



Full Length Article

Physico-chemical structure and combustion properties of chars derived from co-pyrolysis of lignite with direct coal liquefaction residue



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HIGHLIGHTS

- Addition of DCLR raised aromaticity and order degree while reduced porosity of chars.
- Interaction was presented in co-pyrolysis process and changed yield, structure and reactivity of chars.
- Combustion reactivity of chars decreased with the increase of DCLR dosage.
- Raman/FTIR parameters reflected the combustion reactivity of chars.

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ABSTRACT

Co-pyrolysis of lignite with direct coal liquefaction residue (DCLR) is a promising method in the field of clean coal technology. To investigate the influence of DCLR fraction on the physico-chemical structure and combustion reactivity of the co-pyrolysis chars, char samples with different mass fraction of lignite and DCLR were prepared in a quartz tube fixed-bed reactor at 550 °C. Then the physico-chemical structure and combustion properties of co-pyrolysis chars were characterized by Microscope, Scanning electron microscope, Raman Spectrometer, Fourier Transform Infrared Spectrometer, automatic gas sorption analyzer and thermogravimetric analyzer. Results showed that there was interaction of the co-pyrolysis of lignite and DCLR, both on char yield and on char's structure and combustion reactivity. And such interaction became obvious with the increase of DCLR fraction. Compared with lignite char, the addition of DCLR resulted in high aromaticity and ordered structure of co-pyrolysis chars, while the pore structure of chars from co-pyrolysis became less developed. The combustion reactivity of chars decreased with the increase of DCLR fraction. The chars produced during co-pyrolysis were of special structure, which were different from lignite and DCLR chars pyrolyzed individually, and that was the reason for their different combustion behavior and reactivity. With the increase of DCLR dosage, the combustion reactivity of components corresponding to lignite char in co-pyrolysis chars reduced while components to DCLR char were enhanced. In addition, the combustion reactivity of pyrolysis chars showed good correlations with Raman/FTIR parameters.

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1. Introduction

Direct coal liquefaction residue (DCLR) is the important by-product in direct coal liquefaction technology, which accounts for 20–30 wt.% of raw coal [1,2]. DCLR consists of 30–50 wt.% of heavy oils and asphaltenes [3,4], part of these heavy fractions can be recovered through low-temperature pyrolysis which will improve the economic benefits of direct liquefaction process. However, DCLR has low soften point (< 180 °C) and strong cohesiveness for

the existence of the heavy components, which makes it difficult to introduce into the feeding system of the pyrolysis process [5]. In order to solve the problem and take full advantages of DCLR, non-caking or weak-caking raw materials are generally considered to co-pyrolysis with DCLR, low-rank coals are the most commonly used one [6]. The co-pyrolysis of low-rank coals with DCLR has been investigated by many researchers. Liu et al. [7] researched the co-pyrolysis properties of Shenhua DCLR with its raw coal, and analyzed the composition of co-pyrolysis products and the behavior of the released gases. Thermogravimetric characteristics of the co-pyrolysis of Fugu coal and DCLR also have been investigated [8]. Divergent conclusions were obtained about the influence

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of co-pyrolysis of lignite with DCLR on the tar yield [9,10]. Xu et al. [9] studied the co-pyrolysis characteristics of lignite with DCLR and analyzed the morphology changes of co-pyrolysis chars by scan electron microscope (SEM). However, it must be pointed out that current researches on co-pyrolysis of low-rank coals with DCLR are concentrated on the analysis of tar and gas products, few studies extend to physico-chemical structure and reactivity of co-pyrolysis chars. As the major product of co-pyrolysis, the utilization of co-pyrolysis chars influences the economic efficiency of coal processing directly. Therefore further study on the properties of co-pyrolysis chars is very essential.

Combustion is one of the major applications of char which can provide large amounts of energy for power generation [11]. The characteristic of char combustion depends on multiple factors, among which the physico-chemical structure is a key factor influencing the combustion reactivity. After being pyrolyzed, the physico-chemical characteristics of coal such as pore structure and functional groups will change [12,13], and these changes can be characterized by advanced techniques including SEM, Raman Spectrometer, Fourier Transform Infrared Spectrometer, automatic gas sorption analyzer and X-ray diffraction (XRD). Previous researches have indicated that pyrolysis can reduce oxygen content [14] and increase specific surface area of raw coal [15]. Meanwhile aromatic ring size would grow with the enhancement of pyrolysis temperature [16]. These changes consequently result in the difference of char reactivity. Currently, the combustion properties of char are commonly measured by thermogravimetric analyzer (TGA) for its high precision and excellent repetition [17,18]. Combustion characteristic parameters such as combustion characteristic temperatures and combustion reactivity index can also be obtained by the analysis of thermogravimetric data. Researches have recognized that these parameters can give a good assessment to the combustion properties of coal and char [16,19].

DCLR will melt into fluid when heated (soften point < 180 °C). Thus in the co-pyrolysis process, it is likely to enter into internal pores of low-rank coals, which may affect the development of pore structure of co-pyrolysis chars. The low H/C ratio and poor pore structure of DCLR [5] determine its fire resistant properties; it may reduce combustion reactivity of low-rank coal chars during co-pyrolysis. In order to understand the effect of DCLR fraction on the co-pyrolysis process, in this study, we investigated the physico-chemical structure and combustion characteristics of co-pyrolysis chars prepared from lignite and DCLR. Attention was paid to the influence of the mass fraction of DCLR on co-pyrolysis char characteristics. The physico-chemical structure of co-pyrolysis chars was also linked to their combustion properties to provide theoretic reference for their efficient utilization.

2. Experimental section

2.1. Materials

Lignite used in this study was obtained from Yunnan province, China. DCLR was obtained from 6 t/d direct coal liquefaction pilot plant of Shenhua Group in China. Yunnan lignite (YNL) and DCLR were pulverized, passed a 100 mesh sieve (< 154 μm) and stored in a sealed condition. The proximate and ultimate analyses of YNL and DCLR are listed in Table 1.

2.2. Co-pyrolysis

The quartz tube fixed-bed reactor used for pyrolysis experiments is shown in Fig. 1. The length of the quartz tube reactor is 60 cm and inner diameter is 2.5 cm. The flat-temperature zone of the electricity furnace (SK2-2.5-13D, Tianjin) is 8 cm. In each run,

approximately 3 g of sample was put into a quartz boat with length of 6 cm, inner diameter of 2 cm and height of 1 cm. First, the reactor was passed over N_2 (99.999%) at a flow rate of 300 mL/min for 20 min. After the air in reactor was removed, sample was heated from ambient temperature at 10 °C/min to the desired pyrolysis temperature. The tar produced during pyrolysis was in vapor phase and would be entrained out of the reactor by flow gas. The residence time of sample was 30 min at the final temperature. Then the sample was cooled to room temperature in N_2 stream and collected from a quartz boat. Tar and water products were collected in a cooler, and then separated according to ASTM D95-05^{e1} (2005) using toluene as solvent. First, pyrolysis experiment was carried out at 450, 550 and 650 °C, and the mass fraction of DCLR in samples was 0, 20, 100%, respectively. Tar yield of DCLR pyrolysis at 450, 550 and 650 °C was 16.96, 26.18 and 17.05%, which was far more than the maximum yield of lignite tar (550 °C) with 4.30%. Meanwhile, tar yield with 20 wt.% DCLR at 550 °C (11.18%) was also larger than that of 450 (9.68%) and 650 °C (7.51%). Therefore the co-pyrolysis temperature was designated as 550 °C for the maximum yield of tar of all the test samples. Considering the cohesiveness of DCLR [9,10], the mass fraction of 10, 20, 30% of DCLR was selected. After being fully mixed, the blended samples were pyrolyzed at 550 °C and chars were collected in sealed bags. Chars with 0, 10, 20, 30 and 100 wt.% DCLR were defined as YNC, YDC1, YDC2, YDC3 and DDC, respectively. All of the pyrolysis experiments were repeated at least 3 times to ensure accuracy and reliability of the experimental data, and the results (actual char yield) reported here are the averages of multiple measurements. The relative error of each experiment is less than 0.22%. The proximate and ultimate analyses of char samples are listed in Table 1.

2.3. Characterization

The carbon structure of chars was characterized by a Raman spectrometer (Renishaw in Via, UK) with argon ion laser. The excitation line was 514.5 nm and Raman spectra in the range 800–1800 cm^{-1} were acquired at a resolution of 2 cm^{-1} . Microscope (Zeiss Axio Scope A1, Germany) and a high resolution scanning electron microscope (JSM-7001F, Japan) were employed to investigate the morphological variation of char samples. The changes of functional groups of chars were measured by a Fourier Transform Infrared Spectrometer (VERTEX 70, Bruker, Germany). Chars were fully mixed with dried KBr powder at the mass fraction of 1:200 and the spectra were recorded within wavenumbers of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} . The specific surface area and pore structure of chars were measured by a Micromeritics ASAP2020 adsorption apparatus (Micromeritics, America) using N_2 and CO_2 as the probe gas. The adsorption of N_2 was at 77 K whereas the adsorption of CO_2 was at 273 K. The surface area of samples was calculated by Brunauer Emmett Teller method. The N_2 adsorption was used to analysis macropore and mesopore structure (Barrett-Joyner-Halenda model) whereas the micropore structure was evaluated by CO_2 adsorption (Horvath-Kawazoe method).

2.4. Combustion properties of char

Combustion experiments of chars were conducted by a thermogravimetric analyzer (TGA, Setsys Evolution, SETARAM, France). In order to exclude the influence of diffusion effect on the combustion process, particle size and air flow rate were varied to investigate the combustion characteristics of pyrolysis chars. Experiment results showed that the diffusion effect could be neglected when the char particle size was less than 200 mesh (< 77 μm) and the air flow rate exceeded 80 mL/min. Thus the experiment conditions

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