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Substantial upgrading of a high-ash lignite by hydrothermal treatment followed by $Ca(OH)_2$ digestion/acid leaching

Xueping Liu, Xuantao Wu, Jie Wang*

Department of Chemical Engineering for Energy, Key Laboratory of Coal Gasification and Energy Chemical Engineering of Ministry of Education, East China University of Science and Technology, 130 # Meilong Road, Shanghai 200237, PR China

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ABSTRACT

Hydrothermal treatment (HT) is traditionally used as an approach for upgrading lignite. But this approach has a limited effectiveness for upgrading high-ash lignite. In this study, we explore a new method for substantial upgrading of lignite. The method is first to deoxygenate lignite by HT and then to demineralize lignite by successive $Ca(OH)_2$ digestion/acid leaching (abbreviated as HT-D method). For a lignite enriched with quartz and clays, the O/C atomic ratio and the ash content were reduced from 0.30 to 0.09 and from 24.1% to 3.5% (dry basis), respectively, by an optimal HT-D treatment at both HT and digestion temperatures of 330 °C. The higher heat value (HHV) was increased from 17.4 MJ kg^{-1} to 29.7 MJ kg^{-1} via this treatment, in contrast to a smaller enhancement to 22.1 MJ kg^{-1} via the HT only. The presence of acidic functional groups in the raw lignite was found to strongly impede the alkalization reactions of mineral species. The first HT was a critical step for improving the subsequent demineralization through the elimination of acidic functional groups. Many trace elements including Li, Be, V, Mn, Ga, As, Se, Cr and Pb were removed to a large extent by the HT-D treatment.

1. Introduction

Lignite, as an abundant and worldwide distributed reserve, will be important to secure a stable energy supply in the foreseeable future. However, lignite is a low-rank and inferior coal, which has high moisture, high oxygen content and low calorific value. Most lignite also has high inorganic mineral content. Such properties are deemed to have an adverse impact on many aspects of lignite utilization, such as degrading its market value, lowering its combustion efficiency and creating large amounts of airborne pollutants and solid wastes. Therefore, the upgrading of lignite has been the subject of a number of studies [1–3].

Hydrothermal treatment (HT) offers an efficient and environmentally friendly way to upgrade lignite by dewatering and deoxygenating in a non-evaporative system [4–6]. But an ordinary HT is ineffective for removing mineral matter. Consequently, this approach can improve the energy density and other qualities only to a limited extent for high-ash lignite. The existence of a large portion of incombustible mineral matter in coal not only makes the distant transport unattractive economically but also causes many troublesome problems in nearly all coal conversion processes such as combustion, gasification and liquefaction. It is thus necessary to explore a more effective way to upgrade lignite via deoxygenation integrated with demineralization prior to utilization.

Coal beneficiation or demineralization has been investigated extensively, which can be broadly classified into physical, biological and chemical methods [7,8]. Of these, chemical cleaning is seen as an alternative method to physical beneficiation, allowing for a high removal of mineral matter and other impurities such as sulfur and hazardous trace elements. Especially, the chemical method using stepwise alkali/acid leaching has drawn researchers' considerable interests [9–12], mainly because it can demineralize many coals to an ash content lower than 1% to prepare so-called ultraclean coal, and also because the reagents and processing procedures employed in this method are easily available for industrial production. A more attractiveness comes from the possible recycling of reagents by regeneration processes [11].

Early in 1978, Reggel et al. [9] reported a detailed study on coal demineralization by an alkali/acid leaching method. They used 10% NaOH to digest coal at 225 °C for 2 h and subsequently used dilute HCl or H_2SO_4 to leach the alkalized coal. The ash content was found to decrease from about 10% to lower than 1% for Illinois No. 6 coal and Indiana No.5 coal. But for Elliot coal, the demineralization was not so good. They further proved that increasing temperature to 325 °C was unfavorable for ash removal. Since then, there have been several studies on coal demineralization using a similar method [10–18]. A prevailing research trend is the operation of alkalizing treatment under a

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* Corresponding author.
E-mail address: jwang2006@ecust.edu.cn (J. Wang).

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mild condition to alleviate the loss of organic matter. This is particularly important to lignite because the organic matter in it is readily eluted during the rigorous caustic alkali leaching. Çulfaz et al. [17] performed the demineralization of two Turkey lignites by 0.5–10 M NaOH leaching at 127–187 °C followed by 1 M HCl leaching. The yield of organic matter was found to vary from 97% down to 31% depending on the conditions. A large portion of the organic matter in lignite was extracted with a concentrated NaOH solution even at a lower temperature. Karaca and Önal [18] investigated the demineralization of two Turkey lignites by the successive NaOH/HCl leaching under an atmospheric refluxing condition. They revealed that this method achieved a higher level of demineralization for a calcite-rich lignite, while for a clay-rich lignite with 30.3% ash content, the ash removal was very low. Most recently, Behera et al. [12] studied the demineralization of a high-ash Indian lignite by a successive NaOH/H_2SO_4 leaching at atmospheric pressure and boiling temperature. A maximum ash removal was attained with the use of 2.5 M NaOH and 20% H_2SO_4, but not higher than 48%. To sum up, the NaOH/acid leaching method can demineralize bituminous coal to a high level, but this method is not amenable to high-ash lignite.

Since NaOH can terribly erode equipment and aggressively destruct coal structures, Fan et al. [19] tried to employ relatively gentle Na_2CO_3 as a leaching reagent in place of NaOH. However, this reagent was not as effective as NaOH unless the coal firstly underwent an extensive oxidation. With a similar consideration, Wang and Tomita [20] explored a coal demineralization method by the hydrothermal digestion with cheaper and less corrosive $Ca(OH)_2$ followed by the dilute HCl leaching. They found that under the optimized conditions, the ash content decreased from 8.8 to 15.4% to 1% for three of the four Australian bituminous coals tested. They ascertained that a main mechanism was the hydrothermal reactions of $Ca(OH)_2$ with kaolinite and quartz in coal to form acid-leachable calcium aluminosilicates or calcium silicates. Compared to NaOH, $Ca(OH)_2$ has a distinctive advantage of being less destructive to coal even under a severer digesting conditions. However, up to date, no literature has addressed the demineralization of lignite by the $Ca(OH)_2$ digestion/acid leaching method.

In this work, we have found that lignite could not be effectively demineralized by direct use of the $Ca(OH)_2$ digestion/acid leaching method, differing from the case of demineralizing bituminous coals. We have proposed a specific approach for lignite demineralization, with a detailed discussion on its chemical principle. In this approach, lignite is firstly subjected to hydrothermal treatment, and then to demineralization by the $Ca(OH)_2$ digestion/HCl leaching method. This approach can be alternatively used to upgrade lignite by deoxygenation and demineralization.

2. Experimental

2.1. Coal samples and reagents

A Chinese lignite (YX lignite) used in this study was mined from Yuxi district of Yunnan province. The coal was ground and sieved to the particle size of 0.074–0.15 mm. This lignite contained 24.1% ash (dry basis) composed primarily of silica and alumina, but with little sulfur. The main crystalline mineral species in it were quartz, kaolinite and mica. Its proximate and ultimate analyses as well as the mineral matter characterizations will be shown in the "Results and discussion" section. All of calcium hydroxide, sodium hydroxide, hydrochloric acid used in the digestion and leaching experiments were the chemical reagents of analytic-grade purity, purchased from Shanghai Lingfeng Chemical Co. Ltd.

2.2. Demineralization methods

2.2.1. Direct demineralization method (DD method)

A 15 g sample of lignite was blended with a proportion of $Ca(OH)_2$ and 250 mL of deionized water in a 350 mL stirring autoclave. After being tightly sealed, the slurry was heated with an electric furnace at a heating rate of about 10 °C/min from room temperature to 300 °C and a stirring speed of 70 rpm, and then kept at the final temperature for a period of time. The steam pressures erected autogenously at the final temperature of 300 °C was about 8.0 MPa. After the autoclave was taken out from the furnace and cooled down in front of an electric fan, the alkalized slurry was recovered as thoroughly as possible, and then was filtered using a Buchner funnel. The solid was subsequently leached with an excess amount of 5% HCl at room temperature upon stirring for 15 min. After filtration, the solid was leached once again with 5% HCl at boiling temperature for 30 min. The demineralized lignite was obtained successively by filtration, hot water washing, deionized water rinse, and drying in an electric vacuum oven at 60 °C.

2.2.2. Stepwise hydrothermal treatment and demineralization method (HT-D method)

In this method, a key process step distinct from the DD method was the HT of lignite sample without additive prior to demineralization. Briefly, a 15 g sample of lignite was immersed in 250 mL of deionized water in the autoclave, and heated to a desired temperature (250–330 °C) for 1 h. The pressures were autogenously elevated to 3.1–12.3 MPa depending on the temperature. After filtration, the wet sample of hydrothermally treated lignite was entirely transferred to the autoclave. It was then subjected to demineralization by the $Ca(OH)_2$ digestion/HCl leaching method in the same manner as described above. The amount of $Ca(OH)_2$ added, autoclaving temperature and holding time were adjusted in different experiments to optimize the demineralization. Fig. 1 shows two routes to demineralizing lignite with the regulated variables. For convenience, the treated samples obtained in different steps are denoted by abbreviated symbols. For example, HTL300 denotes a lignite obtained by the hydrothermal treatment at 300 °C, and HT300-DL250-2.0-3 stands for a demineralized lignite obtained by the $Ca(OH)_2$ digestion of a HTL300 sample at 250 °C with the $Ca(OH)_2$/ash mass ratio of 2.0 for 3 h, followed by the acid leaching, and so on. Being stated specifically, NaOH or a mixture of NaOH and $Ca(OH)_2$ was used in lieu of $Ca(OH)_2$ for the lignite digestion.

2.3. Analysis methods

To characterize the changes of lignite properties during the HT, alkalization and demineralization, the samples obtained through each of treatment steps were collected, as depicted in Fig. 1. In this case, all

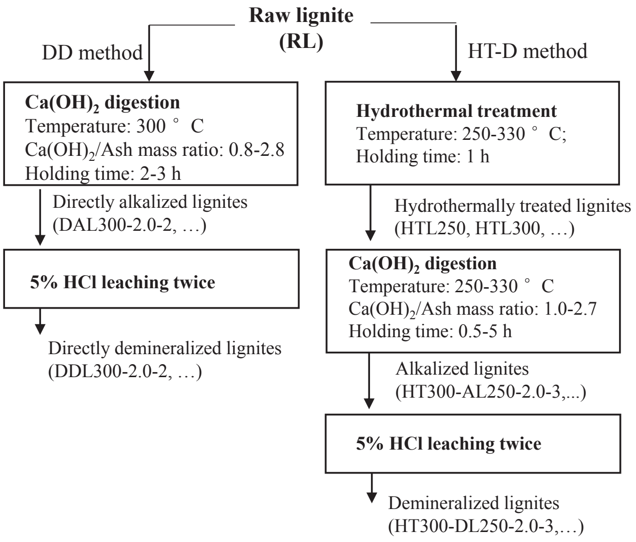

Fig. 1. The stepwise experimental procedures of DD method and HT-D method as well as the related sample nomenclature.