

Analytical determination of temperature of ignition and extinction of carbon particles with regard to thermal radiation and simultaneous reactions

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Abstract

The article provides a method of analytical determination of temperature of ignition and extinction (of critical temperatures of the surrounding gas) and their degeneration depending on diameter of carbon particles. An analysis has been conducted with regard to the influence of the radiation heat transfer in conditions of simultaneous behavior of core heterogeneous reactions of carbon oxidation with the oxygen of gas mixture. It is shown that the point of minimum on the extinction curve and the points of degeneracy delimitate both the area of firing (hysteresis area) and the area of self-ignition of the carbon particle. An analysis has been conducted in respect of the influence which the concentration of oxygen has on the extinction downpoint temperature and on the behavior of degeneration of hysteresis loops at particle temperature dependence on temperature of the gaseous oxidizer and particle temperature dependence on its diameter in conditions when the values of the oxidizing agent concentration and gas temperature are constant. It was determined that the minimum point on the extinction curve and the degeneracy point in the area of large sizes are conditioned with radiation heat loss. In the area of small-sized particles, to the left of the minimum point, decreased diameter of the particles results in degeneration of the critical temperatures of ignition and extinction when the diameter of extinction is reached. An analysis has been made in relation to the influence of the initial critical temperature of particle on the temperature and the diameter of ignition. The limits of variation of the initial temperature of the particle to the extent of temperatures and diameters of ignition and extinction degeneration have been determined.

Key words: CARBON PARTICLE, DIAMETER, TEMPERATURE OF SELF-IGNITION, EXTINCTION, HYSTERESIS, RADIATIVE HEAT TRANSFER

Formulation of scientific problem and its meaning.

Maintenance of sustainable firing and self-ignition as well as further combustion of coke particles is required in various areas of its application. For example, burning of pulverized coal takes place in the combustion zone of a blast furnace or pulverized-coal-fired furnaces. In the first case the final product is carbon monoxide, CO, whereas in the second case the final product is carbon dioxide CO₂. This purpose and ensuring of complete combustion of the particles are achieved, as a rule, by varying the temperature of the gaseous mixture, fraction of oxygen in the mixture, size and concentration of the coal dust on entry to the reaction chamber [1-2]. Specifically, the size of particle plays a decisive role. High heat interchange from the very fine particles even to the heated gas serves to their self-ignition. As shown below, for large particles, the function of the radiation heat exchange in the processes of ignition and extinction determines

the minimum temperature of extinction and, consequently, ultimate value of the initial temperature of the particle's firing, and the degeneracy of the temperatures of ignition and extinction.

Problem research analysis.

It is known that the main heterogeneous reactions occurring on the surface of the carbon particle are the reactions of oxidation of carbon to carbon monoxide CO and carbon dioxide CO₂. At representative temperatures in metallurgical furnaces the process of formation of CO and CO₂ is determined by the collision mechanism between active molecules of oxygen and active atoms of carbon. That is why the oxygen takes the first order position in the kinetic equation. However, at low temperatures, it is more likely that CO₂ will be generated, a more stable oxide characterized with larger thermal effect and lower activation energy compared with the reaction of CO formation. As the temperature increases the active oxygen molecule

may interact with two atoms of carbon resulting in formation of two molecules CO. Semenov's theory allows us to determine approximately only the critical conditions for self-ignition of carbon particles assuming that one reaction is taking place in the kinetic area and there is no heat transfer due to radiation [3]. However, in the general case, including conditions of spontaneous and induced extinction, this problem has not been solved analytically [4].

At the same time, the experimental determination of the critical temperatures and extinction diameters under various external parameters is quite time-consuming task [5].

$$\frac{1}{6}c_c\rho_c d \frac{\partial T}{\partial \tau} = q_{eff}(T, T_g, Z_{ok}, d) = 0, T(\tau = 0) = T_b,$$

$$\frac{1}{2}\rho_c \frac{\partial d}{\partial \tau} = \frac{M_c}{M_{O_2}}(k_1 + 2k_2)\rho_g Z_{O_2,S}, d(\tau = 0) = d_b,$$

$$q_{eff} = q_{ch} - q_h, q_h = \beta c_g \rho_g Le^{-1+m} (T - T_g) + \varepsilon \sigma (T^4 - T_w^4),$$

$$\beta = \frac{D_a}{d_*}, d_* = \frac{d}{Sh}, Sh = NuLe^{-m},$$

$$q_{ch} = Q_1 k_1 (1 + Q_2 k_2 / Q_1 k_1) \rho_g Z_{O_2,S},$$

$$Z_{O_2,S} = \frac{Z_{O_2}}{1 + Se}, Se = \frac{k_1 + k_2}{\beta},$$

$$k_1 = k_{01} \exp\left(-\frac{E_1}{RT}\right),$$

$$k_2 = k_{02} \exp\left(-\frac{E_2}{RT}\right), Q_1 > Q_2, E_1 < E_2.$$

Where: - q_{eff} is effective thermal power density, Vt/m^2 ; q_{ch} - surface density of chemical thermal extraction, Vt/m^2 ; q_h - the surface density of cumulative heat losses Vt/m^2 ; Q_1, Q_2 - the heat effect of reaction of carbon oxidation to carbon dioxide and carbon **monoxide**, calculated per **1 kg of oxidant J/kgO_2** ; E_1, E_2 - energy of activation, J/mol ; k_1, k_2 - constants of chemical reactions; β - oxidizer mass transfer coefficient; the number Se - diffusion-kinetic relation; R - universal gas constant, $J/(mol \cdot K)$; T_w - temperature of walls, K ; ρ_g - density of gas, kg/m^3 ; C_g - gas specific heat, $J/(kg \cdot K)$; D_a - the coefficient of diffusion

The aim of this work is the analytical determination of critical temperatures and corresponding diameters of ignition, spontaneous and induced extinction of the carbon particles.

Physical and mathematical model.

Stable and critical modes of heat and mass transfer on the surface of carbon particle, defined by the temperature of the gaseous medium T_g , the relative mass concentration of the oxidizing agent Z_{ok} , the temperature T and the particle diameter d , are determined from the conditions of stationarity [6].

of the oxidant in the mixture, m^2/s ; ε - the emissivity factor of the particle's surface, σ - Stefan-Boltzmann constant, $Vt/(m^2K^4)$; Le - Lewis criterion; Sh - Sherwood criterion; m - the exponent depending on relation of the Sherwood criteria to Nusselt criteria from the criterion of Lewis.

Thermal-physical properties of gas dependence on temperature and pressure (p - gas pressure):

$$D_a = D_{a0} \left(\frac{T_*}{T_0}\right)^{n+1} \frac{p_0}{p}, c_g = c_{g0} + \Omega(T_* - T_0),$$

$$\rho_g = \rho_{g0} \frac{T_0}{T_*} \frac{p_0}{p}, T_* = 0.5(T + T_g).$$

All stationary states which are formed as the result of change of gas temperature, particle size, gas mixture speed, oxidant concentration, and accordingly particle temperature variations are described by differential equation:

$$-\frac{\partial q_{eff}}{\partial T} \partial T = \frac{\partial q_{eff}}{\partial T_{g\theta}} \partial T_{g\theta} + \frac{\partial q_{eff}}{\partial d_*} \partial d_* + \frac{\partial q_{eff}}{\partial Z} \partial Z. \quad (1)$$

Using this differential equation we can undertake a study of critical gas temperature dependence on carbon particle diameter. At constant values of particle diameter and oxygen concentration Z_{ok} the differential equation of stationary states (1) can be repre-

sented as follows:

$$\frac{\partial T_g}{\partial T} = - \frac{\partial q_{eff}}{\partial T} / \frac{\partial q_{eff}}{\partial T_g} \Big|_{Z_{ok} = const, d_* = const}$$

$$T_g = T + \frac{\varepsilon \sigma (T^4 - T_w^4)}{c_g \rho_g \beta} - \frac{Z_{ok}}{1 + Se} \frac{Q_1 k_{01} (1 + Q_2 k_2 / Q_1 k_1)}{c_g \beta} \exp\left(-\frac{E_1}{RT}\right) \quad (2)$$

$$\text{or } T_g = T + d_* \frac{\varepsilon \sigma (T^4 - T_w^4)}{c_g \rho_g D_a} - \frac{Z_{ok} d_*}{1 + d_* (k_1 + k_2) / D_a} \frac{Q_1 k_{01} (1 + Q_2 k_2 / Q_1 k_1)}{c_g D_a} \exp\left(-\frac{E_1}{RT}\right)$$

In critical points i and e, corresponding to self-ignition and extinction of the carbon particle, the Semenov condition is fulfilled $\partial q_{eff} / \partial T|_{i,e} = 0$. As the value $\partial q_{eff} / \partial T_g$ is always positive, so $\partial T_g / \partial T|_{i,e} = 0$. The equation $\partial^2 T_g / \partial T^2|_{i,e} = 0$ corresponds to the degeneration of critical and hysteretic conditions

From now on as the characteristic dimension of the particle we will use a value $d_* = d / Sh$, which

From the condition about stationarity of particle temperature we obtain gas temperature dependence on stationary temperature of a certain size carbon particle at a constant concentration of the oxidizing agent in the air (Fig. 1):

includes not only the particle size but also Sherwood criterion which acts as Reynolds number function. For fixed spherical particle Sherwood criterion is equal to two.

In a similar way from the temperature stationarity condition we can obtain particle diameter dependence on stationary temperature $d_*(T)$ we will present in the form of [6, 7]:

$$d_* = \frac{D c_g \rho_g (T - T_g)}{Q_1 k_{01} (1 + Q_2 k_2 / Q_1 k_1) Z_{o_2} \rho_g (A_0 \pm \sqrt{B_0^2 - A_0 C_0})} \exp\left(\frac{E_1}{RT}\right), \quad (3)$$

$$A_0 = \frac{(k_1 + k_2)(T - T_g)}{Q_1 k_1 (1 + Q_2 k_2 / Q_1 k_1) Z_{o_2}}, \quad C_0 = \frac{\varepsilon \sigma (T^4 - T_w^4)}{Q_1 k_1 (1 + Q_2 k_2 / Q_1 k_1) \rho_g Z_{o_2}}$$

$$B_0 = \frac{1}{2} (1 - A_0 - C_0)$$

At constant values of T_g, T_w, Z_{ok} the differential equation of stationary conditions (1) the following can be represented:

$$\frac{\partial d_*}{\partial T} = - \frac{\partial q_{eff}}{\partial T} / \frac{\partial q_{eff}}{\partial d_*} \Big|_{Z_{ok} = const, T_g = const, T_w = const}$$

In critical points i and e, corresponding to self-ignition and extinction of the carbon particle the Semenov condition is fulfilled $\partial q_{eff} / \partial T|_{i,e} = 0$. As the value $\partial q_{eff} / \partial T_g$ is not equal to zero, so $\partial d_* / \partial T|_{i,e} = 0$. $\partial^2 d_* / \partial T^2|_{i,e} = 0$ meets the degeneration of critical and hysteretic conditions.

Analysis of findings.

The calculations, as an example, were performed for anthracite coke of ASH (AIII) grade at the following parameters: $Q_1 = 12,34$ MJ/kgO₂, $Q_2 = 6,86$ MJ/kgO₂; $E_1 = 140$ kJ/mol, $E_2 = 154$ kJ/mol, $k_{01} = 6,5 \cdot 10^4$ m/s, $k_{02} = 12,5 \cdot 10^4$ m/s. Invariables: $D_{a0} = 3,2 \cdot 10^{-4}$ m²/s; $\rho_{g0} = 0,277$ kg/m³; $c_{g0} = 1185$ J/(kg·K);

$T_0 = 1273$ K; $\Omega = 0,18$ J/(kg·K²); $\varepsilon = 0,78$; $n = 0,75$, $Le = 1$.

Fig. 1a shows air temperature dependence on stationary temperature of the carbon particle of specified diameter and constant oxygen concentration. At low-temperature branch we can observe practically linear growth of the particle temperature with increase of gas temperature, that is explained by negligibly low heat losses for heat emission and practical absence of chemical reactions. At achieving of critical points of gas and particle temperatures (point i, self-ignition, maximum on the dependence $T_g(T)$) intermittent transition to high-temperature branch occurs (Fig. 1a). Further gas temperature increase leads to practically linear growth of the particle temperature. Self-ignition occurs for the particles [5-7], the size of which is greater than critical d_{*i} (fig. 1b).

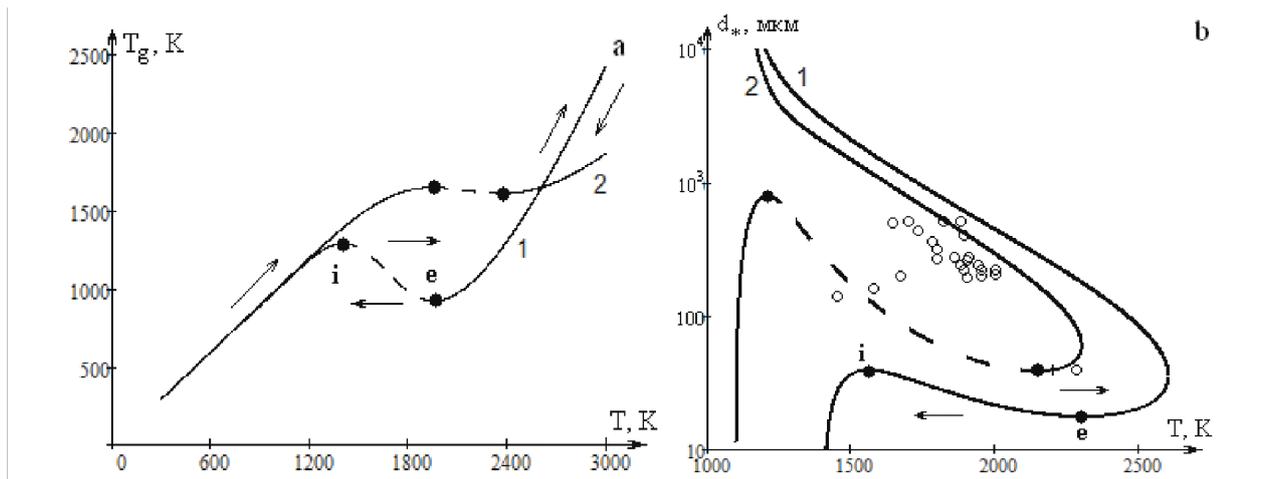


Figure 1. a) Gas temperature and b) particle diameter dependence on stationary temperature of the carbon particle at relative mass oxygen concentration $Z_{ok} = 0.23$ and $T_w = 1100$ K. a) 1 – $d_* = 50 \mu\text{m}$, 2 – $d_* = 10 \mu\text{m}$; б) 1 – $T_g = 1400$ K (o – experiment); 2 – $T_g = 1100$ K.

Full lines – stable (high and low temperature) modes, dotted – unstable critical conditions, related to the influence of initial particle temperature on critical ignition parameters.

The visible non-conformity of calculated and experimental data is explained not by taking account at this stage of Stefan flow, leading to combustion temperature decrease (the impact is stronger with temperature growth), and heat release inside particles pores (the impact is lower with temperature growth) [8-9].

If one reduces the gas temperature on high temperature branch so the achieving of critical points T_g and T (point e, extinction, minimum at $T_g(T)$ dependence) will result in intermittent transition to low-temperature branch. In the interval $T_i < T_{b.cr} < T_e$ the

dependence $T_g(T)$ describes the impact of initial temperature of the particle T_b on the ignition temperature (hysteretic mode). With the growth of particle initial temperature its ignition occurs at lower gas temperature (Fig. 1a).

To determine critical temperatures of self-ignition $T_{gi}(d_*)$ and extinction $T_{ge}(d_*)$ we use extremum conditions at the gas temperature dependence (2) on stationary particle temperature $\partial T_g / \partial T = 0$. As the result we obtain an equation for Semenov's number:

$$1 + (2 + A - B)Se - (1 + 2A + C)Se^2 + ASe^3 = 0, \tag{4}$$

$$A = \frac{4\varepsilon\sigma T^3}{c_g \rho_g (k_1 + k_2)}, \quad B = \frac{Z_{ok}}{c_g RT^2} \frac{Q_1 E_1 k_1 + Q_2 E_2 k_2}{k_1 + k_2},$$

$$C = \frac{Z_{ok}}{c_g RT^2} \frac{(Q_1 - Q_2)(E_1 - E_2)k_1 k_2}{(k_1 + k_2)^2}.$$

Two-of-three equation real roots (4) are positive:

$$Se|_i = u \left(-\frac{1}{2} - i \frac{\sqrt{3}}{2} \right) + v \left(-\frac{1}{2} + i \frac{\sqrt{3}}{2} \right) - \frac{2A + C + 1}{3A}, \tag{5a}$$

$$d_*|_i = \frac{D_a}{k_1 + k_2} \left(u \left(-\frac{1}{2} - i \frac{\sqrt{3}}{2} \right) + v \left(-\frac{1}{2} + i \frac{\sqrt{3}}{2} \right) - \frac{2A + C + 1}{3A} \right), \tag{5b}$$

$$Se|_e = u + v - \frac{2A + C + 1}{3A}, \tag{6a}$$

$$d_{*|e} = \frac{D_a}{k_1 + k_2} \left(u + v - \frac{2A + C + 1}{3A} \right), \quad (6b)$$

$$u = \sqrt[3]{-q - \sqrt{q^2 + p^3}}, \quad v = \sqrt[3]{-q + \sqrt{q^2 + p^3}}, \quad p = \frac{3A(2 + A - B) - (2A + C + 1)^2}{9A^2}$$

$$q = \frac{(2A + C + 1)^3}{27A^3} - \frac{(2A + C + 1)(2 + A - B)}{6A^2} + \frac{1}{2A}$$

Substitution of the dependencies (6) and (5) into (2) allows to obtain in parametric form the ignition and extinction critical temperature dependencies

on diameter of the particle $d_{*|i,e} = d_{i,e}(T)$, $d_{*|i,e} = d_{i,e}(T)$ (Fig. 2).

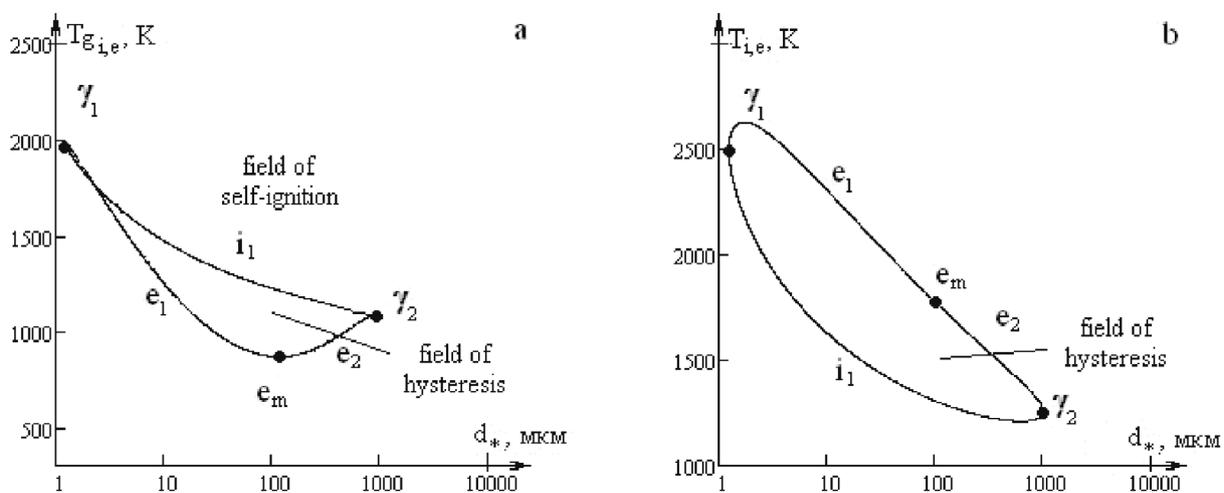


Figure 2. Dependencies of critical values of a) gas temperatures and b) carbon particle temperatures on its diameter without taking into consideration Stefan flow at $T_w = 1100$ K, $Z_{ok} = 0.23$, obtained on the dependencies (2), (5) и (6).

As it is seen from Fig. 2, in the result we have enclosed (hysteretic) area, limited by the obtained dependencies: self-ignition curve (point i) and extinction curve (point e). Hysteretic area is limited along the diameter from above and from below by degeneracy points.

On the extinction curve $T_{g,e} = f(d_e)$ we can observe a minimum, which is explained by the contest of two processes: on one hand, with particle diameter increase, there is a decrease of thermal flow density by molecular-convective way, on the other hand, the relative role of thermal radiation in total heat losses increases and mass flow density and hence the speed of reactionary thermal emission decrease. The minimum extinction temperature and its determinative particle diameter are obtained from the condition of minimum $T_g(d)$.

$$\frac{\partial T_g}{\partial d_*} = 0, \quad \frac{\partial T_g}{\partial T} = 0.$$

$$T_g = T - \frac{\varepsilon \sigma (T^4 - T_w^4)}{c_{pg} \rho_g (k_1 + k_2)} Se^2$$

$$Z_{O_2} = \frac{\varepsilon \sigma (T^4 - T_w^4)}{(Q_1 k_1 + Q_2 k_2) \rho_g} (1 + Se)^2$$

To the left of the minimum point (point e_m) for small sizes the radiation heat losses are small and are of no consequence. To the right of the minimum point the degeneracy point is sensitive to the temperature of the walls. At lower temperatures of the walls the degeneracy point γ_2 rises up, and a minimum point results at the self-ignition temperature dependence on the diameter of the particles.

$$1 + \frac{4\varepsilon\sigma T^3}{c_{pg}\rho_g\beta} = \frac{\varepsilon\sigma(T^4 - T_w^4)E_{ef1}}{c_{pg}\rho_g\beta RT^2} \left(1 + Se - \frac{E_{ef2}}{E_{ef1}} Se\right),$$

$$\left(1 + \frac{4\varepsilon\sigma T^3}{c_{pg}\rho_g(k_1 + k_2)}\right) Se = \frac{\varepsilon\sigma(T^4 - T_w^4)E_{ef1}}{c_{pg}\rho_g(k_1 + k_2)RT^2} Se \left(1 + Se - \frac{E_{ef2}}{E_{ef1}} Se\right)$$

$$E_{ef1} = \frac{Qk_1E_1 + Q_2k_2E_2}{Qk_1 + Q_2k_2}, E_{ef2} = \frac{k_1E_1 + k_2E_2}{k_1 + k_2}$$

At larger values of the wall temperature the degeneracy point γ_2 is shifted to the lower temperatures area. Only in the case of equality of gas and wall temperatures it is observed to reach a horizontal plateau of the self-ignition temperature dependence on the particle diameter at the degeneracy point γ_2 .

The obtained dependences allow to estimate conditions of self-ignition and firing of carbon particles under these external conditions. The considered processes are possible for particles with sizes $d_{\gamma_2} < d_* < d_{\gamma_2}$. For a selected diameter of this range a particle self-ignition is observed at gas temperatures $T_g > T_{gi}$. The smaller the particle, the harder it to ignite because of increase from the unit surface of heat exchange to the gas. As noted above ignition of particle is possible at temperatures of the

gas $T_{ge} < T_g < T_{gi}$. The most favorable conditions for ignition of the carbon particle are for particles which sizes are close in d_{em} . As this takes place, with an increase in particle size the range of the minimum initial temperatures of the particle (ignition temperatures) $T_i < T_b < T_e$ (fig. 2b) goes down towards lower temperatures.

It is important to analyze the effect of concentration of an oxidizing agent on hysteresis area. Fig. 3 shows dependences of gas temperatures and particle size, corresponding to boundary points (γ_1, γ_2, e_m), on concentration of oxidizer. Areas of ignition and extinction in diameter are expanding with increasing concentration of the oxidizing agent.

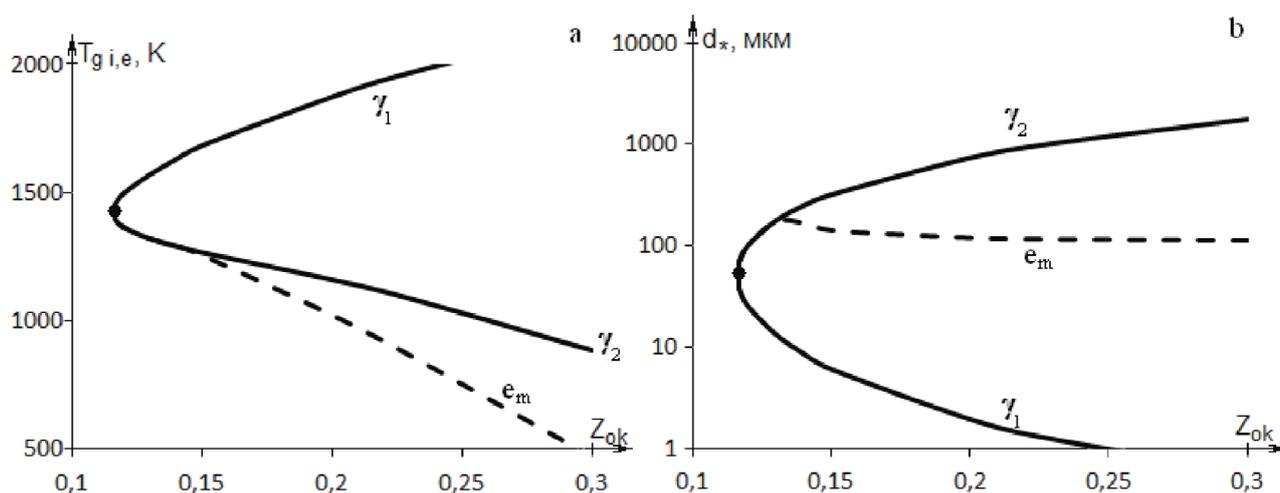


Figure 3. Influence of oxygen concentration on the parameters of degeneracy and limit values of extinction a) gas critical temperatures and b) critical diameters of particles defining hysteresis dependences $T_w = 1100$ K.

Naturally there is some minimum value of oxidizer concentration at which it is impossible neither to ignite, nor inflame a particle.

The diameter corresponding to optimum conditions of ignition (d_{em}) quite poorly decreases with an increase of oxidizer concentration. For the most interesting concentrations of the oxidizer $d_{em} > 100$

microns.

It should be noted that for this analysis the specified diameter has been selected which is Sh times smaller than the real size. Sherwood number for a spherical particle is greater than 2 and increases with growth of the level of convection.

Conclusions and prospects for further researches.

The proposed method allows to estimate quickly the ranges of parameters of the "carbon particles - gas" system, leading to the beginning of stable combustion and gasification of solid carbon particles, as well as the parameters of spontaneous and forced extinction. Although it is important to consider the influence of Stefan flow (mass flow directed from particle) and internal reaction in the pores on the critical conditions of endothermic heterogeneous reaction. Taking into account these factors we can explain more accurately the data regarding the combustion temperature of carbon particles [8-9].

References

1. Yaroshevskiy S.L. Reserves of combined blast efficiency at blast-furnace shops in Ukraine. Study of blast-furnace smelting processes. 2006. 366 p.
2. Kuniyoshi Ishii. Advanced pulverized coal injection technology and blast furnace operation. Eastbourne, Elsevier Science Ltd . 2000. 325 p.
3. Frank – Kamenetskiy D. A. Diffusion and heat transfer in chemical kinetics, Moscow Science. 1987, 491 p.
4. Zolotko A.N., Ushakova N.A., Demirova M.V. Heterogeneous ignition of individual particle with simultaneous chemical reactions on its surface. Physics of aerodisperse systems. 2010, No 47, p. p. 91-99.
5. Atsushi Makino (2013). Critical size for the particle burn-out of solid carbon and/or boron as the high-energy-density fuel. Combustion and Flame. Volume 160, Issue 3, p.p. 742-744.
6. Kalinchak V. V., Chernenko A. S., Zinchenko Y. A. (2013). Ignition, combustion and extinction of carbon particles at parallel-sequential formation of carbon oxides. Metal and casting in Ukraine. No 10, p.p. 21-27.
7. Kalinchak V.V., Chernenko A.S. (2013). Combustion and spontaneous extinction of porous carbon particles in nitrogen-oxygen mixtures at room temperatures. Physics of combustion and explosion. T. 49, No 2. p.p. 80-88.
8. Kalinchak V.V. (1994). Influence of radiation on critical conditions of heat and mass exchange at simultaneous reactions on particle surface. Physics of combustion and explosion. No 4, p.p. 63-74.
9. Kalinchak V. V., Orlovskaya S. G., Kalinchak A. I., Dubinskiy A. I. (1996). Heat and mass exchange of carbon particle with air taking into account of Stefan flow and radiation heat loss. Thermal physics of high temperatures. T.34, No 1, p.p.83-91.

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