Fuel Processing Technology 151 (2016) 40–49

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

Effects of atmospheric gas on pyrolysis characteristics of briquetted lignite and surface properties of semi-char

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ARTICLE INFO

Article history:
Received 30 December 2015
Received in revised form 24 May 2016
Accepted 25 May 2016
Available online 4 June 2016

Keywords:
Briquetted lignite
Low temperature pyrolysis
Semi-char
Ignition temperature
Pyrolysis atmosphere

ABSTRACT

The physicochemical properties of semi-char produced by the pyrolysis of binder cold-briquetted lignite (BCBL) in a fixed bed reactor at 600 °C under different atmospheres of CO, CO_2, CH_4, H_2, and N_2 were investigated comprehensively. Using the N_2 BET method, the specific surface area of the different semi-chars were in the range of 1.71–2.53 ($m^2\ g^{-1}$), the pore volume and average pore diameter of the CO semi-char were lowest, and the N_2 semi-char values were highest. In contrast, the Dubinin CO_2 method at 0 °C gave specific surface areas of semi-chars in the range 165–192 ($m^2\ g^{-1}$). The CO, N_2 and CH_4 semi-chars had the largest diameter, and the H_2 semi-char had the lowest diameter. The TGA test indicates the ignition temperature of BCBL was lower than different semi-chars. The FTIR spectra of BCBL and different semi-chars revealed that the removal rate of the oxygen-containing functional groups showed the highest efficiency under CO atmosphere, thus representing that CO could help to cleave the ether bond. The C1s, O1s, N1s, and S2p spectra of semi-chars under different atmospheres were analyzed by XPS. Raman analysis was also conducted to study the degree of structural orderliness in different semi-chars, which has great significance to the compressive mechanical strength of it. The semi-char produced in an atmosphere of CO_2 showed a more condensed crystalline structure and lowest compressive mechanical strength among all the semi-chars.

1. Introduction

Low-ranked coals (LRCs) are very abundant in several regions throughout the world and constitute a significant resource for both energy and chemical feedstock. However, in spite of their abundance and relatively low market price, LRCs have not been utilized to nearly the same extent as high-ranked coals. Lack of interest in LRC is mainly due to its high water (25–60 wt.%) and oxygen contents [1–4]; moreover, they are more susceptible to spontaneous combustion. This enforces restrictions on both their storage in stockpiles and in their transportation. Furthermore, mechanized mining technologies impose restrictions on the yield of lump coals, which account for only 15 to 20% of the mined coals, resulting in the shortage of lump coal and higher percentage of pulverized coal. Efficient utilization of pulverized coal plays a significant role in solving the demand-and-supply conflict of lump coal [5].

To date, extensive research efforts have been devoted to the methods and techniques to improve the quality of inferior coal, which mainly include drying, briquetting, and pyrolysis techniques [6–8]. The main products of pyrolysis of binder cold-briquetted lignite (BCBL) are semi-char, tar, and gas pyrolyzates. Compared with lignite and gas coal, the semi-char obtained from BCBL develops a porous structure, high reactivity, and higher compressive mechanical strength. Moreover, semi-char can also be used as a metallurgical reducer, fixed bed gasifier, and hydrogasifier, producing methane [9,10]. Activated coke with huge specific surface areas and high adsorption capacities was made by our research team by special activation treatment, which can be effectively used for the treatment and purification of flue gases and wastewater. Therefore, briquetting and pyrolysis play an important role in the development and efficient multi-level utilization of low-ranked pulverized lignite.

Despite the existence of significant body of literature, there have been only very few reports concerning the effects of atmospheric gas on the characterization of the semi-char [11]. A study on the influence of coke oven gas (COG) components on char characteristics in a fixed bed reactor indicated that the char obtained under coke oven gases was not fundamentally different from that under either pure hydrogen or an inert atmosphere [11]. Addition of oxygen into the reaction atmosphere produces an obvious increase in the char surface area due to the

Abbreviations: ad, air dried base; BCBL, binder cold-briquetted lignite; BET, Brunauer–Emmett–Teller; COG, coke oven gas; daf, dried and ash-free base; DFT, Density Functional Theory; FTIR, Fourier transform infrared; LRCs, low-ranked coals; N-5, pyrrolic nitrogen; N-6, pyridinic nitrogen; N-Q, quaternary nitrogen; N-X, oxidized nitrogen; XPS, X-ray photoelectron spectra; TG, thermogravimetry analyzer.

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http://dx.doi.org/10.1016/j.fuproc.2016.05.035
0378-3820/

Nomenclature

$C(\lambda_L)$	the wavelength prefactor
$(dw/dt)_{max}$	the highest weight loss rate (%/min)
La	the microcrystalline size
I_D	the intensity of D band
I_G	the intensity of G band
T_{max}	the temperature corresponding to highest weight loss rate (°C)
t_{max}	the time corresponding to highest weight loss rate (min)
V_f	the weight loss rate at terminate temperature (%)

Greek symbols

λ_L	the wavelength (nm)

opening of closed pores via oxidation; however, introduction of additional steam (at mass ratio of steam/coal = 0.15) into the pyrolysis reaction results in somewhat higher total surface area of the char [12]. Therefore, our group used a self-developed fixed bed reactor to study the pyrolysis properties of BCBL under different atmospheres. Further, the semi-char samples from the pyrolysis tests were characterized in detail by N_2 BET and Dubinin CO_2 measurements, Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. The results of this study may provide a theoretical and technical basis for the BCBL pyrolysis, lignite upgradation and coal-gasification technology, which may have potential applications in fuel utilization.

2. Materials and methods

2.1. Sample preparation

Lignite and gas coal were collected, respectively, in Inner Mongolia and Xinzhou, China. They were pulverized to pass through a 200-mesh sieve (particle size of <74 μm) followed by desiccation in a vacuum oven at 80 °C for 24 h prior to use. The following proportions of lignite (65%), gas coal (30%) and modified coal-based binder (5%) were mixed, and quantitative amounts of water were poured into the mixture and stirred. The mixture was put into a honeycomb steel mold, and BCBL was then prepared under the pressure of 220 KN at the room temperature of 20 °C. A flow-chart of the process representing the preparation of the briquette is shown in Fig. 1. And the preparation method of MB was shown in Fig. S1. Prior to pyrolysis trials, the coal samples were dried at 110 °C for 3 h in vacuum, and then ground to obtain particles sized in the range 2 to 3 mm.

2.2. Pyrolysis experiments

A schematic of the pyrolysis experimental equipment is shown in Fig. 2. Pyrolysis was performed in a temperature-programmable electrically-heated pyrolysis furnace with a quartz reactor. Fig. 2 demonstrates that BCBL sample (20 g) is transferred to the reactor tube, after replacing air with nitrogen. The reactor was heated up to 600 °C at 20 °C min^{-1} and kept at that temperature for 30 min. The semi-

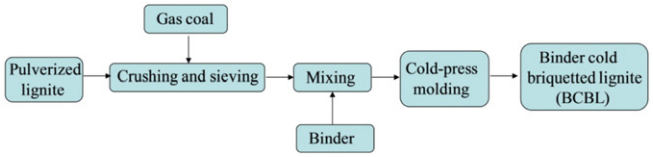

Fig. 1. Flow chart of the process representing the preparation of BCBL.

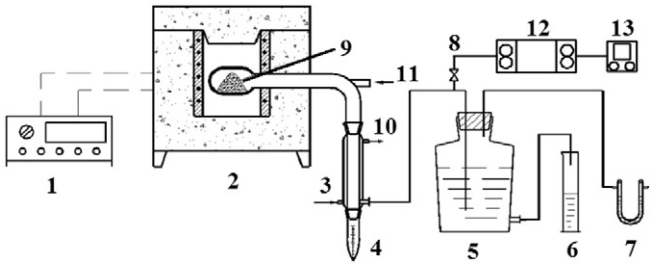

Fig. 2. Diagrammatic representation of the process of low-temperature carbonization of BCBL. (1. Temperature controller; 2. Low-temperature carbonization furnace; 3. Inlet of cooling water; 4. Gas cooling device; 5. Bottle for gas; 6. Metering device; 7. U-shaped tube of air pressure; 8. Injection System; 9. Briquetted lignite; 10. Outlet of cooling water; 11. Carrier gas; 12. Gas chromatography; and 13. Chromatography Workstation.)

char obtained at 600 °C has higher compressive mechanical strength and gasification reactivity in our previous study of reference [13]. Meanwhile, the yields of semi-char, moisture and tar pyrolyzed above 600 °C was almost stable, which means most of volatiles has been released in pyrolysis as shown in Fig. S2. Therefore, 600 °C was selected as the pyrolysis temperature [14]. The same experimental apparatus and methods were adopted during the pyrolysis of samples under different atmospheric gases.

2.3. Analytical methods

In order to study the spontaneous combustion tendency of the raw BCBL and different semi-chars, the thermal properties of BCBL and semi-chars were studied by a thermogravimetry analyzer (Netzsch STA-409CD). The test was performed from 20 to 950 °C under an air flow of 70 mL min^{-1} with a heating rate of 20 °C min^{-1}. Size of the raw materials is below 80 μm. Weight of the sample for TG testing is 20 mg.

The properties of coal and semi-char such as specific surface area and mesopore structure were determined by using a TriStar 3020IIanalyzer (Micromeritics instruments, USA) to measure N_2 adsorption at −196 °C. The total pore volume, average aperture, and pore size distribution of BCBL and semi-char were determined by using Density Functional Theory (DFT), which were calculated on-line by using the computer program [15]; The micropore surface area, pore volume, average pore diameter, and pore size distribution of BCBL and semi-chars were determined using the same TriStar 3020IIanalyzer to measure CO_2 adsorption at 0 °C, and the Dubinin-Astakhov equation [16] was applied based on a micropore filling model.

The sample (0.09–0.2 mm particle size) was powdered and mixed with KBr powder to obtain 1% concentration and then the mixture was pressed into a pellet. FTIR spectra were recorded using a PerkinElmer FTIR spectrometer (USA) in the spectral range 4000–600 cm^{-1} with a resolution of 4 cm^{-1} at room temperature. The spectrum represents an average of 10 scans per sample and the baselines of the spectra were corrected using PerkinElmer interactive software.

The XPS was performed using an ESCALAB 250 spectrometer (ThermoScientific, USA) fitted with non-monochromatic Al K X-ray radiation source. The X-ray source was operated at 200 W, and 60 eV pass energy was used for narrow scans.

The carbon structures in BCBL were studied by Raman spectroscopy using a Renishaw spectrometer, equipped with a silicon-based charge coupled device detector. BXFM microscope, equipped with a 50× LWD objective was used. The 532 nm line of the argon laser was used for excitation with a laser power of 20 mW. The spectra were recorded in the range 800–1800 cm^{-1} with an acquisition time of 20 s. The microcrystalline size L_a is represented by using the following equation, valid in the range 400 nm < λ_L < 700 nm as previously reported [17]:

$$L_a = C(\lambda_L)[I_D/I_G]^{-1} \quad (2.1)$$