Full Length Article

Moisture removal mechanism of low-rank coal by hydrothermal dewatering: Physicochemical property analysis and DFT calculation

Junhong Wu [a], Jie Wang [b], Jianzhong Liu [a,*], Yumeng Yang [a], Jun Cheng [a], Zhihua Wang [a], Junhu Zhou [a], Kefa Cen [a]

[a] State Key Lab of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China
[b] Zhejiang Energy Group R & D, Hangzhou 310000, China

HIGHLIGHTS

- The free and bound water in lignite were quantified before and after HTD.
- The removal of free water was associated with the collapse of macropore.
- The bound water was reduced because of the removal of oxygen functional groups.
- DFT calculation on the interaction energy between lignite and water were carried out.

ARTICLE INFO

ABSTRACT

High moisture content greatly restricts the large-scale utilization of low-rank coals (LRCs). Hydrothermal dewatering (HTD) is a promising technique for dewatering and upgrading LRCs. Chinese lignite from XiMeng Mine in Inner Mongolia was upgraded by HTD. The effects of pore structure and oxygen functional group content on moisture distribution were investigated. Thermogravimetric analysis, mercury intrusion porosimetry, and chemical titration were conducted to characterize the physicochemical properties of coal samples. Results show that a substantial amount of moisture was removed, the coal composition was modified, and the energy density was significantly improved after HTD. Both free-phase and bound-phase moisture in lignite were significantly removed. Free water removal was associated with the collapse of macropore structures caused by shrinkage forces. The bound water was remarkably reduced as a result of the removal of oxygen functional groups, such as phenolic hydroxyl and carboxyl. During HTD, the oxygen functional groups were decomposed, and the hydrogen bonding between water and hydrophilic sites was destroyed, thereby leading to a weakening of the water-holding capacity of lignite. Four representative model molecules with different polarities were used to study the intermolecular interactions between lignite and water. The interaction energies of model molecule···water complexes were determined by density functional theory (DFT) calculation. The types of non-covalent interactions of both hydrophobic and hydrophilic sites in lignite with water were vividly demonstrated using color-mapped reduced density gradient isosurface. The carboxyl and hydroxyl groups are extremely liable to interact with water via hydrogen bonding with large interaction energy and exhibiting strong hydrophilicity. On the other hand, the alkanes and benzene rings interact with water via van der Waals attractions and show hydrophobic effects.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The high moisture content of low-rank coals (LRCs) is a major obstacle to their economic utilization. Such obstacle significantly affects the economics of coal transportation and the efficiency of coal utilization processes, such as combustion and gasification [1]. For coal water slurry (CWS) preparation, the vast amount of inherent water bounded on the coal surface cannot flow freely between coal particles to reduce the viscosity, thereby leading to inferior slurry ability [2,3]. Therefore, substantial efforts for LRC upgrading to increase its energy density, promote its market value, and make it a transportable fuel have been regarded as a promising way toward clean and highly efficient utilization [4,5].

* Corresponding author.
  E-mail address: jzliu@zju.edu.cn (J. Liu).

Given the structural complexity and component diversity of coal, water adsorption on coal surface is complicated. However, both pore structure and coal component are crucial in assessing the water adsorption characteristics of coal. Water adsorption on coal surface is expected to occur in three steps: monolayer sorption, multilayer sorption, and capillary condensation [6]. Various literatures reveal that the BET monolayer capacity of coal for water adsorption correlates well with the amount of hydrophilic functional groups rather than the surface area, whereas the pore size distribution is the dominant factor affecting multilayer adsorption and capillary condensation [7]. Generally, the polar groups in porous carbonaceous materials are the primary sites for water vapor adsorption at low relative pressure (P/P_0 < 0.5), whereas water vapor adsorption in hydrophobic pores may occur for P/P_0 > 0.5, depending on pore size and the availability of functional groups. The water molecules adsorbed on the hydrophilic surface groups act as nucleation sites for further water adsorption. In addition, three-dimensional water clusters and networks develop with increasing relative pressure. This condition arises because surface groups, such as hydroxyl and carboxyl groups, can act as either hydrogen bond acceptors or donors during water adsorption on coal surface [8]. The surface morphology and pore structure of coal are irregular and complex because of its different pore structures, such as cracks, capillaries, and open and closed pores. The porous structure of LRCs mainly comprises meso- and macropores, which is also correlated with its high moisture content [9]. Kaji et al. [6] found that the decrease in the pore surface area makes the coal surface inaccessible to water because of the plugging of small pores during pyrolysis. Hayashi et al. [10] analyzed the relaxation characteristics of water adsorbed in the pores, and found that the pore water roughly decreased in a linear manner with the pore dimension. Overall, it is generally accepted that the abundant oxygen functional groups as well as pore structures result in high moisture content in LRCs.

Hydrothermal dewatering (HTD) technology has several advantages over conventional dewatering methods, such as decarboxylation and irreversible dewatering, and has a comparatively superior product quality. Because of these unique features, HTD has been extensively applied to modify LRCs [11–13]. Previous efforts to investigate HTD upgrading of LRCs have been devoted toward: (1) the effect of HTD conditions on the treated coal properties [14–16]; (2) the properties of gas-, solid-, and liquid-phase products [17–21]; (3) the effect of HTD treatment for LRC on its slurrying, pyrolysis, combustion, and gasification behaviors [22–25]; (4) the disposal of wastewater produced from HTD [26,27]. Although nearly all these research reveal that the moisture content remarkably decreases after HTD upgrading, less is known about the mechanism that affects how the hydrophilic functional groups as well as pore structures in LRCs change, and further affects moisture distribution during HTD upgrading.

The changes of moisture distribution, pore structures, and oxygen functional group contents of lignite were investigated after HTD. A theoretical explanation is given on how HTD modifies the lignite concerning hydrophilic functional groups and pore size distribution, and further irreversibly removes the moisture with different forms. Furthermore, a definitive insight into the interactive nature of both hydrophilic and hydrophobic functional groups with water in lignite is provided by density functional theory (DFT) calculations. A high level of calculation on the interaction energies is carried out. Meanwhile, reduced density gradient (RDG) analysis is employed to identify the types of non-covalent interactions between coal and water.

2. Material and methods

2.1. Material

The coal used in this study was typical Chinese lignite, XiMeng (XM), which was collected from Inner Mongolia, China. Both raw and upgraded coals were exposed to a constant temperature (25 °C) and humidity (65%) to reach equilibrium. Then the moisture content was measured, and it referred to as equilibrium moisture (M_{eq}). The elemental analysis of coal samples was measured using a LECO-CHNS 932 Elemental Analyzer, and the oxygen content was calculated by difference. The proximate analysis was determined according to ISO11722, ISO1171, and ISO562, and the calorific value was measured using the adiabatic bomb calorimetric method in accordance with ISO1928.

2.2. HTD procedure

The HTD procedure was the same as described in the previous literature [28,29]. A mixture of raw coal and deionized water at a 1:2 proportion was added into the reactor. The reactor was heated to the desired temperatures and then maintained for 60 min. After HTD, the upgraded coals were labeled as HTD-200, HTD-250, HTD-280, HTD-300, and HTD-320 based on the numbers of HTD temperature in degree of Celsius.

2.3. Thermogravimetric analysis

Thermogravimetric (TG) analysis of raw and upgraded coals was carried out using a TA TGA-DSC Q600 thermogravimetric analyzer under nitrogen atmosphere. For each test, about 12 mg of coal was added and quickly heated to 70 °C. The sample was dried at 70 °C for 60 min. During isothermal drying, the flow rate of sweep gas (nitrogen) was set to 120 ml/min.

2.4. Pore structure

Meso- and macropores are the dominant porous structures of LRCs. Mercury intrusion porosimetry (MIP) is widely used to characterize the pore structure of lignite, especially for meso- and macropores. The MIP tests of coal samples were conducted on an AutoPore IV 9500 (Micromeritics Instrument Corporation). The intrusion accuracy of AutoPore IV 9500 was ±1% of full-scale intrusion volume. The relation between pressure and pore diameter was determined following the Washburn equation for cylindrical pores [30].

2.5. Oxygen functional group content

Oxygen functional groups of raw and hydrothermally dewatered coals, including carboxyl, phenolic hydroxyl, and total acid groups, were determined by chemical titration [31]. More detailed description of the method has been reported in previous literature [22].

2.6. DFT calculations

Four representative model molecules with different polarities in lignite, namely, benzoic acid, phenol, benzene, and ethylbenzene, were taken into account in analyzing the intermolecular interactions with water. The geometry optimization and vibrational frequency analysis for the model molecule··· water complexes were carried out at the M062X-D3/6-311+G(d, p) level by Gaussian 09