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EVALUATION OF THE POROSITY OF A COKE PARTICLE ACCORDING TO ITS COMBUSTION DATA

The dependence of the density of a porous coke particle on its diameter at the particle combustion in the external diffusion mode is analyzed. It is shown that, for the large values of the internal diffusion-kinetic ratio, $Se_v > 5$, the required dependence can be obtained in the analytic form. The analytic formulas are found to be different for the bulk and Knudsen diffusion modes inside the pores. A graphical comparison of the obtained dependences with the empirical power-law dependence is carried out to evaluate the power exponents in the analytic dependences. The corresponding results make it possible to evaluate the effective specific surface area of the pores.

K e y w o r d s: particle, coke, combustion, porosity, diameter, density.

1. Introduction

If coal dust is used as a fuel, there arises an important issue concerning the prognosis of its burnout degree. Most of the works focus attention on the combustion kinetics and do not evaluate such properties as the particle diameter, density, porosity, the specific surface area of pores, and, all the more, variations of those parameters during the combustion. There are some experimental data on the changes of the diameter and the density of coke particles of various coal blends [1–4]. Despite that there is a large variance among them and the combustion of every coal must be analyzed separately, the dependence of the particle density ρ on the particle diameter d can be approximated by the formula

$$\frac{\rho}{\rho_0} = \left(\frac{d}{d_0}\right)^{\alpha}. \tag{1}$$

Different approaches and different measurement methods were applied in the relevant studies. In general, the fuel type, sizes of fuel particles, and combustion conditions (in particular, the combustion temperature) strongly affect the combustion regime. Furthermore, during the process of particle burning, both the particle porosity and the specific surface area of pores vary.

Most of the literature data are presented for high temperatures (1200–2200 K) and small particle sizes (from 10 to 100 μm). Those parameters are typical of the combustion of a pulverized coal torch [5]. As a rule, the density and the diameter of burning particles decrease in time in accordance with dependence (1), where the power exponent α acquires different values depending on external conditions.

As a parameter that allows the combustion mode of the particle to be identified [6, 7], the efficiency factor η is used. It is defined as the ratio between the effective reaction rate, which takes the mass transfer of an oxidant into account, and the rate of a chemical reaction. Its value varies within the interval $0 < \eta < 1$ and depends on the morphology of a particle material, as well as on the diameter and the specific surface area of pores. As a rule, larger values of the particle porosity, the specific surface area, and the pore diameter lead to higher particle combustion rates.

The combustion stage of a coke particle is considered to be the slowest. Its duration is governed by such factors as the oxidant diffusion to the outer particle surface and the surface of the pores in the carbon matrix, as well as the temperatures of the gas mixture and the particle itself. A specific feature of large coal particles is the fact that volatile gases escape from them before the combustion stage begins. Thus, only the coke residue burns. Coal coke with a high content of volatile gases is quite porous. Therefore, the change in the particle porosity during the combustion

can be substantial, although a lot of researchers believe that inner reactions play an insignificant role in the course of particle combustion.

At low temperatures, the surface reactions control the total reaction rate, and the reaction takes place in all pores ($\eta = 1$). The particle size remains practically constant, whereas the particle density gradually decreases.

At very high temperatures, the diffusion of an oxidant restricts the reaction rate. The reaction mainly takes place at the external surface of the particle ($\eta = 0$), and the oxidant concentration in the particle is close to zero. Therefore, the particle density remains unchanged during the combustion, whereas the particle diameter decreases.

The most interesting case, which is considered in this work, is an intermediate interval of combustion temperatures, when the density and the diameter of the particle decrease simultaneously in the course of particle combustion. Such oxidation regimes are usually established by reducing the oxygen concentration in the mixture (e.g., down to 5–10 vol%) [8]. In this case, the particle combustion temperature becomes considerably lower. A similar effect can be achieved, if the mixture temperature is low (cold mixtures). In the latter case, the combustion mode is implemented by the forced ignition [9].

The aim of this work was to analyze the dependences of the density of a porous carbon particle on its diameter to find regularities of the particle combustion in the external diffusion mode. Another aim was to analyze how the power exponent α in formula (1) depends on the origin of coal particles and their internal structure (porosity).

2. Formulation of the Problem

For the process of particle combustion, we may assume that this reaction runs in the diffusion region, and the particle combustion temperature changes rather weakly. The particle diameter decreases owing to chemical reactions I and II that run at the outer particle surface, whereas the particle density decreases owing to the reactions running in the pores. Then the decrease of the diameter d and the density ρ of a carbon particle in time can be described by the equations [10]

$$\rho \frac{\partial (d^2)}{\partial t} = - \left(\frac{100 - X_A}{100} \right)^{-1} \times$$

$$\times \frac{4M_{\mathrm{C}}}{M_{\mathrm{O}_2}} D_g Sh \rho_g Y_{\mathrm{O}_2} \frac{(k_1 + 2k_2)}{(k_1 + k_2 + k_v + U_{s0})}, \qquad (2)$$

$$d^2 \frac{\partial (\rho)}{\partial t} = - \left(\frac{100 - X_A}{100} \right)^{-1} \frac{6M_{\mathrm{C}}}{M_{\mathrm{O}_2}} \times$$

$$\times D_g Sh \rho_g Y_{\mathrm{O}_2} \frac{(k_1 + 2k_2)}{(k_1 + k_2 + k_v + U_{s0})} \frac{k_v}{(k_1 + k_2)}, \qquad (3)$$

$$d \, (t = 0) = d_0, \rho \, (t = 0) = \rho_0.$$

Here, ρ_{gs} is the density of a surrounding gas near the particle surface, kg/m³; M_{C} and M_{O_2} are the molar masses of carbon and oxygen, respectively, kg/mol; k_1 and k_2 are the rate constants of chemical reactions I and II, respectively; k_v is the effective constant of the inner reaction; Y_{O_2} is the relative mass fraction of oxygen in the gas; D_g is the oxygen diffusion coefficient in the gas, m²/s; ρ_0 is the initial particle density, kg/m³; and X_A is the mass fraction of ash in coal.

For experimenters, it is more convenient, if the dependences of the relative particle diameter and density on the unburned mass fraction of the particle are determined separately [1–3]. With a certain approximation, these dependences can be described by the following power-law formulas

$$\frac{\rho}{\rho_0} = \left(\frac{m}{m_0} \right)^{\frac{\alpha}{3+\alpha}}, \quad \frac{d}{d_0} = \left(\frac{m}{m_0} \right)^{\frac{1}{3+\alpha}}. \qquad (4)$$

The power exponents in dependences (4) vary within the limits $0 \le \frac{1}{3+\alpha} \le \frac{1}{3}$ and $0 \le \frac{\alpha}{3+\alpha} \le 1$.

To evaluate the rate of particle density change, let us divide formula (3) by formula (2). As a result, we obtain

$$\frac{\partial \rho}{\partial d} = 3 \frac{\rho}{d} \frac{k_v}{k_1 + k_2}. \qquad (5)$$

In the general case, the inner reaction constant depends on both the particle diameter and density. It is determined by the particle porosity χ and the specific surface area of the pores F_v as follows [11]:

$$k_v = \frac{2D_v}{d} (Se_v \coth Se_v - 1), \qquad (6)$$

where

$$Se_v = \sqrt{\frac{F_v d^2 (k_1 + k_2)}{4D_v}}$$

is the inner diffusion-kinetic ratio (the inner Semenov criterion), which determines the ratio between the

oxygen reaction rate and the oxygen mass transfer in the pores; D_v is the oxygen diffusion coefficient in the pores, m^2/s; and F_v is the specific surface area of the pores (the total surface area of the pores per unit volume of the particle), m^{-1}. Expression (6) does not allow the dependence $\rho(d)$ to be obtained in the analytic form. However, if the criterion $Se_v \geq 5$, this expression can be simplified:

$$k_v = \sqrt{D_v F_v\,(k_1 + k_2)}, \tag{7}$$

which testifies to the independence of this constant on the external diameter of the particle.

Let us assume that the inner diffusion coefficient and the specific surface area of the pores do not depend on the particle density. Then $k_v = $ const. By integrating Eq. (5), we obtain the power-law dependence of type (1), where

$$\alpha = 3\sqrt{\frac{D_v F_v}{k_1 + k_2}} = \text{const.}$$

3. Dependence of Particle Density on Particle Diameter

The internal diffusion coefficient and the specific surface area of the pores depend on the parameters of particle's internal structure and morphology. In order to take the bulk and Knudsen diffusions of oxygen in particle's porous structure into account, the effective diffusion coefficient D_{eff} can be used. It can be calculated according to the following expression [1, 12]:

$$\frac{1}{D_{\text{eff}}} = \frac{1}{D_g} + \frac{1}{D_{\text{K}}}. \tag{8}$$

Here,

$$D_{\text{K}} = \frac{2}{3} r_p \bar{u} \tag{9}$$

is the Knudsen diffusion coefficient for oxygen, which characterizes the transport through the pores the diameter of which is less than the free path length of oxygen;

$$r_p = 2\frac{\chi}{F_v}$$

is the average pore radius, m;

$$\bar{u} = \sqrt{\frac{8RT}{\pi \mu_{\text{O}_2}}}$$

is the velocity of the thermal motion of oxygen molecules, m/s;

$$\chi = 1 - \frac{\rho}{\rho_{\text{tr}}}$$

is the particle porosity; and ρ_{tr} is the density of the particle substance (matrix), kg/m^3.

Expression (9) for the Knudsen diffusion coefficient D_{K} was obtained in the framework of the kinetic theory of gas diffusion in a straight cylindrical pore [12]. To describe the oxygen diffusion coefficient in the pores, D_v, the relation [1, 12]

$$D_v = \frac{\chi}{\tau} D_{\text{eff}} \tag{10}$$

is used, where τ is the coefficient of pore tortuosity. The latter is introduced to take such factors into account as the tortuous path along which oxygen must diffuse, the influence of the intersection of separate pores, as well as various unknown degrees of anisotropy and heterogeneity in the varying pore structure. The value $\tau = \sqrt{2}$ is put for randomly oriented homogeneous pores [12]. As a rule, the value $\tau = 1.5$ is adopted.

From Eq. (8), one can see that the average pore radius depends on the specific surface area of the pores: $F_v = \rho F_m$, where F_m is the specific pore surface area in 1 kg of coke. The characteristic values of F_m are quite different. For instance, a value of 850 m^2/kg is indicated for electrode carbon with the density $\rho = 1600 \div 1700$ kg/m^3 [13]. For American coal with the density $\rho = 900 \div 1400$ kg/m^3 (the true density $\rho_{\text{tr}} = 1300 \div 1600$ kg/m^3), the specific pore surface is $100 \div 400$ m^2/kg [12]. For spherocarb particles with the density $\rho = 560$ kg/m^3, we have $F_m = 864 \times 10^3$ m^2/kg [3]. Some other values are: $F_m = 2 \times 10^3$ m^2/kg for petroleum coal, $F_m < 0.1 \times 10^3$ m^2/kg for metallurgical coke, and $F_m = 16.7 \times 10^3$ m^2/kg for charcoal [14].

Macropores are the largest pores [12, 15]. Their radius r_p exceeds 0.5×10^3 Å, and their specific surface area is $(0.5 \div 2) \times 10^3$ m^2/kg. The radius of intermediate pores is 8 Å $< r_p < 0.5 \times 10^3$ Å, and their specific surface area is up to 70×10^3 m^2/kg. The size of micropores is $r_p < 8$ Å, and their specific surface area is $(6 \div 17) \times 10^5$ m^2/kg.

With the increase in the carbon content in coke from 70% to 95%, the share of micropores in the total pore volume monotonically increases from 23%

to 75%, whereas the share of macropores decreases monotonically from 75% to 23% [12]. The volume ratio of intermediate pores reaches a maximum of 30% when the carbon content in coke equals 80%.

For the Knudsen diffusion mechanism to be applicable, the condition $Kn = l_p/d_p \gg 1$ for the Knudsen number Kn has to be satisfied. If we consider the temperature dependence of the free path length $l_p = l_{p0}T/T_0$, then, e.g., $l_p = 0.35$ μm at a particle temperature of 1500 K. According to Eq. (8), for characteristic values of the anthracite porosity ($\chi = 0.1$) and the specific surface area of pores ($F_v = 1.5 \times 10^6$ m^2/m^3), we obtain the average pore radius $r_p = 0.13$ μm ($d_p = 0.26$ μm). Therefore, the Knudsen diffusion regime can be active for the specific surface areas of pores $F_v > 10^7$ m^2/m^3. The corresponding value of the internal diffusion coefficient D_v is about 10^{-6}–10^{-7} m^2/s, which agrees with the data given in work [12].

Thus, for the Knudsen diffusion, we have

$$D_v F_v = \frac{4}{3} \frac{\bar{u}}{\tau} \chi^2,$$

and the explicit form for the internal reaction constant does not include the specific surface of pores. As a result, similarly to what was done in works [6, 7], Eq. (5) is transformed into the equation

$$\frac{d}{\rho} \frac{\partial \rho}{\partial d} = \alpha_0 \left(1 - \frac{\rho}{\rho_{tr}}\right). \tag{11}$$

Its solution can be represented in the form

$$\frac{\rho}{\rho_0} = \frac{\left(\frac{d}{d_0}\right)^{\alpha_0}}{1 - \left[1 - \left(\frac{d}{d_0}\right)^{\alpha_0}\right] \frac{\rho_0}{\rho_{tr}}}, \tag{12}$$

where

$$\alpha_0 = 3\sqrt{\frac{4\bar{u}}{3\tau} \frac{1}{k_1 + k_2}},$$

and d_0 and ρ_0 are the initial particle diameter and density, respectively. Thus, the coefficient α_0 depends on the pore tortuosity, the particle temperature, and the kinetic parameters of chemical reactions. A specific feature of this dependence is that α_0 does not depend on the specific surface area of pores in this case.

If the specific surface area of pores is not large [13], $D_{\text{eff}} \approx D_g$, and the coefficient of internal oxygen dif-

fusion is proportional to the molecular diffusion coefficient,

$$D_v = \frac{\chi}{\tau} D_g, \quad D_g = D_{g0} \left(\frac{T}{T_0}\right)^{n+1} \frac{P_0}{P}. \tag{13}$$

The specific surface area of the pores is a function of the particle porosity [13]:

$$F_v = F_{v0} \frac{\chi (1 - \chi)}{\chi_0 (1 - \chi_0)}, \tag{14}$$

where F_{v0} is the initial specific surface area of the pores, and χ_0 the initial porosity. The substitution of Eqs. (13) and (14) into Eqs. (5) and (7) leads to the equation

$$\frac{d}{\rho} \frac{\partial \rho}{\partial d} = \alpha_1 \left(1 - \frac{\rho}{\rho_{tr}}\right) \sqrt{\frac{\rho}{\rho_{tr}}}, \tag{15}$$

where

$$\alpha_1 = 3\sqrt{\frac{D_g F_{v0}}{\chi_0 (1 - \chi_0) \tau (k_1 + k_2)}}.$$

Its solution reads
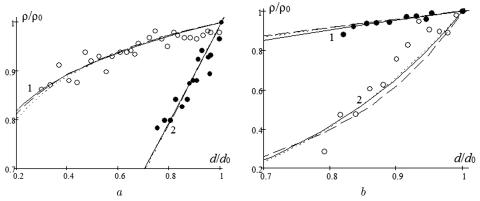
$$\left(\frac{d}{d_0}\right)^{\alpha_1} = \frac{\left(1 + \sqrt{\rho/\rho_{tr}}\right) \left(1 - \sqrt{\rho_0/\rho_{tr}}\right)}{\left(1 + \sqrt{\rho_0/\rho_{tr}}\right) \left(1 - \sqrt{\rho/\rho_{tr}}\right)} \times$$
$$\times \exp\left(2\sqrt{\frac{\rho_{tr}}{\rho_0}} - 2\sqrt{\frac{\rho_{tr}}{\rho}}\right). \tag{16}$$

So, in this case, the coefficient α_1 explicitly depends on the specific surface area of the pores.

4. Analysis of Results and Discussion

Thus, on the basis of experimental data obtained for the dependence of the coke particle density on the particle diameter, it is easy to find the experimental value of the power exponent α in dependence (1). The next step consists in the graphical comparison of dependences (12) and (16) with dependence (1) in order to determine the power exponents α_0 and α_1 at which the best agreement of those dependences takes place.

The results of processing the experimental data obtained for the coke and charcoal particles, whose parameters are quoted in Table 1, are depicted in Figure. The results for charcoal particles are obtained following the method of work [9]. Namely, charcoal particles were heated in a furnace to a temperature of 600–650 K. At this temperature, when being taken

Dependences of the density of a burning coke particle on its diameter: petroleum coke [2] (hollow circles) and spherocarb [3] (solid circles) (*a*); charcoal, $\rho_0 = 450$ (solid circles) and 350 kg/m^3 (hollow circles) (*b*). The evaluation formulas are (1) (solid curves), (12) (dotted curves), and (16) dashed curves

Table 1. **Parameters of cokes and calculated power exponents**

Coke type	E_1, kJ/mol	T_{bur}, K	d_0, μm	ρ_0, kg/m^3	α	α_0	α_0 by (17)	α_1
Petroleum coke	82.7	2000	85	1400	0.125	0.353	0.169	0.43
Spherocarb	84.0	1800	140	450	1	1.25	1.19	2.9
Charcoal − 1	75.0	1200	13200	450	0.45	0.55	0.50	1
Charcoal − 2	75.0	1200	11200	350	4	4.5	4.35	15

out from the furnace, the particle ignited and burned in the air environment at room temperature. The particle was mounted on a metal suspension which, in turn, was mounted on a microbalance. The evolution of the particle diameter in time was determined with the help of digital microscopy.

The obtained values of power exponents are given in Table 1. Attention is drawn by their substantial discrepancy. In work [6], a comparison of the power exponents α and α_0 was carried out, and the following approximate dependence for evaluating α_0 was proposed:

$$\alpha_0 = \alpha \left(1 + 0.25 \frac{\rho_0}{1000}\right). \tag{17}$$

However, the α_0-values calculated using this relation turned out substantially different from ours. In particular, according to formula (17), we have $\alpha_0 = 0.169$ for petroleum coke, $\alpha_0 = 1.12$ for spherocarb, and $\alpha_0 = 0.50$ and 4.35 for charcoal.

To evaluate the parameters characterizing the internal coal structure, let us consider the problem of isothermal combustion of coke particles giving rise to

Table 2. **Parameters of cokes and calculated power exponents**

Coke type	F_{v0}, m^2/m^3	F_{m0}, m^2/kg	Se_{v0}	D_{eff}/D_g
Petroleum coke	1.2×10^4	8.5	13.5	0.909
Spherocarb	2.5×10^5	530	51	0.987
Charcoal − 1	2.4×10^4	44	778	0.996
Charcoal − 2	2.0×10^6	5710	7390	0.749

the change of both the particle diameter and density. For this purpose, we have to numerically solve Eq. (5) in the general case, i.e. taking Eqs. (6) and (8) into account. This equation can be solved using the Cauchy method.

For each type of coke, a specific pore surface F_{v0} was determined (Table 2) at which the solution of Eq. (5) was graphically consistent with the empirical dependence (1). This was necessary to do in order to identify the dominating mechanism of diffusion in the pores. For this purpose, the effective oxygen diffusion coefficient was compared with the Knudsen and bulk diffusion coefficients in the gas. As a result, which of

the analytic solutions – Eq. (12) or Eq. (16) – can be used for the further analysis was determined.

The bulk diffusion is observed in all examined types of coal. Therefore, the obtained value of the power exponent α_1 can be used to find the specific surface area of the pores (Table 2). The calculated value agrees with the value obtained from the numerical solution of the exact model (5).

In general, the values obtained for the specific surface area of the pores turned out one to three orders of magnitude smaller than the values obtained using the BET or D-R methods. This is a result of the fact that, when a coke particle is burning, only some part of the whole pore surface is engaged, namely, this is a part that is close to the external particle surface. Therefore, the values obtained for the specific surface area of the pores can be regarded as effective.

5. Conclusions

Hence, the analytic relations between the density and the diameter of a burning coke particle can be derived for some combustion conditions, when the internal diffusion-kinetic ratio is large, $Se_v > 5$. In particular, when describing the diffusion of oxygen in the pores as the Knudsen diffusion, the obtained analytic expression includes the relative particle diameter raised to the power α_0. A similar result can be obtained by assuming the molecular diffusion of oxygen in the pores of coke particles. The obtained analytic power-law dependences are qualitatively different from the empirically obtained power-law dependence (1) with which they can be compared graphically. The obtained values of power exponents can be used to evaluate the effective specific surface area of the pores in coal coke.

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ОЦІНКА ПОРУВАТОСТІ ЧАСТИНКИ
КОКСУ ВУГІЛЛЯ ЗА ДАНИМИ ЇЇ ВИГОРАННЯ

Р е з ю м е

Проводиться аналіз залежності густини від діаметра поруватої частинки коксу при її горінні в зовнішньому дифузійному режимі. Показано, що при значеннях внутрішнього дифузійно-кінетичного відношення $Se_v > 5$ можливо в аналітичному вигляді отримати потрібну залежність. Вигляд аналітичної залежності різний у припущенні об'ємної дифузії і дифузії Кнудсена всередині пор. Проводиться їх графічне порівняння з емпіричною степеневою залежністю. Отримані таким чином значення показників степеня в аналітичних залежностях дозволяють оцінити ефективну питому поверхню пор.