

Experimental Study of Single Coal Char Particle Combustion Mechanism*

J. MARKOŠ**, R. ŽAJDLÍK, B. REMIAROVÁ, and Ľ. JELEMENSKÝ

*Department of Chemical and Biochemical Engineering, Faculty of Chemical and Food Technology,
Slovak University of Technology, SK-812 37 Bratislava
e-mail: markos@cvt.stuba.sk*

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An experimental study of single coal char particle combustion at different conditions is presented. Based on the results of thermogravimetric measurements and on the analysis of pore structure development during the combustion, the mechanism of combustion was described. It was shown that the combustion, depending on operating conditions (temperature, oxygen content), could proceed both by the shell progressive mechanism and by the reaction-diffusion mechanism with diffusion of oxygen as a rate-controlling step. At low temperatures and low oxygen contents in the feed stream, oscillations of temperature inside the pellet could be observed.

At present time, coal is mostly used as a source of energy and heat by combustion with air in industrial combustors (fluidized bed, grate combustors, fixed bed, moving bed). Coal combustion is a complicated process, which consists of various partial processes, depending on the coal history (age of coal, composition of coal, source of the coal mine, *etc.*). A lot of papers are available in the literature dealing with the experimental study of coal combustion and theoretical (mathematical) description of the coal combustion process. In our earlier paper [1], we presented a brief review of these works. Since coal is a natural material and its properties vary from mine to mine, a number of papers present a comparison of combustion of various samples from different sources at the same conditions (temperature, oxygen feed concentration, *etc.*). In our previous papers [2–4], we have studied the combustion mechanism of brown coal from the same source (mine Cigeľ, Slovakia) at different conditions. Steep temperature and content (oxygen, carbon dioxide, carbon monoxide) gradients exist in industrial combustors, depending on their constructions and performance conditions. It means that the moving coal particle in the bulk volume of the combustor can be surrounded by different environment during its existence in the combustion equipment. This fact can significantly influence the overall rate of combustion. As a result, ash particles outgoing from the device contain various amounts of noncombusted carbon, which decreases the efficiency and increases the negative en-

vironmental impact of the process.

The aim of the presented paper was an experimental study of single coal char particle combustion at different initial temperatures and different oxygen contents in the feed stream. Our attention was focused especially at low temperatures and low oxygen contents. The combustion experiments proceeded at a different degree of burnout and the resulting particles were analyzed to obtain the information about their microporous structure. A combustion mechanism and conditions of its change were determined from the obtained data.

THEORETICAL

Combustion of coal is a complicated process and the main oxidation products are carbon dioxide and carbon monoxide. The principal heterogeneous exothermic reactions between solid carbon and gaseous oxygen are coupled with homogeneous exothermic oxidation of carbon monoxide to carbon dioxide and heterogeneous endothermic reaction of carbon dioxide with solid carbon. However, the reaction mechanism of formation of individual products has been subject of many discussions. Besides of principal reactions, numerous reactions of other elements and compounds present in the system take place [1].

Coal combustion consists of two steps:

1. After the entry of a coal particle into the combustion device, a rapid release of humidity and volatile

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**The author to whom the correspondence should be addressed.

compounds is observed. These volatile compounds are then burned in the gaseous phase. As a result of degasification, the microporous structure of the particle is changed [3, 4].

2. The resulting coal char particle starts burning itself with the combustion rate in orders of magnitude lower than that of combustion of volatile compounds but the major part of the heat released in the combustor is generated in this phase.

From the chemical reaction point of view, the coal char particle combustion represents a noncatalytic gas—solid reaction system. This process can be described by the general reaction-diffusion mechanism assuming interfacial and intraparticle gradients [6], which can be simplified to the shell progressive mechanism. This mechanism can be applied for some limiting cases [5], especially for a nonporous original particle, high temperature and high reaction rate with respect to the diffusional transport through the ash layer. The mathematical model equations, describing the single coal char particle combustion depend then on the combustion mechanism applied. Since the principal reactions which take place inside the particle are strongly exothermic, the burning particle can be overheated and the model equations have to take into account variations of the temperature inside the particle. In the case of the reaction-diffusion mechanism, the solid reactant (carbon) is consumed in the whole volume of the particle, which results in a continuous change of the particle porosity and consequently, the change of effective diffusivity [6]. On the other hand, if the combustion mechanism can be described by the shell progressive model, the particle of the coal char is divided into two parts: the shell, formed by ash without any carbon, and the core, formed by original coal char. The reactions proceed only on the very sharp interface between the shell and core. It means that the radius of the core is decreasing with time, but the microstructure of the core remains constant. On the contrary, the width of the shell is growing but its microstructure is constant, too.

EXPERIMENTAL

The experimental equipment used in this study was in detail described in our previous works [2—4]. The thermogravimetric method was applied with on-line measurements of the mass of the single coal particle together with on-line measurements of the flue gas composition, temperatures in the particle centre, on the particle surface and in the gas phase close to the surface. Combustion experiments consisted of several steps: preparation of the particle, drying, devolatilization, and burning of the resulting coal char [2—4]. The experimental conditions are summarized in Table 1. The combustion of particle proceeded to different degrees of burnout (25 %, 50 %, 75 %, and 100 %). The porous structure of original and partially combusted

Table 1. Experimental Conditions of Combustion

Temperature/°C	460—800
Pressure/Pa	1.01×10^5
Inlet content of oxygen/mole %	5—15
Mass of the coal particle/kg	0.4×10^{-3} — 0.6×10^{-3}
Mass of the degassed particle/kg	0.2×10^{-3} — 0.3×10^{-3}
Original coal particle diameter/m	8×10^{-3} — 1×10^{-2}
Coal char particle diameter/m	7×10^{-3} — 8×10^{-3}
Flow rate of gas/(m ³ s ⁻¹)	$(1.4—5.6) \times 10^{-5}$

particles (the specific surface area, specific volume of pores, pore size distribution, and porosity) was determined from adsorption and desorption isotherms of nitrogen at liquid nitrogen temperature (SORPTOMATIC 1900, Fisons, Milan, Italy) and by mercury penetration (POROSIMETER P2000, Fisons, Milan, Italy) [7]. The sorption method is suitable for the identification of the micropore and mesopore structure (up to 50 nm of pore radius); the porosimetry is applied for the determination of the macroporous structure (pore radii above 50 nm).

RESULTS AND DISCUSSION

The original coal particle after the drying procedure has a micropore specific surface area of about $4 \text{ m}^2 \text{ g}^{-1}$ and a macropore specific surface area of about $6 \text{ m}^2 \text{ g}^{-1}$ with a porosity less than 10 %. After degassing, these values increased especially in the micropores region. The coal char particle has a micropore specific surface area of about $100 \text{ m}^2 \text{ g}^{-1}$, the macropore specific surface area increased slightly up to $10 \text{ m}^2 \text{ g}^{-1}$ with an overall porosity change to 15 %. This means that after degassing, the original, practically nonporous compact particle of coal changes to a porous particle with a predominantly micropore structure.

After the combustion of coal char particles, the following observations were made depending on combustion conditions:

1. High temperature (above 500 °C), wide range of feed oxygen content

A typical dependence of mass vs. time during combustion for two initial temperatures (527 °C and 627 °C) and 15 mole % feed oxygen content is presented in Fig. 1. A very quick loss of the particle mass with a high overheating of the particle (from 150 to 250 °C) could be observed. These dependences were very similar at higher temperatures and oxygen contents ranging from 5 to 21 mole %. At these conditions, it was possible to distinguish two different regions in the profile of a partially burned particle: a white or gray (ash shell) region and a black region (char core) with a sharp interface between them. It followed from the pore structure analysis that the ash shell structure

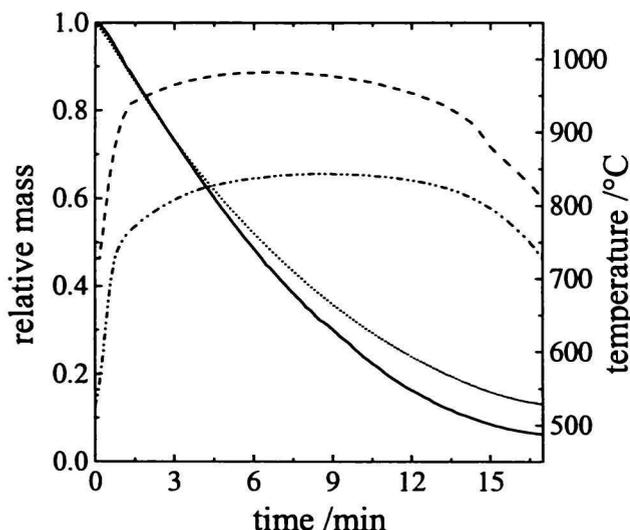


Fig. 1. Combustion of coal char particle at different initial temperatures and 15 mole % feed oxygen content. The mass of particle and temperature in the centre of the particle vs. time; 527°C: solid line and dot-dashed line, respectively; 627°C: dotted and dashed line, respectively.

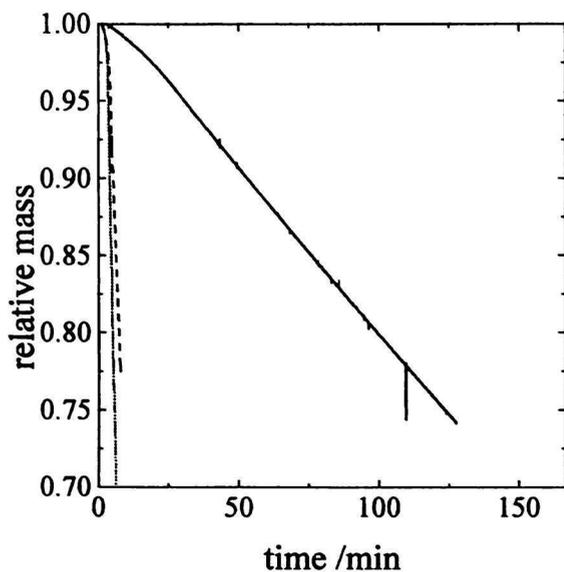


Fig. 2. Combustion of coal char particle at a low temperature (460°C) and different oxygen contents. The mass of particle vs. time dependences. Solid line – 5 mole %, dashed line – 10 mole %, dotted line – 15 mole %.

is made predominantly of macropores with a porosity of about 70 %. On the other hand, the noncombusted core structure was made by micropores and it was very similar to the structure of coal char. Some variations of the coal char structure at high temperatures are discussed in [7]. This phenomenon is probably caused by the diffusion and reaction of the formed carbon dioxide inside the core. We concluded from these results that at high temperatures and a wide range of oxygen content, the combustion could be described by

the shell progressive mechanism. In our previous work [2, 4] we developed such a model for a nonisothermal particle and a very good agreement of the model with experiment was found.

2. Low temperature, high feed content of oxygen (more than 5 mole %)

At low temperatures below 500°C but at high contents of oxygen, the mechanism of coal char combustion was similar to that one described in the previous part. Fig. 2 shows the comparison of the time dependence of the relative mass of particles burning at the same initial temperature (460°C) but different feed contents of oxygen. It is evident that the decrease of particle mass was very sharp at higher contents of oxygen. Also in this case, we concluded from the microstructure of the particle (ash shell, noncombusted core) that a shell progressive model could be used for the combustion mechanism.

3. Low temperature (less than 500°C), low feed contents of oxygen (less than 5 mole %)

At these conditions, when the content of oxygen in the feed stream to the reactor was less than or equal to 5 mole %, the combustion proceeded with a different rate than in cases 1 and 2, as can be seen from Fig. 2. The analysis of pores at different degrees of burnout showed some development of the microstructure: starting from coal char, the specific surface area made by micropores and mesopores grew up to 160 m² cm⁻¹ with a relatively small specific area formed by macropores (about 35 m² cm⁻¹) when the degree of burnout was 50 %. By increasing the burnout to 75 %, the values of specific surface area were changed to 140 m² cm⁻¹ at micro- and mesopores and to 45 m² cm⁻¹ at macropores. It was not possible to visually distinguish any different zones in the particle profiles. An assumption followed from these results that at low temperature and low feed oxygen content, the combustion mechanism could be described by the reaction-diffusion model both with diffusion and kinetic limitations with a porosity change depending on the degree of conversion. The last argument could also be supported by Fig. 2 (solid line) and Fig. 3. These figures present the results obtained by burning the coal char particle with an initial temperature of 460°C and 5 mole % of oxygen in the feed stream. Fig. 2 shows that the mass depletion was monotonic and very slow and that, after 130 min, the particle lost only 25 % of its initial mass. In addition, the temperature in the particle centre increased not more than by 5°C from the initial value and remained constant during the whole experiment. Fig. 3 shows a completely different behaviour of combusted particles even when the initial conditions were the same. The mass vs. time dependence exhibited several time periods with differ-

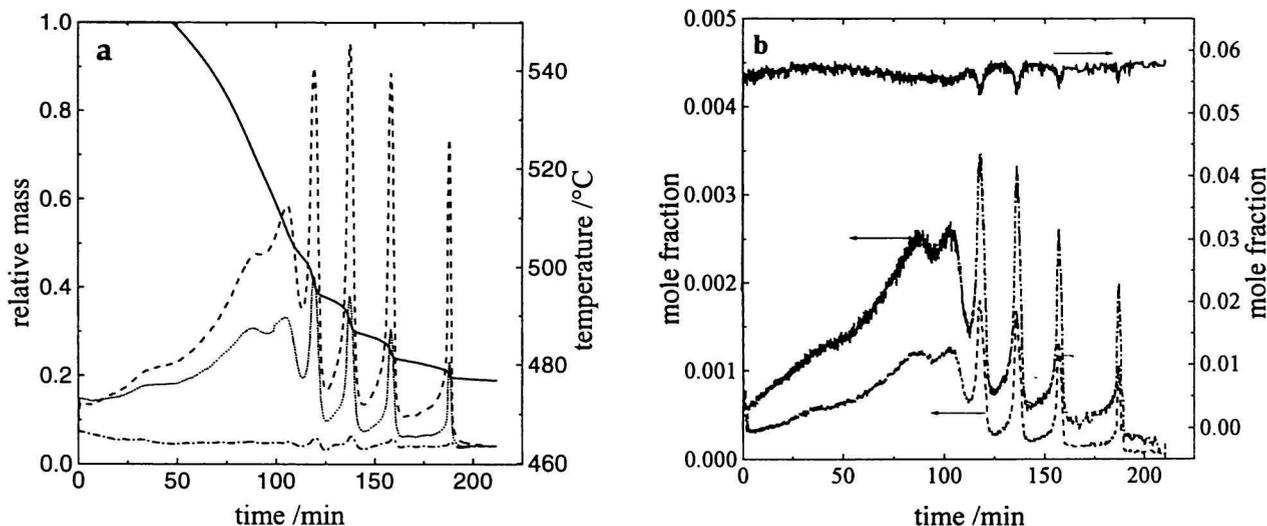


Fig. 3. Combustion of coal char particle at 460°C and 5 mole % oxygen content. *a*) Time dependences of the mass of particle (solid line), temperature in the centre of the particle (dashed line), temperature on the geometrical surface (dotted line), temperature of the gas phase close to the particle surface (dot-dashed line); *b*) Flue gas composition vs. time. Oxygen – solid line, carbon dioxide – dashed line, carbon monoxide – dot-dashed line.

ent rates of mass depletion. The periods with accelerated rate of mass depletion were correlated with the oscillations of temperature in the centre of the particle, at the geometrical surface and also in the gaseous phase close to the particle surface. The same oscillations could be observed in the flue gas composition (Fig. 3b).

In the first case (Fig. 2), the process was limited by the oxygen transport through the microporous structure. Since the content of oxygen and also the temperature were low, the reaction proceeded very slowly, with small heat release and therefore it could not be accelerated. We have to point out that in some experiments, the oxygen flux into the particle was not sufficient to ignite the reaction. Even in the case that this reaction started to proceed, it extinguished after some time. In the other cases, an initially very slow chemical reaction was ignited, which was probably caused by the accumulation of oxygen in the growing pores and the temperature in the particle increased (in some periods by more than 80°C). The rapid acceleration of chemical reaction caused a rapid consumption of oxygen in the particle pores, which was not sustained by the diffusion transport inside the particle. The reaction then extinguished and the temperature fell down. A new ignition of the reaction occurred after some oxygen accumulated again in the pores.

This case shows one fact, which is typical for natural materials such as carbon. Even in the case that carbon from the same mine is used, its properties vary from the piece to piece. Therefore particles at the same conditions exhibit a different behaviour.

CONCLUSION

A study of single coal char particle combustion at different conditions is presented. The coal char particles were burnt at wide ranges of the initial temperature and feed oxygen content. From the thermogravimetric measurements and porous structure analysis, we were able to conclude the following:

At high temperatures and high content of oxygen, the combustion proceeds by a shell progressive mechanism, which results in the division of the particle into two different parts: ash shell and coal char noncombusted core. If the temperature is sufficiently high then the ash shell (formed predominantly by oxides of Al and Si) can melt. These molten oxides do not have any porosity and form a large resistance against the oxygen transport inside the particle, that is why the reaction extinguishes. This situation can occur for instance in the bottom part of grate combustors where both the temperature and oxygen content are high.

At low temperatures and low oxygen contents, the combustion proceeds by the reaction-diffusion mechanism. The overall rate of the process can be controlled by the diffusion, the rate of oxygen transport is not sufficient to sustain its consumption by the chemical reaction. The reaction is very slow with small heat release, the particle needs a very long residence time in the combustor for a complete conversion. This situation can occur in the upper part of industrial combustors. This described and discussed situation leads to an insufficient utilization of carbon content in coal.

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