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A study of chemical structure changes of Chinese lignite during fluidized-bed drying in nitrogen and air

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ABSTRACT

A Chinese lignite coal was dried in a fluidized-bed reactor in the presence of air and nitrogen to examine the effect of temperature, particle size, gas flow rate, and sample mass. The changes of chemical structure during drying were investigated using FTIR technique. The drying rate is shown to increase with increasing drying temperature and gas flow rate, and decreasing particle size. It has been found that the aliphatic hydrogen absorbance decreased with increasing drying temperature. These changes in aliphatic absorption were more significant after drying in air compared to in nitrogen. In air drying the absorption of oxygen-containing functional groups increased gradually with increasing temperature up to 200 °C and declined thereafter due to the decomposition of these groups to release CO and CO_2 or react with nearby hydroxyl groups to produce esters. Carbonyl groups decreased progressively with temperature in nitrogen while carboxylate and aromatic carbon absorption increased up to 250 °C and decreased thereafter. During air drying, the aromatic carbon absorption remained relatively unchanged suggesting the reaction of aliphatic groups with oxygen may be a primary oxidation mechanism.

1. Introduction

It is estimated that nearly half of the world's coal reserves consist of lignite. Lignite is a cheap fuel and usually low in sulfur. But its high moisture content (25–60%) causes serious application problems [1]. Grinding, separation and classification of high moisture coals are difficult to handle. Low rank coals also tend to spontaneously combust [2]. The high moisture content of coals is a matter of concern in coal-fired power plant efficiency [3]. It is important to reduce their moisture content to increase the product quality [4,5]. In recent years, increasing environmental concerns have been raised globally to coal industry because of the emission of air pollutants from coal firing. In particular, the green house gas (GHG) emission has caused global warming [6]. Development of clean coal technologies in order to decrease the GHG emissions is critical in future application of low rank coals such as lignite.

Vorres [7] used a thermogravimetric analyzer to study the drying characteristics of Wyodak subbituminous coal and found that the rate of drying is affected by the temperature, gas flow, and sample thickness. He also found that there is a unimolecular mechanism for the initial 60–85% weight loss. A transition occurs to a slower mechanism until about 1% of the water remains [7]. In a study on dehydration of a bituminous coal using the TGA technique [8], it was observed that with the increase of the sample temperature at a steady rate a sample mass undergoes a sharp decrease in the first few minutes, which is followed by a progressive decrease at the later time of an experiment. Water liberated from coal matrix can be classified into two major stages, which corresponds to the liberation of water stayed in the big voids and coal pores in the form of water clusters and multilayer water on the surface of the coal pores [8]. Fluidized-bed dryers (FBD) are used extensively for the drying of wet particulate and granular materials, and even slurries, pastes, and suspensions that can be fluidized [9,10]. The main advantages of fluidized-bed technology in drying applications are large contact surface area between solids and gas, better temperature control, more uniform temperature distribution in the bed, higher thermal efficiency and drying intensity [11–14]. Drying of lignite depends on the temperature, gas flow rate, sample thickness, and particle size [11,15,16].

Oxidation affects technological properties of coal in a sense that softening and swelling properties, heat of combustion, calorific values, and coking and caking characteristics decrease significantly [17–19]. Infrared spectroscopy is a useful method in determining the chemical changes during oxidation of coal and many researchers have investigated the chemical changes during the oxidation process of coal using FTIR [20–26]. The main effects of oxygen on coal structure are related to an increase in oxygen functionalities with a simultaneous decrease in

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aliphatic hydrogen content [27,28]. Initial stage of oxidation involves the reaction between molecular oxygen and certain aliphatic groups such as methylenes α to aromatic rings to produce peroxides and hydro-peroxides and hydroxyl species [20,29]. Peroxides and hydro-peroxides groups start to oxidize to hydroxyl, carbonyl (ketones), and carboxyl groups at temperatures as low as 50 °C in the early stages of oxidation [17,22,23,29–34]. Liotta et al. [20] working on simulative weathering of coal reported the formation of ether linkages as a dominant oxidation mechanism. Ketonic carbonyl and carboxyl groups decompose at temperatures higher than 150 °C to produce lower molecular weight structures like carbon dioxide. Aromatics are usually more stable than aliphatic groups even up to 150 °C [17,35,36] and the increase in the ratio of aromatic to aliphatic carbons as a function of oxidation time in air at 105 °C is reported [37]. On the other hand, drying of a low-rank coal in an inert atmosphere results to a decrease of oxygen containing polar functional groups [38]. Decrease in these groups will cause a decrease in the moisture-holding capacity of the coal [39,40]. Removal of water from coal causes the decrease in hydroxylic and carboxylic groups in coal as there is a linear dependence between these two factors [39,41].

Systematic study is desirable for Chinese lignite coals which are relatively rich coal resources in North China. In this study, the drying of Chinese Shenhua No. 6 coal in a laboratory-scale batch fluidized-bed dryer is reported. Many researchers have reported the low temperature oxidation that causes spontaneous combustion of coal but little is reported in literature on the air oxidation during hot air drying of coal. The oxidation of lignite during air drying in fluidized bed at high temperatures (up to 250 °C) is investigated in this study. Chemical structure changes accompanying drying of lignites in an inert atmosphere (nitrogen) is also studied and the results are compared with those dryied in air. The objective of this study is to investigate the changes in aliphatic structure and oxygen containing functional groups as a function of drying temperature.

2. Experimental

2.1. Fluidized-bed drying

A Chinese lignite coal, Shenhua No. 6 coal from Inner Mongolia in north China, was used in the experiments and its proximate analysis data is as follows: total moisture (ar), 39.04%; volatile matter (ad), 38.59%; fixed carbon (ad), 56.37%; ash (ad), 5.03%; total sulfur (ad), 0.21%. All samples were crushed and sieved to obtain four size fraction samples (i.e., 75–111, 111–154, 154–224, and 224–355 μm) for fluidized-bed drying experiments. The drying experiments were carried out in a fluidized-bed dryer setup shown in Fig. 1. The quartz fluidized-bed dryer was heated in an electric furnace (SY60, Shenyang General Furnace Manufacturing Co., Ltd., China). The reactor was taken out at the end of each drying experiments and weighed using a digital balance (Satorius BT224S, Germany) in order to measure the weight loss of coal samples during drying. Nitrogen and air were used as fluidizing mediums in drying characteristics and oxidation experiments, respectively.

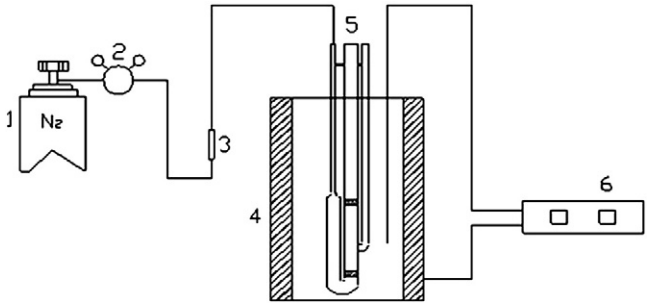

Fig. 1. Schematic diagram of the experimental rig using a fluidized-bed dryer. 1: nitrogen gas cylinder, 2: regulator, 3: gas flow meter, 4: electric furnace, 5: fluidized-bed dryer, 6: temperature controller.

The moisture content values and the drying rate values were calculated through the following equations:

$$X = \frac{W_{w.s} - W_{d.s}}{W_{d.s}} \quad (1)$$

$$R = \frac{(W_{w.s})_1 - (W_{w.s})_2}{(W_{d.s})(t_2 - t_1)} \quad (2)$$

where, X is moisture content (g moisture/g dry coal) at any time, $W_{w.s}$ is initial coal sample weight, $W_{d.s}$ is dried coal weight, R is drying rate ((g evaporated moisture)/ (g dry coal . second)) and t is drying time.

2.2. FTIR spectroscopic analysis

Infrared spectra of the raw coal, coal dried air at 150, 200 and 250 °C, and dried in nitrogen up to 300 °C were analyzed using a Thermo Fisher Nicolet IS5 mid FTIR spectrometer. KBr pellets were prepared by grinding around 2.5 mg of dried coal with 200 mg KBr. Infrared spectra of the lignite sample for the 4000–400 cm^{-1} region were studied by curve fitting analysis using a commercially available data-processing program (OriginPro, OriginLab Corporation). The assignment of the bands in the infrared spectra was made according to literature [21,23,25,42–44]. Initial approximation of the number of bands and peak positions were obtained by examining second derivatives of the spectral data. Gaussian and Lorentzian functions were used as mathematical functions for band shapes at aliphatic hydrogen and carbonyl stretching region [23,43,45]. The initial set of peak parameters was left optimized until convergence of the data was achieved.

3. Results and discussion

3.1. Drying characteristics

3.1.1. Effect of particle size

To investigate the effect of coal particle size on the drying characteristics of lignite, different particle size fractions were dried at 200 °C, with 200 l/h gas flow rate and using 2 g coal sample mass. The results are shown in Fig. 2. Since the initial moisture contents of different size fraction samples were not the same, in order to compare the results, they are normalized to 100% moisture loss. As can be seen in Fig. 2a, with decreasing the coal particle size the weight loss during drying increased and the drying time (which is defined as to achieve the complete drying of a coal sample) became shorter. Fig. 2b clearly shows that samples with smaller particle sizes had a higher drying rate at the beginning of drying while had faster falling rate at the later stage than larger particle sizes. This result is in good agreement with those reported in the literature [10,11]. Larger surface area in smaller particle size results in a faster particle heating rate and better heat transfer from drying medium to the center of particle and moisture transfers more easily from inside the particle to the surface upon heating. Decreasing particle size enhances both convective gas to particle and particle to particle heat transfer under fluidized-bed drying conditions [46]. Decrease of particle diameter also means the smaller resistance to internal heat transfer. At a fixed solids holdup, the decrease of particle diameter is accompanied by an increase in heat and mass transfer area, which in turn would decrease drying time [47].

3.1.2. Effect of drying temperature

In order to investigate the effect of drying temperature on drying characteristics of lignite, drying experiments were carried out at