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Structural characterization and oxidation study of a Chinese lignite with the aid of ultrasonic extraction

Xiaoxing Zhong [a, b], Manman Wang [c], Guolan Dou [a, b, *], Deming Wang [a, b], Yun Chen [a], Yuxin Mo [a], Yi Zhang [d]

[a] School of Safety Engineering, China University of Mining & Technology, Xuzhou 221116, China
[b] Key Laboratory of Gas and Fire Control for Coal Mines, Xuzhou 221116, China
[c] Sanquan Medical College, Xinxiang 453003, China
[d] Xuzhou Anyun Mining Technology Inc., Xuzhou 221116, China

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ABSTRACT

Chinese lignite coal from the Beizao mine which located in Shandong Province of China was studied using a combination of ultrasonic extraction under mild conditions (which generate minimal chemical changes) in conjunction with modern analytical instrumental techniques. This procedure allowed the development of a structural model. Calculations with the Gaussian 09W package generated an optimized structural geometry and also determined the activities of various functional groups. The initial stages of oxidation were found to consist of the oxidation of hydroxyl groups, the rupture of C–O and C–C bonds, and the dehydrogenation of carboxyl groups. In contrast, both the decarboxylation and decarbonylation reactions were determined to require significant energy inputs and thus occur only at high temperatures. *In situ* Fourier transform infrared analyses were used to confirm the results of the theoretical calculations.

1. Introduction

Coal is an increasingly important and valuable energy source with numerous uses. A fundamental hazard associated with coal is self-heating, a phenomenon that has been of practical importance for more than a century [1]. Low rank coal, accounting for 50–60% of the total coal resources in China, is primarily found in the northwest Jurassic coal-bearing basin, the Cenozoic down-faulted basin in the northeast, and the northern carboniferous-Permian coal-accumulating basin in the west. Low rank coal is composed mostly of lignite and low metamorphic bituminous coal, with lignite accounting for 5.74% of China's coal reserves. These reserves are widely distributed in the northwest, northeast and eastern regions of the country. It is well known that low-rank coal is prone to spontaneous combustion and so, in these areas, coal seams have undergone spontaneous combustion to generate fires that have seriously impacted the ability to safely produce coal. It is therefore important to study the oxidation characteristics of lignite as a means of predicting or mitigating such hazards.

Of particular interest in recent years has been the study of the correlations between the chemical structures of coals and spontaneous combustion [2,3]. As such, various analytical techniques, such as Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR), and X-ray diffraction (XRD) have been used in the study of chemical structures of coals. Ibarra et al. [4] used FTIR spectroscopy to study a series of coals varying in rank from peat to semi-anthracite, and found that this technique can be successfully used to determine aromaticity, hydrogen distribution and oxygen-containing species in coals. Thermogravimetry (TG)–FTIR has also been used to determine the oxygen content of coals [5]. Carbon-13 (^{13}C) NMR spectra, which provide direct measurements of the chemical structure of organic matter, were obtained for a large number of New Zealand coals ranging from peat to semi-anthracite, and four NMR parameters (f_a, S_{ox}, f_{CO2H} and f_{COH}) were examined [6]. Knicker et al. [7] found that solid-state ^{15}N NMR spectroscopy may add substantially to our understanding of the nature and diagenesis of nitrogen structures in coals. XRD analysis is also a useful means for evaluating carbon stacking structures [8].

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* Corresponding author. School of Safety Engineering, China University of Mining &Technology, Xuzhou 221116, China.
E-mail address: gldoucumt@163.com (G. Dou).

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However, these studies only provide the rough structures of coals and do not allow the more detailed structural analyses needed in the study of coal oxidation. A combination of solvent extraction under mild conditions, which causes little chemical change to coals, combined with modern analytical instrumental techniques may provide an essential and effective approach to the investigation of coal compositions and structures [9–12]. This method provides valuable information concerning coal structures, although both the time required for experimental trials and limited extraction efficiencies remain problematic with regard to coal oxidation studies. Ultrasonic irradiation is a powerful tool in modern chemistry and has attracted significant attention because of its advantages of convenience, mild conditions, short reaction times, and high efficiency. This process has become increasingly popular in recent years [13,14]. Ultrasonic technology has also been applied to the extraction of coal [15–17] and has been shown to enhance extraction yields. Many investigators [18–20] report that relatively small molecules with masses less than 500 Da may represent about 30–40% of coal, and so the small molecules that are obtained by extraction may be representative of the overall reactivity of coal samples, at least to some extent. Therefore, in the present work, Beizao (BZ) coal, a typical lignite coal from China, was extracted using various organic solvents, together with the application of ultrasonic irradiation. The raw coal, extracted coal, and extraction residues were all characterized by FTIR and ^{1}H NMR to determine the structure of BZ coal in detail. Based on the data obtained, the oxidation activity of the coal was analyzed using the Gaussian 09W software package. In addition, a series of *in situ* diffuse reflectance FTIR studies were used to examine the low-temperature oxidation of BZ coal to validate the results obtained from Gaussian 09W.

2. Materials and methods

2.1. Sample origin and preparation

The coal used in this study was a lignite coal obtained from the Beizao mine in Shandong Province, China. The coal was ground to a particle size of 0.18–0.38 mm and then dried overnight under vacuum at 313 K prior to experimental trials. The results of proximate and ultimate analyses of the coal are summarized in Table 1.

2.2. Organic solvents

The organic solvents used in this work included methanol (CH_3OH), tetrahydrofuran (THF), pyridine (Py), carbon disulfide (CS_2) and *N*-methyl pyrrolidone (NMP). All chemicals were analytical grade.

2.3. Ultrasonic extraction of coal samples

Prior to ultrasonic extractions, a 5-g sample of dried coal was combined with 20 mL of an organic solvent in a flask, with mixing, and then extracted for 8 h under ultrasonic (40 Hz) irradiation at room temperature. The mixtures were subsequently kept overnight and then filtered. The solid filtrate was then extracted with fresh solvent in the same manner as described previously.

2.4. FTIR measurements

In situ FTIR spectra were acquired using a Nicolet 6700 spectrometer, providing spectra in units of cm^{-1}. A KBr powder background was collected prior to sample analysis as a baseline reference. Each ground coal sample was placed in the reaction chamber, the chamber dome was put in place, and dry air at a flow rate of 100 mL/min was allowed into the reaction chamber, entering from its base and exiting from the top. A temperature controller was connected to the reaction chamber and the chamber was heated to 220 °C at a rate of 1 °C/min. The region from 650 to 4000 cm^{-1} was scanned with 4 cm^{-1} resolution, adding 64 scans per spectrum. For each sample, a series of spectra were collected at 30 s intervals.

2.5. Liquid-state NMR experiments

^{1}H NMR spectra were recorded on a Varian NMR system (UNITY INOVA 400). The chemical shifts were reported in parts per million (δ) relative to the trimethylsilane internal standard (at 0 ppm) in $CDCl_3$. The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz).

3. Results and discussion

3.1. FTIR results

Fig. 1 shows the FTIR spectra of the BZ coal. In total, there are 16 peaks in the spectrum, and these are summarized in Table 2. The 3650–3100 cm^{-1} region corresponds to the –OH stretching vibrations (ν) of water, alcohols, phenols, carboxylic acids and similar groups. Of

Table 1
Proximate and ultimate analyses of BZ coal.

Proximate analysis, %				Calorific power, kJ/g	Elemental analysis, %		Real density, g/cm^3
Moisture/M_{ad}	Ash/A_{ad}	Volatile/V_{ad}	Fixed carbon/F_{Cad}	$Q_{net,\ ad}$	H_{ad}	S_{td}	ρ
19.13	13.32	31.30	36.26	23.78	4.49	0.66	1.54