Single Coal Char Particle Combustion in the Carbon Dioxide Atmosphere*

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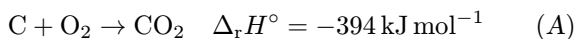
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The combustion of single coal char particle in carbon dioxide atmosphere was studied. In experiments, brown coal from coal mine Cígeľ (Slovakia) has been used. The combustion was monitored using the TGA method. The experimental equipment allowed to study the mass of the particle and temperatures inside of the particle and on its geometrical surface. Time dependences of these parameters were measured during combustion in different gas mixtures of carbon dioxide and argon (5—100 vol. % of CO_2) and in the temperature range 800—1300 °C. For some samples, the properties such as pore size distribution, specific surface area, and porosity were determined by the mercury porosimetry and the nitrogen sorption method. The results showed that coal char particle combustion proceeded *via* a homogeneous mechanism. The microstructure properties of a partially combusted particle showed an important increase in the specific surface area compared to the original coal char particle, which was mainly formed by micropores. Such partially combusted particle can be used as a cheep adsorbent.

The mechanism of coal combustion is very complicated. It consists of various processes, which proceed at various rates. Their duration depends on the combustion conditions and the origin of coal. The combustion process of single coal particle starts immediately after its entry into the combustion device. In the first step, a rapid release of humidity and volatile compounds occurs due to a high temperature. Then, after the release of volatile substances, both the coal char as a solid residue and volatile substances start burning independently. The process of coal char oxidation is not simple. Besides heterogeneous reactions of carbon with oxygen or carbon dioxide, homogeneous reaction of carbon monoxide oxidation takes place [1].

The main heterogeneous reactions, which can be assumed, are

$$C + O_2 \rightarrow CO_2 \quad \Delta_r H^\circ = -394 \, \text{kJ mol}^{-1} \quad (A)$$

$$C + 1/2O_2 \rightarrow CO \quad \Delta_r H^\circ = -110 \, \text{kJ mol}^{-1} \quad (B)$$

$$C + CO_2 \rightarrow 2CO \quad \Delta_r H^\circ = 174 \, \text{kJ mol}^{-1} \quad (C)$$

and the main homogeneous reaction is the oxidation of carbon monoxide to carbon dioxide

$$CO + 1/2O_2 \rightarrow CO_2 \quad \Delta_r H^\circ = -284 \, \text{kJ mol}^{-1} \quad (D)$$

Even more complex reaction schemes are available in literature. These involve partial reactions as the chemisorption of gaseous reactants and consecutive decomposition reactions of surface complexes. In addition, if the combustion proceeds in air, reactions of nitrogen to nitrogen oxides can occur, especially at higher temperatures [1].

Combustion of coal char is a typical noncatalytic gas—solid reaction process, which can proceed somewhere between two limiting mechanisms: the homogeneous and the shell progressive [2]. In our previous works [3, 4], we determined the narrow region of the conditions (low temperatures, low oxygen concentrations), in which combustion proceeds by homogeneous mechanism. At other conditions, the shell progressive model can describe the mechanism of the coal char combustion.

The lumped kinetic scheme (*A*—*D*) is usually used to describe mathematically the process of coal char combustion. From these reactions, only the reaction (*C*) can be studied separately. All other reactions, *i.e.* (*A*), (*B*), and (*D*) proceed simultaneously as parallel and consecutive reactions. Moreover, only the reaction
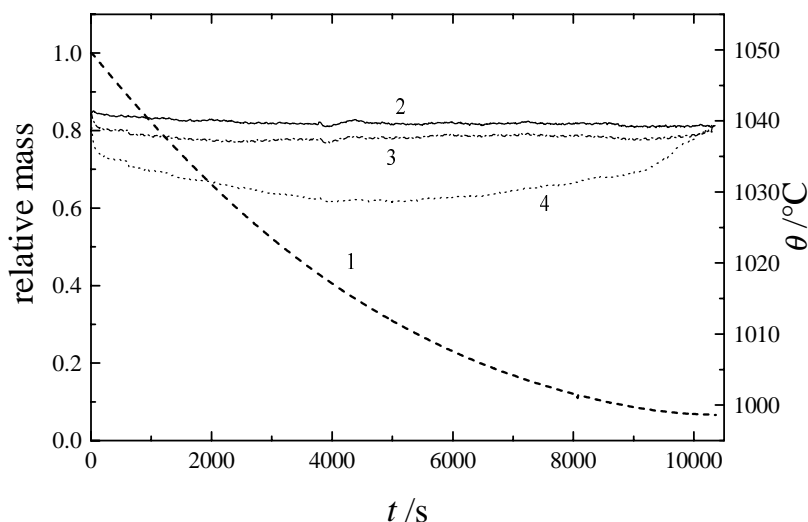
Fig. 1. Coal char combustion by CO_2 (5 vol. %) at temperature 1040 °C. Time dependence of the relative mass of particle (*1*) and the temperature bulk gas flow (*2*), close to the particle surface (*3*) and inside of the particle (*4*).

(*C*) is endothermic, whereas the others are strongly exothermic.

The aim of this work was the investigation of combustion of a single coal char particle in the atmosphere of carbon dioxide (pure or in the argon mixture). Based on experiments, performed in laboratory equipment described in detail in our previous work [3] and on the micropore structure analysis, both the mechanism of the process and conditions, under which this reaction significantly influences the overall process of combustion, were determined.

EXPERIMENTAL

Coal from the coal mine Cígeľ (Slovakia) was used. Coal char was prepared by slow degassing of the original coal particle in nitrogen up to 1100 °C. The combustion experiments were carried out in an equipment described previously [3]. Atmosphere with different carbon dioxide concentrations (5—100 vol. %) in argon was used. The initial temperatures of combustion varied within the range from 800—1300 °C. The particle diameter was about 1 cm. The volumetric flow-rate of the inlet feed was about 100 dm^3 h^{-1}. Combustion of the particle was conducted up to the desired mass of the particle (50 %—100 % of the carbon burnout). The mass of the particle, temperature in the particle centre, particle surface, and temperature of gas closed to the geometrical surface of the particle were measured continuously.

The overall reaction activity of the coal char particle depends on the accessibility of the internal surface of coal char to the gaseous reactant (CO_2), which is determined by its pore structure. Using the principles of gas adsorption (SORPTOMATIC 1900, Fisons, Milan, Italy) and mercury penetration (Porosimeter P2000, Fisons, Milan, Italy), the identification of the pore structure of the original, degassed, partially and completely burned particles was performed.

RESULTS AND DISCUSSION

Figs. 1 and 2 show the time dependence of relative particle mass and temperatures in the centre, on the geometrical surface and in the gas phase close to the particle. The feed concentrations of CO_2 in the experimental run were 5 vol. % (Fig. 1) and 100 vol. % (Fig. 2), respectively. The initial temperature was 1040 °C in both cases. The experiments were prolonged until a complete carbon burnout in the particle has been reached. Figs. 1 and 2 show that the rate of the process was very strongly influenced by the concentration of carbon dioxide when the reaction time was practically four times shorter in the case of pure carbon dioxide atmosphere. On the other hand, a very fast reaction inside the particle in the case of a pure carbon dioxide atmosphere caused a rapid decrease in the temperature in the particle which was about 40 °C in the centre of the particle and 15 °C on the surface of the particle. If the external heat transfer is not sufficient to sustain the heat consumption in the particle, the resulting large temperature drop in the particle can significantly decrease the reaction rate in the particle.

Figs. 3 and 4 present the time dependences of carbon conversion in the particle at different conditions. We can conclude from these results that both temperature and the concentration of carbon dioxide in the bulk gas phase strongly influence the overall rate of the process. Fig. 3 reveals that there was no difference between runs with pure carbon dioxide and those with 50 vol. % of CO_2. This could be caused, as we discussed above, by a significant decrease of temperature in the coal char particle at the beginning of the run with pure CO_2, and a consecutive decrease in the reaction rate. On the other hand, at the lower bulk
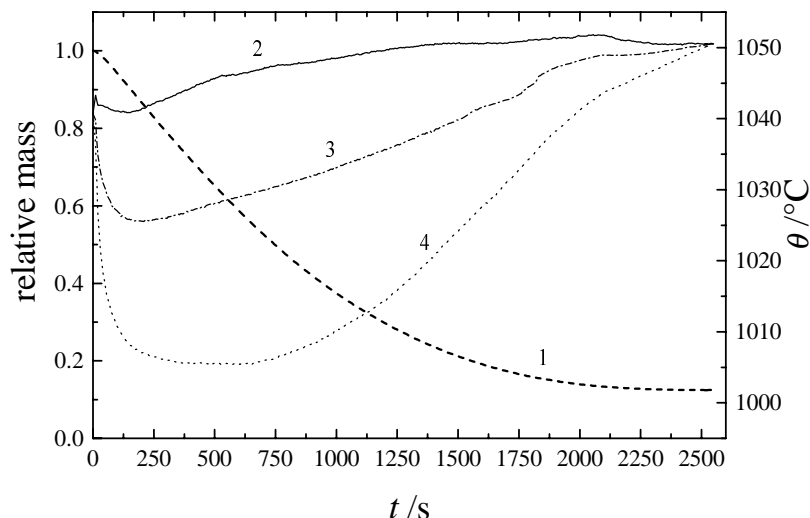
Fig. 2. Char combustion by CO$_2$ (100 vol. %) at temperature 1040 °C. Time dependence of the relative mass of particle (*1*) and the temperature bulk gas flow (*2*), close to the particle surface (*3*) and inside of the particle (*4*).
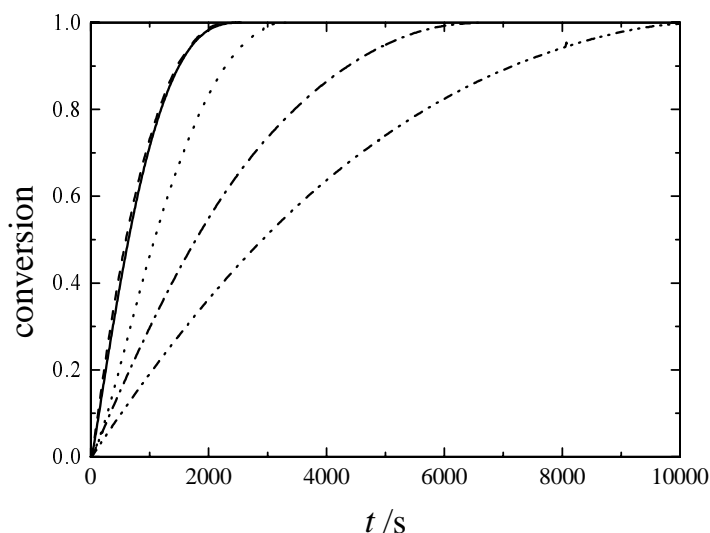

Fig. 3. Carbon conversion *vs.* time for different initial mole fraction of carbon dioxide in argon at 1040 °C (—— 1.00, – – – 0.50, · · · 0.25, — · — 0.10, — · · — · · 0.05).

concentrations of CO$_2$ and temperatures, the time dependences of the conversion were as expected.

The pore size distributions of the original coal char particle obtained by standard sorption and mercury porosimetry methods are shown in Figs. 5 and 6, respectively. These are compared with the pore size distribution of 50 % burnout particles obtained at different atmospheres and of ash after complete combustion of the particle.

Fig. 7 gives the comparison of the specific surface area formed by different pore regions for particles burned at different conditions. For illustration, there is also the specific surface area of a particle, with 50 % burnout in the atmosphere with 5 vol. % of oxygen at 460 °C where the mechanism of combustion was homogeneous.

Fig. 7 further shows that the specific surface area of the original coal particle can be negligible. After the degassing of the particle, the specific surface area was significantly increased. The pore structure was formed by micropores, mesopores, and with a small fraction of macropores. On the other hand, the specific surface area of ash, after complete burnout of carbon, was formed mainly by macropores with the pore radius greater than 500 nm.

In the case of the particle combustion in an atmosphere with low concentration of oxygen and low temperature, the specific surface area after a 50 % burnout was increased to the value of about 200 m^2 g^{-1}, and was formed predominantly by mesopores (about 50 %). The contribution of micropores was 30 % and of macropores 20 %. The particle was homoge-
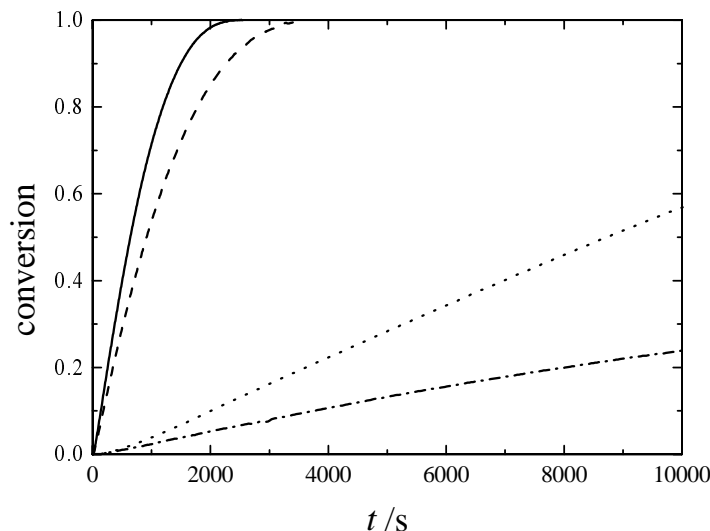
Fig. 4. Carbon conversion *vs.* time for different initial temperatures in atmosphere of pure CO_2 (——— 1040 °C, – – – 950 °C, $\cdots$ 850 °C, $- \cdot - \cdot$ 740 °C).
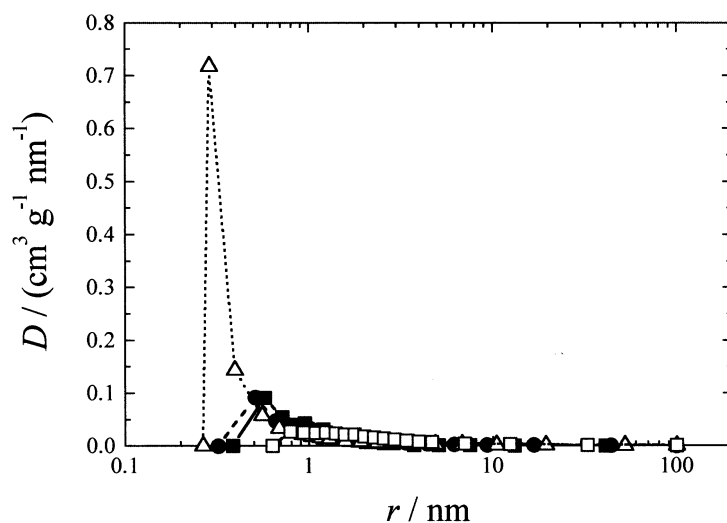

Fig. 5. Changes of the pore structure of the coal char particle in the microporous region depending on the combustion conditions and degree of combustion (0 % (——■——), 50 % in 5 vol. % CO_2 (– ● –), 50 % in pure CO_2 ($\cdot \cdot \triangle \cdot \cdot$), and 100 % burnout ($- \cdot \square - \cdot$)), initial temperature 1040 °C.

neous at these combustion conditions and of the mechanism of the process was assumed to be homogeneous as well. At higher temperatures or higher concentrations of oxygen, the combustion proceeded by the shell progressive mechanism and the particle was divided to two regions: a shell formed by ash with a pore structure formed mainly by macropores, and a core with a pore structure very close to the structure of the coal char particle.

If the particle was burnt in the atmosphere containing carbon dioxide, the pore structure after the partial burnout depended on the bulk carbon dioxide concentration combustion conditions (Figs. 5—7). The internal surface was formed by micro- and mesopores in both cases. When pure carbon dioxide was used, a significant increase in the specific surface area,

comparable with the one obtained at combustion in the oxygen atmosphere, was observed (Fig. 7). In the latter case, micropores with the pore radius less than 1 nm formed a predominant part of internal surface (Fig. 5). On the other hand, if the combustion was performed in the atmosphere with 5 vol. % of CO_2, the specific surface area was lower (approximately 60 % of the specific surface area obtained with pure CO_2) and was created mainly by mesopores. This can be explained by different rates of the reaction and diffusion in the particle. When combustion proceeds with pure carbon dioxide, the reaction rate is higher than that in the case of burning in the atmosphere containing 5 vol. % of CO_2. Because the reaction is strongly endothermic, the heat consumption by this reaction can significantly decrease the temperature inside the par-
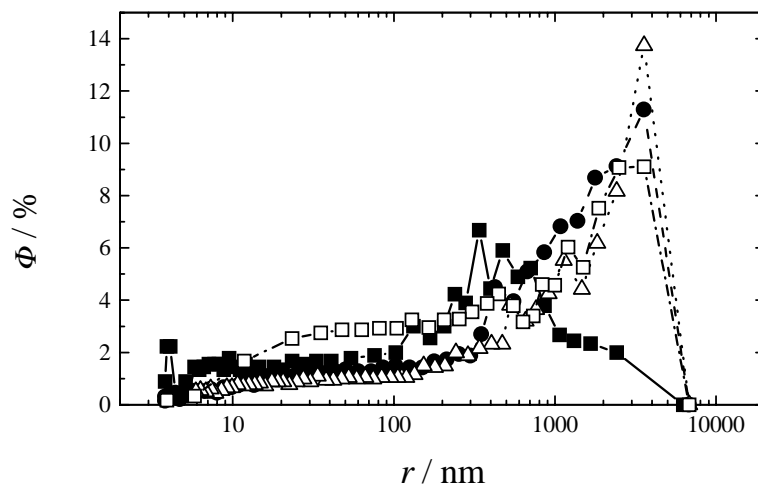
Fig. 6. Changes of the pore structure of the coal char particle in the mesoporous region depending on the combustion conditions and degree of combustion (0 % (—■—), 50 % in 5 vol. % CO$_2$ (– ● –), 50 % in pure CO$_2$ ($\cdots\triangle\cdots$), and 100 % burnout (– · □ – ·)), initial temperature 1040 °C.
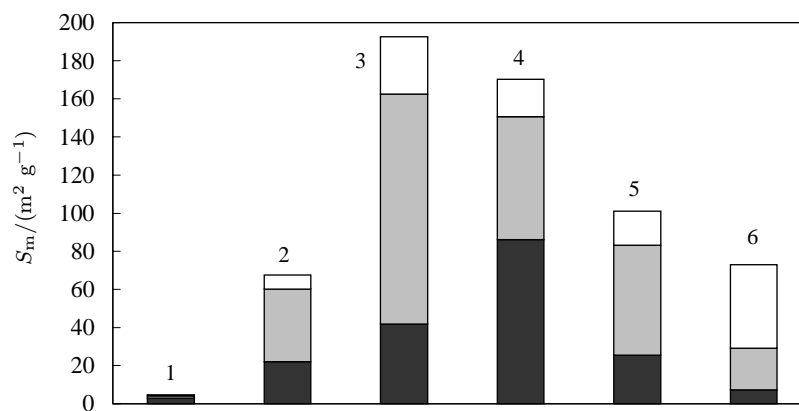

Fig. 7. Comparison of specific surface area of particles burned at different conditions. 1 – coal particle, 2 – coal char particle, 3 – 50 % burnout in 5 vol. % O$_2$ in Ar at 460 °C, 4 – 50 % burnout in pure CO$_2$ in Ar at 1040 °C, 5 – 50 % burnout in 5 vol. % O$_2$ in Ar at 1040 °C, 6 – ash (□ macropores, ▨ mesopores, ■ micropores).

ticle (Fig. 2) and consequently decrease the reaction rate. The diffusional flux of CO$_2$ into the coal char particle should be much higher in the case of pure CO$_2$ because of a higher concentration gradient. This allows carbon dioxide to penetrate towards the interior of the particle, and react in its whole volume.

CONCLUSION

The study of single coal particle combustion in carbon dioxide is presented. Combustion experiments were carried out in equipment by applying the TGA method. We can conclude from the pore structure of partially burned particles that the combustion of particle proceeds by a homogeneous mechanism in a wide range of temperature and concentration of carbon dioxide. On the contrary, oxidation of coal char particle by oxygen proceeds by a shell progressive mechanism [3, 4]. The homogeneous mechanism can

be assumed only at low temperatures and low oxygen concentrations. When the particle is burnt with oxygen by the homogeneous mechanism, the pore structure of partially burnt particle is created mainly by mesopores. On the contrary, the pore structure of a particle partially burnt in carbon dioxide is formed by micropores with a narrow zone of pores with the radius less than 1 nm. This fact indicates that it is possible to prepare cheep adsorbents with specific surface area comparable with some industrial adsorbents (about 200 m^2 g^{-1}) by partial burning of coal char particle in carbon dioxide. Such an adsorbent is useful in the case when for economical reasons there is no interest to desorb adsorbed compounds and it is more convenient to burn the adsorbent together with adsorbed compounds.

SYMBOLS

D differential pore size distribution function
$$\text{cm}^3\ \text{g}^{-1}\ \text{nm}^{-1}$$

ΔH° standard reaction enthalpy kJ mol^{-1}

r pore radius   nm

S_m specific surface area $\text{m}^2\ \text{g}^{-1}$

t time   s

Φ relative volume of pores   %

θ temperature   ℃

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