Fuel 219 (2018) 288–295

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Water occurrence in lignite and its interaction with coal structure

Li Feng*, Chuanzhou Yuan, Lianzhen Mao, Chuanyong Yan, Xiangang Jiang, Jie Liu, Xiangchun Liu

Key Laboratory of Coal Processing and Efficient Utilization of Ministry of Education, School of Chemical Engineering and Technology; National Engineering Research Center of Coal Preparation and Purification, China University of Mining & Technology, Xuzhou 221116, China

ARTICLE INFO

Keywords:
Lignite
Water occurrence state
Coal-water interaction
The binding energy

ABSTRACT

Essentially, the difficulty in dehydration technology of lignite depends on the energy state of water in lignite. The fundamental understanding of the water occurrence and energy state in lignite as well as its physical-chemical interaction with coal structure is helpful to the upgrading of lignite. In this paper, the water occurrence in lignite and the changes of oxygen-containing functional groups, pore structure, and water holding capacities at different drying temperatures were researched by DSC, NMR, FTIR and BET, respectively. The binding energies (calculated by DFT using model compounds) of different forms of water in lignite were also summarized. The relationships between energy state and occurrence mode of water in lignite as well as dehydration difficulty and structural changes during dewatering were clarified. The Results show that the energy state of water in lignite divided into three levels. The water in free and pore is in the lowest energy level. Its binding force with coal is pretty weak. So this type of water is easily vaporized and re-adsorbed. It is the main in removed moisture. Generally, the temperature removed free water mainly focused on below 100 °C, and the dehydration temperature of pore water mainly focused on 100–200 °C. The water bonded in hydrogen-bond and capillary confinement is in the middle energy level. The dehydration temperature mainly focused on 200–400 °C. The oxygen-containing functional groups of samples change a little and the re-adsorbed property improves a little after dehydrated. The water mainly produced by chemical reaction above 400 °C is in the highest energy level. Though this type of water does not belong to the natural occurrence of water in lignite, the re-adsorbed property improves much, and it plays the key role in stabilizing the dehydrated lignite interface.

1. Introduction

The high moisture content of lignite results in lower calorific value and higher fuel consumption; in the meanwhile it increases transportation cost and risk of spontaneous combustion. However, the application of lignite will be enhanced in the future due to its huge recoverable deposit, low mining cost and high reactivity [1–3]. Consequently, it is of great importance to upgrade the quality of lignite through dehydration before utilization. The key to dehydration technology lies in the understanding to the water occurrence and energy state in lignite and its physical-chemical interactions with coal structure.

Water exists in lignite in different forms. There are two relatively new techniques used to determine the types of water in coal: proton nuclear magnetic resonance (NMR) spectroscopy [4] and differential scanning calorimetry (DSC). It is commonly accepted that water exists in a free phase and a bound phase [5]. Norinaga et al. [6] used DSC and proton NMR methods to quantify different types of water in various coals ranging from lignite to bituminous. Based on the congelation characteristics of water, they classified the water into three types: free water that is identical with bulk water, bound water that freezes at a lower temperature than free water, and nonfreezable water that never freezes in the present temperature range. This conclusion was confirmed by Yi Fei et al. [7]. They used DSC to prove that lignite contains a third type of water, ‘bound’ water, which can be clearly distinguished from non-freezable and free water. Arash Tahmasebi et al. [8] investigated the types of water in low-rank coals by DSC and X-ray diffraction (XRD) analyses based on the freezing characteristics. Two types of water were detected during freezing process in DSC experiments: free and freezable bound water. These two types of water accounted for 18.22–78.25% of total water in coal. The presence of the third type of water, namely “non-freezable water”, was confirmed in DSC heating process experiments. Lynch et al. [9,10] used ^{1}H NMR technique to measure the relaxation characteristics of water in coals. They found that most of the water associated with brown coal is mobile above 0 °C and not bound to the surface. Allardice et al. [11] measured the total

---

* Corresponding author.
E-mail address: 8422127@alu.fudan.edu.cn (L. Feng).

https://doi.org/10.1016/j.fuel.2018.01.097
Received 21 April 2017; Received in revised form 17 January 2018; Accepted 25 January 2018

value of non-freezing water in the coal and some hydrothermally-dried products using both ^1H NMR and DSC. Hayashi et al. [12] found that there were three components with different transverse relaxation times (T_2), which could be attributed to free water, pore water (freezable bound water and nonfreezable water), and mobile hydroxyls on the basis of the NMR relaxation characteristics of water absorbed in the pores.

The water occurrence in the coal has been defined in various terms, such as freezable and no-freezable water, free water, pore water, surface water, molecular water, internal water, capillary water, adsorbed water and crystal water [4,8]. But there still lacks a widely-acknowledged classification and all the previous classifications mainly depend on the analytical techniques. In the attempt to establish such a coherent classification system, the water occurrence state in lignite as well as the interaction between coal-water and coal structure should be taken into account simultaneously [4].

Coal–water interactions in lignite are very complicated. Many researches have been conducted in this field [13–22]. Kaji et al. [23] found a linear relationship between these hydrophilic sites and the water-holding capacity of coal. The relationship between equilibrium moisture content and polar groups is that the oxygen functional groups have greater affinity to chemically bind the moisture, making the surface more hydrophilic. Mu and Malhotra [24] studied the coal–water interactions by FTIR technique coupled with desorption approach. They observed different desorption kinetics for four O—H stretch vibrations, suggesting various desorption pathways for various types of water. Feng et al. [25] researched the physicochemical structure and moisture re-adsorption characteristics of Zhaotong lignite after hydrothermal and thermal upgrading. Han et al. [26] explored the relationship between pore structure and water occurrence in pore using partially gasified lignite char. Tang et al. [27] conducted a theoretical study to investigate the interactions between the lignite monomer and water molecules. Wang et al. [28] researched energetic and vibrational frequency shifts of water molecules confined inside single-walled carbon nanotubes by means of DFT study.

Although the above researches exist, the relationships between energy state and occurrence mode of water in lignite as well as dehydration difficulty and structural changes during dewatering reported few. This paper will focus on these researches.

Moisture determination is very important in researching the upgrading of lignite. The fractional mass loss method is a common method. But there may be errors using this method because released substances are not only water during heating of lignite. Karl-Fischer method was put forward by Karl-Fischer in 1935. It only measures the water content through chemical reaction. The method works over a wide concentration range from ppm up to 100% and supplies reproducible and correct results. But this method usually uses in many other areas and rarely applies in coal field. These two methods were used simultaneously and compared in measuring moisture content during dewatering of lignite in this paper, which reported few.

The desiccator method [29–31] is a classical and common method to measure equilibrium moisture content (EMC). But the experimental period is relatively long because the sample mass is relatively more and the reached equilibrium time is too long. We improved the experimental details based on the original method. Thus the experimental time is reduced. We also provide a criterion to judge the equilibrium.

2. Experiment

2.1. Sample

Lignite sample in this experiment was taken from Shengli (SL) Coal Mine, Inner Mongolia autonomous region, China. First, crush and grind the sample; then sieve it under a 200 mesh; then dry it with a vacuum oven at 105 °C for 4 h to constant weight. The ultimate and proximate analysis can be obtained by elementary analyzer (Vario MACRO cube, Germany) and an automatic industrial analyzer (5E-MAG6700, Kaiyuan, China) respectively. The results are shown in Table 1.

Table 1
Proximate and ultimate analyses of the lignite.

Sample	Proximate analysis (wt%)				Ultimate analysis (wt% daf)				
	M_{ar}	A_{db}	V_{db}	FC_{db}	C	H	N	S	O*
SL	31.91	22.28	32.41	43.32	65.71	4.92	1.26	2.42	25.69

ar: as-received basis.
db: dry basis.
daf: dry and ash-free basis.
* By difference.

2.2. Moisture content

The moisture content of the sample was measured with a moisture meter (915 KF Ti-Touch with 832 KF drying oven, Metrohm) by Karl-Fischer method.

2.2.1. Karl-Fischer method

The sample is heated in an oven located upstream from the cell and the released water is transferred by a flow of dry carrier gas to the titration cell where it is determined automatically by a Karl Fischer titration.

Water released from sample can react quantificationally with sulfur dioxide and iodine in Karl-Fischer (KF) reagent (a solution of iodine and sulfur dioxide in a mixture of pyridine and methanol)

$$SO_2 + I_2 + 2H_2\,O \rightarrow H_2SO_4 + 2HI$$

Pyridine is used to neutralize sulfuric acid, and methanol is used as stabilizer.

KF reagent is commercial reagent. It was periodically standardized against distilled water by adding 10 μL directly into the reaction vessel.

Absolute water contents can be determined by volumetric titration. When measured, titration vessel is filled with solvent, pretitrated with KF reagent, and then the sample is added into the titration vessel and titrated with KF reagent.

2.2.2. Moisture determination

First, weigh accurately 0.20 g raw coal (set its mass as m_1) and seal it in a small vial; then put the vial into the heating oven attached to automated titration systems; heat the coal sample under nitrogen purging; and then measure the moisture mass (m_{wi}) by Karl-Fischer method in sequence when the constant weight of dehydration is reached at the following temperature ranges: 20–50 °C, 50–60 °C, 60–80 °C, 80–100 °C, 100–120 °C, 120–140 °C, 140–160 °C, 160–180 °C, and 180–200 °C. The dehydration content (w_i) and the accumulative dehydration rate (r_i) of unit coal sample can be calculated by the following Eq. (1) and Eq. (2) respectively.

$$w_i = (m_{wi}/m_1) \times 100\% \tag{1}$$

$$r_i = r_{i-1} + (w_i/\sum w_i) \times 100\% \tag{2}$$

2.3. Sample drying

The amount of mass loss was measured by the fractional mass release observed in the experimental temperature range.

First, weigh accurately 0.70 g coal sample (set its mass as m_2); then put it a porcelain boat and weigh the overall mass (set its mass as m_3); place the porcelain boat into a tube furnace and then degasify the furnace completely with N_2; keep the constant temperature for 2 h at 50 °C, 100 °C, 150 °C, 200 °C, 250 °C, 300 °C, 350 °C, 400 °C, 450 °C and denote the coal sample as SL50, SL100, SL150, SL200, SL250, SL300,