Reactivity and Kinetic Analysis of Coal Chars Combustion under Oxy-fuel Conditions

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Abstract. The Oxy-fuel combustion of Yunfu bituminous (YFB) chars was studied by isothermal thermogravimetric experiments at 1273K-1573K. The surface area of coal chars prepared at different stages of Oxy-fuel combustion was determined by BET methods. The pyrolysis temperature leads to a slight increase in the average pore diameter and surface area, and the average pore diameter of YFB increases with increasing carbon conversion. Pore structure parameters were calculated by random pore model. Compared to the experimental data, it is found that the random pore model has good ability to depict the reactivity of coal chars Oxy-fuel combustion under high temperature, indicating the random pore model was used to depict the reactivity of coal char combustion in Oxy-fuel.

Introduction

The combustion of coal chars for energy production results in the generation of greenhouse gases, with CO_2 as the major contributor, which are emitted to the atmosphere[1]. There is a general agreement on the need to reduce the emissions of CO_2; although the ways approach the problems are rather different. Combustion of fossil fuels in an Oxy-fuel environment is one of several promising new technologies for having a significant impact on reducing greenhouse emissions[2, 3].

Non-catalytic gas-solid reaction, such as coal combustion as well as gasification, which is influenced by many factors (such as atmosphere, pyrolysis time, temperature), is a very complicated phenomenon, particularly to coal char[4, 5]. It has an abundance of submicropores, of which the surface areas have been thought to be predominant in the char reactions[6-8].

Coal characterization has been extensively studied over the years[9, 10]. The combustion of a porous carbon particle is a kinetic process. Coal char properties not only directly have impact on combustion and/or gasification reactions, but also intensify the complexity of the reaction[5, 6, 8]. Moreover, some researchers have conducted researches to study the emission of NO in Oxy-fuel combustion, and the main factors influencing NO emission have also been carefully investigated[2, 3]. This can be of importance in revealing in-depth reaction mechanism in Oxy-fuel combustion atmosphere.

In this work, the combustion of Yunfu bituminous chars in Oxy-fuel was studied by isothermal thermogravimetric experiments. The characteristics of coal chars combustion at different temperatures were examined in Oxy-fuel.

Experimental Section

Yunfu Bituminous (YFB) coal was used in the present study as the representatives of coal. Coal samples were first crushed and sieved. Fractions in the size range of <0.175mm was used in the experiments. Elemental analysis and proximate analysis were carried out in vario EL-2 and TGA2000 (Navas Instruments, Spain), respectively. Coal properties are shown in Table 1.

Tab.1 Coal Sample Analysis

Sample	Proximate Analysis(wt%, air-dried)				Ultimate Analysis (wt%, air-dried)				
	Moisture	Volatile	Ash	Fixed Carbon	C	H	N	S	O
Yunfu Bituminous (YFB)	10.65	25.91	17.10	46.34	58.03	3.97	1.00	1.26	7.99

Pyrolysis and combustion in the TGA: The experiments were carried out on thermogravimetric balance (STA 409) of Germanic NETZSCH Corporation. Firstly, coal samples were heated at a heating rate of 30k/min up to the final temperature range of 1273K, 1373K, 1473K, 1573K at N_2 atmosphere, and then atmosphere was changed to the mixed gas of O_2/CO_2 with the ratio of 1:4 for 20~30 minutes with a flow rate of 100ml/min.

Chars preparing in a tubular furnace: The tube furnace was first heated up to the temperature range of 1273K-1573K, and then pumped in the mixed gas of O_2/CO_2 with the ratio of 1: 4 at a flow rate of 100ml/min, and finally moved coal chars into heating zone rapidly to stay at predetermined time.

BET surface area analysis: The BET surface area of different coal chars was measured with a Micromeritics ASAP2020 automated gas adsorption apparatus. The adsorption/desorption isotherms (N_2, -196 ℃) were determined using the TriStar 3000 gas absorption analyzer from Micromeritics. To ensure the reproducibility and accuracy of analysis, repeated experiments were accomplished.

Results and Discussion

The influence of temperature: Carbon conversion can be calculated by following equation

$$X = \frac{m_0 - m}{m_0 - m_{ash}} \quad (1)$$

In which m, m_0, and m_{ash} are instantaneous mass of solid reactant, initial mass of solid reactant, mass of solid ash, respectively.

Fig.1 (a) shows variation of the conversion with time for YFB combustion under Oxy-fuel atmosphere. It can be seen that carbon conversion increases with temperature at the same reaction time. The carbon conversions of YFB are 100% for 1573K and 30% for 1273K in three minutes, respectively. The relationships of carbon conversion and reaction rate of YFB chars are shown in Fig.1 (b). It can be seen from the figure that the combustion rate of coal char increases with temperature at the same carbon conversion. The combustion rate shows a maximum in the initial stage at 1473K. At 1373K and 1573K, the combustion rate also shows similar trend, reaching maxima at carbon conversion of 36%, 28%, respectively. It is thought that the pyrolysis of coal char has a significant effect on the combustion process[11, 12]. Higher temperature increases coal char combustion rate, which means that long pyrolysis time leads to a reduction of combustion reactivity[13].

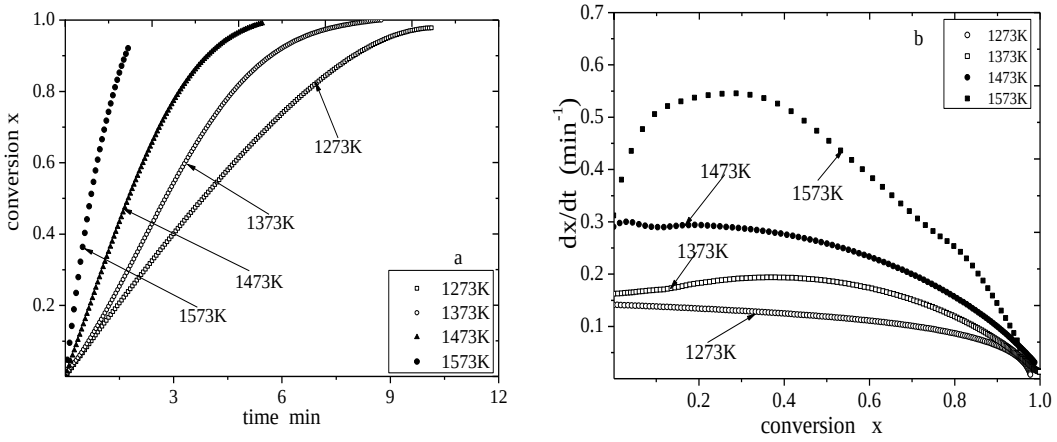

Fig.1 The Effects of Temperature on Conversion and Combustion Rate (*dx/dt*) of Coal Chars

Char properties: As can be seen from Fig.2, the changes of average pore diameter were small, which is consistent with Balci et al. [14]studying results. The pyrolysis temperature leads to a slight increase in the average pore diameter and a reduction of surface area (see Fig.2 and Fig.4). Similar to the changes of YFB at 1573K, the average pore diameter of YFB increases with increasing carbon conversion at 1273K. This phenomenon is mainly related with the pore expansion and coalescence[15]. Fig.3 shows variation of pore volume with carbon conversion during O_2/CO_2 combustion. As can be seen from Fig.3, pore volume shows a maximum at carbon conversion range of 0.2-0.4.

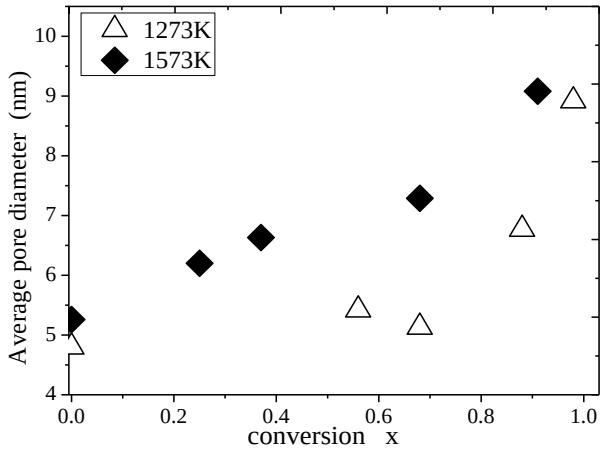

Fig.2 Relationship between Average Pore Diameter and Carbon Conversions

Surface area: To investigate relationship between char O_2/CO_2 combustion process and the variations of char structure, YFB chars were prepared at 1273K and 1573K in O_2/CO_2 using the tube furnace. The correlations between surface area of YFB and carbon conversion is shown in Fig.4. It can be seen that the surface area of YFB increases at 1273K at the initial stage of reaction, this phenomenon is mainly caused by generation of a large number of new pores and micropore expansion[15], and then decreases when the carbon conversion is higher than above 50 %, which is mainly caused by pore collapse.

The random pore model (RPM) developed by Bhatia and Perlmutter[16] as well as Gavalas[17] is supported as being appropriate for application. This model accounting for the effects of pore growth and coalescence has often shown satisfactory agreement between theory and experiment.

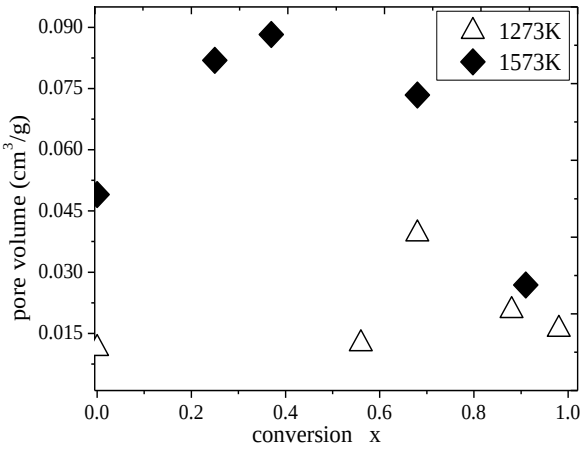

Fig.3 Relationship between Pore Volume and Carbon Conversions

The model equations[16] derived for specific surface area with the conversion is denoted as

$$S = S_0(1-X)\sqrt{1-\psi \ln(1-X)} \quad (2)$$

Where S_0 is surface area of initial pore, S is surface area of pore. ψ is a structural parameter, which is also calculated by porosity per unit volume of reaction solid as follows[18].

$$\psi = 1/\ln(\frac{1}{1-\varepsilon_0}) \quad (3)$$

In which L_0 is the total initial pore length per unit volume, ε_0 is the initial porosity.

The blank points in Fig.4 are the simulated results calculated by random pore model. It can be seen from the figure that the model fits the experimental results well. Obviously, the random pore model can describe the variations of the surface area of coal char during O_2/CO_2 combustion process. But some minor deviations still exists when the RPM predicts the experimental data especially at the middle stage of reaction, which is related with the hypothesis of structure parameter in the random pore model[6, 15].

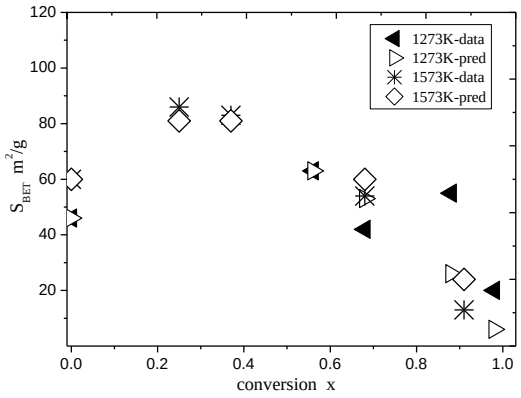

Fig.4 Surface Area and Simulation Results of Coal Chars at Different Conversion Ratios

Conclusions

1) Higher temperature increases coal char combustion rate, and the pyrolysis temperature leads to a slight increase in the average pore diameter and surface area.

2) The coal chars combustion in Oxy-fuel is investigated with the help of random pore model. Compared to the experimental data, surface areas predicted by the model are more satisfied to depict

the experimental results.

3) The random pore model can be recommended as a convenient submodel for predicting the characteristic of coal chars combustion in Oxy-fuel.

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