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Structure characterization and metallurgical properties of the chars formed by devolatilization of lump coals

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ABSTRACT

The thermal pyrolysis of two lump coals used in the Corex process was carried out, and the structure, strength and reactivity to CO_2 of the resulting chars were comprehensively investigated. The results show that the characteristic of the resulting chars is greatly affected by coal properties and carbonization conditions. XLC char forms visible pores because of its good thermoplastic property, and the bigger pores could affect the yields of volatiles. However, fissures are produced in DLC char during pyrolysis due to the non-caking property and cracks appear to decrease the production of pores. With the increasing annealing time and temperature, pore size and pore volume of chars decrease, which can be related to the shrinkage of coal char. The mechanical strength of chars is enhanced with increasing carbonization time and temperature, but the crushing strength of DLC chars is significantly influenced by cracks. Chars produced with longer time and higher temperature primarily display a lower CO_2 reactivity according to the gasification tests. The results further indicate that factors affecting the CO_2 reactivity are different for the two series of chars. The char reactivity index appears to have a linear correlation with the char strength after reaction.

1. Introduction

Understanding of pyrolysis characteristic of coal is continually developing because coal is a complex and heterogeneous substance [1–4]. In the past, many researchers have mainly concentrated in the carbonization of pulverized coals due to the wide application in the ironmaking industry [5–8], such as the coking process which involves the carbonization of blending coals with particle size under 3 mm, and a temperature heating up to 1100 °C in an oxygen deficient atmosphere and a residence time for a dozen hours. However, with the increasing environmental protection and shortage of good quality coking coal, some emerging ironmaking processes have been extensively explored to save resources and energy, as well as to reduce environmental pollution. The Corex process emerges as a more environmentally friendly alternative to the blast furnaces for the melting reduction process, which allows using non-coking coal as a fuel to take the place of cokes. So far, the primary Corex C-2000 including Saldanha Steel in South Africa and Jindal Vijayanagar Steel Limited in India have the capacity of 0.65 and 0.8 mtpa, respectively, and the Corex C-3000 of Baosteel in China has expanded to 1.5 mtpa capacity [9–11]. Although the share of production by the Corex process is very low compared with a world production of 1.5 btpa, the Corex process is one of the most successful technologies in the emerging ironmaking processes.

In the Corex process, lump coals are fed into the top of a gasifier where the temperature is high. The property of the resulting char is greatly affected by the coal particle size, the ambient temperature, etc. Then chars produced from the lump coals form the fixed-bed and have to undergo many complicated physical and chemical changes, such as mechanical movement, gasification reaction and combustion, deteriorating the property of char bed. However, the char bed is crucial to maintain the permeability to allow the reduction gases passing through freely and ensure the sensible heat of gases transferring to the char bed [12]. Hence, a deep understanding on the pyrolysis behavior of lump coals, particularly in the resulting char structure and reactivity, is imperative to ensure the stable operation.

Generally, lump coal may undergo decrepitation when exposed to high temperature, which changes the particle size distribution of the coal [13]. Van Dyk used coal with particle size up to 19 mm to determine the influence of carbonization time and temperature on thermal fragmentation, and the correlation of fragmentation between atmospheric conditions and 2.6 MPa pressure was established [14]. In addition, Yu et al. pointed out that the behavior of individual coal particle during pyrolysis differed markedly from pulverized coals [15–17], for example, the deformation of pulverized coals during pyrolysis takes place along all directions, while the swelling trend of a natural lump coal occurs along the laminated structure [18]. Furthermore, the property of char after pyrolysis is often affected by many factors. Apart from coal properties, annealing temperature and time, heating rate and

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particle size have a strong impact on decrepitation, fracture, swelling and agglomeration, which affects the physical and chemical properties of coal char [19–21]. For example, the strength of coal char is weaken by swelling [22], and the deformation increases with increasing particle size, heating rate and volatile matter [23,24]. The carbonization conditions also have a big influence on pore structure and the transformation of mineral matters because of the uneven distribution of microlithotype composition in lump coal [25].

The devolatilization of lump coal is the first and important step in the coal carbonization process. The devolatilization rate is barely affected for the coal with particle size less than 0.5 mm, while a greater decreasing rate can be found for the particle size up to 1 mm, which can be related to the heat and mass transfer [26,27]. Kim et al. pointed out that the devolatilization rate of lump coals increased with increasing temperature as well as the increasing volatiles present in the coals [28]. In addition, high temperature pyrolysis behavior and kinetics of lump coal in Corex melter gasifier were investigated in our previous work, the mechanism and the kinetics parameters were obtained [11].

Despite a series of researches on lump coals, there is limited information available about the comprehensive performance of the chars formed by devolatilization of lump coals, particularly in the mechanical strength and the reactivity which are crucial to the Corex process. In the present study, the changes of structure and metallurgical properties of coal chars produced under different carbonization conditions, including the pore characteristic, carbon structure, char strength and CO_2 reactivity were studied.

2. Experimental

2.1. Coal sample preparation

Two kinds of lump coals primary used in the Corex process, Xinglongzhuang lump coal (XLC) and Datong lump coal (DLC) were selected. Their proximate and ultimate analyses are presented in Table 1. Table 2 shows the petrographic analysis and caking characteristic of XLC and DLC, and the chemical composition of the coal ash is summarized in Table 3. The proximate analysis shows that the content of volatile matter of XLC is higher than that of DLC. The values of caking index for XLC and DLC are equal to 39 and 0, respectively, which suggest that XLC has a certain caking property and DLC is a typical non-caking coal. It can be seen from an Audibert–Arnu dilatometer test in Table 2 that both of the coals display contraction trend during heat treatment, with the value of 29% and 4% for XLC and DLC compared with their parent coal volume, respectively. The coal particle size was selected between +20 and −30 mm, which is regarded as the optimum mean grain size of coal in the Corex process [29]. Coal sample was dried by heating in a muffle furnace at 120 °C for 2 h to remove the moisture.

2.2. Carbonization process

The carbonization experiments for the two coal samples with large particle size were carried out in a 2 kg coking furnace with the heating element of resistance wire. Approximately 1 kg coal sample was placed in a coking retort with a gas outlet, and with an internal diameter of 100 mm and a length of 500 mm. In order to simulate the influence of different temperatures on the fast pyrolysis process of lump coal, the coking retort with coal sample was put into the isothermal zone of coking furnace after the experimental temperature had reached to 700, 800, 900, 1000 and 1100 °C with an average heating rate between 20 and 30 °C/min that depended on the experimental temperature, and the sample was treated for 1 h. The obtained chars were labeled in the following forms, XChar-700, DChar-700, etc. In addition, the tests of the influence of time on char property were chosen from 0.5 to 2.5 h with the interval of 0.5 h at a constant temperature of 1000 °C, labeled as XChar-0.5, DChar-0.5, etc. When the test was completed, the coking retort with char sample was taken out of the furnace and cooled in air below 100 °C within 40 min.

Table 1
Proximate and ultimate analyses of XLC and DLC.

Sample	Proximate Analysis (wt.%)				Ultimate Analysis (d, wt.%)				
	M_{ad}	A_d	VM_d	FC_d	C	H	N	O[a]	S
XLC	4.0	8.9	35.0	56.1	76.0	4.7	1.1	8.8	0.6
DLC	8.3	14.4	31.4	54.2	69.6	4.1	0.8	10.7	0.3

M: moisture; A: ash content; VM: volatile matter; FC: fixed carbon; ad: air dried basis; d: dried basis.

[a] By difference.

Table 2
Petrographic analysis and caking characteristic of XLC and DLC.

Sample	Petrographic analysis (%)			Caking index[a]	Dilatometry Audibert–Arnu[b] (%)	
	Vitrinite	Liptinite	Inertinite		a	b
XLC	54.5	9.2	26.4	39	29	No dilatation
DLC	48.4	4.6	37.1	0	4	No dilatation

[a] Following Chinese Standard Method (GB/T 5447-1997).

[b] Following Chinese Standard Method (GB/T 5450-1997).

Char sample with particle size more than 10 mm was used to perform the mechanical strength test using I type drum with a metallic drum having an internal diameter of 130 mm and a length of 700 mm. The free chars fell on the bottom of the drum with the rotational speed of 20 rpm and a total of 100 revolutions. The mass of the +10 mm and −3 mm particles was weighed to evaluate the char crushing strength property (CCS) and the abrasion resistance index (ARI), which were calculated by using Eqs. (1) and (2), respectively.

$$\mathrm{CCS} = \mathrm{m}_{+10}/\mathrm{m}_0 \times 100\% \tag{1}$$

$$\mathrm{ARI} = \mathrm{m}_{-3}/\mathrm{m}_0 \times 100\% \tag{2}$$

where m_{+10} is the mass of the +10 mm particles, m_{-3} is the mass of the −3 mm particles, and m_0 is the initial mass of char put into the drum. It should be noted that the higher CCS and lower ARI, the better is the mechanical strength. One of each group experiments was carried out three times in order to verify the reliability, and the obtained error was under 2%.

2.3. Gasification process

Approximately 200 g (±0.1 g) chars with the particles (15–20 mm) after drum test were used to examine the char reactivity with CO_2, as shown in Fig. 1. In the heating process, N_2 (2 L/min) was purged into the retort to flush out the residual oxygen, while the reactant CO_2 was taken the place of N_2 at the flow rate of 5 L/min when the temperature kept at 1000 °C. The infrared gas analyzer (Precision of ±0.5% FS) was used to measure the change of the off gas composition. The data recording started when the sum of the percentage of CO and CO_2 reached to 99.5% and it was stored by the computer collecting system simultaneously. After completion of the test, the char sample was cooled under N_2 atmosphere. The mass of the gasified chars was weighed and

Table 3
Chemical composition (wt%) of the coal ash.

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	SO_3	P_2O_5
XLC	49.58	40.67	4.33	1.56	0.66	0.50	0.34	1.13	1.01	0.10
DLC	41.54	15.13	34.08	1.74	1.52	0.55	0.78	0.76	1.05	0.25