



The effects of pore structure on the behavior of water in lignite coal and activated carbon

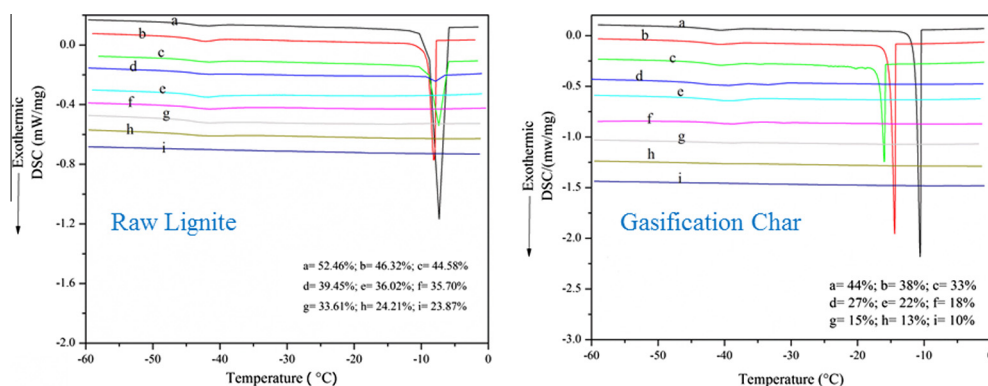


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GRAPHICAL ABSTRACT



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ABSTRACT

The effects of physical structure (pore structure) on behavior of water in lignite coal and activated carbon (AC) samples were investigated by using Differential Scanning Calorimetry (DSC) and low-temperature X-ray diffraction (XRD) techniques. AC samples with different pore structures were prepared at 800 °C in steam and the results were compared with that of parent lignite coal. The DSC results confirmed the presence of two types of freezable water that freeze at -8 °C (free water) and -42 °C (freezable bound water). A shift in peak position of free water (FW) towards lower temperature was observed in AC samples compared to the lignite coal with decreasing water loading. The amount of free water (FW) increased with increasing gasification conversion. The amounts of free and freezable bound water (FBW) in AC samples were calculated and correlated to pore volume and average pore size. The amount of FW in AC samples is well correlated to the pore volume and average pore size of the samples, while an opposite trend was observed for FBW. The low-temperature XRD analysis confirmed the existence of non-freezable water (NFW) in coal and AC with the boundary between the freezable and non-freezable water (NFW) determined.

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1. Introduction

Low-rank coals account for nearly 45% of the global coal reserve [1], which are important energy source in developing countries around the globe and are currently mainly used for generating

electricity [2]. However, these coals contain high moisture content (25–60%) which significantly affects their utilization including combustion, gasification and liquefaction [3,4]. High moisture content in Low-rank coals reduces its conversion efficiencies, increases transportation cost and causes higher carbon dioxide emissions which results in environmental issues [5]. Low-rank coals contain high amount of oxygen functional groups which is the reason for its high hydrophilicity and high moisture holding capacity [6]. On the other hand, low-rank coals have some advantages such as high reactivity, high amount of volatiles, lower mining cost, and lower pollution forming impurities such as nitrogen, heavy metals and sulfur [7]. Hence, these coals need to be upgraded before their use in order to be competitive in energy market. Upgrading of low-rank coal usually involves thermal drying processes [7–10]. Therefore, it is necessary to gain a better understanding of the coal-water interactions, particularly the behavior of water in these coals in order to design more efficient drying and upgrading technologies.

Drying and upgrading affect the physical and chemical properties of low-rank coals [11–14]. Low-rank coals are known to have colloidal gel-like structures that shrink and swell in response to drying and water uptake, respectively [13,15–17]. The reduction in the porosity of coal upon drying is induced by the shrinkage in macropores and so-called transitional porosity [18]. Low-rank coals are mainly comprised of meso- and macro-pores. Pore shrinkage and emptying during drying occurs due to the counteraction of particle contraction and moisture removal [3]. The changes in physical structure of low-rank coal during water removal are important in a sense that can affect the mass transport and chemical reaction mechanism during conversion processes [3]. Deevi and Suuberg [17] observed irreversible shrinkage of coal during drying. With increasing the intensity of drying, more pores would collapse resulting in lower apparent surface area [19].

Water exists in coals in different forms [20]. Researchers have used different definitions to describe various forms of water in coal such as freezable and non-freezable water, free water, pore water, surface water, molecular water, internal water, capillary water, adsorbed water and crystal water [3]. Unsworth et al. [21] defined three types of water, i.e., tightly bound water, loosely bound water and bulk-like water. Norinaga et al. [6] reported two types of freezable water (free water and freezable bound water) and non-freezable water in coals, based on congelation characteristics, which was confirmed by Tahmasebi et al. [22]. It has been reported that water molecules are not only adsorbed on active sites but also form water clusters around functional groups [23]. Water is primarily sorbed on active sites, before formation of water clusters and micropore filling.

Although several studies have reported on drying and thermal treatment of low rank coals, the exact mechanism of the interaction of physical structure of lignite coal with water is not well understood. The purpose of this study is to investigate the water behavior in lignite coal and its AC samples with different physical structures to establish the effects of physical structure of coal on the behavior of water. The amount of FW, FBW, and NFW in coal and AC samples and their correlation with physical properties of samples was also investigated.

2. Experimental section

2.1. Sample preparation

The lignite coal used in this study was from Inner Mongolia region of China and was supplied by Shenhua Energy Co. Ltd., China. The proximate and ultimate analyses of the Shenhua lignite sample are given in Table 1. The raw coal (HL1) was crushed and

Table 1
Proximate and ultimate analyses of HL1 lignite.

Sample	HL1 lignite
Moisture (wt%, ar)	14.39
Volatiles matter (wt%, db)	38.28
Fixed carbon (wt%, db)	46.82
Ash (wt%, db)	14.90
C (wt%, daf)	70.63
H (wt%, daf)	4.38
N (wt%, daf)	1.29
S (wt%, daf)	0.14
O (By difference) (wt%, daf)	23.74

sieved to a particle size of 150–300 μm . In order to obtain AC samples with different physical structures, lignite sample was pyrolyzed at 800 $^{\circ}\text{C}$ under nitrogen flow of 100 ml/min for 30 min in a fixed-bed reactor. The nitrogen used in this study was of a high purity quality (99.99%). Pyrolysis char was then gasified in steam at 800 $^{\circ}\text{C}$ in a vertical fixed-bed tubular quartz reactor with an internal diameter of 2.0 cm heated in an electric furnace to obtain AC samples with different pore structures. AC samples with 22%, 38%, and 62% conversion were obtained with varying gasification residence time. To obtain coal and AC samples with different water loadings, around 20 g of the sample was stirred in de-ionized water in a sealed beaker at room temperature for 24 h. The slurry was then filtered and immediately stored in airtight containers for further experiment. In order to obtain samples with lower water loadings, the wet samples were dried in a vacuum drying oven at 30 $^{\circ}\text{C}$ and 0.1 MPa. By controlling the residence time in drying oven, samples with different water loadings were obtained. The samples with different water contents were immediately stored in airtight containers for further analysis. The water content of coal and AC samples ranged between 10.12% and 52.46% on wet basis.

2.2. Sample characterization

The BET surface area analysis of lignite coal and AC samples was carried out with a specific surface area and pore size analyzer (V-sorb 4800 P). The N_2 gas adsorption method at 77 K was used. The coal and AC samples were first oven-dried at 105 $^{\circ}\text{C}$ and then degassed in the adsorption system at 200 $^{\circ}\text{C}$ to a final pressure of 1.33×10^{-4} Pa. To ensure the reproducibility and accuracy of analysis, experiments were repeated 3 times and the average values were reported. The Barrett–Joyner–Halenda (BJH) model was used to determine the pore size distributions from the desorption isotherm. The BET analysis results are summarized in Table 2.

FTIR technique was used to study the chemical structures of coal and AC samples. A Thermo Fisher Nicolet IS5 mid-FTIR spectrometer was used to obtain infrared spectra of raw coal and activated carbons. KBr pellets were prepared by grinding around 1 mg sample with 100 mg KBr. Prior to FTIR measurements, a reference spectrum was obtained from pure KBr pellets without the addition of any sample. The assignment of the bands in the infrared spectra was made according to the literatures [24,25].

2.3. DSC analysis

Differential Scanning Calorimetry (DSC) analysis was used to study the behavior of water in coal and AC samples with different

Table 2
The BET results of lignite coal and AC samples.

	HL1	AC (22%)	AC (38%)	AC (62%)
Surface area (m^2/g)	3.2	406.91	425.99	395.07
Pore volume (cm^3/g)	0.028	0.11	0.25	0.35
Average pore size (nm)	2.74	4.46	6.20	7.01

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