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Effects of coal drying on the pyrolysis and in-situ gasification characteristics of lignite coals

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HIGHLIGHTS

- Effect of coal drying on lignite pyrolysis was studied by TG-MS and a novel reactor.
- Coal type, final temperature and heating method had key effects during pyrolysis.
- We developed a new method to study morphological changes during char gasification.
- It initially showed shrinking particle mode, and then changed to shrinking core mode.
- Insignificant steam deactivation of char was verified by the active sites mechanism.

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ABSTRACT

Pyrolysis behaviors of two lignite coals with different drying conditions were determined by a thermogravimetric analyzer coupled with mass spectrometer (TG-MS) and a high-frequency furnace. An in-situ heating stage microscope was adopted to observe the morphological changes during char-CO_2 gasification process. It is concluded that the effects of moisture contents in coals on the gaseous release process during coal pyrolysis mainly depend on coal type, final pyrolysis temperature and heating method. The in-situ heating stage experiments indicate that the shrinking particle mode is suitable to illustrate the gasification reaction mechanism in the initial and midterm reaction stages of all the lignite char samples. Although drying conditions have significant effects on coal pyrolysis process under rapid heating, these dewatering conditions result in little noticeable reactivity loss of the char during the subsequent char-CO_2 gasification reaction. The measuring results of catalytic active sites can well explain the similar reactivity of lignite coals with different drying conditions.

1. Introduction

Coal poly-generation is a competitive way for clean utilization of coal in the world. Coal gasification technology, which includes fixed bed, fluidized bed and entrained flow gasification, holds a top position in the coal poly-generation process [1,2]. The raw materials used in coal gasification include lignite coal, bituminous coal, anthracite coal, etc. Recently, lignite coal is getting more and more attentions all over the world due to the overdeveloping of bituminous coal and anthracite coal [3–5]. Ahmed and Gupta conducted pyrolysis and gasification experiments of a lignite coal in a semi batch reactor at reaction temperatures of 800–950 °C, and they conducted the simulation of syngas evolution during pyrolysis using first order, single step mechanism and the FLASHCHAIN mechanism, respectively [3]. Stochastic simulations results fitted well with the experimental yields of CH_4 and other hydrocarbons. Utilization of lignite coal were novelly applied in the fields of carbon fuel cell [6] and co-combustion/co-gasification of coal and biomass [7,8]. Nevertheless, lignite coals were usually dried in an oven at 105 °C under nitrogen before the thermal reaction experiments at high temperatures in most of these researches [3–8], and the effects of water in coals on the reaction characteristics were not considered. As a young coal, lignite coal usually contains high volatiles (30–50 wt.%, dry basis) and moisture contents (20–55 wt.%, as received basis), [9–12] and the moisture contents in some lignite coals can even reach ~70 wt.% (as received basis) [13]. The high moisture content in lignite coal may cause unfavorable limitations in improving thermal efficiency and a low energy output relative to other coals [12,14]. Moreover, excessive moisture contents in coals may have an adverse effect on the process of pneumatic conveying of pulverized coals during the pulverized

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coal gasification system. Therefore, coals are generally dried through direct contact with the warm exhaust gas before entering the gasifier in industrial production [15]. Although this conventional drying process is thermally based, the dewatering process could not guarantee the complete removal of water in coals, and the remained water may take effects on the subsequent coal gasification reaction. Therefore, it is necessary to explore the interactions of carbon matrix with steam produced in-situ (from the water of lignite coal) during the gasification process of lignite coals since these studies are helpful for expanding application range of lignite coals in the industrial gasification.

Binner et al. held the pyrolysis experiments of dry and wet (~25.2 wt.% moisture content) lignite coals at 800 and 1000 °C in a drop-tube reactor [16]. They found that coal pre-drying degrees would affect the behavior of the low concentrations of inorganic species (i.e. Na, Mg, Cl) present in coal, but there was no discernible difference between the dry and wet coal devolatilization rates. Binner et al. also studied the ignition characteristics and peak particle temperatures of Victorian brown coal with different drying conditions (10–30 wt.% moisture content) in a drop tube furnace [17]. It was concluded that the evolution and evaporation of water in the wet case lead to an ignition delay, cooler peak particle temperatures and prolonged char combustion. Yip et al. also concluded the similar results that there was little difference between the lignite char yields from the coals with and without drying in drop tube furnace at the pyrolysis temperature of 1000 °C [18]. Yip et al. suggested that the short char residence time (2 s) in the drop-tube reactor was the main reason leading to little remarkable steam-char interactions, and they found that the interactions between the in-situ steam and char were more significant in a drop-tube/fixed-bed reactor due to a longer duration of interactions between in-situ steam and char. Yip and his co-workers concluded that the inherent moisture in Collie coal had a significant influence on the char yield and reactivity, depending on the pyrolysis conditions [18]. Zeng et al. [19] and Butuzova et al. [20] also carried out their researches to explore the effects of drying conditions of lignite coals on coal pyrolysis and gasification behaviors, and they compared the solid/liquid yield, and char reactivity of lignite coals with or without drying. Although several methods were chosen to study the effects of moisture contents on lignite coal gasification, the reports about the effects of coal pre-drying on gaseous release during the pyrolysis process and the structure changes ((i.e. size, area and morphology)) of char during the in-situ gasification step at high temperatures are still rare, and these researches may provide lots of worthy references for further understanding the in-situ interactions between coal water and carbon matrix during the thermal reactions of lignite coals. Therefore, in the present study, a drop-tube/fixed-bed reactor (fast heating) and a thermogravimetric analyzer-mass (slow heating) were both employed to investigate the effects of moisture contents on the gaseous evolution characteristics during the pyrolysis processes of two typical lignite coals in China, and an in-situ heating stage microscope was adopted to observe the structure changes of lignite char samples during CO_2 gasification to explore the effects of dewatering on the gasification reaction mechanism of lignite char. Moreover, CO_2 chemisorption experiments of chars were carried out to study the relationship between the active sites of char surface and the gasification reactivity of coal char.

2. Experimental section

2.1. Samples preparation

Two lignite coals, Yun-nan zhaotong coal (YN) and Nei-meng hulunbeier coal (NM) were used in this study. The coals were crushed and sieved, and the average diameter of the chosen samples was ~150 μm. The proximate and ultimate analyses and ash fusion temperatures of samples are summarized in Table 1. The as-received lignite was dried at three temperatures (25, 40 and 105 °C, respectively) to prepare different moisture-containing samples. Coal drying at 25 °C was performed with the usage of the BINDER constant temperature and humidity equipment at the condition of 90% of air relative humidity value to form lignite samples with high saturation moisture contents. The moisture contents of different samples are shown in Table 2.

2.2. Slow pyrolysis of coals in TG-MS

Slow pyrolysis experiments of samples with different moisture contents were carried out with a NETZSCH thermogravimetric analyzer (STA 449 F3) coupled with a MS 403C quadrupole mass spectrometry for on-line gas analysis. Typical 15 mg of sample particles were placed in an alumina crucible and heated at 25 °C min^{-1} to the prescribed temperature (1000 °C) under a continuous argon flow of 30 mL min^{-1}. The samples were then held at the final temperature with the duration of 10 min for a complete devolatilization. The response time of the mass spectrometer is less than 2 s. The gas outlet of TGA and the transfer line were all heated to 220 °C to avoid steam condensation. Mass spectrometry identifies the species by using the differences in mass-to-charge ratio (m/z) of ionized atoms or molecules [21]. The gaseous compounds generated during pyrolysis including H_2, CH_4, H_2O, and CO_2 could be easily detected, and their mass-to-charge ratios were set at m/z (2), m/z (16), m/z (18), and m/z (44) separately. CO was not analyzed in our TG-MS experiments because it is difficult to separate CO in the mixture due to spectral interference of the fragmentation of the ions produced by CO_2 [22].

2.3. Fast pyrolysis of coals in a high-frequency furnace

Fast pyrolysis experiments of lignite samples were carried out in an atmospheric pressure high-frequency magnetic field based

Table 2
The moisture contents of different coal samples.

Sample	Moisture wt.%		
	Desiccation at 105 °C	Desiccation at 40 °C	90%-air relative humidity, 25 °C
YN	2.20	11.54	22.03
NM	1.76	9.12	19.39

Table 1
Proximate and ultimate analyses and ash fusion temperature of coal samples.

Sample	Proximate analysis/d, wt.%			Ultimate analysis/d, wt.%					Ash fusion temperature, °C			
	VM	FC	Ash	C	H	N	S	O[a]	DT	ST	HT	FT
YN	42.77	25.93	31.30	47.56	3.60	1.40	0.95	19.21	1172	1197	1204	1211
NM	49.22	40.33	10.45	74.65	3.32	1.20	0.58	9.80	1086	1105	1121	1124

[a] O was calculated by difference.