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Effects of in-situ interactions between steam and coal on pyrolysis and gasification characteristics of pulverized coals and coal water slurry

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HIGHLIGHTS

- In-situ steam gasification presented in pyrolysis processes of pulverized and CWS coals.
- Pore structure showed a distinct effect on gasification reactivity of high-rank coals.
- Carbon microcrystalline structure reflected variations of char graphitization degree.

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ABSTRACT

The effects of water on the pyrolysis and gasification characteristics of coal water slurry (CWS) and pulverized coals with different ranks have been studied in the present work. Rapid pyrolysis characteristics (i.e. char yield, char structure evolution) of raw carbonaceous materials with varied water contents were investigated by using a high frequency furnace at 800–1200 °C. Moreover, gasification characteristics of the pyrolysis char were studied by using a thermogravimetric analyzer (TGA). The results indicate that at the pyrolysis temperature of 800 °C, the char yield of Wu-ran-cha-bu (WRCB) lignite slightly decreased with increasing the water content from 2.1 wt.% to 13.98 wt.%, while that of Yun-nan (YN) lignite showed a more significant decrease with increasing water content from 2.2 wt.% to 11.54 wt.%. This could be attributed to a higher coal reactivity of YN lignite than that of WRCB lignite. When the pyrolysis temperature was at or above 1000 °C, due to more significant in-situ coal-steam interactions, a lower char yield of both the pulverized lignites were observed with increasing water content from 2 wt.% to above 10 wt.%. CWS char presented a higher graphitization degree than pulverized coal char. The carbon microcrystalline structure factors (i.e. L_{002}/d_{002} value) of pyrolysis char increased with coal rank, which might reflect the variation trend of the graphitization degree from low rank coal to high rank coal. During the rapid heat treatment processes, the water evaporation and the in-situ steam-char gasification were favorable for void formation for both pulverized coals with high water contents and CWS. Notably, during the gasification processes of three different rank coals at 1200 °C, a more significant inhibition effect of residual ash on CWS char was observed compared to the pulverized parent coal char with high carbon conversion ($x > 0.9$).

1. Introduction

China is rich in coal, while scarce in oil and gas, so coal accounts for a great proportion in the energy consumption structure of the country. But the utilization of coal has brought about many environmental problems, such as air pollution and acid rain. Thus clean coal utilization becomes a general trend in the world [1]. The gasification technologies of entrained flow, fluidized bed, and fixed bed are the three most commonly applied ones adopted in the poly-generation system of coal basis, which denote the clean utilization trend of coal in China [2,3]. Gasification can convert different carbonaceous materials (such as coal, biomass and petroleum coke) into syngas ($CO + H_2$) under environmental friendly conditions.

The entrained flow gasification has been widely investigated and applied because it is one of the most advanced technologies with the advantage of high capacity, long stability, and convenient operation. The entrained flow gasification technology can be divided into coal water slurry (CWS) gasification and pulverized coal gasification based on the feeding methods of raw materials

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[4–7]. The advantages of slurry feeding of CWS include the following aspects: 1. Stable feeding and operating, easy for high pressure. 2. No extra process steam is needed for coal water slurry gasification when compared to pulverized coal gasification. 3. The mechanical grinding during the slurry preparation process is favorable for a higher activity.

Recently, the low rank coal with lower quality has attracted a great of interests for its abundance in China and the gradual exhaustion of high quality coal. The volatile content of low rank coal can reach 30–50 wt.% on a dry basis, and the water contents can reach 20–55 wt.% on as received basis [8–11]. Moreover, it often presents low slurry ability, which could bring high operation cost for CWS gasification. Therefore, the pulverized coal gasification may be an ideal alternative way for better utilization of low rank coals.

In general, reactions in gasifiers are complicated processes including evaporation of water, volatiles pyrolysis, combustion, and char gasification. The water in coal takes important effects on both of the two coal gasification processes: 1. As the water content in CWS was in the range of 30–40 wt.%, thus water play an important role in the gasification process of CWS. During the CWS process, the interactions of water with coal during rapid devolatilization process will further affect the reaction mechanism of the subsequent char gasification stage; 2. During the pulverized coal gasification process, although coals experience drying process before entering gasifiers, the dehydration process can not remove all the water of coals, and the residual water would affect the subsequent pyrolysis and gasification reactions in gasifiers, especially for the low rank coal [7].

Prationo et al. [12] found that the contribution of inherent water to char-steam reaction was vital during the oxy-fuel combustion of wet Victorian brown coal when the oxygen concentration was 21%, which was because of the long duration of the unevaporated steam as a thick cloud on coal char surface. In another research, Prationo et al. [13] concluded that in the oxy-fuel combustion mode, the inherent water could interrelate with CO_2, which led to significant delay of the ignition of the wet coal particle and its propagation velocity and flame intensity. Binner et al. [14] explored the peak particle temperatures and ignition characteristics of Victorian brown coal containing different water contents (10–30 wt.%) by using a drop tube furnace. The characteristics of cooler peak particle temperatures and ignition delay of the wet coal were also concluded. Moreover, Binner et al. [15] investigated pyrolysis characteristics of lignite with different water contents by using a drop-tube reactor, and it was found that there was little difference of char yields between the wet and dry coal at the pyrolysis temperatures of 800 °C and 1000 °C. Yip et al. [16] considered that the residence time of char particles in the drop-tube reactor was too short (2 s), which might result in little significant coal-steam interactions, and the interactions between coal matrix and the in-situ steam became more remarkable in the drop-tube/fixed-bed reactor due to a longer time of duration of coal-steam interactions. Butuzova et al. [17] and Zeng et al. [18] also explored effects of coal drying conditions on pyrolysis and gasification behaviors of pulverized lignite, and the yield of solid or liquid product, and char reactivity of lignites with different water contents were compared. Butuzova et al. [17] found that water could take part in thermal hydrolysis reactions during pyrolysis and change the package method of the aromatic rings, which led to the different variation trends of pyrolysis products with increasing water contents. Zeng et al. [18] concluded that changes of the dewatering temperature might lead to different variation trends for effects of coal/char physical structure and NaCl contents on char and tar yields, and char reactivity.

As is well known, coal gasification include two processes, that is, coal pyrolysis and char gasification. Many researchers separated these two processes, and studied them respectively [19–23]. In our study, we also separated and explored the pyrolysis and gasification processes, respectively. Although some progress was made on investigating the effects of water contents on the pyrolysis and gasification characteristics of lignite, most of these researches were aimed at the reaction characteristics of pulverized lignites containing different water contents. The structure evolution characteristics (i.e. morphology, size and area) of both CWS and pulverized coal chars, which could provide a lot of reference values for further understanding the interactions of in-situ steam with coal matrix during CWS and pulverized coal gasification processes, were still rarely reported.

It is necessary to study the effects of water on the pyrolysis and gasification characteristics of both CWS and pulverized coals. For the CWS gasification, three coals with different ranks were chosen, that is, Wu-ran-cha-bu lignite (WRCB), Shen-fu bituminous coal (SF), and Zun-yi anthracite (ZY); For the pulverized coal gasification, two lignites, that is, Wu-ran-cha-bu lignite (WRCB) and Yun-nan lignite (YN) with varied water contents were chosen. Rapid heating pyrolysis of all the raw materials were held in a high frequency furnace at 800–1200 °C to investigate effect of water on the pyrolysis characteristics of different rank coals. Many researchers adopted CO_2 as a gasification agent to evaluate the reactivity of different char samples [24–27]. Moreover, CO_2 gasification of coal char may play an important role in oxy-combustion environments with flue gas recirculation (FGR) [28–31]. To give clarity to the likely impact of CO_2 gasification on the oxy-combustion of pulverized coal chars, it is also necessary to study char-CO_2 reactivity characteristics. Therefore, the char gasification reaction with CO_2 was examined by using a thermogravimetric analyzer (TGA) to explore the relation between the dewatering conditions at the pyrolysis stage and the reactivity of the produced char at the subsequent gasification stage in this research.

2. Experimental section

2.1. Samples preparation

During the first part research, Nei-meng lignite (WRCB) and Yun-nan lignite (YN) were chosen to prepare for the pulverized coal with different water contents. All the coal samples were ground and sieved with the screen of 80–120 mesh, and the average diameter was analyzed by Malvern Mastersizer 2000 laser particle size analyzer, which was around 150 μm. The as-received lignite was put in the BINDER constant temperature and humidity equipment at the condition of 25 °C, 90% of air relative humidity for 24 h to form coals with high water contents. The relative humidity denotes the ratio of the actual partial pressure of water vapor to the saturation vapor pressure of water at the condition of 25 °C, atmosphere pressure, which was examined on the basis of Sonntag's formula with respect to saturation vapor pressure on water [32]. The relative humidity was measured by using a MA150 infrared ray water apparatus in our study. The water determination was repeated for three times, and the relative error was within ±3%.

Coals obtained at 25 °C, 90% of air relative humidity were then dried at 40 °C and 105 °C to remove the external water and the total water of coals according to the method introduced in GB/T 211-2007 of China [33]. Therefore, coals of various inherent water and total water, and coal in dry basis were considered, respectively. The pulverized lignites with three different water contents were designated as WRCB-90% relative humidity, 25 °C, WRCB-40 °C, and WRCB-105 °C, respectively.

During the second part research, WRCB lignite, SF bituminous coal, and ZY anthracite were chosen to prepare for the coal water