Chemical Engineering Thermodynamics

Evolvement behavior of microstructure and H₂O adsorption of lignite pyrolysis☆

Yingyue Teng, Shijun Lian, Quansheng Liu *, Yuzhe Liu, Yinmin Song, Runxia He, Keduan Zhi

College of Chemical Engineering, Inner Mongolia University of Technology, Inner Mongolia Key Laboratory of Industrial Catalysis, Hohhot 010051, China

ABSTRACT

The effect of pyrolysis on the microstructure and moisture adsorption of lignite was investigated with low field nuclear magnetic resonance spectroscopy. Changes in oxygen-containing groups were analyzed by Fourier transform infrared spectroscopy (FTIR), and H₂O adsorption mechanism on the surface of lignite pyrolysis was inferred. Two major changes in the pore structure of lignite char were observed as temperature increased in 105–200 °C and 500–700 °C. Pyrolysis temperature is a significant factor in removing carboxyl and phenolic hydroxyl from lignite. Variation of ether bond content can be divided into three stages; the content initially increased, then decreased, and finally increased. The equilibrium adsorption ratio, content of oxygen-containing groups, and variation of pore volume below 700° were closely correlated with each other. The amount of adsorbed water on char pyrolyzed at 700 °C increased. Moreover, the adsorption capacity of the lignite decreased, and the adsorption state changed.

© 2016 The Chemical Industry and Engineering Society of China, and Chemical Industry Press. All rights reserved.

1. Introduction

Lignite is characterized by low heat value but high transportation cost [1], which limits its wide application; these characteristics are attributed to its high porosity (similar to plastic material) and high moisture content (25%–60%). Heat treatment is one of the effective solutions to the limitations of lignite. Pyrolysis can reduce the moisture content and spontaneous combustion tendency of lignite, but increase the heat value. However, pores and cracks are abundant on the surface of heat-treated lignite, which re-absorb moisture in wet environment. Such re-absorption lowers the heat value of lignite and may increase spontaneous combustion [2]. The pore specific surface area of lignite expands as temperature rises, accompanied with the production of microcracks in low-temperature phase [3,4]. Numerous open holes within the lignite are developed after low-temperature dehydration, and the number of mesopore reaches the maximum at 140 °C. Re-absorption is significantly influenced by specific surface area [5,6]. –OH and C=O are the main oxygen-containing functional groups that influence reabsorption and have different moisture absorption performances [7–9]. Chemical property changes of low-rank coal are mainly caused by damages in coal surface and oxygen-containing functional groups during drying [10]. After absorbing a certain amount of moisture, low-rank coal becomes less sensitive to low-temperature oxidation and spontaneous combustion [11]. Porous structure and oxygen-containing functional group are related to coal hydrophilicity [12]. Existing state of moisture

can be determined through diffuse reflectance infrared spectroscopy and low field nuclear magnetic resonance (¹H NMR) [13–15].

Among the study methods of pore diameter and specific surface area, mercury porosimetry and gas adsorption require sample pre-processing, which destroys the cellular structure of samples, thereby making it difficult to determine the existing state of moisture. Nevertheless, a few investigations have been conducted on the porous structure and existing state of moisture in heat-treated lignite by ¹H NMR technology. This technology is a non-invasive measurement for moisture content and existing state in coal samples. Most existing studies focus on low-temperature and middle-temperature zones (<600 °C), and only a few discuss coal treatment at higher temperature. Moreover, no uniform adsorption mechanism has been developed yet. A systematic comprehension on porous structure, functional group changes, and the moisture adsorption mechanism of lignite could be obtained through high-temperature heat treatment. Basing on previous research [16,17], this study conducted a systematic survey on porous structure and moisture adsorption characteristics of heat-treated lignite (<950 °C) by using ¹H NMR. Relationships of moisture adsorption with porous structure and functional groups, as well as the moisture adsorption pattern, were investigated. Moisture adsorption mechanism was further analyzed. Research results could provide theoretical bases for industrial use of lignite.

2. Materials and Methods

2.1. Coal sample

Lignite samples were collected from Shengli 2# Mine in Xilinguole League in Inner Mongolia, China. The samples were crushed into

2–4 mm and 0.037–0.075 mm particles. An industrial analyzer (5E-MAG6700), an element analyzer (5E-CHN2000), and an infrared sulfur meter (5E-IRS II) that were manufactured by Changsha Kaiyuan Company were employed for industrial and element analyses. Results are listed in Table 1.

Table 1
Proximate and ultimate analyses of trial coal samples

Proximate analysis /%					Ultimate analysis /%			
M_{ad}	A_d	V_{daf}	FC_{daf}	C_{daf}	H_{daf}	O_{daf}	N_{daf}	$S_{t,d}$
8.24	10.83	39.43	63.8	76.63	3.85	16.15	0.98	2.13

2.2. Heat treatment

Heat treatment of lignite was conducted in a drying oven (5E-MIN6150) and then in a fixed-bed reactor (Fig. 1) under N_2 atmosphere.

Drying temperatures were set at 25 °C, 50 °C, 75 °C, and 105 °C, and pyrolysis temperatures were set at 200 °C, 300 °C, 500 °C, 700 °C, and 950 °C. Coal samples (8–10 g), with a particle size of 2–4 mm, were placed into a drying oven or a fixed-bed reactor. The rate of temperature was 25 °C min^{-1}, and the maximum temperature was maintained for 1 h. Heat-treated samples were called SLH. The samples were stored in a sealed bag and then placed in a drying vessel.

Thermogravimetric (TG) curve was analyzed with a Diamond TG/DTA 6300 thermogravimetric analyzer (Japan). Coal samples (15–20 mg), with a particle size of 0.0374–0.0750 mm, were placed into the crucible of a TG analyzer. Air in the instrument was replaced with carrier gas (argon) prior to the experiment. Temperature program was initialized as soon as the flow rate achieved stabilization. The inflow rate of carrier gas was 100 ml·min^{-1} and the temperature increased from room temperature to 950 °C at a rate of 25 °C min^{-1}.

When carbocoal was prepared in a fixed bed reactor, gas chromatography was performed with a TCD detector (Beijing Analyzer Plant) to analyze H_2, CO_2, CO, and CH_4 in pyrolysis products. The separation column was filled with TDX02. The column box and TCD temperatures were 160 °C and 180 °C, respectively. The carrier gas was Ar, with a flow rate of 34 ml·min^{-1}. Sampling interval was 5 min.

2.3. Pore structure and existing state of water

The principle of ^{1}H NMR [18] shows that the chemical environment of the proton and the transverse relaxation time (T_{2i}) are different. Shorter T_2 results in smaller degree of freedom (DOF) of protons, whereas longer T_{2i} results in greater DOF of protons. More products are likely to be released with a greater degree of binding of moisture in the sample. T_2 can reveal the occurrence state of moisture content in coal. Inversion of T_{2i} spectrum in different waves represents the water state, and wave covered amplitude value represents the relative content of the moisture state; thus, samples after immersion in water by moisture measuring the relative amount of known pore distribution. Studies show that [14], due to the low field conditions, even if coal is present in trace amounts along the magnetic minerals nor to the measuring result caused by, the coal in solid-state ^{13}C nuclei and ^{1}H nuclear signal will be blocked, will not affect the detection results.

^{1}H NMR (VTMR20-010V-T; Shanghai Niumag) was performed to test the water content and porous structure. Testing parameters include the following: resonance frequency, 21.306 MHz; magnetic intensity, 0.5 T; coil diameter, 10 mm; and magnetic temperature, 35.00 °C. Sample signal values were collected using nuclear magnetic resonance analysis software and CPMG sequence. On this basis, T_{2i} spectrum was obtained through inversion with SIRT algorithm. Coal samples (1–1.25 g) were placed into a detector oven. The detection limit of water was 10 mg.

2.4. Moisture adsorption

The moisture adsorption experiment was performed in the SHBY-40B standard curing box (Jiangsu Wuxi Southern China Experimental Instrument Inc.). SLH were paved on a 35 mm culture dish, which was then placed into a temperature-constant and humidity-constant box. Temperature was set at 30 °C. The relative humidity (RH) was set at 85% and 95%. The first 6 h was divided into three phases, with 2 h for each phase. The interval time between phases was 30 min. Samples were weighed every 1 h or 2 h, and then every 12 h. Equilibrium moisture adsorption is reached if the difference between two adjacent weights is smaller than 0.01 g. The corresponding adsorption ratio is viewed as the balance adsorption ratio. Adsorption ratio is calculated as follows:

$$\text{Adsorption ratio} = (m_t - m_0)/m_0 \times 100\% \tag{1}$$

where m_0 is the mass of lignite sample and m_t is the mass of lignite sample after water absorption.

2.5. Fourier transform infrared spectroscopy (FTIR) analysis

Oxygen-containing functional groups were tested using an FTIR infrared spectrometer (NEXUS670; American Nicolet Corporation). The KBr method was performed to prepare the samples. The samples and KBr were mixed at a ratio of 1:120. Infrared spectrum was obtained within the range of 400–4000 cm^{-1}, and scanning time was set at 25 s. The resolving power and wavenumber accuracy were 0.125 and 0.001 cm^{-1}, respectively.
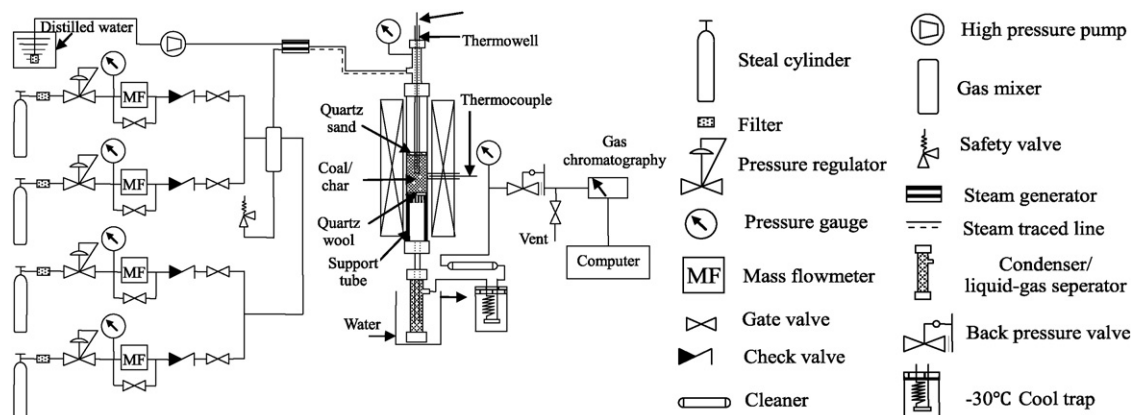
Fig. 1. Flow charts of a fixed-bed reactor.