Pore fractal structures and combustion dynamics of cokes derived from the pyrolysis of typical Chinese power coals

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A B S T R A C T

The pore fractal structures and combustion dynamics of cokes derived from the pyrolysis of 18 typical Chinese power coals were investigated to use the said cokes for boiler combustion and power generation after pyrolysis gas extraction. When the total contents of volatile matter and moisture in raw (air-dried) coals increased from 15.22% to 39.49%, the pore fractal dimensions of the pyrolyzed cokes gradually increased from 2.30 to 2.84 because of the decrease in the activation energies of coal pyrolysis. The average pore diameters of the coke particles gradually decreased, and the peaks of the differential specific surface area formed at a pore diameter of 3.7 nm gradually increased. Accordingly, the ignition temperatures of cokes gradually decreased from 617 °C to 486 °C. Their activation energies also gradually decreased, which resulted in an increase in fixed carbon burnout efficiencies from 84% to 91%. This indicated that cokes derived from lignite pyrolysis had larger pore fractal dimensions and therefore had lower ignition temperatures and higher burnout efficiencies than those from lean coal and anthracite pyrolysis.

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1. Introduction

The total coal consumption of China is about 3.6 billion tons per year, approximately 50% of these coals are burned for power generation, and installed coal-fired power generation capacity accounts for about 70% of the total installed capacity. Meanwhile, approximately 530 thousand of coal-fired industrial boilers exist in China, and the coal consumption of these boilers is approximately 730 million tons annual. Pollutants, such as SO_2, NO_x and PM2.5, are generated during coal combustion. Compared to the lack of treatment to the pollutants produced by industrial boilers, coal-fired power plants deploy plenty of pollution control equipments with a pollutant removal rate of as high as 95% to 99%. When a pyrolyzer is equipped in front of the coal-fired boilers of large thermal power plants and volatile matter in coal pyrolysed to generate coal gas firstly, the coal gas can be converted into natural gas for small and medium industrial boilers. The remaining cokes continue to be used for electricity generation in coal-fired power plants. The pollutant emissions of both power plant boilers and industrial boilers (i.e., after deep desulphurisation, denitration and dust removal) are hopeful to meet higher standards of pollutant emission, thereby resulting in remarkable economic and environmental benefits.

The abundant pore structures of cokes are formed from their parent coals during pyrolysis and have important influences on the subsequent ignition and combustion of cokes. The effects of pyrolysis on the pore structures of cokes such as volume distribution and porosity have

been studied either by experiments or numerical models for a long time [1–3]. Feng et al. [4] found that the surface area and volume of the micropores of cokes did not change with carbon conversion when the coal/char is gasified in air, while those of the mesopores and macropores increased with increase of carbon conversion. However, all the pores with different size increased in surface area and volume with increase of carbon conversion in CO_2 gasification. Yamashita et al. [5] presented a new reaction model to express the gasification behavior of char particles and concluded that the wall thickness of the coke particle contributed remarkably to the transition temperature between the chemical-reaction rate control regime and the pore-diffusion rate control regime and temperature had only a small effect on fragmentation behavior in the case of small char particles. Subsequently, it was found that coal and char pores were fractal-like and the fractal pore properties had also been extensively investigated either by experiments or numerical models [6–13]. Mahamud et al. [14] investigated the fractal characterization of four bituminous coals and the corresponding coal sample oxidized in air at 543 K for different time periods and indicated that the evolution of the fractal dimension of coals with oxidation is determined by the balance between the two main mechanisms of pore development: the oxidation of the pore surface that tends to lower the fractal dimension and the access of mercury to previously non-accessible regions that tends to increase the said dimension. Wang et al. [15] studied the evolution of pore structures during coal devolatilization using mercury porosimetry to classify pore structures into either micropores or macropores based on fractal theory. Hu et al. [16] investigated the variations of fractal dimensions of parent coals and chars with different burn-off ratios and demonstrated that the particle surface fractal

dimensions which were determined by SEM image analysis of three Chinese coals firstly increased and then decreased with increasing carbon burn-off ratios and the internal surface fractal dimensions which were determined by N_2 isotherm adsorption/desorption of three Chinese coals changed similarly to their specific areas development. Chen et al. [17] numerically investigated coal pyrolysis processes and found that both the porosity and volatile contents of the parent coal can linearly affect the fractal dimension of the final char pores after pyrolysis then a formula was obtained to predict the fractal dimension of char pores from its parent coal properties by curve fitting numerous results. Fei et al. [18] modified the structure parameter ψ of the random pore model (RPM) according to experimental analysis and constructed a fractal RPM to analyse the O_2/CO_2 isotherm combustion of coal chars at different temperatures. The literature modifies only the structure parameter ψ at carbon conversions under 0.7 and illustrates that the influence of pore structure on gas diffusion is related to temperature and the reaction stage. Although the influences of carbonization procedure of different coals on the pore structure characterization of their cokes were revealed and most pore fractal structures of cokes were investigated in current researches, the influences of the coal properties and pyrolysis characteristics on the fractal dimensions of their cokes and the effect of pore fractal dimensions of the coal chars on their combustion processes were investigated limited.

In summary, although the pore fractal characteristics of raw coals and pyrolyzed cokes are reported in the literature, the effects of pore fractal structure on the ignition and the combustion of pyrolyzed cokes are seldom reported. Therefore, an in-depth study of the effect of the pore fractal structures of cokes derived from the pyrolysis of typical Chinese power coals on the ignition and combustion characteristics of cokes is necessary. In the present work, 18 typical Chinese power coals (including lignite, bituminite and anthracite) were used. The effects of the composition of raw coals and the activation energy of pyrolysis on the pore fractal structures and the fractal dimensions of pyrolyzed cokes were studied. Moreover, the influences of the pore fractal structures of pyrolyzed cokes on ignition temperature, activation energy of combustion and fixed carbon burnout efficiency were analysed.

2. Experimental materials and methods

2.1. Coal samples and coke preparation

A total of 18 frequently used and typical power coals in the coal-fired power plants in China were used for the experiments. The chemical compositions of the coal samples are shown in Table 1. The 18 coal samples employed in this study included 8 high-volatile lignites (Xilutian, Leling, Wujia, Hongmiao, Gushan, Shenfu, Fengshuigou and Yima coals), 7 medium-volatile bituminites (Zaozhuang, Changguang, Xinwen, Yuanbao, Huangling, Datong and Huainan coals), 2 low-volatile lean coals (Luan and Liuqiao coals) and 1 anthracite with very low volatile matter (Jincheng coal). The 18 coal samples were crushed in a ball grinder and sieved through a 80-mesh sieve. Air-dried particles with a size range of ≤200 μm were used in the coal pyrolysis experiments, which were conducted on a thermogravimetric balance. A total of 1 g of the air-dried coal samples was placed firstly into a ceramic crucible and then in a muffle furnace preheated to 920 °C. After isolated air heating for 7 min at the constant-temperature region of the muffle furnace, the crucible was removed into a desiccator and was cooled at room temperature. The pyrolyzed coke samples were used to test the pore structure and coke combustion experiments on the thermogravimetric balance.

2.2. Pyrolysis of coals and combustion of cokes

Experiments involving the pyrolysis of 18 raw coals and the combustion of cokes were conducted on thermogravimetric balance (SINKU RIKO-5000RH, Japan), and the test materials were placed in a platinum crucible. The experimental conditions of coal pyrolysis were as follows: the combustible mass (the sum of the volatile matter and fixed carbon) of the coal sample was kept at 2.0 ± 0.1 mg; N_2 was used as the protecting gas with a flow rate of 50 ± 2 ml/min; the temperature was increased from room temperature to 900 °C at a heating rate of 40 °C/min. The experimental conditions of coke combustion were as follows: the combustible mass (fixed carbon) of coke was kept at 2.0 ± 0.1 mg; at an air flow of 50 ± 2 ml/min, the temperature was increased from room temperature to 1000 °C at a heating rate of 40 °C/min.

The activation energies of 18 raw coals in pyrolysis and those of 18 pyrolyzed cokes in combustion were calculated with thermogravimetry (TG) curves based on the Doyle–Ozawa method. The activation energy was calculated using the following equation:

$$\ln[-\ln(1-\alpha)] = \ln\frac{AE}{\beta R} - 2.315 - 0.4567\frac{E}{RT} \qquad (1)$$

where α is the sample conversion ratio, A is the frequency factor, E is the activation energy, β is the heating rate, and R is the gas constant. A linear regression was fitted to the data points on the graph of '$\ln[-\ln(1-\alpha)]$' versus '$1/T$' based on the TG curves at different sample conversion ratios. The line slope was used to calculate E.

Table 1
Chemical composition of typical Chinese power coals on an air-dried basis.

No.	Coal names	Proximate analysis				Net calorific value (kJ/g)	Ultimate analysis				
		Moisture (%)	Ash (%)	Volatile matter (%)	Fixed carbon (%)		Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulfur (%)	Oxygen (%)
1	Xilutian	9.05	13.43	34.88	42.64	20.73	56.82	3.09	0.93	1.17	15.51
2	Leling	4.19	19.45	33.19	43.17	23.91	59.22	4.08	1.02	4.38	7.66
3	Wujia	8.07	19.38	32.60	39.95	19.29	54.05	3.22	0.88	0.91	13.49
4	Hongmiao	8.19	19.70	32.04	40.06	19.0.13	52.39	3.12	0.77	1.32	14.51
5	Gushan	6.85	22.45	31.77	38.93	19.15	52.93	3.08	0.73	1.03	12.95
6	Shenfu	6.60	9.56	31.49	52.35	26.22	66.34	3.61	0.95	0.38	12.56
7	Fengshuigou	9.11	20.59	31.46	38.83	18.14	50.44	2.63	0.80	0.62	15.81
8	Yima	9.47	14.19	30.02	46.32	23.80	58.44	2.92	0.83	0.44	13.71
9	Zaozhuang	1.84	18.10	29.43	50.63	27.73	65.88	4.06	1.22	0.88	8.02
10	Changguang	1.58	37.95	29.16	31.30	19.02	45.34	3.76	1.11	3.74	6.51
11	Xinwen	2.98	22.23	28.80	45.99	23.78	59.78	3.62	1.16	0.71	9.52
12	Yuanbao	7.97	26.31	27.75	37.97	17.39	48.52	3.11	0.74	1.83	11.53
13	Huangling	3.85	23.68	26.98	45.49	24.49	58.93	3.42	1.12	0.85	8.15
14	Datong	2.50	14.42	26.06	57.02	28.75	68.55	3.92	0.81	0.69	9.11
15	Huainan	1.62	25.47	23.32	49.59	25.70	61.26	3.32	1.09	0.52	6.72
16	Luan	1.45	18.19	13.77	66.59	27.76	71.28	3.55	1.24	0.34	3.95
17	Liuqiao	1.00	14.62	10.44	73.94	30.65	75.90	3.14	1.15	0.42	3.81
18	Jincheng	4.62	20.16	6.17	69.05	26.88	67.42	2.00	0.97	0.28	4.55