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MECHANISM OF COAL CHAR BURNING AT A LOW OXYGEN CONTENT IN THE FEED STREAM

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Abstract

Evolution of the internal pore structure during the combustion of two different types of coal chars is compared. In this study brown coal char prepared from brown coal (coal-mine Nováky) by drying and devolatilization, and commercial black coal char (provided by U.S. Steel Košice) were used. Particles were combusted to different degrees of burnout at an initial temperature of 800°C in a low oxygen containing atmosphere (5 vol%).

It was shown that the combustion of both types of coal chars proceeds via the same shell progressive mechanism, despite differences in their original internal pore structure. The internal surface area of the brown coal char particles mainly belongs to the region of micropores, while for the black coal char is typical its macropore structure. Inside the brown coal particle cores pore structure evolution was observed. This change of the structure was caused by the reaction between solid carbon and carbon dioxide, due to which the specific surface area in the region of micropores significantly increased.

Keywords: coal char, combustion, internal pore structure, thermogravimetry

Introduction

The design of an industrial equipment for coal combustion/gasification needs a good knowledge and proper understanding of the mechanism of coal combustion. This is important especially in case, when the design of a combustor/gasifier and conditions of its optimal performance are proposed on the basis of mathematical modelling and simulation of the combustion process.

Numerous papers dealing with the experimental study and mathematical description of the coal combustion process appeared in the literature. In our previous paper [1] we presented a brief review of these works. Single coal particle represents the smallest part of an industrial combustor. Therefore, it seems to be very important to analyse the processes which proceed inside the particle (i.e. reaction and diffusion of all components involved in the process) together with the evolving coal char structure.

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After the entry of a coal particle into the combustor, a rapid release of volatile compounds takes place [2]. These compounds are burned outside the coal particle. The resulting coal char particle is then burned itself as a slower step of the process. The combustion of a char particle involve following three heterogeneous reactions between solid carbon and gaseous oxygen or carbon dioxide

$$\mathrm{C}(s)+\mathrm{O_2} \quad \mathrm{CO_2} \tag{1}$$

$$\mathrm{C}(s)+1/2\mathrm{O_2} \quad \mathrm{CO} \tag{2}$$

$$\mathrm{C}(s)+\mathrm{CO_2} \quad 2\mathrm{CO} \tag{3}$$

and one homogeneous oxidation of carbon monoxide.

$$\mathrm{CO}+1/2\mathrm{O_2} \quad \mathrm{CO_2} \tag{4}$$

A relatively large number of theoretical works concerned with the change of the internal pore structure of a single coal char particle during the combustion is available in the literature [3–7]. The results of these authors have revealed a strong dependence of the pore structure of a coal particle on the origin and pre-treatment of coal. It has been shown that the original coal structure is characterized by a non-uniform pore size distribution with randomly oriented pores. Evolution of the pore structure during the combustion process is characterized by the growth of individual pores and coalescence of neighbouring pores. In our earlier paper [8] we have determined some combustion conditions for both the shell progressive mechanism and the reaction–diffusion mechanism in case of brown coal char.

The aim of this paper was an experimental investigation of the behaviour of two different coal chars and changes of the internal pore structure during the combustion process in a low oxygen containing environment (5 vol%). The brown coal char was prepared from brown coal (coal-mine Cígeľ, Slovakia), the black coal char was a commercial char provided by U.S. Steel Košice. The combustion experiments were performed in such a manner that different degrees of burnout were achieved. Then, the pore structures of the resulting particles were analysed. Spherical coal char particles with a diameter of about 7 mm were used for the experiments presented here. This size is typical for fluidized bed combustors. In such combustors, steep temperature and concentration gradients of oxygen, carbon monooxide and carbon dioxide exist. These result in different conditions for particle combustion.

Experimental

Preparation of particles

Two types of coal char were used for our experiments: commercial char (black coal) from U.S. Steel Košice, and coal char prepared by devolatilization of brown coal (coal-mine Nováky). Particles for our experiments were obtained by cutting the original material to pieces of spherical shape with a diameter of about 7 mm. Particles prepared from the commercial char were used in the combustion experiments directly. Particles from brown coal were pre-treated by the following procedures:

1) Drying in flowing nitrogen at 100°C for 4 h. To avoid particle rupture, the heating rate of 2°C min^{-1} was used at heating temperatures up to 100°C.

2) Devolatilization which ensured the removal of volatile substances by heating to a temperature of 800°C in flowing nitrogen. The heating rate was 2 and 5°C min^{-1} at heating temperatures up to 500 and 800°C, respectively.

Combustion measurements

The combustion experiments were carried out in a set-up described in [9]. This system allowed to perform measurements at different experimental conditions, i.e. initial temperature, heating rate, mass of the particle, compositions of the feed stream. The scheme of this experimental set-up is shown in Fig. 1.

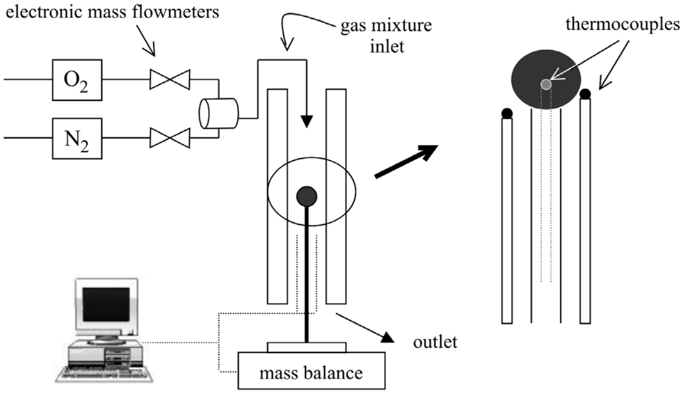


Fig. 1 Experimental set-up

The single particle was placed in the centre of the furnace tube using a thin ceramic rod. This rod was standing on a digital mass balance. The temperature in the centre of the particle was measured by a thermocouple located inside the ceramic rod. The temperature of the gas phase was measured by a thermocouple placed below the particle. Both the mass and the temperature of the particle were scanned with a frequency of 20 s. The furnace consisted of an open ceramic tube. The temperature inside the tube was regulated within the range of 20–1600°C by a programmer. The feed stream with the desired content of oxygen in nitrogen was obtained by a system consisting of two rotameters and electronic mass flowmeters.

To obtain ash from both types of fuels it was necessary to burn particles totally. This was the case when the mass of the sample remained constant. In order to obtain partially combusted particles the following procedure was done: after having reached the desired decrease of the mass, the inlet gas stream was switched to the stream consisting nitrogen and the experiment was stopped. The particle was withdrawn from the furnace at ambient temperature. The experimental conditions are given in Table 1.

Table 1 Experimental conditions for combustion of a single particle

Temperature/°C	800
Pressure/Pa	$1.01\ 10^5$
Inlet concentration of oxygen/mol%	5
Mass of particles/kg	$0.5\ 10^{-3}$–$1.0\ 10^{-3}$
Mass of degassed particles of coal char/kg	$0.3\ 10^{-3}$–$0.7\ 10^{-3}$
Particle diameter/m	$7\ 10^{-3}$–$10\ 10^{-3}$
Flow rate of gas/$m^3\ s^{-1}$	$2.8\ 10^{-5}$

Characterization of the pore structure

The internal pore structure of particles can be characterized by the following physical characteristics: specific surface area, specific volume of pores, pore size distribution and porosity. These quantities were determined by:

- the measurement of adsorption and desorption isotherms of nitrogen at the boiling point of nitrogen by applying the instrument Sorptomatic 1900 (Fisons Instruments, Milano Italy)
- mercury porosimetry using Porosimeter 2000 (Fisons Instruments, Milano, Italy).

The sorption method was suitable for the identification of the micropore structure; the porosity was applied for the determination of the macropore structure.

Due to the non-uniform pore structure of coal [10, 11] the pore size distribution was determined by a method based on the ‘ink bottle’ model for the pore shape.

We need to point out that the coal and coal char used for our experiments are natural materials. Therefore, their properties vary from piece to piece, even in case of coal stemming from the same coal-mine. Hence, the results presented here were obtained from several particles (5–10) and averaged.

Results and discussion

In our study, changes of the internal pore structure during combustion of two types of carbon material were investigated. For this purpose coal char CC1 prepared from brown coal by devolatization of original carbon in our experimental set-up and commercial black coal char CC2 were used. The differences between these two materials are given in Table 2 and Fig. 2. In this figure photographs of both materials before combustion and after total burning are presented. These pictures reveal the difference in porosity of both chars and ashes. Coal char CC1 (Fig. 2a) is apparently without pores and the geometrical surface of its particles is compact and bright. Coal char CC2 visually presents a very outstanding macropore structure (Fig. 2c). This observation was confirmed by the micropore structure analysis. The specific surface area of CC1 was about 17 $m^2\ g^{-1}$ in the region of macropores, and about 98 $m^2\ g^{-1}$ in the region of micropores at a total porosity of about 14%. On the other hand, it was not possible to determine the properties of micropores for CC2 by the sorption method.

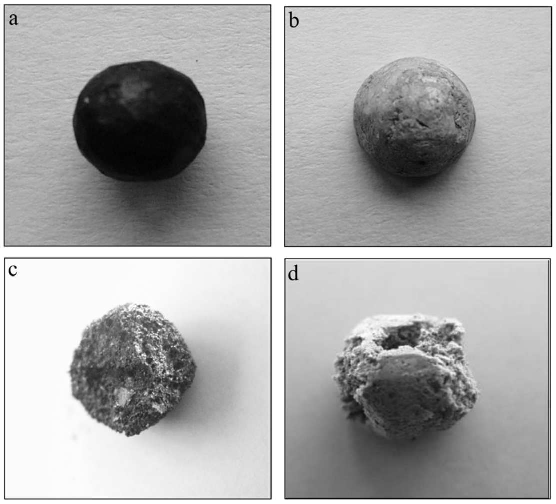


Fig. 2 Single particles of brown coal char, commercial char and both types of ashes. a – brown coal char, b – ash from brown coal char, c – commercial char, d – ash from commercial char

This was caused by a very small internal surface area of micropores area which is out of the instrument region. The specific surface area of macropores of this coal char was about 8 $m^2 g^{-1}$ at 15% total porosity.

The same analysis of ash, after the total burnout (when the mass of the particle remained constant) is shown in Figs 2b and 2d for ash obtained from CC1 and CC2, respectively. The corresponding specific surface areas are presented in Table 2. Both ashes exhibited practically the same value of porosity, but they were quite different from the mechanical point of view. The ash from CC1 was very fine and soft, and in some cases disintegrated to powder due to manipulation. The ash from CC2 was mechanically a little bit more stable than the ash from CC1, but it also could be very easily disintegrated.

Table 2 Porosity and values of the specific surface area detected by two methods, (S – sorption method, P – mercury porosimetry)

	Porosity/%	Specific surface area-S/ $m^2 g^{-1}$	Specific surface area-P/ $m^2 g^{-1}$
Original brown coal	13	0.4	4.6
Brown coal char	14	98.3	17.3
Brown coal ash	68	21.8	23.9
Black coal char	15	–	8.29
Black coal ash	50	–	6.29

From the above mentioned results it can be concluded, that the brown coal char CC1 has a bimodal character of the pore structure. Nearly all the internal surface belongs to the region of micropores. The black coal char structure is formed predominantly by macropores. The overall chemical reactivity (rate of combustion reactions) depends on the temperature, oxygen content and the accessibility of the internal surface area to gaseous reactants (O_2, CO_2). This accessibility is determined by the pore structure of the coal char particle. In Fig. 3 time dependence of the particle mass is depicted. The loss of the particle mass is proportional to the rate of the chemical reaction. A very small difference between the time dependences of particle mass for CC1 and CC2 can be observed. It is evident, that the internal surface area of micropores may not be accessibile to the gaseous reactants unless the feeder pores are large enough. Therefore, for the principal combustion process, i.e. oxidation of carbon by oxygen under given experimental conditions (high temperature, low oxygen content), the same diffusional resistance *vs.* oxygen transport inside the particle can be assumed for both coal chars. If particles are burned to some degrees of burnout, after cutting it was possible to distinguish visually two different regions in the particle profile for both types of coal chars (Fig. 4). These were: a gray region, formed by ash

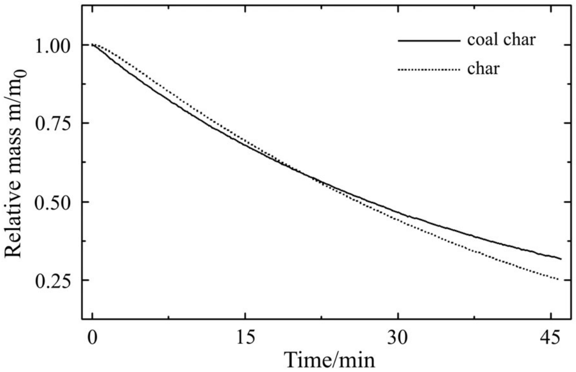
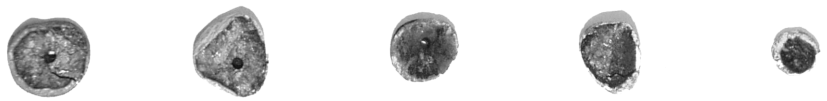


Fig. 3 Time dependences of the relative mass of brown coal char (CC1) and commercial char (CC2) during combustion

Fig. 4 Detail of the brown coal char particle combusted to 50% degree of burnout at an initial temperature of 800°C

with a high porosity (Table 2), i.e. ash shell, and a black region (char core). Between these regions a sharp interphase was observed. Accordingly, we can conclude that under our experimental conditions combustion of both types of coal chars proceeds by the shell progressive mechanism. This is possible not because of the non-porous structure of the original particle (which is predominantly made of macropores) but as a consequence of low content of oxygen and a very high value of the reaction rate at the experimental temperature. Oxygen is immediately consumed by the reaction at the shell–core interphase. The ash shell with a macroporous structure of high porosity does not represent any diffusional resistance. The core radius is continuously decreasing, as can be seen in Fig. 5. In this figure are presented coal char cores from particles (with practically the same original particle radius) combusted to different degrees of burnout.

Analysing the pore structure of the cores from partially burned particles a change of the micropore structure of the brown coal char was observed during the combustion process (Fig. 6). A progressive evolution of the specific surface area of micropores could be noticed. We could see that at the beginning of combustion, the specific surface area represented by micro- and mesopores grew practically twofold (up to 200 $m^2\ g^{-1}$). This phenomenon was probably caused by reaction (1) which took place at the shell–core interphase. Carbon dioxide could diffuse into the core and due to high temperature (around 850–900°C) it reacted with carbon (reaction (3)). As a consequence of carbon consumption, the micropore structure was changing. At the beginning of this structure evolution, new micropores were formed which are responsible for the increase of values of the specific surface area. Later, at higher degrees of



20% 30% 40% 50% 75%

Fig. 5 Cores of brown coal char particles with different degrees of burnout

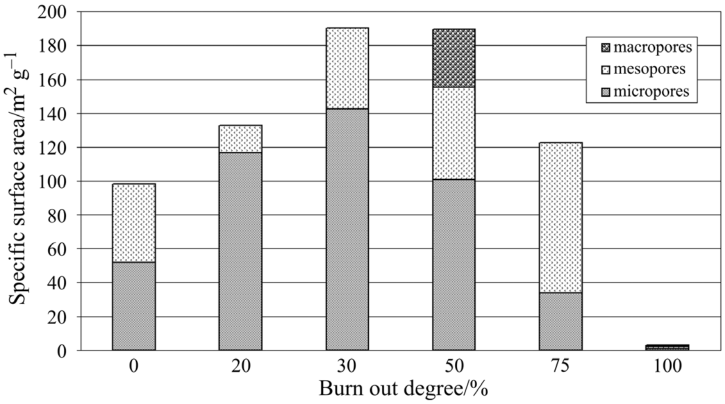


Fig. 6 Evolution of the specific surface area in the cores of brown coal char during combustion, determined by the sorption method

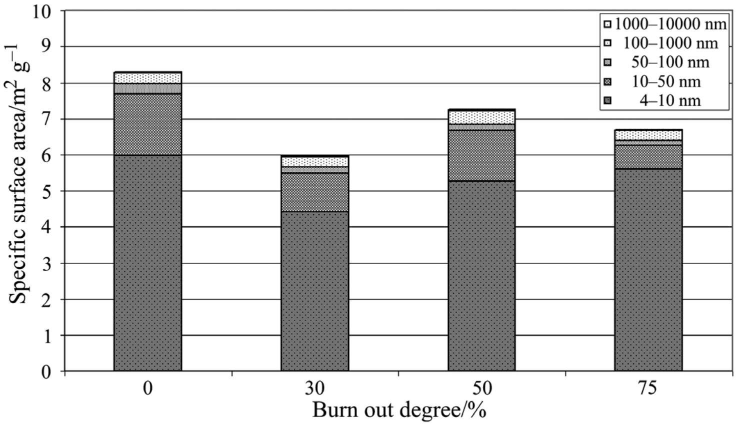


Fig. 7 Evolution of the specific surface area in the cores of black coal char during combustion, determined by mercury porosimetry

burnout (more than 50%, Fig. 6) the walls between micropores collapsed and the values of the specific surface area decreased. Carbon monoxide, as a product of reaction (3), diffused out of the core, and reacted with oxygen in the ash pores (reaction (4)). For coal char CC2 which originally did not exhibit a micropore structure, this phenomenon, was not manifested. The changes in the micropore structure of the core were not dominant (Fig. 7). In any case, also reaction (2) could be assumed in the particle core. However, the extent of this reaction was not sufficient to change the macropore structure. The decay of the particle core proceeded faster than the evolution of its pore structure.

Conclusions

In this work changes of the pore structure during combustion of two coal chars were investigated. The particles of these coal chars were burned at 800°C in a gas stream containing 5 vol% of oxygen. The pore structure of the original particles, particles burned to different degrees of burnout and of the resulting ashes were determined by a sorption method and by mercury porosimetry.

It was shown that the internal structure of the brown coal char is made of micro- and macropores, with a high internal specific surface area of micropores. The structure of the black coal char is only made of macropores. In spite of these differences the course of combustion of both types of particles is the same; it proceeds via the shell progressive mechanism. The formed ashes exibit in the ash shell similar properties; they are very soft, fine and mechanically unstable. It means, that in industrial fluidized bed combustors in which moving particles of burned coal char particles are in contact, the attrition of ash can occur unless its falling down from the particles proceeds. Then, the diffusional resistance of ash disappears, and oxidation reactions take place solely on the geometrical surface of the particles. This fact should be taken into account in modelling single particle combustion.

Analysing the pore structure of the core of brown coal char with different degrees of burnout, a change of the micropore structure was observed. This phenomenon could be explained by diffusion and reaction of the carbon dioxide inside the core, consumed carbon and formation of new micropores. Because this reaction is endothermic, the heat consumption by this reaction with increased CO concentration in the flue gas should be considered in designing a combustor. This phenomenon was not observed for black coal char. This difference is caused by the different micropore structure of both types of coal char.

The obtained experimental results have shown that at 800°C and a low concentration of oxygen the combustion proceeds by the shell progressive mechanism. Such conditions could be expected in the central part of the fluidized bed in industrial combustors. In our previous paper [6] we have shown that at a low temperature (less than 460°C) in a low oxygen containing atmosphere the mechanism of combustion proceeds via a diffusion–reaction mechanism. These conditions exist in the top part of a combustor in which, due to slow reactions, a single particle needs a very long residence time in a combustor for total conversion.

The mathematical model of a real combustor should take into account all above mentioned mechanisms of single coal particle combustion, on the assumption that intraparticle transport properties (effective diffusion coefficient, effective thermal conductivity, attrition of the ash) change with respect to the evolution of its internal pore structure.

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