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Full Length Article

Transformation behaviors of C, H, O, N and S in lignite during hydrothermal dewatering process

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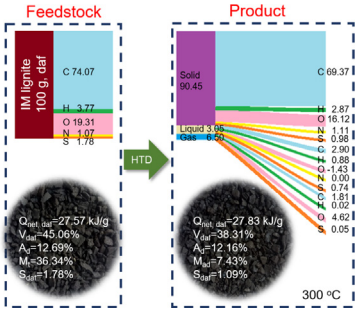
GRAPHICAL ABSTRACT



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ABSTRACT

Lignite resources are abundant in China, but high moisture contents limit their utilization. With a view to making optimal use of beneficial elements (C, H, O) and effectively control the release of harmful elements (N and S) in lignite during drying, two lignites, one from Inner Mongolia (IM) and one from Yunnan (YN) province, were hydrothermally dewatered (HTD) at 230 °C, 270 °C and 300 °C. The solid, liquid and gaseous products were characterized by proximate and ultimate analyses as well as Fourier transform infrared spectroscopy (FT-IR), chemical oxygen demand (COD) analysis, Raman laser analysis and gas chromatography. Based on these data, the transformation behaviors of C, H, O, N and S contained in the raw lignite as they partition into the HTD products (solid, liquid and gas) were investigated. Results show that the effects of HTD on the elemental transformations depend on the coal properties. HTD is more effective for YN lignite than for IM lignite. IM liquid products have lower COD contents, resulting from less dissolution of IM lignite. CO_2 and CO are released during HTD and their amounts increase with temperature for both IM and YN lignites. High temperature leads to a significant loss of carbon in the solid product; this corresponds with increases of the carbon content in the gas and liquid phases. Hydrogen, nitrogen and sulfur in lignite are mainly transferred into the liquid phase. A large proportion of the oxygen-containing functional groups in the lignite decompose, causing its transfer out of the solid and into the gas and liquid phases.

1. Introduction

Coal is the primary source of energy in China. With increasing consumption of coal, low rank coal, especially lignite, has become a very important part of the energy supply, due to abundant reserves and low prices. However, the high moisture content of lignite results in

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lower calorific value and higher transportation cost, which restricts its large-scale utilization [1]. Therefore, an efficient dewatering technology is essential for clean and highly efficient utilization of lignite. Technologies for dewatering lignite include rotary drying [2], fluidized-bed drying [3–6], microwave drying [7–9], mechanical thermal dewatering (MTE) [10,11], hydrothermal dewatering (HTD) [12–16] and organic solvent upgrading [17]. HTD is a non-evaporative technology, which removes water in liquid form, and thus, could save the latent heat of water evaporation [18]. Thus, HTD has attracted much attention because of its significant advantages.

Many studies have focused on the properties of HTD lignite [12,19–21]. It is reported that a number of changes can occur as a result of HTD processing, including: (1) The moisture content in HTD lignite can be reduced to below 10% [15,21], and the moisture re-adsorption performance also efficiently inhibited [19]; (2) The volatile matter and oxygen content decrease, while the fixed carbon and carbon content increase, thus improving the lignite quality [21]; (3) Oxygen-containing functional groups, such as carboxyl, hydroxyl and carbonyl groups, can be irreversibly removed [22]. Overall, HTD exerts significant influences upon the properties of lignite, thereby affecting its utilization processes, such as combustion [23], gasification [24,25], pyrolysis [26,27] and slurrying [28,29] behaviors. Besides the solid product, there are liquid and gaseous products produced by HTD as has been discussed in some prior research [29–33]. The decomposition of lignite surface structures produces gases, such as CO_2, CO, H_2, and H_2S. At the same time, the organic matter and some ions (such as cation: Na^+, Fe^{3+} and Al^{3+}; anion: SO_4^{2-}, NO_3^- and Cl^-) are leached out from lignite into the liquid phase, and their contents increase with increasing HTD temperature [29,32]. These recent gains in understanding about the composition of solid, liquid and gaseous products have provided a good foundation for studying the HTD process further.

In order to explore the HTD process more deeply, a few literatures have investigated the elemental partitioning of C [30], N [34], S [34,35], and some trace elements [36] into the solid, liquid and gaseous product phases. However, detailed investigation on the overall mass balance during HTD and the broader transformation of all main elements (C, H, O, N and S) contained within the lignite is still lacking. Thus, further explorations of the HTD upgrading mechanism are warranted. This study aims to investigate transformation behaviors of C, H, O, N and S in lignite so as to provide theoretical guidance for optimizing HTD processing conditions, so as to obtain a dewatered solid product which is clean and of high quality, and to minimize the waste-water problems. With this purpose in mind, two lignites from China were treated by HTD at a sequence of temperatures (230–300 °C). Then, the solid, liquid and gaseous products were obtained and analyzed to determine the mass balance and the partitioning of elements as a consequence of HTD treatment.

2. Experimental

2.1. Materials

Two typical Chinese lignites, one from Inner Mongolia (IM) and one from Yunnan (YN) province, which are two of top lignite-producing provinces in China, were selected. The lignites were milled and then sieved under N_2 to reduce the oxidation of the coal surface and to obtain the particle sizes of 0.83–3.35 mm. The total moisture contents (M_t) of Inner Mongolia raw coal (IM-RC) and Yunnan raw coal (YN-RC) were determined to be 36.34% and 51.61% respectively, by measurement at 110 °C in a N_2 oven according to GB/T 211-2007 [37]. Additionally, the basic properties of two RCs are presented in Table 1. For IM-RC and YN-RC, the former should belong to higher rank lignite with lower moisture content and the latter to lower rank lignite with higher moisture content. They are different in contents of V_{daf} (45.06% and 69.28%), C_{daf} (74.07% and 66.12%) and O_{daf} (19.31% and 26.69%), which would make the data more comparative.

2.2. Hydrothermal dewatering

HTD experiments were carried out in an 1 L autoclave with an electric heating jacket and a magnetic stirrer, as shown in Fig. 1. A mixture of as-received raw coal (100 g in dry basis) and deionized water at an 1:2 proportion were added into the autoclave. After sealing, the air in the autoclave was exhausted by vacuum pump. Subsequently, the autoclave was raised to the desired temperature (230 °C, 270 °C or 300 °C) and held for 30 min under magnetic stirring at a constant speed of 200 rpm. When the autoclave had cooled to ambient temperature, the gas products were measured through a gasometer and collected in a reservoir bag under ambient temperature (25 °C) and pressure (101 kPa). To make the data more understandable, the gas volume obtained under ambient temperature was converted into those under standard conditions (0 °C, 101 kPa). The solid and liquid products were separated by filtration. The products obtained at 230 °C, 270 °C and 300 °C were labelled as HTD230, HTD270 and HTD300, respectively. The yield ($Y_{solid,\ d}$) of the solid products was calculated by formula (1).

$$Y_{solid,d} = \frac{m_{solid}}{m_{raw}} \times 100\% \quad (1)$$

where, $Y_{solid,\ d}$ represent the yield of solid products on the dry basis (wt %, d); m_{raw} and m_{solid} are the masses of raw coal and solid products obtained after HTD process on the dry basis respectively (g, d).

2.3. Analysis of HTD products

The proximate and ultimate analyses of the solid products were determined according to GB/T 212-2008 [38] and GB/T 31391-2015 [39], as listed in Table 1.

The Bruker Vertex 70 Fourier transform infrared spectroscopy was used to examine chemical structure change of the solid products. Sample (0.5 mg) and KBr (100 mg) were mixed and pressed into a pellet. The pellet was then immediately measured in the range of 4000–500 cm^{-1} with 32 scans.

H_2S was measured by a gas chromatography (Haixin GC-950) coupled to a flame photometric detector (FPD), while other gases, such as CO, CO_2, H_2 and CH_4, were measured by a Raman laser spectrometer (RLGA-174b).

The liquid was evaluated by chemical oxygen demand (COD) analysis according to GB/T 11914-89 [40].

3. Results

3.1. Solid products

As shown in Table 1, the moisture content (M_{ad}), volatile matter content (V_{daf}), oxygen content (O_{daf}) in IM-RC are significantly lower than those in YN-RC, while the calorific value ($Q_{net,\ daf}$) of the former is higher than the latter, indicating that the quality of IM lignite is slightly better than that of YN lignite.

After HTD processing, the moisture contents of solid products at 300 °C decrease to 7.43% for IM lignite and 4.47% for YN lignite. Clearly, the extent of moisture removal for YN lignite is greater than that for IM lignite. There are also continuous decreasing trends in volatile matter and increasing trends in calorific value with increasing temperature both for IM and YN lignites. Ultimate analyses in Table 1 show that the carbon contents increase and oxygen contents decrease after HTD. The atomic ratios of O to C ($A_{O/C}$) and H to C ($A_{H/C}$) also decrease with increasing temperature. These changes all demonstrate an improvement in the quality of HTD solid product for IM and YN lignites, relative to their parent lignites. More importantly, HTD is more beneficial for YN lignite than for IM lignite.

The removal percentages of C, H, O, N and S elements in solid products for IM and YN lignites are displayed in Fig. 2. The proportions of S removed from these two lignites by HTD are much higher than the