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Effect of waste liquid produced from the hydrothermal treatment of both low-rank coal and sludge on the slurryability of coal sludge slurry

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HIGHLIGHTS

- More than 85 wt% carbon was retained in the HT solid products.
- TOC and pH value increased rapidly with an increase in the amount of sludge.
- Alkanes, phenols and heterocyclic were the main organics in the HT waste liquid.
- Heterocyclic increased and amines slightly decreased with the sludge amount increased.
- The better slurryability of CSS were prepared using the HT waste liquid.

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ABSTRACT

Effects of temperature and the amount of sludge on the physicochemical properties of the waste liquid products produced from the hydrothermal treatment (HT) of both low-rank coal and sludge were investigated. The slurryability of coal sludge slurry (CSS) prepared with HT solid and waste liquid product was also analyzed. An increase in the amount of sludge led to a decrease in the solid yield, calorific value and fixed carbon of solid products decreased, particularly the solid yield which reached 63.8 wt% in the HT of sludge at 300 °C. However, more than 85 wt% carbon was retained in the solid products, which is beneficial for the energy densification. The Total Organic Carbon (TOC) content increased significantly with an increase in the amount of sludge and attained a concentration of 60 g/L. The same trend was observed in the pH value of waste liquid, owing to the presence of ammonium nitrogen organics. Alkanes, phenols, and heterocyclic were the main organic compounds produced from the HT of Inner Mongolia Coal (IMC), Yunnan Coal (YNC) and sludge at 300 °C, respectively. CSS prepared using the HT waste liquid instead of water has a higher fixed-viscosity concentration and better stability due to the presence of dissolved organic compounds and ions.

1. Introduction

Low-rank coal with highly volatile matter (VM) content and reactivity has been widely applied in gasification or combustion technology [1,2]. Remove of moisture from low-rank coal before large-scale utilization is of absolute necessity to improve its calorific value. Previous studies [3–6] demonstrated that the hydrothermal treatment (HT) of low-rank coals greatly reduced its moisture content and re-absorption ability, subsequently improving its calorific value. Organic and inorganic compounds dissolved in the waste liquid products after HT heavily contribute to the added complexity of wastewater treatment of these liquid products [7–10]. Racovalis et al. [8] found that the concentration of organics in the waste liquid products increased exponentially when the temperature was increased from 250 to 350 °C. They reported a maximum level of nearly 7 g/L Total Organic Carbon (TOC) in the HT of Loy Yang coal at 350 °C [8]. This is consistent with the results of Yu et al. [7] and Wu et al. [9]. Additionally, Mursito et al. [10] demonstrated that sugars, furans, organic acids, alcohols, phenol and phenol derivatives were dissolved into the waste liquid during the HT of tropical peat. Evidently, it is essential to develop the process that treat the wastewater efficiently and recover the energy obtainable from combustible organic compounds in the waste liquid. Nakagawa et al. [11] developed a novel Ni/carbon catalyst to hydrothermally gasify the organic compounds dissolved in the wastewater after the HT of brown coal, producing the combustible

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gas rich in methane and hydrogen. Coal-water slurry (CWS) gasification/combustion technology is one of the most mature processes that incorporate the use of organic waste liquid produced from HT. Not only can organic waste liquid improve the slurryability and reduce the amount of water used for the preparation of CWS but also avoids the loss of combustible organic compounds [7,9,12,13]. Yu et al. [7] found that the mass concentration of CWS increased from 44.4 wt% for raw lignite to 59.1 wt% for the HT of lignite. Additionally, it was observed that the waste liquid from the HT of lignite can be used to improve the slurryability of solid products due to the organic compounds and the dissolved minerals present in the waste liquid [7]. Xie et al. [13] demonstrated that phenol in the industrial wastewater acted as a surfactant, thereby reducing the viscosity of CWS. In addition, the stability of CWS was improved by the presence of ammonia nitrogen organics in the waste liquid. However, Zhang et al. [14] found that the polarity of coal particle surface was transformed by small oxygen-containing organic molecules in the wastewater, henceforth negatively impacting the slurryability of CWS. Therefore, it is necessary to investigate the organics composition of the waste liquid from the HT of low-rank coal and evaluate the effect of organic compounds on the slurryability of CWS.

As reflected in previous works [15–18], sewage sludge is important to improving the combustion/gasification performance of coal and enhancing the stability of coal sludge slurry (CSS). The flocs structure of sludge prevents the settlement of coal particles in the CSS but absorbs enormous quantities of free water, resulting in a reduction of the mass concentration of CSS [18–20]. Although high-concentration CSS can be obtained by modifying the sludge with a surfactant [20], an alkali [18,20,21] or through thermal pretreatment [22], the addition amount of sludge is less than 20 wt% on a dry coal basis. Additionally, high-rank coal is consistently used to prepare the high concentration CSS. HT of sewage sludge not only can destroy the flocs structure and reduce its moisture content but also can decompose substantial amounts of organic and inorganic pollutants, including N, S, and heavy metals [23–26]. Danso-Boateng et al. [27] detected the presence of organic compounds, such as acids, alkenes, phenolic and aromatic compounds, in the waste liquid produced by the hydrothermal carbonization of sewage sludge. The same organics compositions have been reported in the literature [28,29]. An increase in temperature led to an observed increase in the concentration of TOC, chemical oxygen demand (COD) and biochemical oxygen demand (BOD) whilst the volatile fatty acid (VFA) concentration decreased. Nonaka et al. [30] demonstrated that there were positive synergistic effects on the coalification of solid products in the HT of both low-rank coal and biomass. In addition, the solid products became hydrophobic and incapable of re-adsorbing the lost moisture. Thus, the HT of both low-rank coal and sewage sludge can handle a huge amount of sludge, enhance the coalification of solid products and reduce the emission of pollutants in industrial applications [31]. Besides, co-slurry of coal and sludge prepared with the solid and liquid products of HT has the following advantages: (1) The water contained in the sludge can be converted into the free water through HT. Consequently, the amount of water used to prepare CSS is reduced; (2) Most organic compounds in the waste liquid products can be used to improve the slurryability of CSS; (3) Avoids extreme loss of copious amounts combustible organics; (4) Sludge particles improves the rheological behavior of CSS. However, few studies have explored the physicochemical properties of waste liquid products in the HT of both low-rank coal and sewage sludge. Moreover, the co-slurry properties of CSS prepared with HT solid and waste liquid products have not been thoroughly investigated and therefore require extensive attention.

In this work, solid and waste liquid products produced from the HT of both low-rank coal and sludge were collected and subsequently characterized. The fuel characteristics of solid products and physicochemical properties of waste liquid were analyzed, including TOC, PH, anions, cations, and dissolved organic compounds. Furthermore, the fixed-viscosity concentration and stability of CSS prepared with the solid and waste liquid products were fully investigated to study the effect of waste liquid on the slurryability of coal sludge slurry.

2. Experimental

2.1. Materials

Two low-rank coals, Inner Mongolia Coal (IMC) and Yunnan Coal (YNC) (particle size less than 200 μm) were used for the hydrothermal treatments. Digested municipal sewage sludge (MSS) after mechanical dewatering was obtained from a wastewater treatment plant in Nanjing, China. All the samples were sealed to prevent the moisture loss. The fuel characteristics of raw IMC, YNC, and MSS are shown in Table 1.

2.2. Procedure of HT

The HT experiments were carried out in a 1 L batch-type reactor. Fig. 1 shows the schematic of the reactor. The weighted raw low-rank coal and sludge were fed to the reactor basing on the required mixing ratio. Following that, deionized water was also fed to the reactor. In each experiment, 200 g of mixed feedstock materials (raw coal and sludge) and 450 g of deionized water were fed to the reactor. The air in the reactor was discharged using the nitrogen gas (4 MPa). The agitator was then set to 700 rpm. The reaction temperature was controlled in the range of 150–300 °C at a heating rate of 5 °C/min for a reaction time of 1 h. After the reaction, the reactor was rapidly cooled to room temperature using running water. The gas products were collected in the gas collection bag whilst the waste liquid and solid products were collected from the reactor and subsequently separated by suction filtration. After filtration, the solid products were placed in a temperature humidity incubator (25 °C, 65% humidity) to reach the equilibrium state for the further fuel properties analysis and slurryability experiments. The waste liquid products were stored in glass bottles and kept at a constant temperature of 4 °C for further analysis. The solid yield was determined by the weight ratio of solid residue and raw materials on a dry basis. Operating conditions were labeled using a format of "HT-xxx-xx", where "xxx" is the mixing ratio of low-rank coal, "xx" is the reaction temperature. For example, "HT-0.9IMC-150 °C" represents the HT of both 90 wt% IMC and 10 wt% MSS at 150 °C.

2.3. Analysis

The ultimate and proximate analysis of raw materials and solid products were determined using an Elemental Analyzer (LECO-CHNS 932, USA) and an Infrared Rapid Analyzer (5E-MACIII, China). The calorific value of samples was measured using the adiabatic bomb calorimetric method. A TOC analyzer (Shimadzu TOC 5000A VCSH, Japan) was used to determine the TOC of waste liquid products. Organic compounds in the waste liquid were measured based on the EPA 625 method. The waste liquid was extracted three times by CH_4Cl_2 under the respective PH conditions of 2, 7, and 12. The three types of extracted liquid were mixed with the same volume as the measurement sample of GC–MS. The composition of organic compounds in the waste liquid products was measured by GC–MS (Agilent 7890A-5975C, USA) using a capillary column Agilent HP-5 ms 30 m × 0.25 mm × 0.25 μm. The initial temperature was maintained at 40 °C for 3 min, followed by a