



Effects of phenolic hydroxyl and carboxyl groups on the concentration of different forms of water in brown coal and their dewatering energy



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ABSTRACT

Oxygen functional groups as primary adsorption site of water are one of key factors controlling water re-adsorption and drying behaviors of brown coal. The dewatering energy of brown coal because of different oxygen functional groups is still unclear. Thus, two kinds of oxidized brown coal samples carrying more phenolic hydroxyl or carboxyl groups with similar pore structures were chosen. The concentrations of different water forms of the samples were determined from the moisture holding capacity at constant humidity and temperature and from the results of dewatering experiments analyzed by thermogravimetry coupled with differential scanning calorimetry. The results showed that the concentrations of three forms of water, i.e. free water, capillary water, and molecular water, showed good correlations with concentration of carboxyl groups. Comparison of ¹H NMR analysis of dried and moisturized samples showed that the types of oxygen functional groups predominantly affected the water environment in coal. IR spectra of dried and adsorbed D₂O samples showed that OH–π hydrogen bond due to carboxyl groups was easier broken than that due to phenolic hydroxyl groups. The water desorption energy of primary site and dewatering energy of samples with more carboxyl groups were lower than that of samples with more phenolic hydroxyl groups, because hydrogen bonding energy of water bonded to hydroxyl oxygen of carboxyl groups was lower than that of water bonded to hydroxyl oxygen of phenolic hydroxyl groups.

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1. Introduction

Oxygen functional groups as primary adsorption site of water are one of key factors controlling water re-adsorption and drying behaviors of brown coal [1,2]. About 20% of water in bed-moist brown coal bonds with surface oxygen functional groups [2–4], which makes it uneconomical to dry brown coal from the viewpoint of energy consumption. The high energy consumption can be attributed to overcoming direct hydrogen bonding of water to oxygen functional groups and weaker bonding of water at a secondary site to water directly bonded to coal oxygen functional groups [5,6]. In this connection, determining the effect of oxygen functional groups on dewatering energy is important for investigating the high energy consumption during dewatering processes of brown coal.

The oxygen functional groups are sensitive to drying temperatures and drying atmospheres. The concentrations of oxygen functional groups such as phenolic hydroxyl, carbonyl and methoxyl groups decrease with drying temperature increasing in inert gases and steam and increase gradually with temperature increasing up to 200 °C in air

[7–9]. Phenolic, alcoholic, free carboxylic acid, carboxylate, carbonyl groups approximately break down at 150 °C, 200 °C, 150 °C, 200 °C and 150 °C, respectively [10]. In evaporative thermal drying, where the brown coal is directly or indirectly in contact with heated nitrogen, air, flue gas or superheated steam. The concentrations of oxygen functional groups such as phenolic hydroxyl, carbonyl and methoxyl groups decrease during the drying process, so that the water re-adsorption ability is changed [7,9,11–13]. In non-evaporative dewatering processes, such as hydrothermal dewatering, mechanical thermal expression, hot oil-immersion and microwave drying, the oxygen functional groups are damaged, and the oxygen/carbon atomic ratios are decreased [14–17,51]. Since dewatering methods and conditions differ in their effect on different oxygen functional group concentrations, it is important to assess the relative merit of different dewatering methods with respect to water re-adsorption.

A good correlation between the equilibrium moisture content (EMC) at 52% relative vapor pressure (RVP) and the carboxylic acid content for a range of eleven international coals and less significant correlation between EMC with the phenolic group content are reported [18]. The EMC at 51.4% RVP or less for the acid-washed brown coal samples showed moderately good correlation with the carboxylic acid concentration, but much weaker correlation with the phenolic content [19]. The author

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interpreted that the research in reference [18] covered a much larger carboxylic acid concentration range than in the study of Fei Yi et al. [19]. Furthermore, the order of oxygen functional groups' hydrophilicity of dewatered brown coal is: carboxyl group > phenolic hydroxyl group > carbonyl group > methoxyl group and good correlations between the oxygen functional groups with EMC at 77% RVP are reported [8]. Obviously, there are some discrepancies on the relationship between phenolic hydroxyl and EMC, and the dewatering energy of brown coal due to different oxygen functional groups is still unclear.

Investigating dewatering process with thermogravimetry coupled with differential scanning calorimetry (TGA-DSC) gives quantitative information about the change of mass and heat. Previous studies [2,20,21] have shown that at least three forms of water differing in desorption heat from brown coal or sludge have been distinguished and at least two types of water can be obtained according to the drying rate curve [9]. Determination of sorption isotherms using intelligent gravimetric analyzer (IGA) provides a quantitative record of the variation of sorbed material with sorbate pressure and derives information on the thermodynamics of the sorption processes [19,22,23]. Isosteric heat of sorption can be estimated through BET model and modified BET model [6,23]. Modified BET model, which overcomes the limitation of the BET model, is applicable to the relative humidity in the range of 0.05–0.35 and can estimate the water sorption on primary and secondary sites [24]. To monitor the pathway of selected target molecules and for structure elucidation in organic chemistry, H/D isotope exchange and IR spectroscopic investigation have been frequently applied [25–27]. Hydrogen bonding energy can be calculated by corrected density functional theory-D function of ω B97X-D. The function performed quite well in the test cases energies of the hydrogen-bonded conformers, where the root-mean-square error was only 0.59 kcal/mol [36]. Compared with B97-D, B3LYP-D, BLYP-D, ω B97X, and ω B97, corrected density functional theory-D function of ω B97X-D includes further atomization energies, reaction energies, non-covalent interaction energies, equilibrium geometries, and a charge-transfer excited state [56].

This work attempts to study the individual effects of oxygen functional groups on the concentration of different forms of water and dewatering energy of brown coal, with the pore structure parameters that might affect equilibrium moisture content holding constant.

2. Experimental

2.1. Samples preparation

2.1.1. Preparation of samples with different oxygen functional groups

Yunnan brown coal of China was selected. It was crushed and sieved to a particle size under 100 mesh.

To minimize the interference of metal cation on the concentrations of different forms of water, brown coal sample was demineralized. Crushed coal (6.0 g) was immersed into HCl aqueous solution (5 mol/L, 40 mL) at 60 °C for 60 min, afterwards, the sample was filtered. And then, HF aqueous solution (1.13 g/mL, 40 mL) was added and operated under the same conditions. At last, the demineralized sample was filtered and rinsed with boiling distilled water to eliminate the residual acid until the pH of filtrate reached nearly 7. All of the acid treatment operations were performed in a chemical fume hood to prevent inhalation of corrosive vapor of hydrofluoric acid. The demineralized coal was denoted as DC.

To introduce different oxygen functional groups into coal samples and keep pore structures that might affect the content of forms of water almost the same, DC was mild oxidized by low concentrations of H₂O₂ and HNO₃ aqueous solution, respectively. Firstly, DC (10.0 g) was mixed with H₂O₂ aqueous solution (5% vol., 300 mL). The mixture was heated at 60 °C for 2 h while being mixed with a magnetic stirrer. Afterwards, the mixture was filtered and rinsed with distilled water until the pH of filtrate was 7. The oxidized sample was denoted as HO5. Samples oxidized by 8% vol. H₂O₂ aqueous solution and 2.5 and

3% vol. HNO₃ aqueous solution under the same condition were denoted as HO8, HN2.5, and HN3, respectively.

In order to keep the oxygen functional groups and pore structures of oxidized samples almost intact, subsamples of DC, HO5, HO8, HN2.5, and HN3 were dried in a vacuum oven at 30 °C for 24 h, which were denoted as dried samples. Rest of the samples was not dried, which were denoted as undried samples.

Table 1 shows the elementary analysis of the dried samples by a Vario El Cube elemental analyzer (Vario EL cube; Hanau, Germany). Notably, the oxygen content was determined individually. Compared with DC, the carbon content of oxidized samples was lower and their oxygen content was higher. The sequence of atomic O/C ratio was: HN3 > HN2.5 \approx HO8 > HO5 > DC. The results suggested that oxygen functional groups were introduced into the oxidized samples. The oxidation degree of HO8 and HN2.5 was almost the same.

2.1.2. Adsorbed D₂O samples preparation

In order to reveal the interaction between oxygen functional groups and water molecule, the liquid D₂O (99.9% D, Aladdin Reagent) was employed. A subsample of each of the above dried samples (about 0.5 g) was weighed into a porous plastic basket, put into a self-made constant temperature and humidity incubator, as shown in Fig. 1, and maintained at 30 °C. Before adsorption, the valve was opened, the incubator was evacuated until the liquid D₂O was boiling and then immediately closed the valve. After at least 3 days, when adsorption equilibrium had been reached, the basket was taken out. The adsorbed D₂O samples of DC, HN3, HN2.5, HO5 and HO8 were denoted as RDC, RHN3, RHN2.5, RHO5 and RHO8, respectively.

2.2. Moisture holding capacity measurement of undried samples

A subsample of each of the above undried samples (about 2.0 g) was weighed into a glass dish, put into a constant temperature and humidity incubator (DSC1H-100-RT-P-AR, Beijing Chuanteng Instruments & Equipments Co., Ltd) and maintained at 30 °C under relative humidity (RH) of 96%. After about 7 days, when adsorption equilibrium had been attained, the dishes were taken out, weighed immediately, and then dried in a vacuum oven at 30 °C for 24 h. After drying, these dishes were weighed again. These experiments were repeated twice. The moisture holding capacity (MHC) (g/g, db) of samples was calculated by Eq. (1).

$$MHC = \frac{w_1 - w_2}{w_2 - w_3} \quad (1)$$

where w_1 is the weight of the dish and sample after water re-adsorption, (g), w_2 is the weight of the dish and sample after drying in the vacuum oven, (g), and w_3 is the weight of the empty dish, (g). Similar samples held in the incubator under similar conditions but not dried in the vacuum oven afterwards, denoted as moisturized samples, were

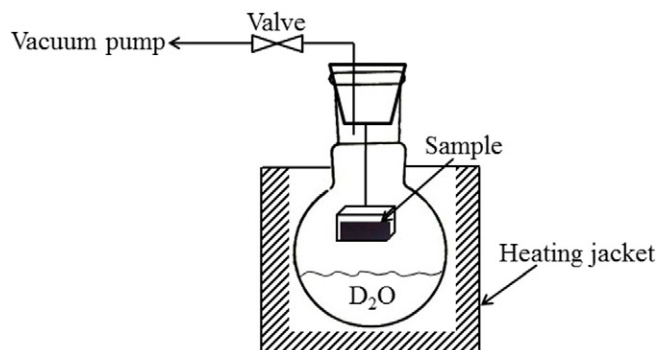


Fig. 1. Schematic diagram of the self-made incubator for adsorption D₂O.

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