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Modeling of coal particle combustion

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Modelovanie horenia častice uhlia

Príspevok je zameraný na experimentálne a teoretické sledovania priebehu horenia častice uhlia. Experimenty boli realizované v zariadení, založenom na princípe termogravimetrickej analýzy. Boli zistené, že počas spaľovania časticu uhlia tvorí z nespálené jadro a vrstva popola. Horenie častice neovplyvňuje porézne vlastnosti v nespálenom jadre. Výrazne vyššia porozita vo vrstve popola indikuje nízky difúzny odpor pre reaktanty. Experimentálne výsledky potvrdili opodstatnenosť použitia škrupinového modelu pre matematický opis procesu horenia častice uhlia. Podľa tohoto modelu, prebieha reakcia na rozhraní medzi vyhorenou vonkajšou škrupinou popola a nezhoreným jadrom. Polomer tohto jadra sa s dĺžkou horenia zmenšuje. Kinetické parametre reakcie (aktivačná energia, frekvenčný faktor, poriadok reakcie), boli získané optimalizáciou experimentálnych údajov. V príspevku je poukázané na to, že navrhnutý škrupinový model dobre opisuje proces horenia častice uhlia.

Key words: častica uhlia, spaľovanie, porézna štruktúra uhlia, kinetické merania, škrupinový model.

Introduction

Coal is the oldest mineral resource used as an energy supply. However, coal combustion has a serious environmental impacts linked to emissions of gases and dust into the atmosphere. Coal contains a considerable amount of elements like sulphur, nitrogen and trace amount of other elements (chlorine, heavy metals). During the coal combustion the oxides of sulphur and nitrogen are emitted to the environment. With the increasing coal consumption these environmental problems become more energing.

The fluidized bed combustion is one of the advanced combustion technologies. A fluidized bed consists of a collection of coal particles suspended in an upward gas flow. A single coal particle represents the basic component of this process. For the better understanding and mathematical description of the coal combustion process, it is helpful to have a more information about the internal pore structure and changes in the coal particle during the reaction.

The objectives of this paper are the following:

- to estimat the pore structure characteristics of a single coal particle,
- to study the effects of degassing and combustion process on the pore distribution in a coal particle,
- to realize the combustion experiments based on the application of TGA method using a single coal particle.
- to describe the combustion process using the shell progressive model
- to obtain the model parameters (activation energy, frequency factor, order of reaction) by optimization of the experimental data.

Experimental

Pore structure characterization of a single coal particle

The coal pore structure depends on its origin and pretreatment. In experimental studies (Laurendeau,1978), Sotirchos and Amundson, 1984), it has been shown that original coal pore structure is characterized by a bimodal pore distribution. Nearly all the internal surface area belongs to the region of micropores ($r_P < 1$ nm) and mesopores (1 nm $< r_P > 25$ nm), while the large pores ($r_P >$

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25 nm) account for a significant part of the total porosity. The overall chemical reactivity depends on the accessibility of the internal surface area to the gaseous reactants which is determined by the pore structure of the coal particle. Micropores may not be accessible to the gaseous reactant unless the feeder pores are large enough.

In our experiments coal from the coalmine Cígeľ, Slovakia was used. The composition of this coal was determined by the element analysis: 47 %w carbon, 4,6 %w hydrogen, 1 %w nitrogen and 3 %w sulphur. We estimated the pore structure of the original coal particle, the degassed particle and the partially combusted particle. Using the principles of gas adsorption and mercury penetration (ASTM Standards, Designation D3663, 1987), (IUPAC Document, 1985), the identification of the pore structure was performed. Gas adsorption is defined as the physical adsorption of an inert gas onto a clean surface at low temperatures. The gas - nitrogen is physically adsorbed into a degassed sample at the temperature of liquid nitrogen (-196 ^{o}C). During the isothermal adsorption the thermodynamic theory predicts that the isotherm has a linear portion in the region of the monolayer. Then BET theory can be used for the calculating the specific surface area. The micropore and mesopore size distribution calculation utilizes the hysteresis between adsorption and desorption isotherms. But, in our system containing micropores, the pore size distribution was calculated using the Horvath and Kawazoe calculation method (1983). The surface characterization by the mercury intrusion works on the principle of the nonwettability of solids by some liquids. As mercury forms an obtuse contact angle with solids, it follows that a positive pressure must be applied to allow mercury to penetrate the porous surface. The mercury intrusion techniques generate parameters such as the pore size distribution in the macropores region, specific surface and the total porosity. The determination of the physical characteristics was carried out with a fully automatic instruments - Sorptomatic 1900 and Porosimeter 2000[2] fy Fisons.

Our experiments have shown that the specific surface area of the original coal particle is negligible. Degassing of the coal particle has an important influence on its pore structure which is characterized by a bimodal pore distribution - micropores (r_P < 1 nm) and pores (r_P > 10 nm). The removal of volatile organic compounds has an influence on the accessibility of the micropore region. The total porosity increased from 5 % to 10%. In order to study the changes in the coal pore structure during the combustion process, we the determined physical characteristics of the partially combusted particle. The cross section of a partially combusted particle is shown in Figure 1. This particle consists of the noncombusted core and the ash layer. We estimated the parameters of both of the core and in an ash. The pore size distribution in a micropore region and the total porosity in the core of the partially combusted particles are shown in Figure 2. The physical characteristics for the ash layer are presented in Figure 3.

The combustion experiments

The combustion experiments were realized for these reasons:

- to study the pore structure changes in the coal particle,
- to estimate the parameters which have a strong influence on the particle behavior,
- to obtain the kinetic data for the mathematical description of combustion by the shell progressive model.

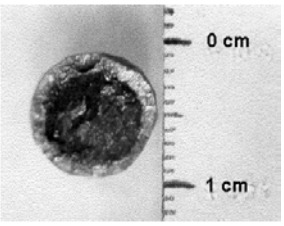

Fig.1. Cross section of a partially combusted particle.

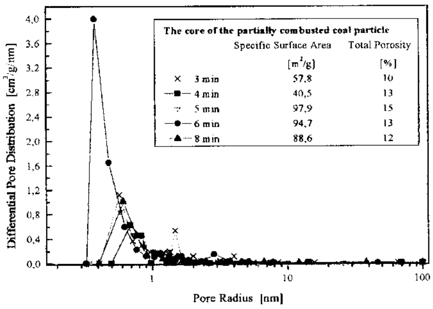

Fig.2. Pore size distribution in the non-combusted core of the particle for the different combustion time.

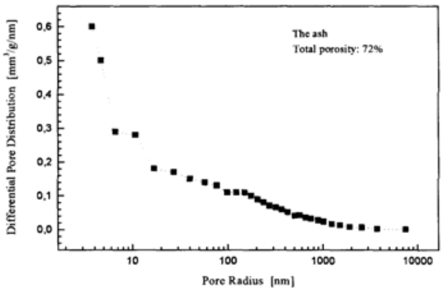

Fig.3. Pore size distribution in the ash layer determined by the mercury porosimetry.

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[2] Instruments purchased with the support of the European Union in the framework of the TEMPUS JEP 1125

Equipment

The combustion experiments were carried out with the equipment based on the application of the TGA method using a single coal particle. This system allowed to measurements at different experimental make conditions (temperature, mass of a particle, feed stream composition). The scheme of this experimental system is shown in Figure 4. The TGA equipment consisted of :

- the gas mixer with four rotameters,
- the furnace - an open ceramic tube with a heating inductor (the temperature inside the tube is regulated by a programmer in the range 100-1600 ^{o}C) ,
- the digital mass balance,
- the analyzer a mass spectrometer combined with the gas chromatograph TRIO 1000[3] fy Fisons.

The single coal particle was placed in the center of the furnace tube using a thin ceramic rod. This rod was standing on the digital mass balance. The temperature in the center of the coal particle was measured by a thermocouple (E type) located inside the ceramic rod. The gas phase temperature was measured by a thermocouple (J-type) placed under the coal particle (detail in Figure 4). The combustion products were analyzed by the quadrupole mass spectrometer using an autosampler. The frequency of sampling was 20 sec. The mass and the temperature of the coal particle were scanned with an frequency 3 sec.

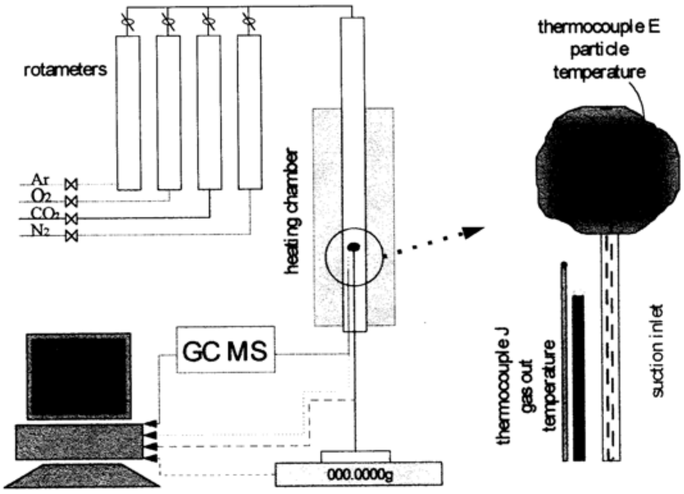

Fig.4. Experimental eguipment.

Experimental procedure

The chemical composition and physical properties of the coal used in this study were mentioned above. The spherical particle (diameter 5-10 mm) were obtained by cutting the coal.

The experimental procedure consisted of three consecutive steps:

1. **Drying** in flowing air or nitrogen at 100 ^{o}C for 4 h. To avoid the particle rupture, the heating rate up to 100 ^{o}C was 2 ^{o}C /min.
2. **Degassing** (carbonization) involved the removal of volatile substances by heating to 800 ^{o}C in flowing nitrogen. The heating rate to 500 ^{o}C was 2 ^{o}C /min and to 800 ^{o}C was 5 ^{o}C /min.
3. **Combustion** of the particle at 800 K (527 ^{o}C). The degassed particle was kept in flowing nitrogen or argon. After switching the feed stream on the stream consisted of air, the particle started burning itself. The experiment was finished when the mass of the particle was constant. The volumetric flow rate of the gaseous phase was in the range 50-350 l/h.

In order to obtain an information about the content of nonvolatile substances in the coal particle, many thermogravimetric analyses were carried out. We studied the mass changes of the particle in the temperature range 100 ^{o}C - 800 ^{o}C. The content of the volatile substances at 800 ^{o}C

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[3] Instrument purchased with the support of the European Union in the framework of the TEMPUS JEP 1125

was 4 %. It means, that the effect of these substances on the combustion process of the degassed particle is negligible.

Mathematical model of coal particle combustion

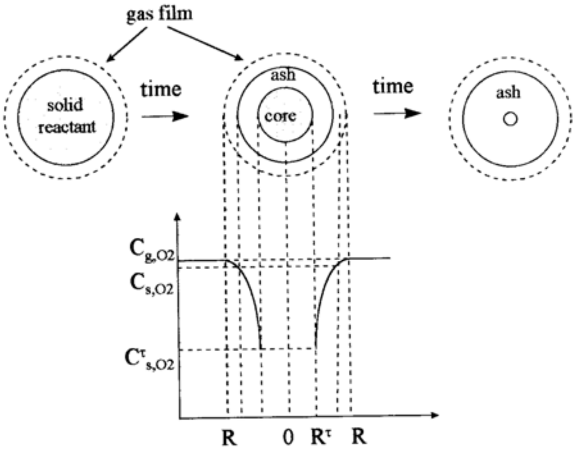

Fig.5. Schematic representation of the sharp-interface model.

The combustion of the coal particle starts at the surface proceeds to the inside of the particle (Figure 1). In this period, the process of combustion can be limited by the transport of oxygen through the gas-solid interface as well as exhausted outer shell - (ash) layer. Solid phase changes during the combustion its inside structure. As inner mentioned above, the exhausted outer shell has a different porosity from that of the unreacted core. The experiments confirmed that the combustion of the coal particle is a real process with a sharp - interface between the exhausted outer shell and the unreacted core of the solid. From these results a model based on the shell progressive mechanism with a shrinking unreacted core has been proposed. The reaction is assumed to occur at a sharp interface between the exhausted outer shell and the unreacted core of the solid. The unreacted core shrinks in size as the reaction proceeds - Figure 5.

The particle is burned by the heterogeneous reaction

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

In the deriving the equation for this model, the following assumptions are made:

- nonisothermal conditions and the temperature gradient in the particle is neglected,
- constant pressure,
- constant pellet size during the combustion,
- the coal particle is complete devolatilized, at the zerotime,
- pseudo-steady state for the gas components as was shown by (Froment and Bischoff, 1989).

The rate of the reaction (1) can be expressed as

$$\xi = k_{\infty} \exp\left(-\frac{E}{RT}\right) C^{n}_{sO_2} C^{m}_{sC} \tag{2}$$

List of symbols

C	*concentration*	*$mol.m^{-3}$*
E	*activation energy*	*$J.mol^{-1}$*
k_{∞}	*frequency factor*	*$m^{4}.mol^{-1}.s^{-1}$*
m	*reaction order*	
n	*reaction order*	
T	*temperature*	*°K*
R	*gas constant*	*$kj.kmol^{-1}.K^{-1}$*
Greek symbols		
ξ	*rate of reaction based on 1 m^2 of reaction surface*	*$mol.m^{-2}.s^{-1}$*

Subscripts

s	*solid phase*

where the rate of the reaction is based on 1 m^2 of the reaction surface.

The model equations solution and the optimization technique are described in Jelemenský at al., (1998).

The model kinetic parameters ($k_{1\infty}$, E_1, m, n) have been received by the optimization of 20 experimental data sets for the constant temperature of inlet air T^{o}_{g} = 800 K.

In the model, the enthalpy balance was not used, because at every step of calculating the model equations the experimentally measured temperature of the coal particle as well as around the particle was considered (Figure 6). In this way a problem with the estimation of the chemical, physical and process quantities (related to the heat transfer process) was avoided.

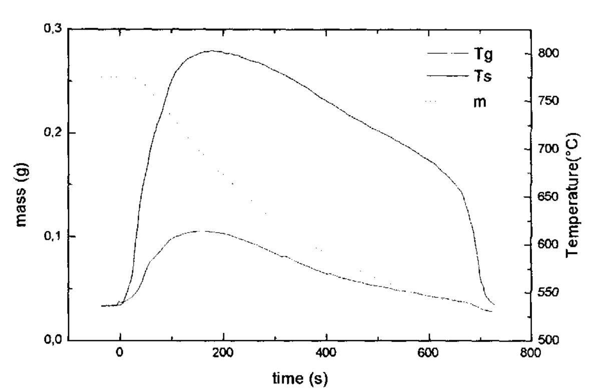

Fig.6. Combustion of the coal particle, time dependencies of experimental: Tg-the temperature of the combustion products, Ts-temperature of the particle, m-mass of the particle.

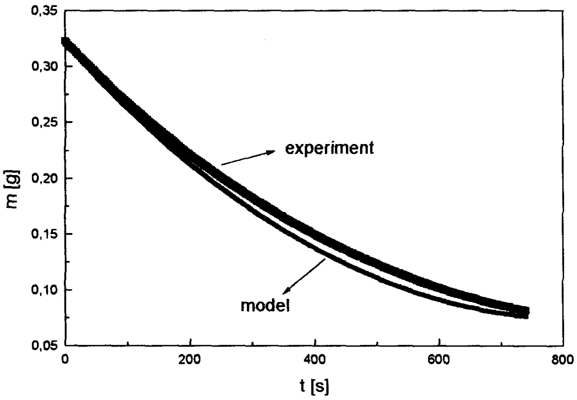

Fig.7. Comparison of the experimental and calculated mass of the coal particle during combustion.

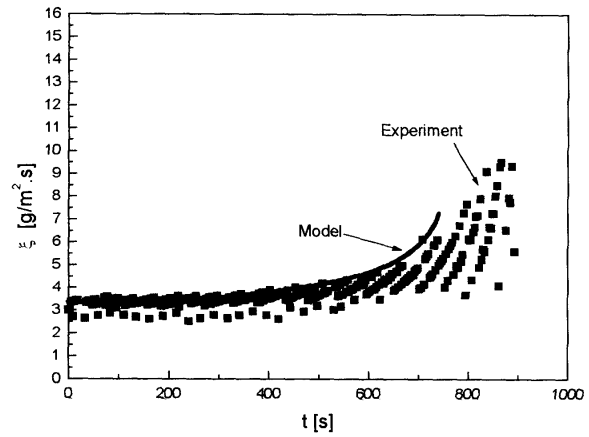

Fig.8. Reaction rate as a function of time.

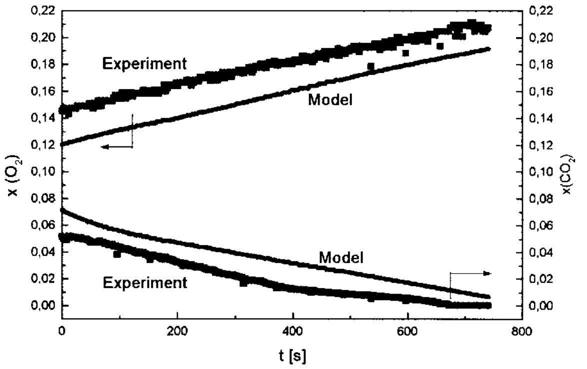

Fig.9. Concentration of oxygen and CO_2 in the outlet gas as a function of the combustion time.

Conclusions

The experimental and theoretical investigation of a single coal particle combustion is presented. The combustion experiments were carried out in the equipment based on the application of TGA method. During the combustion process, it appeared the particle consisted of two regions - the noncombusted core and the ash layer. The combustion does not affect the changes of the pore distribution and porosity in the core of the partially combusted particle. The porosity of the ash layer indicates the low diffusional resistance for the reactants. Obtained experimental results confirmed that the shell progressive mechanism can be apply for the mathematical description of the single coal particle combustion. The reaction is assumed to occur at a sharp interface between the exhausted outer shell and the unreacted core of the solid. The unreacted core shrinks in size as the reaction proceeds. The model parameters (i.e. activation energy, frequency factor and order of reaction) have been received by optimization of experimental data from the thermogravimetry set-up. From the optimization follows that the reaction of oxygen with carbon is of the first order. Furthermore, the activation energy of reaction , E_1 =100 kJ/mol and frequency factor, $k_{1\infty}$ =3000 m^4/mol.s.

It was found that the model quantitatively describes the decrease of the particle mass during the combustion.

Furthermore, the model prediction of the fuel gas composition is in a qualitative agreement with the experimental observations.

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