

POROUS CARBON PARTICLE COMBUSTION IN AIR

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Abstract

Theoretical investigation of porous carbon particle combustion in air is presented. The diffusive-kinetic model considering heat and mass transfer both inside the porous particle and over particle surface as well as kinetic equations of both heterogeneous and homogeneous reactions is investigated. It is shown the homogeneous reaction may be considered as diffusive-limited reaction for rather large size of the particle. Two regimes of the carbon particle combustion are observed: (1) high-rate regime for large internal surface of the particle and (2) low-rate regime for the particle with lower internal surface. The temperature of the particle is decreased with rate of the particle combustion increasing in high-rate regime because inside the particle the endothermic reaction of carbon with carbon dioxide is occurred. In low-rate regime the temperature of the particle is increased with rate of the particle combustion increasing because the reaction of carbon with oxygen takes place inside the particle. The dependence of the rate of the particle combustion on the value of internal surface is determined. The distributions of the concentrations and flows of reactants on radial coordinate as well as rates of the reactions are determined both inside the porous particle and outside the particle..

Introduction

In the theory of porous carbon particle combustion and gasification next positions have to be taken into account [1]: the intensity of the combustion process is depended as on kinetics of the chemical reactions so on mass and heat transfer of reactants and reactions products (2) burning out of carbon particle takes place on the internal surface inside the particle and at the particle external surface (3) the products of the carbon particle interaction with oxygen are both carbon monoxide and carbon dioxide.

The absence of the kinetics equations of the heterogeneous reactions of carbon with gaseous reactants is a main hindrance for theory of carbon particle combustion and gasification development.

The diffusive-kinetic model for porous carbon particle combustion in pure oxygen has been considered [2, 3]. Two regimes of the carbon particle combustion are existed: (1) low-rate and high-rate regimes. The heterogeneous reactions of carbon with oxygen are occurred in both low-rate and high-rate regimes of the particle combustion in pure oxygen. The difference between the regimes of the particle combustion was connected with formation of carbon dioxide in low-rate regime and consumption of carbon dioxide inside the porous particle in high-rate regime. It is interesting to consider the combustion of the carbon particle in environment with lower concentration of oxygen, for example, in air because oxygen may be supplied totally in homogeneous reaction over particle surface and that does not reach the particle surface. Besides such kind of carbon particle combustion is more impotent for practice.

Diffusive-kinetic model of porous carbon particle combustion

The diffusive-kinetic model considers porous carbon particle having radius a what is burning out in air in a furnace with wall temperature T_w . The model considers the equations of diffusion and heat transfer what are written in form of elements (carbon and oxygen) and full enthalpy conservation.

$$\text{div} \Sigma \frac{m_j I_j}{\mu_j} = \frac{W_s}{\mu_c} \quad (1)$$

$$\text{div} \Sigma \frac{n_j I_j}{\mu_j} = 0 \quad (2)$$

$$\text{div}(I_j h_j + I_h) = s W h_c - I_R \delta(r-a) \quad (3)$$

Here $j=1, 2$ and 3 correspond to CO_2 , CO and O_2 , $I_R = \sigma(T_0^4 - T_w^4)$ is heat losses by radiation, m_j and n_j are numbers of carbon and oxygen atoms in molecular of substance considering. The rate of carbon consumption inside the particle equals to sum of the rates of heterogeneous reactions of carbon with reactants and that is proportional to the value of the internal surface of the porous particle. If mass flow of gas through unit surface is denoted $U = \varepsilon \rho u$ than the mass flows of substances and heat may written in form

$$I_j = U z_j - \varepsilon \rho D \text{grad} z_j, \quad I_h = U c T - [\varepsilon \lambda_g + (i - \varepsilon) \lambda_c] \text{grad} T \quad (4)$$

Here λ_g and λ_c are coefficients of heat conductivity in gas and in solid carbon.

The equation of gas discontinuity is

$$\text{div} U = R_s \quad (5)$$

The equation for pressure alteration inside the porous particle is determined by Darcy' law

$$\varepsilon u = -\frac{k}{\mu} \text{grad} P \quad (6)$$

Besides the diffusive equation for carbon dioxide including kinetic equations for chemical reactions have to be considered

$$\text{div} I_3 = -\left(\frac{\mu_3}{\mu_c} R_o - \frac{\mu_3}{\mu_c} R_c + \frac{\mu_3}{2\mu_1} \varepsilon R_g\right) \quad (7)$$

Here R_c and R_o are the rates of heterogeneous reactions of carbon with carbon dioxide and with oxygen correspondingly and R_g is the rate of homogeneous reaction.

Boundary conditions for equations (1)-(7) are

$$r = 0, \quad U = 0, \quad I_j = 0, \quad I_h = 0, \quad \frac{dP}{dr} = 0 \quad (8)$$

$$r = \infty, \quad z_j = z_j^\infty, \quad T = T_w, \quad P = P_0 \quad (9)$$

Equations (1)-(3) may be integrated over radial coordinate. Excluding the summary rate of carbon consumption from equations (1) and (5) and integrating the equations with boundary conditions (8) the next correlations between flows of different substances are received

$$\sum \frac{m_j I_j}{\mu_j} = \frac{U}{\mu_c} \quad (10)$$

$$\sum \frac{n_j I_j}{\mu_j} = 0 \quad (11)$$

$$\sum I_j h_j + I_h = U h_c - I_R \frac{a^2}{r^2} \theta(r-a) \quad (12)$$

The left side of the equation (12) includes the summary flow of full enthalpy in gas and the flow of heat inside the solid carbon. If heat effects of the reactions are high and porosity of the particle is rather high as well the heat flow in solid carbon will be negligible in comparison with flow of full enthalpy in gas.

The equations (10)-(12) may be integrated over radial coordinate once more with boundary conditions (9) if it is assumed the criteria Lewis equals to unit. In the result of integrating in account of $c = c_{in} + \sum z_j (c_j - c_{in})$ next equations may be received

$$\sum \frac{m_j z_j}{\mu_j} = e^{-\eta} \left(\sum \frac{m_j z_j^\infty}{\mu_j} - \frac{1}{\mu_c} \right) + \frac{1}{\mu_c} \quad (13)$$

$$\sum \frac{n_j z_j}{\mu_j} = e^{-\eta} \sum \frac{n_j z_j^\infty}{\mu_j} \quad (14)$$

$$r > a: \quad \sum z_j (h_j + c_j T) = e^{-\eta} \left[\sum (z_j^\infty + c_j T_w) + \frac{I_R}{U_0} \right] - \frac{I_R}{U_0} \quad (15)$$

$$r < a: \quad \sum z_j (h_j + c_j T) = e^{-\eta} \left[\sum (z_j^\infty + c_j T_w) + (1 - e^{-\eta_0}) \frac{I_R}{U_0} \right] \quad (16)$$

Here $\eta = \int_r^{\infty} \frac{U}{\varepsilon \rho D} dr$

The equation (6) may be integrated on radial coordinate also if it's assumed the value p/ρ is not altered inside the particle

$$\begin{aligned} r < a & \quad P^2 = P_0^2 + \frac{\eta - \eta_0}{\kappa} ; \\ r > a & \quad P = P_0 \end{aligned} \quad (18)$$

Here $\kappa = k\rho_0/2\mu\rho D p_0$ is parameter determining gas penetration of porous particle and alteration of pressure inside the particle and $\eta = \eta_0$ if $r = a$. $\eta_0 = aU_0/\rho D$ is dimensionless' rate of the particle combustion.

Regimes of the porous carbon particle combustion in air

The equations (13)-(16) are valid both in gas phase over particle surface and inside the porous particle. Consequently these equations are valid at the particle surface as well.

The solution of the equations (13)-(16) at the particle surface has a sense if concentrations of all substances at the particle surface are positive values. This condition determines a domain where the solutions of the equations are existed. Such domain is shown in fig.1 for case of carbon particle combustion in air in a furnace with wall temperature $T_w = .1500$ K. The domain is restricted by curves a , b and c where concentrations of CO_2 , CO and O_2 equal to zero correspondingly. The point A where the rate of the particle combustion reaches maximum value corresponds to diffusive-limited rate of the particle combustion $\eta_0 = 0.159$. Besides curves 1 and 2 are shown in the fig.1 where the flow of carbon dioxide equals to zero and condition of homogeneous reaction equilibrium is fulfilled correspondingly.

The rate of the homogeneous reaction $2CO + O_2 = 2CO_2$ is determinate by the equation [4]

$$R_g = \frac{d[CO_2]}{dt} = 1.05 \cdot 10^{10} \exp(-14293/T)[CO][O_2]^{0.5}[H_2O]^{0.25} \quad (19)$$

where concentrations are determined in units mol/liter

The dependence of the rate of the homogeneous reaction on concentration of steam is rather weak. However, the presence of steam is need for this reaction caring out. In the following calculations the dependence of the rate of homogeneous reaction on concentration of steam is not taken into account.

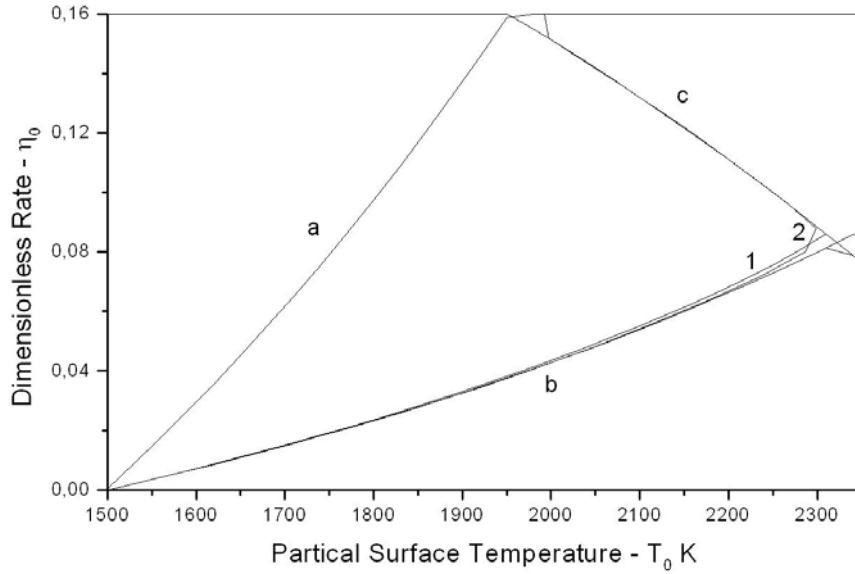


Figure 1 The domain where the solutions of the equation are existed.
 1 – flow of carbon dioxide equals to zero, 2 – equilibrium of homogeneous reaction.

It may be assumed the homogeneous reaction is carried out in diffusive-limited regime for rather high temperature what is realized in process of carbon particle combustion. The diffusive-limited regime is realized if the rate of the homogeneous reaction determining by the equation (19) is higher the rate of the reaction R_d determining by the diffusive flows of reactants.

The diffusive-limited rate of the homogeneous reaction is determined from the equation

$$\frac{1}{\xi^2} \frac{dJ_1}{d\xi} = W_d \quad (20)$$

Here $J_1 = \varepsilon \rho D I_1 / a^2$ and $W_1 = \varepsilon \rho D R_d / a^2$ are dimensionless flow of carbon dioxide and diffusive-limited rate of the homogeneous reaction.

If the homogeneous reaction is carried out in diffusive-limited regime the concentrations of reactants will equal to equilibrium concentrations. So the condition of the homogeneous reaction equilibrium is written in form

$$z_2 z_3^{1/2} = k_e z_3 \quad (21)$$

Here k_e is constant of the reaction $CO + 0.5O_2 = CO_2$ equilibrium determined from [5].

From the condition that diffusive-limited rate is lower the kinetic rate of the homogeneous reaction next correlation may be received

$$a \geq (\rho D R_d / R_g)^{1/2} \quad (22)$$

Figure 2 shows the dependence the minimum radius of carbon particle when correlation (22) is fulfilled on radial coordinate over particle surface. The calculations have been fullfielded for case of the rate of the particle combustion $\eta_0 = 0.14$ and for furnace temperature $T_w = 1500 K$. So it may be considered the equilibrium of the homogeneous reaction is valid for radius of carbon particle more $12 \mu k\mu$.

If the assumption about equilibrium of homogeneous reaction is valid the real dependence of the particle combustion rate on the particle surface temperature is determined by curve 2 in the fig.1. In this case two regimes of the carbon particle combustion in air may be considered: (1) low-rate regime where temperature of the particle is increased with rate of the particle combustion increasing and (2) high-rate regime where the temperature of the particle is decreased with the rate of the particle combustion increasing.

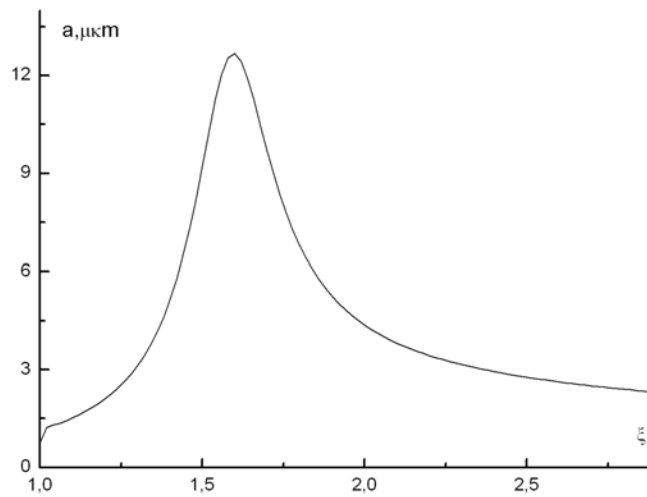


Figure 2. The dependence of minimum radius of the particle on radial coordinates when the homogeneous reaction is carried out in diffusive-limited regime.

Figure 3 shows the dependence of the flows of substances to the particle surface on the rate of the particle combustion in air for furnace temperature $T_w = 1500 K$ and for size of the particle corresponding parameter $A = a / \rho D = 1$ what is correspond to $a \approx 1 \cdot 10^{-4} m$. In the high-rate regime oxygen is supplied in the homogeneous reaction over particle surface practically totally and that does not reach surface of the particle. The consumption of carbon determining the rate of the particle combustion is occurred by mean of endothermic reaction of carbon with carbon dioxide because the temperature of the particle is decreased with rate of the particle combustion increasing.

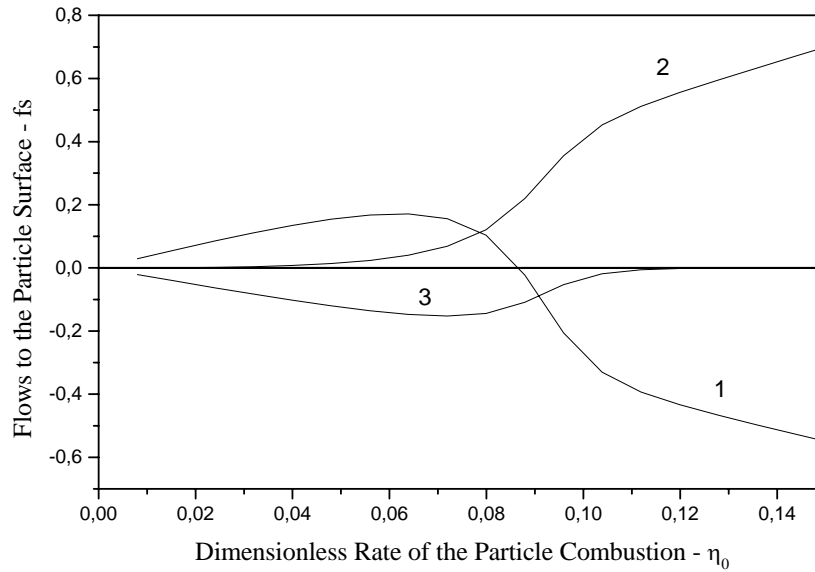


Figure 3. Dependence of the substances flows to the particle surface on the rate of the particle combustion in air: 1 - CO_2 , 2 - CO , and 3 - O_2 .

In the low-rate regime of the particle combustion oxygen reaches the particle surface and the reaction of oxygen with carbon is occurred inside the porous particle. The product of the particle combustion in low-rate regime is carbon dioxide (see fig.3). The homogeneous reaction over particle surface in low-rate regime is practically absent.

Figure 3 shows the high-rate regime of the carbon particle combustion in air is occurred if the rate of the particle combustion $\eta_0 > 0.1$ but low-rate regime is realized if $\eta_0 < 0.06$. At the middle rates of the particle combustion ($0.06 < \eta_0 < 0.1$) is carried out transition regime. In this regime the flow of oxygen to the particle is decreased but flow of carbon dioxide is altered the direction with rate of particle combustion increasing.

Processes inside the porous carbon particle

The rate of porous carbon particle combustion is depended on summary rates of heterogeneous reactions what is proportional to internal surface of porous carbon particle. The rate of porous carbon particle combustion has to be determined from the consideration of processes inside the porous particle. It may be done if kinetic equations for heterogeneous reactions of carbon with oxygen and with carbon dioxide are known.

The kinetic equation of the reaction of carbon with carbon dioxide to unit of the internal surface may be considered as known [6]

$$R_c = 760 \exp(-30205 / T) \rho \frac{\mu_c}{\mu_3} z_3 \quad (23)$$

The dependence of the rate of porous carbon particle combustion on particle temperature for case of the particle combustion in oxygen is presented in [7]. This dependence for low rate of the particle combustion and for the particle temperature near to furnace temperature may be written in form

$$R_o = 2.023 \cdot 10^2 \exp(-25070 / T) \rho \frac{\mu_c}{\mu_1} z_1 \quad (24)$$

Using the equations for the rates of heterogeneous reactions (23)-(24) the equation of discontinuity (5) may written in form

$$\frac{1}{\xi^2} \frac{d\beta}{d\xi} = (\Phi_o + \Phi_c) S \quad (25)$$

$$\frac{d\eta}{d\xi} = -\frac{\beta}{\xi^2} \quad (26)$$

Here $\Phi_o = R_o A$ and $\Phi_c = R_c A$ are the dimensionless rates of the reactions of carbon with oxygen and with carbon dioxide correspondingly, $S = sa / \varepsilon$ and function $\beta = \xi^2 d\eta / d\xi$ determines the rate of gaseous flow of the reactions products.

The internal surface of the carbon particle may be altered [8] with carbon particle burning out. However here it will be assumed the internal surface of the particle is constant and that is not depended on radial coordinate.

The equations (13)-(15) together with condition of the homogeneous reaction equilibrium (21) may be solved and concentrations and temperature are determined as a function η . So the rates of the reactions Φ_c and Φ_o are the function of η also. In this case the equations (25)-(26) may be integrated with boundary conditions

$$\xi = 0, \quad \beta = 0; \quad \xi = 1, \quad \eta = \eta_0, \quad \beta = \beta_0 = \eta_0 / \varepsilon_0 \quad (27)$$

Here ε_0 is porosity at the particle surface.

So the distributions of function β and η as well as concentrations and temperature on radial coordinate ξ inside the porous particle are determined. The additional boundary condition. (27) gives the possibility to determine the parameter S corresponding to the rate of the particle combustion η_0 . The dependence of the parameter S on the rate of the particle combustion is shown in fig. 4. In the high-rate regime the rate of the particle combustion is increased with parameter S increasing. But in the low-rate regime the value of the parameter S is not increased with the rate of the particle combustion increasing monotony. So, two rates of the particle combustion are realized for the same value of the parameter S . The decreasing of the parameter S with η_0 increasing is connected with sharp increasing of the particle temperature in low-rate regime. Because the rate of the particle combustion η_0 is increased with the particle temperature increasing stronger then that is increased with parameter S increasing. It may be assumed the

realization of different regimes of the particle combustion for the same internal surface of the particle is connected with process of the particle ignition. If the carbon particle is ignited by mean of high temperature of environment gas the high-rate regime of the particle combustion is realized but if the particle is ignited by means of radiation when the temperature of the particle is higher the environment gas the low-rate regime of the particle combustion will be realized.

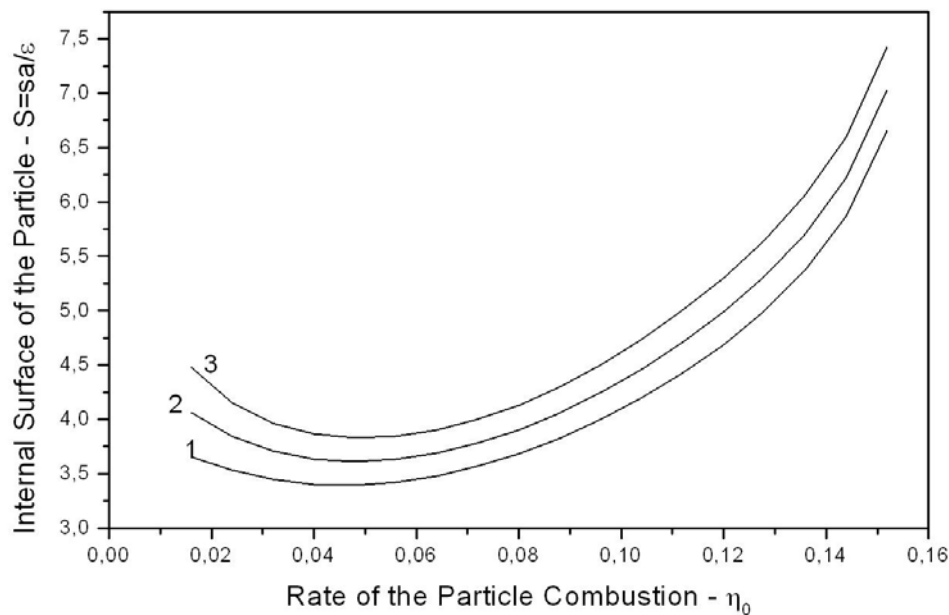


Figure 4. Dependence of parameter S on the dimensionless rate of the particle combustion for different furnace temperature : 1 - $T_w=1300$ K, 2 - 1500 K, 3 – 1700 K.

Conclusion

The theoretical diffusive-kinetic model is considered for porous carbon particle combustion in air. The investigations show:

- two regimes of the carbon particle combustion in air are realized in dependent on the value of the internal surface of the particle: (1) low-rate regime and (2) high-rate regime,
- in the high-rate regime the endothermic heterogeneous reaction of carbon with carbon dioxide is occurred therefore the temperature of the particle is decreased with the rate of the particle combustion increasing,
- in the low-rate regime the heterogeneous reaction of carbon with oxygen is occurred,
- the homogeneous reaction of carbon monoxide with oxygen is carried out in diffusive-limited, equilibrium regime for the carbon particle rather large size,
- the dependence of the carbon particle combustion rate on the value of the internal surface of the porous particle is determined,
- the distributions of reactants concentrations and flows as well as rates of heterogeneous and homogeneous reactions on radial coordinate inside the porous particle are determined as well.

Nomenclature

a	radius of the particle
C_j	heat capacity of gaseous substances to kmoll
c_j	heat capacity of gaseous substances to kg
D	diffusivity
I_j	fluxes of substances
I_h	flux of heat
H_j	enthalpies of substances formation from elements to kmoll
h_j	enthalpies of substances formation from elements to kg
h_c	enthalpy of solid carbon
k	gas penetration of porous particle
m_j	numbers of atoms of carbon in molecular of substance
n_j	numbers of atoms of oxygen in molecular of substance
R_g	rate of homogeneous reaction
R_c	rate of the reaction of carbon with carbon dioxide
R	rate of carbon consumption in heterogeneous reactions
R_{o1}	rate of carbon consumption in the reaction $C + O_2 = CO_2 + 2H_2$
R_{o2}	rate of carbon consumption in the reaction $2C + O_2 = 2CO$
P	pressure in units of atmosphere
r	radial coordinate
s	internal surface of the particle
T	temperature
T_w	temperature of furnace
T_0	temperature of the particle surface
U	mass flux of gas
u	velocity of gas
z_j	mass fractions

z_j^∞ mass fractions in environment

z_j^0 mass fractions at the particle surface

Greek symbols

λ heat transfer coefficient in gas

μ viscosity of gas

μ_j molecular mass of gaseous substances

μ_C molecular mass of carbon

ε porosity of the particle

ρ density of gas

σ Stephan-Boltsman constant

Indexes j:

1 CO_2

2 CO

3 O_2

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