 0.01125\,(1 - \text{Tar})\, O^{OH},$$

$$CH_x\colon\ Y_0 = 0.01000\,(1 - \text{Tar})\, H^{al}\,(1 + 12/x), \qquad (8)$$

$$H_2\colon\ Y_0 = 0.01000\,(1 - \text{Tar})\, H^{ar},$$



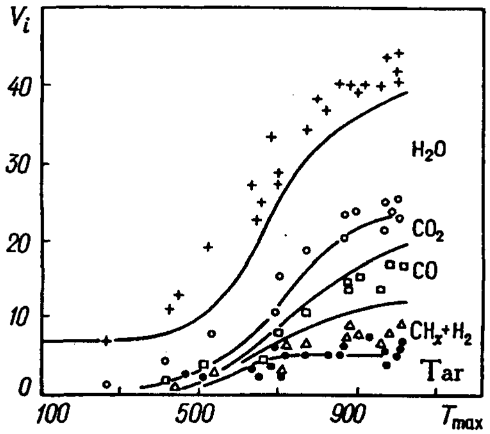


Fig. 1. Initial tar content (Tar) vs. the degree of coal metamorphism under high-speed pyrolysis conditions. The ambient pressure is $p_a = 10^{-5}$ MPa (1), 0.01 (2), 0.1 (3), 1 (4), 10 (5). Tar, C, daf%.

Fig. 2. Comparison of calculated and experimental yields of volatile components versus the maximum heating temperature for lignite from the state of Montana. The ambient pressure is $p_a = 0.1$ MPa. $V_i$, wt.%; $T_{max}$, °C.

$$\text{HCN: } Y_0 = 0.01930\,(1 - \text{Tar})\,\text{N}^{\text{daf}},$$

$$\text{tar} : Y_0 = \text{Tar}.$$

An important parameter of the process is the initial tar content (Tar) entering expressions (8) for the initial concentrations $Y_{i0}$. As results of experimental investigations show, Tar depends mainly on the type of coal and the pressure of the ambient gas $p_a$. In [15] an attempt was made to determine the empirical dependence of Tar on the elemental composition of the organic mass of coal and the pressure for fine coal particles from an analysis of numerous experimental data. We approximated these data by the simpler relation

$$\text{Tar} = 0.106z^2 \exp(-0.16z^2)\,[1 - 0.357 \arctan(0.5 \log p_a)], \tag{9}$$

where Tar is measured in mass fractions (daf), and $p_a$, in atm. In Fig. 1 results calculated by formula (9) are compared to the expermental data reported in [15]. For coarse coal particles the pressure inside a particle differs from $p_a$, and for fixed $r$ it is a function of $t$. Nevertheless, as the results given below show, the change in the pressure inside a particle is considerably smaller than the range of $p_a$ shown in Fig. 1. Therefore in the case of coarse particles, too, expression (9) can be used for determination of Tar.

The kinetic model suggested was employed for a test calculation of the yield of volatile the components as applied to combustion conditions of powdered coal in combustion chambers. As an example, we chose lignite from the state of Montana with a moisture content $W = 6.8$, an ash content $A = 9.9$, and the following elemental composition: $C^{daf} = 71.2$; $H^{daf} = 4.6$; $O^{daf} = 21.8$; $N^{daf} = 1.1$; $S^{daf} = 1.3$. Figure 2 shows calculated results in a comparison with experimental data of [16] (coal particles were heated at a rate of $10^4$ K/sec to a temperature $T_{max}$ and then cooled at a rate of 200 K/sec).

3. The algorithm suggested for calculation of the fields of $N_i$, $p$, $\rho$, $\varepsilon$, and $T$ inside a particle was used in combination with the kinetic model of release of the volatile components to calculate the dynamics of pyrolysis of coarse coal particles. As the first step in the calculation procedure, the initial concentrations of the functional groups $Y_{i0}$ were calculated by relations (8), (9). Next at a fixed moment of time $t$ the temperature field $T(r, t)$ was determined using expression (6), and then the rates of release of the functional groups into the pore space of the particle $G_i(r, t)$ were calculated. The next step was determination of the porosity $\varepsilon(r, t)$ by formulas (4), (1), and (2) beginning from the initial distribution $\varepsilon(r, 0) = \varepsilon_i$ and of the mass flows $N_i(r, t)$ and the pressure $p(r, t)$. The concentration of the gas components $y_i(r, t)$ was determined next from $y_i = N_i/N$, where $N = \sum\limits_i N_i$.

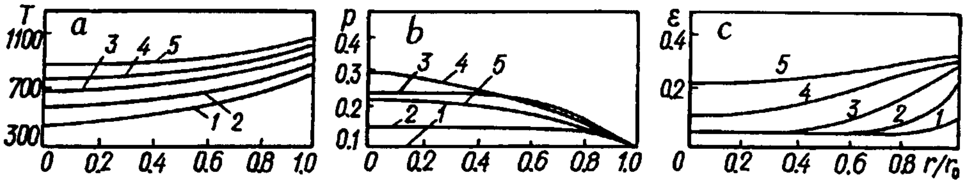


Fig. 3. Distributions of the temperature (a), pressure (b), and porosity (c) inside a particle of bituminous coal of radius $r_0 = 2.5 \cdot 10^{-3}$ m. The time of the pyrolysis process is $t = 10$ sec (1), 20 (2), 30 (3), 40 (4), 50 (5). The initial temperature of the particle is $T_0 = 300$ K, the ambient temperature and the ambient pressure are $T_a = 1400$ K, $p_a = 0.1$ MPa. $T$, K; $p$, MPa.

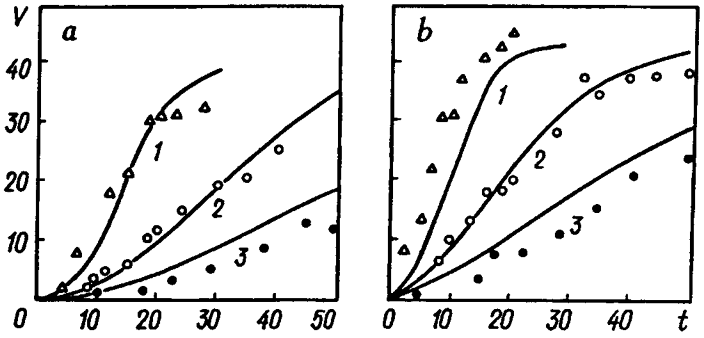


Fig. 4. Calculated and experimental total yields of the volatile components vs. the pyrolysis time for bituminous coal: $r_0 = 1.5 \cdot 10^{-3}$ m (1) 2.5 (2), 3.5 (3); $T_0 = 300$ K; $T_a = 1400$ K (a), 1700 (b). $V$, daf%; $t$, sec.

For the calculation we chose, as an example, bituminous coal with a moisture content $W = 1.5$, an ash content $A = 28.9$, and the elemental composition $C^{daf} = 83.9$, $H^{daf} = 5.3$, $O^{daf} = 8.3$, $N^{daf} = 1.7$, $S^{daf} = 0.8$. For the density, thermal conductivity, and heat capacity of the coal particles we took the following values: $\rho_s = 1.5 \cdot 10^3$ kg/m$^3$, $\lambda_s = 0.15$ W/(m·K), $c_s = 2.4 \cdot 10^3$ J/(kg·K) [17]. The viscosity and thermal conductivity of the surrounding medium (air) were calculated by the formulas $\eta = 1.34 \cdot 10^{-6} T_a^{1/2}$ kg/(m·sec), $\lambda_a = 2.11 \cdot 10^{-3} T_a^{1/2}$ W/(m·K) [18]. It was assumed that the increase in the particle porosity was caused by an increase in the micropore radius [4], i.e., the radius $a$ of the macropores, through which the volatile components escaped outward, did not change in the course of pyrolysis. The value was taken for $a$ $4 \cdot 10^{-7}$ m.

Figure 3 illustrates the distributions of the temperature $T$, pressure $p$, and porosity $\varepsilon$ inside a porous particle of radius $r_0 = 2.5 \cdot 10^{-3}$ m for different times of the process for $p_a = 0.1$ MPa and $T_a = 1400$ K. It is seen that the particle heating and, correspondingly, the process of pyrolysis last approximately a minute. The pressure inside the particle increases to about 0.3 MPa and then decreases to $p_a$. Figure 4 represents a comparison of the calculated total yield of volatile components $V$ with experimental data of [19] for particles of different sizes for different ambient temperatures. The calculated results are seen to be in rather good agreement with the experimental data.

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## NOTATION

$\rho$, gas density; $\varepsilon$, particle porosity; $y_i$, mass fractions of the gas components; $R_i$, rate of formation of the volatile components per unit volume of the particle; $G_i$, rate of release of the functional groups from the organic mass of coal; $N$, total mass flow of the volatile components released from the particle; $\rho_s$, density of the solid substance of the particle; $A^c$, ash content of the dry mass of coal; $A_{sec}$ and $E_{sec}$, kinetic parameters of the secondary reactions; $y_{tar}$, mass fraction of tar in the volatile components; $\xi_i$, mass fractions of the components in the products of thermal destruction of tar; $p$, pressure; $a$, mean radius of the pores; $\eta$, gas viscosity; $v_0$, mass-mean velocity of the gas inside the particle; $R$, gas constant; $T$, gas temperature; $\mu_i$, molecular weights of the gas components; $V_i(t)$, total releases of the volatile components to the surrounding medium in the time $t$; $r_0$, particle radius; $r$, radial coordinate inside the particle; $c_s$ and $\lambda_s$, heat capacity and thermal conductivity of the solid substance of the particle; $T_a$ and $\lambda_a$, ambient temperature and ambient thermal conductivity; Nu, Nusselt number; Bi, Biot number; Re, Reynolds number; Pr, Prandtl number; $Y_i$, concentrations of the functional groups in coal (kg/kg of the initial organic mass of coal); $A_i$, $E_i$, and $\sigma_i$, kinetic parameters of liberation of the functional groups from coal; Tar, initial tar content in coal.

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