Study on Effects of Low-Temperature Preheating on Ignition and Combustion of Weakly Caking Coal

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1 Introduction

Coal is an important resource in the energy field, and how to achieve the efficient utilization of coal is always the focus of research. According to the use of coal, it is currently categorized into thermal coal and coking coal. Thermal coal is primarily used for thermal power generation. Coking coal, on the other hand, is heated to high temperatures under air-insulated conditions to produce the coke needed to make iron in blast furnaces. Coking coal is divided into bituminous coal according to the degree of deterioration, mainly including gas coal, fat coal and weakly caking coal, etc. Proximate analysis, caking property (Caking Index, Char Residue Characteristic), and characteristics of coal macerals (Vitrinite Reflectance, Vitrinite Content) are currently the main methods for evaluating coking coal. However, weakly caking coal, which rarely meets the requirements of caking processes, is seldom used as coking coal. Moreover, when used as thermal coal, weakly caking coal tends to cause caking and slagging issues. Therefore, how to achieve the efficient use of weakly caking coal is the focus of the research.

The caking property of coal is usually defined as the ability of the coal to bind itself or inert materials when heated in isolation from the air [1]. Taylor found that coal forms anisotropic flow-polymerised liquid crystals during heating, and the amount of this substance determines the strength of the coal caking property [2]. This substance is known as plastic mass, which is a viscous mixture of gas, liquid and solid phases coexisting when coal is heated to a certain temperature [1]. The liquid phase material in it is the main cause of caking. Studies have shown that there are three main sources of liquid phase in plastic mass [3]: (1) the generation of free radicals from the bridging bonds in coal to produce liquid phase products. (2) the transformation of aliphatic structures in coal into liquid aliphatic hydrocarbons. (3) the transformation of aromatic structures in coal into small molecules of aromatic hydrocarbons. From the mechanism, the researchers found an effective way to change weakly caking coal. Yoshida investigated the effect of heating rate on caking property and showed that when the raw coal was rapidly heated up to 400-500°C at a rate greater than 100°C/min, the caking property was significantly enhanced [4]. Matsuura found that the thermal decomposition reaction of plastic mass was limited when the coal was rapidly heated up, which in turn enhanced the caking property [5]. In order to achieve the combustion and gasification utilization of weakly caking coal, researchers treated the weakly caking coal by pre-

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oxidation [6,7]. The results showed that the caking index decreased significantly after pre-oxidation, and no caking occurred in the subsequent combustion.

The above studies have shown that the caking property of coal can be adjusted by pretreatment, but there are fewer studies on the specific composition of substances that change during pretreatment and on the ignition and combustion of weakly caking coal by pretreatment. Therefore, in this study, the separation of weakly caking coal fractions was achieved by acid pickling and low-temperature ashing. Meanwhile, the specific changes occurring in the coal fractions during low-temperature preheating were investigated by using technical analyses such as FTIR and Raman. The ignition and combustion processes of different samples before and after low-temperature preheating were observed using the heating stage microscope. Moreover, the effects of low-temperature preheating on the ignition and combustion of weakly caking coals were grasped.

2 Experimental

2.1 Coal samples preparation

In order to conduct a comparative analysis of the physicochemical properties of the weakly caking coal, three raw coal samples were chosen: coal HL (weakly caking coal), coal SM (non-caking bituminous coal from Shannxi Province of China), and coal SH (anthracite from Shanxi Province of China). All samples were pulverized to a particle size range of 0-0.12 mm. The results of property characterization are summarized in Tables 1 and 2.

Table 1: Proximate and ultimate analysis of coal

Sample	Proximate analysis (wt. %)				Ultimate analysis (wt. %)					$Q_{net,ar}$ (MJ/kg)
	M_{ad}	A_{ad}	FC_{ad}	V_{daf}	C_{ad}	H_{ad}	O_{ad}[a]	N_{ad}	S_{ad}	
HL	0.96	29.50	44.12	36.55	56.06	3.64	8.23	0.98	0.63	21.90
SM	8.72	5.88	57.10	33.14	70.40	3.44	10.17	0.89	0.50	26.97
SH	1.02	20.42	72.45	7.78	72.21	2.37	2.69	0.92	0.37	25.96

[a] by difference

Table 2: Parameters related to caking property

Sample	CRC	$G_{R.I.}$	Gray-King Assay			
			Coke Type	CR_{ad}/%	Tar_{ad}/%	$Water_{ad}$/%
HL	5	27	E	81.3	9.4	4.1
SM	3	0	B	73.3	6.8	12.4
SH	2	/	/	/	/	/

The coal samples were subjected to acid pickling and low-temperature ashing to separate the organic and inorganic components. Acid pickling was carried out conducted in accordance with the Chinese National Standard GB/T 7560-2001. The low-temperature ashing method followed the Chinese national standard GB/T 212-2008 and the ignition temperature of raw coal, allowing the coal sample to slowly heat up to 450°C in the muffle furnace, and then maintaining this temperature for 3 h. During the process, the furnace door was kept with a gap of about 15 mm.

2.2 CRC

As shown in Table 2, CRC and $G_{R.I.}$ are both used as the evaluation index of caking property. In this paper, CRC was mainly used for the rapid evaluation of caking, and the normalized method was as follows: (1) Preheating a muffle furnace to 900 ± 10°C; (2) Loading a lidded porcelain crucible containing 1.0 ± 0.1 g sample into the furnace for 7 min; (3) Cooling to ambient temperature followed by mass measurement; (4) Determining CRC through morphological examination of the residue. According to Chinese National Standard GB/T 212-2008, coal samples are classified as non-caking (CRC 1–3), weakly caking (CRC 4–5), or strongly caking (CRC 6–8).

2.3 Low-temperature preheating

The porcelain crucible was placed in a muffle furnace preheated to the target temperature under air atmosphere. After the crucible reached thermal equilibrium, a measured coal sample was added for heating. When the preset time elapsed, the treated sample was removed, cooled to room temperature, and weighed to obtain the low-temperature preheating sample.

3 Results and discussion

3.1 Acid pickling and low-temperature ashing

The samples obtained after acid pickling were weighed, and the results are shown in Table 3. The mass of the samples decreased after acid pickling, and the mass loss was close to the ash content of the raw coal. To elucidate the impact of acid pickling on the inherent components of coal, the proximate analysis and mass loss of coal samples were used to calculate the changes in moisture, volatile matter, ash, and fixed carbon in 1 g of raw coal before and after acid pickling. As shown in Figure 1, the ash content of three coal samples decreased significantly after acid pickling, while the changes in the other components were relatively small. This indicates that acid pickling effectively removed most of the ash from the raw coal, achieving the extraction of organic components.

The results of low-temperature ashing are shown in Table 4. After low-temperature ashing, the mass of coal samples decreased substantially.

Table 3: Mass change of coal samples before and after acid pickling

Sample	Mass before acid pickling/g	Mass after acid pickling/g	Mass loss/%
HL	6.03	3.96	34.33
SM	6.00	5.13	14.50
SH	6.01	4.88	18.80

Table 4: Mass change of coal samples before and after ashing

Sample	Mass before ashing/g	Mass after ashing/g	Mass loss/%
HL	0.99	0.25	74.80
SM	1.01	0.07	92.95
SH	1.00	0.86	85.65

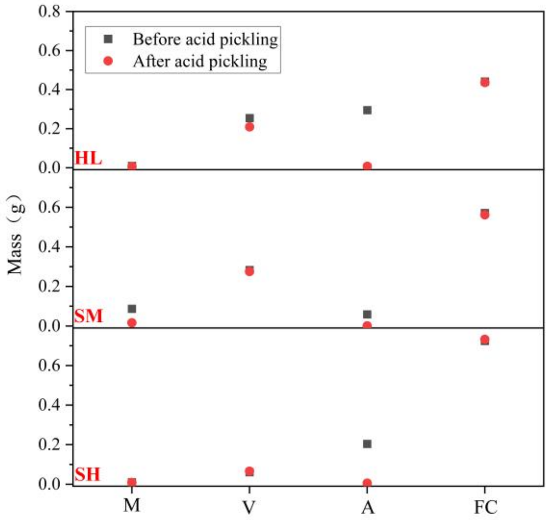


Figure 1: Mass change of each component before and after acid pickling

The CRC of samples obtained by acid pickling and low-temperature ashing was analyzed, and the results are shown in Figure 2. The CRC of HL after acid pickling remained at 5, consistent with the raw coal, while the CRC of HL after low-temperature ashing decreased to 2. For SM and SH, the CRC remained unchanged before and after treatment.

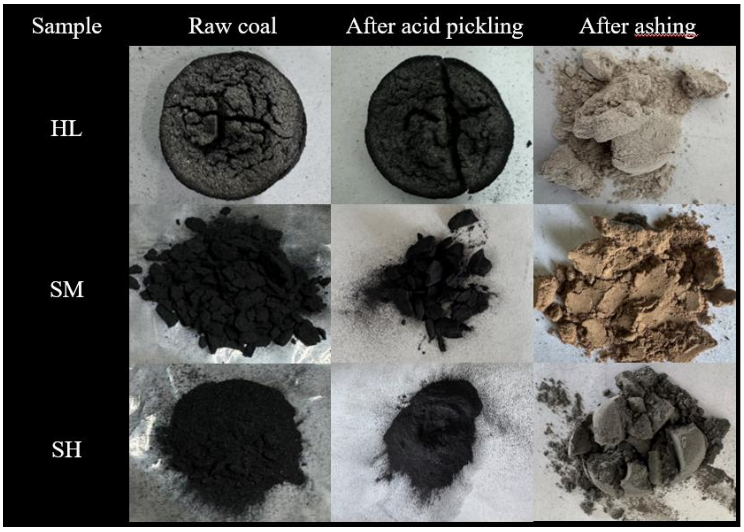


Figure 2: Change in CRC of coal samples

These results indicate that the organic components in weakly caking coal are the main cause of caking. Furthermore, acid pickling can effectively extract organic components without significantly altering structural integrity.

3.2 Low-temperature preheating

HL were subjected to low-temperature preheating at different temperatures and time as the experimental method, with specific parameters listed in Figure 3. During the experiment, it was observed that the coal ignited when the temperature reached 400°C. Therefore, the temperature range was set between 100°C and 300°C. The CRC of the samples after low-temperature preheating is presented in Figure 3. The results indicate that heating HL at 100°C for less than 300 s had no effect on CRC. However, heating at 200°C for 300 s reduced the CRC to 3, and heating at 300°C for 15 s reduced it to 2. Furthermore, the longer the preheating time, the more pronounced reduction in CRC.

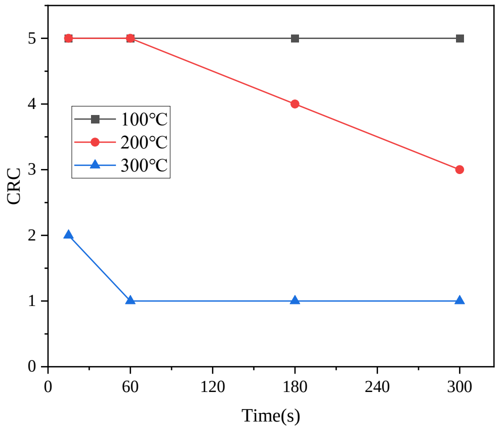


Figure 3: Changes in CRC of HL after low-temperature preheating

3.3 FTIR and Raman

Different functional groups in coal have different characteristic vibration frequencies, thus corresponding to different infrared spectroscopy characteristic absorption peaks. According to the principles of organic chemistry and infrared spectroscopy, the functional groups corresponding to each absorption peak of coal are shown in Table 5 [8,9]. The position and description of Raman peak spectrum bands used in this article are shown in Table 6 [10].

Table 5: The band assignments for functional groups in coal FTIR spectra [8,9]

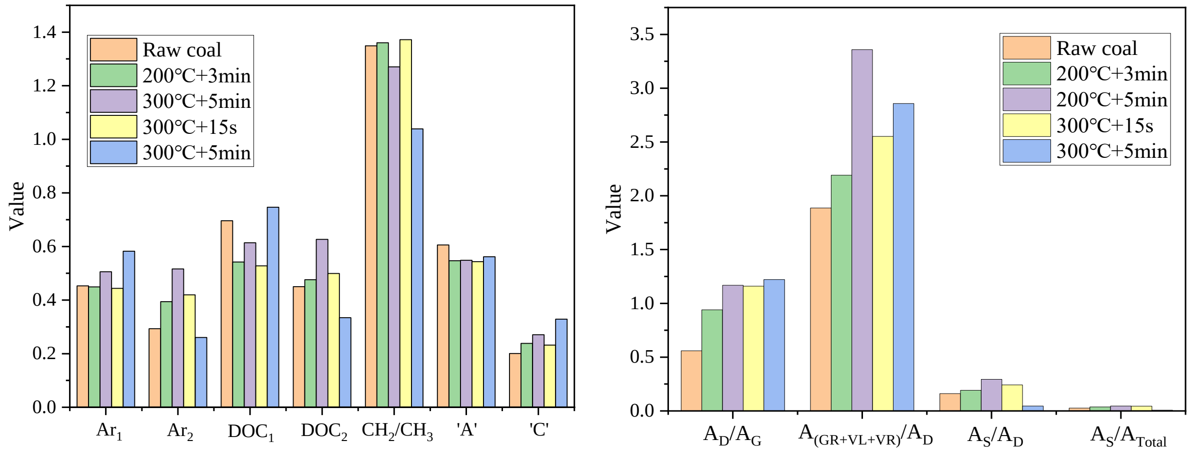
Region(cm^{-1})	Modes of functional groups
3100-2990	Aromatic CH stretching
2990-2800	Aliphatic CH_x stretching
2990-2940	Asymmetric CH_3 stretching
2940-2900	Asymmetric CH_2 stretching
1760-1650	Carbonyl/carboxyl C=O stretching
1650-1530	Aromatic C=C ring stretching
900-700	Aromatic CH out of plane bending

Table 6: Band assignment of Raman spectrum for coal [10]

Band name	Band position/cm^{-1}	Description
G_L	1700	Carbonyl group C=O
G	1590	Aromatic ring quadrant breathing; alkene C=C
G_R	1540	Aromatics with 3-5 rings; amorphous carbon structures
V_L	1465	Methylene or methyl; semi-circle breathing of aromatic rings
V_R	1380	Methyl group
D	1300	D band on highly ordered carbonaceous materials
S_L	1230	Between aromatic rings and aromatics with not less than 6 rings aryl–alkyl ether; para-aromatics

S	1185	$C_{aromatic}$–C_{alkyl}; aromatic(aliphatic)ethers; C–C on hydroaromatic rings; hexagonal diamond carbon sp^3
S_R	1060	C–H on aromatic rings; benzene(ortho-di-substituted)ring
R	960-800	C–C on alkanes and cyclic alkanes

The content of different functional groups in coal was determined according to the percentage of peak area of each band, and the relevant parameters were calculated, as shown in Figure 4.



(a) FTIR (b) Raman

Figure 4: FTIR and Raman structural parameters of various coal samples

4 Conclusions

(1) The organic components in weakly caking coal are the main cause of caking. Using the acid pickling method described in this study, the organic components could be extracted without significantly altering structural integrity. Furthermore, the results of CRC and heating stage microscope show that the caking property of the organic components was similar to the raw coal, while the inorganic components exhibitted non-caking.

(2) The caking property of weakly caking coal can be disrupted by low-temperature preheating . Higher temperatures and longer durations led to more pronounced reductions in caking property. The results of FTIR and Raman show that after low-temperature preheating, the aromaticity of weakly caking coal was increased. Meanwhile, the aliphatic hydrocarbon length was shortened, the degree of branching was reduced, and the content of aliphatic carbon-hydrogen also decreased.

(3) The caking property of coal has a significant impact on its ignition and combustion performance. Heating stage microscope analyses revealed that weakly caking coal exhibitted caking behavior under the nitrogen atmosphere, while this phenomenon was not observed under the air atmosphere. Moreover, it had been noted that the combustion efficiency of weakly caking coal declined following the caking process.

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