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Research Paper

Effect of hydrothermal dewatering on the pyrolysis characteristics of Chinese low-rank coals

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HIGHLIGHTS

- Typical lignites with various ranks are upgraded through hydrothermal dewatering.
- van Krevelen diagrams show the artificial carbonization reactions process.
- Upgraded coals exhibit weak pyrolysis characteristics similar to bituminous coal.
- Products from stable and saturated components (p-xylene, phenol, CH_4) increase.
- Products from unstable and unsaturated components (CO_2, CO, formic acid) decrease.

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ABSTRACT

This paper describes the effect of the hydrothermal dewatering (HTD) on the pyrolysis characteristics of low-rank coals (LRCs). The effect of HTD on the characteristics of LRCs was explored based on scanning electronic microscopy and N_2 adsorption analyses. The pyrolysis behaviors and gas products were determined using a TG-FTIR instrument. The results show that the crosslink structure and overall gel structure were broken. The pore structure expanded to the micropore region, and the surface area and total pore volume initially increased and then decreased as the treatment temperature increased. The TG-DTG results confirmed that the pyrolysis process moved towards the high-temperature and bituminous coal region. The characteristic parameters of pyrolysis indicated that the thermal stability of the coal structure was improved. According to the TG-FTIR results, the amount of released gas products from stable and saturated components (such as p-xylene, phenol and CH_4) increased, whereas the amount of released gas products from unstable and unsaturated components (such as CO_2, CO and formic acid) decreased. The unstable structure and components of the LRCs were decomposed and transformed, and a stable structure and phase were created. Moreover, pyrolysis activity declined, and thermal stability improved.

1. Introduction

Coal accounts for 39.3% of the fuel used for global electricity generation [1]. Coal use is particularly prevalent in China, which is the world's largest producer and consumer of coal [2]. Coal supplies 67.5% of China's primary energy and more than 75% of China's electricity [3]. However, the country's coal resource endowment conditions are poor, and its reserves of low-rank coals (LRCs) total approximately 190.3 billion tons (41.18% of the total coal reserve) [4]. The utilization of LRCs (including lignite, brown coals and sub-bituminous coals) is expected to become increasingly important. Unfortunately, the inherent limitations of LRCs, such as high moisture and oxygen contents, high transportation costs, high CO_2 emissions, low calorific values, and high propensities for spontaneous combustion, greatly restrict their large-scale application [5]. Thus, upgrading LRCs by increasing their energy value is of considerable importance, and dewatering is the first critical step in this process [6].

Hydrothermal dewatering (HTD, wet torrefaction, hot compressed water, or hot water pretreatment) is a popular research topic. HTD is a non-evaporative method that effectively removes water from coal and improves the chemical structure of LRCs [7]. The HTD process has been developed for almost a century, with the original aim of simulating the mechanisms of natural coalification in the laboratory [8,9]. This method involves a thermochemical conversion process at temperatures

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typically between 200 and 350 °C, and the vessel pressure is autogenously generated to stop water from evaporating [10]. Many chemical reactions, such as hydrolysis, dehydration, deoxygenation, decarboxylation, demethanation, polymerization, and aromatization, can occur during this process, and artificial carbonization can result in the modification of LRC characteristics [11].

Recent investigations into upgrading LRCs with HTD have generally focused on (1) the effects of HTD conditions on the properties of the treated coal, including the temperature, residence time, dry coal/water ratio, and so on [12–14]; (2) the properties of gas-, liquid-, and solid-phase products [15–18]; (3) the disposal of wastewater produced from HTD [19–22]; (4) the effect of the HTD treatment of LRC on its slurryability [23–26]; (5) the thermal conversion and utilization of upgraded coal, including liquefaction [27,28], pyrolysis, gasification, combustion [29–33], caking and coking [34,35]; (6) pollutant migration and emission characteristics during the HTD process, such as trace elements [36], sulfur [37], nitrogen [38,39], and ash [40]; and (7) the upgrading mechanism and simulation of HTD for LRCs [7,41].

Previous studies mainly focused on the effects of HTD related to changes in physicochemical properties and aimed to enhance the performance of LRCs in the preparation of coal water slurry. A few studies have focused on the effects on thermal conversion behaviors and the utilization of upgraded LRCs. Umar et al. [31,32] studied the changes in the combustion characteristics of three Indonesian LRCs with upgraded brown coal (UBC), hot water drying (HWD) and steam drying (SD). They found that the ignition temperature of the upgraded coals increased and that the maximum combustion rate increased significantly. After upgrading, the combustion peak of volatile matter decreased slightly, whereas the char combustion process was obviously strengthened. In addition, the combustion characteristics of the HWD and SD processes were superior to those of the UBC process because the former were conducted at lower temperature and pressure. The author has studied the influence of HTD on the gasification and combustion characteristics of LRCs [30,33], and the results suggest that the process indeed changes the physicochemical properties of LRCs, improving their coal rank, delaying thermal conversion processes towards the high-temperature region, increasing the activation energy of the process and upgrading the characteristics of LRCs to levels comparable to those of high-rank coals (HRCs). Pyrolysis is the first essential step in the coal conversion process and has an important effect on coal gasification and combustion. Volatile releases during the pyrolysis stage control the ignition behavior, flame temperature and combustion stability. Thus, the effects of HTD on the pyrolysis characteristics of LRCs should be studied in detail. Liu et al. [29] studied the effects of HTD on the pyrolysis kinetics and CH_4 release characteristic of two lignites. They divided the thermogravimetric process into three stages. The results showed that the initial temperatures of each pyrolysis stage of HTD products were higher than those of raw coals. The temperatures at which CH_4 appeared during the pyrolysis process increased. The activation energy also increased after HTD upgrading, indicated that thermal stability was improved. However, volatile matter contains many species, and changes in their release before and after the HTD process is also important for thermal conversion behaviors.

In this paper, three typical LRCs with different geological ages were hydrothermally dewatered and upgraded at 250 and 300 °C. The effects of the HTD temperature on the pyrolysis performance and volatile release characteristics of the upgraded coals and on the coal composition, microscopic morphology and pore size distribution were studied. The kinetics were also measured and modeled using the Coats–Redfern integral method.

2. Experimental

2.1. Coal sample

The typical LRCs selected for this study were from the three largest coal-producing areas in China: Zhao Tong (ZT), Yi Min (YM), and Zhun Dong (ZD). These LRCs formed during different geological ages, namely, the Tertiary, Late Jurassic, and Early or Middle Jurassic, respectively. Da Tong (DT) bituminous coal was used for comparison as an HRC. The raw coals were crushed and sieved through a 2.5-mm mesh before the upgrading process. The raw and upgraded coal samples were milled for 30 s in a ring mill and were then sieved through a 74-μm mesh for analysis.

2.2. HTD upgrading process

The HTD process was performed in a bench-scale hydrothermal reaction system (WeiBa WHFS-2). The system included a 2-L cylindrical autoclave with a maximum pressure of 25 MPa and maximum temperature of 350 °C. The end HTD temperatures in this study were 250 °C and 300 °C, and the detailed process description was shown in a previous work [33]. All upgraded coals were abbreviated based on the coal type initials and treatment temperature, such as "ZT-250" and "ZT-300".

2.3. Scanning electronic microscopy (SEM)

The surface morphologies of the raw and upgraded coals were observed using a SEM (SIRON-100) at a voltage of 25 kV with various amplifier times.

2.4. N_2 adsorption

The pore structures, including the Brunauer–Emmett–Teller (BET) surface area, pore volume, and pore size distribution, of the raw and upgraded coals were obtained through N_2 adsorption measurements using a commercial instrument (ASAP 2010, American Micromeritics Co. Ltd.). Each coal sample (approximately 0.2 g) was placed in a sealed glass tube and then degassed at 250 °C for 4 h in a nitrogen stream. After degassing of the coal samples, the glass tube was placed in the instrument, and measurements were performed. The surface area was calculated using the BET equation, and the Barret–Joyner–Halenda (BJH) model was used to determine the pore distribution and volume.

2.5. Thermogravimetric and Fourier transform infrared spectroscopy (TG-FTIR)

A Mettler-Toledo TGA/SDTA 851e thermo-balance coupled with a Nicolet NEXUS 670 FTIR was used to study the pyrolysis and devolatilization characteristics of raw and upgraded coals. Specifically, 10 mg of dried coal sample was placed in an aluminum crucible and heated at 15 °C/min within the temperature range of 40–1000 °C under a steady nitrogen flow of 60 ml/min. Volatiles released during coal pyrolysis were rapidly transported into the FTIR gas cell by pure nitrogen. The Teflon tube and FTIR gas cell were preheated to 180 °C before each experiment to prevent the condensation of volatiles. A deuterated triglycine sulfate pyroelectric detector was used to detect gaseous products because of its rapid response and low noise. The spectrum scope ranged from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

Volatile release characteristics were studied based on the analysis of FTIR spectra, which were obtained online during TG runs. TG analysis coupled with FTIR has been widely applied to study the compounds that evolve during the pyrolysis of coal. Such analyses provide continuous important information regarding devolatilization, including the identification of major volatile species and the typical temperature range of release. Detailed methods and operations can be found in [42,43]. In this study, CO_2, CO, CH_4 and formic acid were chosen as light components in volatile matter, and the heavy components chosen included p-xylene and phenol, which are representative of benzene-containing species and tar. Their standard spectra and main characteristic absorption bands are given in Fig. 1 and Table 1 [43,44].