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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...
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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].

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].

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

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

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

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

$q_{ch} = Q_k k_1 \rho_g Z_{O_2,S}, \quad Z_{O_2,S} = \frac{Z_{O_2}}{1 + Se}, \quad Se = \frac{k_1 + k_2}{\beta},$

$k_1 = k_{01} \exp \left( \frac{-E_1}{RT} \right), \quad k_2 = k_{02} \exp \left( \frac{-E_2}{RT} \right), \quad Q_1 > Q_2, E_1 < E_2.$

Where: $q_{eff}$ - is effective thermal power density, $\text{W/m}^2$; $\rho_{ch}$ - surface density of chemical thermal extraction, $\text{Wt/m}^2$; $\rho_{ch}$ - the surface density of cumulative heat losses $\text{Wt/m}^2$; $Q_1, Q_2$ - 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; $\beta$ - oxidizer mass transfer coefficient; the number $Se$ - diffusion-kinetic relation; $R$ - universal gas constant, $J/(mol\cdot K)$; $T_w$ - temperature of walls, $K$; $\rho_g$ - density of gas, $kg/m^3$; $C_g$ - gas specific heat, $J/(kg\cdot K)$; $D_a$ - the coefficient of diffusion of the oxidant in the mixture, $m/s$; $\varepsilon$ - the emissivity factor of the particle’s surface, $\sigma$ - Stefan-Boltzmann constant, $\text{Wt/(m}^2\text{K}^4)$; $Le$ - 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):

$D_a = D_{a0} \left( \frac{T_s}{T_0} \right)^{n_p} \rho_{g0} c_g = c_{g0} + \Omega (T_s - T_0),$

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

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:

$\frac{\partial q_{eff}}{\partial T} = \frac{\partial q_{eff}}{\partial T_g} + \frac{\partial q_{eff}}{\partial d} + \frac{\partial q_{eff}}{\partial Z}. \quad (1)$

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-
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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):

\[ T_g = T + \frac{\varepsilon \sigma (T^4 - T_w^4)}{c_g \rho_g \beta} \frac{Z_{ok}}{1 + S\varepsilon} - \frac{Z_{ok} d_s}{c_g \rho_g D_a} \frac{Q_{t_0} (1 + Q_2 k_2 / Q_1 k_1)}{1 + d_s(k_1 + k_2) / D_a} c_g k_1 \exp \left( - \frac{E_1}{RT} \right). \quad (2) \]

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

From now on as the characteristic dimension of the particle we will use a value \( d_s = d / Sh \), which 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 \( d_s(T) \) we will present in the form of [6, 7]:

\[ d_s = \frac{D c_g \rho_g (T - T_g)}{Q_{t_0} (1 + Q_2 k_2 / Q_1 k_1) Z_{ok} \rho_g (A_0 \pm \sqrt{B_0^2 - A_0 C_0})} \exp \left( \frac{E_1}{RT} \right), \quad (3) \]

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

\[ \frac{\partial d_s}{\partial T} = -\frac{\partial q_{eff}}{\partial T} \bigg|_{d_s = const, T_g = const, T_w = const}. \]

In critical points i and e, corresponding to self-ignition and extinction of the carbon particle the Semenov condition is fulfilled \( \partial q_{eff} / \partial T \bigg|_{i,e} = 0 \) As the value \( \partial q_{eff} / \partial T \) is not equal to zero, so \( \partial d_s / \partial T \bigg|_{i,e} = 0 \). \( \partial d_s / \partial T \bigg|_{i,e} = 0 \) 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: \( Q_1 = 12.34 \text{ MJ/kgO}_2; \ Q_2 = 6.86 \text{ MJ/kgO}_2; \ E_1 = 140 \text{ kJ/mol}, \ E_2 = 154 \text{ kJ/mol}, \ k_{on} = 6.5 \cdot 10^4 \text{ m/s}, \ k_{off} = 12.5 \cdot 10^4 \text{ m/s}. \) Invariables: \( D_0 = 3.2 \cdot 10^{-4} \text{ m/s}, \ \rho_{g0} = 0.277 \text{ kg/m}^3; \ c_{g0} = 1185 \text{ J/(kg-K)}; \)

\( T_0 = 1273 \text{ K}; \ \Omega = 0.18 \text{ J/(kg-K);} \ \varepsilon = 0.78; \ n = 0.75, \ Le = 1. \)

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 \( d_s \) (Fig. 1b).
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 $b$ 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 $T_{gi}(d_i)$ and extinction $T_{ge}(d_i)$ we use extremum conditions at the gas temperature dependence (2) on stationary particle temperature $\frac{\partial T_g}{\partial T} = 0$. As the result we obtain an equation for Semenov’s number:

$$1 + (2 + A - B)Se - (1 + 2A + C)Se^2 + ASE^3 = 0,$$

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

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

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

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

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

$$Se|_e = u + v - \frac{2A + C + 1}{3A}.$$
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 \( d_{i,e} = d_{i,e}(T) \) (Fig. 2).

As it is seen from Fig. 2, in the result we have enclosed (hysteric) area, limited by the obtained dependencies: self-ignition curve (point i) and extinction curve (point e). Hysteric 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–convectional 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 \( T_g(d) \).

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 \( y_2 \) rises up, and a minimum point results at the self-ignition temperature dependence on the diameter of the particles.
At larger values of the wall temperature the degeneracy point $\gamma_2$ 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 $\gamma_2$.

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 $d_{\gamma_2} < d_{\gamma_1} < d_{\gamma_2}$. 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 $d_{\gamma_m}$. As this takes place, with an increase in particle size the range of the minimum initial temperatures of the particle (ignition temperatures) $T_i < T_b < T_{ei}$ (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 ($\gamma_1$, $\gamma_2$, $e_m$), on concentration of oxidizer. Areas of ignition and extinction in diameter are expanding with increasing concentration of the oxidizing agent.

![Figure 3](image)

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($d_{\gamma_m}$) quite poorly decreases with an increase of oxidizer concentration. For the most interesting concentrations of the oxidizer $d_{\gamma_m} > 100$ 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