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Studies on low-temperature pyrolysis characteristics and kinetics of the binder cold-briquetted lignite

Jun Liu, Yongfa Zhang*, Ying Wang, Lei Chen

Department of Key Laboratory of Lignite Science and Technology, Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan, China

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ABSTRACT

In this study, pyrolysis process of the binder cold-briquetted lignite (BCBL) was studied comprehensively. The effects of temperature in the range of 350–650 °C, heating rate in the range of 5–20 °C/min, the residence time at constant temperature in the range of 30–120 min, pyrolysis atmosphere of H_2, CO, CH_4, CO_2 and N_2 and the particle size in the range of 0.45–6 mm were investigated. The main generated gas species were quantified by two gas chromatographs: H_2, CO, CO_2, CH_4 and trace amounts of C_2H_4 and C_2H_6. A semi-quantitative method was established to proceed the pyrolysis kinetics fitting by the thermal analysis–mass spectrometry (TA–MS) signals of pyrolytic products. The kinetic parameters of different gas pyrolysates were calculated by the first-order kinetics. The activation energies for H_2, CO, CO_2, CH_4, C_2H_4 and C_2H_6 were found to be close to the reference results. The results reported in this work may provide a theoretical and technical basis for the BCBL pyrolysis and lignite upgrading technology which may have potential application in fuel utilization.

1. Introduction

Lignite takes a large proportion of low-rank coals which is more than 40% of the total global coal reserves [1,2]. Due to its large reserves, lignite is playing an increasingly important role in supplying primary energy in many countries. However, lignite has low heating value, high moisture, high oxygen content and carbon ratio. Furthermore, lignite combustion without any pretreatment inevitably results in a great deal of dust, a serious environment pollution and a low fuel efficiency [3–5]. Meanwhile, the mechanized mining technologies impose restrictions on the yield of lump coals, which only takes account for 15–20% of the mineral coals, resulting in the shortage of lump coal and the high percentage of pulverized coal. Efficient utilization of pulverized coal is more and more significant to solve the lump coal's demand-and-supply conflict.

Briquetting and drying of pulverized lignite can efficiently improve the heating value, decrease the spontaneous combustion tendency [6,7]. Therefore, briquetting technology is playing an important role in the development and utilization of low-rank pulverized lignite. It includes the stamping briquetting technology, the roll briquetting technology, the screw extrusion briquetting technology, and the ring forming technology concerning the lignite briquetting technologies [8]. There are the key parameters for pressure, temperature and moisture content during the briquetting process [9]. Lignite decreases in moisture, increases in heating value and becomes a high-quality fuel after the hot press upgrading. However, it is easy to crack and reabsorb water and fail to store or transport. At present, pyrolysis of briquetted lignite is prior to the simple briquetting for the reduced water and volatile content which can meet the international standards for solid smokeless fuels.

In the process of pyrolysis, the briquetted lignite is transformed to the semi-coke which can be used as carbon reducer, high-quality gasification material and fuels, and the liquid and gaseous products can also be extracted during the pyrolysis process. It achieves an efficient multi-level use of resources. There were certain research foundations on pyrolysis characteristics of the briquetted lignite. Chu et al. [10] studied gas evolution characteristics of the binderless hot-briquetted lignite during pyrolysis. Blesa et al. [11] studied the effect of the

* Corresponding author.
E-mail address: yongfaz@yeah.net (Y. Zhang).

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pyrolysis process on the physicochemical and mechanical properties of smokeless fuel briquettes. It was obtained by Xu et al. [12] that under the higher pressure of the atmosphere of H_2, residence time had an effect on secondary reaction of volatile, but with the residence time prolonged, the total carbon conversion and the amount of gas produced remained, the yield of CH_4 increased, but gas production rate of C_2 declined linearly instead. Zhu et al. [13] studied the gas evolution characteristics of lignite and its briquette, the results show that: in the pyrolysis temperature of 550–850 °C, the semi-coke yield of briquette is 2–6% higher than lignite, the tar yield of briquette is 2–3% higher than lignite and the gas yield of briquette is 4–9% less than lignite. Xu et al. [14] studied the pyrolysis characteristics of lignite binderless briquette and raw coal. However, to the authors' knowledge, a systematic study about the BCBL's gas pyrolysates characteristics has not been reported in literature. Therefore, it is necessary to do much work to understand pyrolysis mechanism of the briquetted lignite in order to increase development of low-rank pulverized coals and lignite.

Hence, in order to study the thermochemical reaction kinetics during pyrolysis, BCBL was pyrolyzed with different heating rates, terminal temperature, residual time, pyrolysis atmosphere and particle size on a fixed bed reactor and on a TA–MS analyzer in this paper. The kinetic parameters of different gas pyrolysates were calculated by a semi-quantitative method, and better linear regression could be achieved by the first-order kinetic model. The results reported in this work may provide a theoretical and technical basis for the BCBL pyrolysis and lignite upgrading technology which may have potential application in fuel utilization.

2. Experimental

2.1. Sample preparation

The investigations were performed on a lignite sample collected from the deposit in Inner Mongolia, the certain proportion of low-rank pulverized lignite (65%), gas coal (30%), and the binder (5%) were prepared into cylindrical shape briquetted lignite under the 220 kN pressure. The preparation process flow is shown in Fig. 1. The particle size of GC experiment sample by 20 g is 20 mm × Φ10 mm.

2.2. Pyrolysis process

A schematic diagram of the pyrolysis experimental equipment is shown in Fig. 2. It was performed in a temperature-programmable electrically-heated pyrolysis furnace with a self-developed quartz reactor. As shown in Fig. 2, the BCBL sample (20 g) was transferred to the reactor. The heater was connected to a programmer and controller. Nitrogen with flow rate of 50 mL/min was used to remove the air in the reactor before the pyrolysis until nitrogen content was up to 99.5% in the gas at the exit. Under the heating rate of 20 °C/min, temperature increased from 20 °C to the terminal temperature of 600 °C. When the sample reached 600 °C, keeping it at the residence time of 30 min. The yield of gaseous products was determined by gas-collecting method of drainage water.

2.3. Gas pyrolysates analysis

Two high-sensitivity gas chromatographs (HP 6890A GC) equipped with a thermal conductivity detectors (TCD) were respectively used to quantify the main pyrolysates gaseous species including H_2, CO, CO_2, CH_4, C_2H_4 and C_2H_6. For one of the gas chromatograph which was equipped with two TCDs and twin channels, the injector temperature was 50 °C, and the column temperature was 40 °C, hydrogen was used as carrier gas with the flow rate of 40 mL/min. Samples were injected into a 5 A molecular sieve column to quantify the gaseous species of O_2, N_2, CH_4 and CO. A GDX-502 column was used to quantify the gaseous species of CO_2, C_2H_4 and C_2H_6. For the other gas chromatograph which was equipped with a 5 A molecular sieve column, it was used to quantify the gaseous species of H_2, nitrogen was used as carrier gas with the flow rate of 40 mL/min, the injector and column temperatures were 80 °C. During the pyrolysates experiment, the gas was sampled simultaneously into a 1 mL syringe for testing with two gas chromatographs to obtain the yields of each species.

2.4. TA–MS analysis

TA–MS measurements were performed by a simultaneous thermal analyzer (Netzsch STA-409CD) coupled with a quadrupole mass spectrometer (Balzers QMA 400). In the interface between the two subunits, a skimmer coupling system was used to prevent the unnecessary condensation of evolved gases (i.e., tar production). Thermal gravimetric (TG) and DTG analyses were done to understand thermal properties of the BCBL in helium atmosphere at heating rates of 20 °C/min. And the flow rate of helium carrier gas is 100 mL/min. Size of the raw materials is below 80 μm. Weight of the sample for TG and DTA testing is 20 mg.

The mass spectrometer was in the electron impact (EI) ionization mode at the electron energy of 70 eV and provided mass spectra up to 512 a.m.u. every 2 min. This study primarily discusses the mass spectra of 2, 15, 18, 27, 28, 30, 32, 44 a.m.u, which are assigned to represent H_2, CH_4, H_2O, C_2H_4, CO, C_2H_6, O_2, and CO_2, respectively. During the experiments, about 20 mg of sample (40 mesh sieved) was put in a ceramic crucible for each batch, and then heated in the TA–MS apparatus from room temperature to about 900 °C at the heating rate of

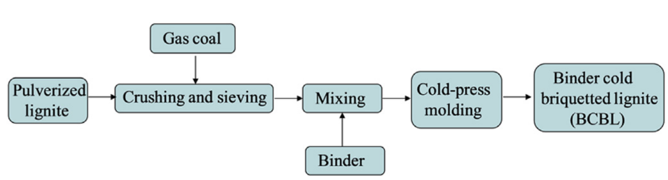

Fig. 1. Preparation process flow diagram of the BCBL.

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