



Insight into the structural features of Zhaotong lignite using multiple techniques



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HIGHLIGHTS

- Zhaotong lignite (ZL) mainly consists of aliphatic (52.3%) and aromatic (42.2%) carbons.
- Each aromatic cluster in ZL contains 2 rings on average.
- Oxygen and nitrogen in ZL mainly exist in C–O moieties and pyrrolic structures, respectively.
- Cleavage of C_{al}–O and C_{al}–C_{al} bonds should be the major reactions during ZL ethanolsis.
- Pyrroles, indoles, and carbazoles account for most of the neutral nitrogen forms in ZL.

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ABSTRACT

The chemical structures of Zhaotong lignite (ZL) were characterized with multiple direct tools, including solid-state ¹³C nuclear magnetic resonance (NMR), X-ray photoelectron spectrometer (XPS), Fourier transform infrared (FTIR) spectrometer, and thermogravimetric (TG) analyzer, combined with ZL ethanolsis and subsequent electrospray ionization Fourier transform ion cyclotron resonance mass spectrometer (ESI FT-ICR MS) analysis of the resulting ethanol-soluble portion (ESP). According to ¹³C NMR analysis, ZL mainly consists of aliphatic (52.3%) and aromatic (42.2%) carbons. Methylene is the most abundant among the aliphatic carbons. Each aromatic cluster contains 2 rings on average and the number of substituents on each aromatic ring is 3 or 4. XPS analysis suggests that oxygen atoms mainly exist in C–O moieties, which is consistent with ¹³C NMR and FTIR analyses, and pyrrolic nitrogen species are the main nitrogen form in ZL. Based on TG analysis, cleavage of C_{al}–O and C_{al}–C_{al} bonds should be the major reactions during ZL ethanolsis. A series of neutral nitrogen compounds (NNCs, i.e., pyrrolic nitrogen) in the ESP were detected by negative-ion ESI FT-ICR MS analysis. The identified NNCs are N₁O_x (x = 0–5) class species with 3–13 double bond equivalent (DBE) values and 10–31 carbon numbers, in which N₁O₂ class species are predominant NNCs. According to DBE distributions of NNCs, pyrroles, indoles, and carbazoles account for most of the neutral nitrogen occurrences in ZL. Such multiple characterizations proved to be an effective method for fully understanding the chemical structures of coals, especially lignites.

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1. Introduction

Lignites are abundant fossil resources [1], but their high ash yield, high water content, low calorific value, and poor thermal stability make them difficult in the current industrial use. Therefore, it is necessary to develop efficient conversion processes to minimize such disadvantages. Zhaotong lignite (ZL) from Yunnan Province has attracted much attention because of its easy minability and

abundant deposit in China. Taking high oxygen content of the lignite into account, we tried to depolymerize ZL under relatively mild conditions using ethanol as the solvent to obtain oxygen-containing species, especially phenols [2].

A deep insight into the chemical structures of coals is significantly important for efficient utilization of coals, especially for obtaining value-added chemicals from coals [3–5]. Coals are too complex to be elaboratively characterized. It is common to understand original structural information on coals with direct characterization tools, such as solid-state ¹³C nuclear magnetic resonance (NMR) [6–8], Fourier transform infrared (FTIR) spectrometer [9,10], and X-ray photoelectron spectrometer (XPS) [11–13].

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Nomenclature

ESI	electrospray ionization	NMR	nuclear magnetic resonance
ESP	ethanol-soluble portion	NNCs	neutral nitrogen compounds
DBE	double bond equivalent	OCMs	oxygen-containing moieties
DTG	differential TG	TG	thermogravimetric
FT-ICR MS	Fourier transform ion cyclotron resonance mass spectrometer	XPS	X-ray photoelectron spectrometer
FTIR	Fourier transform infrared	ZL	Zhaotong lignite

Analyses with such tools greatly facilitate the understanding of carbon skeleton structures and functional groups along with oxygen, nitrogen, and sulfur forms in coals. In addition, thermogravimetric (TG) analysis of coals was also usually conducted because most of the coal conversion processes involve in thermal reactions [14,15].

Although nitrogen contributes a small portion to the mass of coals, the environmental pollution, especially acid rain, photochemical smog, and greenhouse effects resulting from the emission of NO_x during coal combustion, is still an urgent problem [16–18]. A full understanding of nitrogen forms in coals is necessary to develop better methods for nitrogen removal. As a non-destructive technology, XPS analysis cannot provide detailed information on nitrogen occurrences in coals at molecular level. Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS), which possesses ultrahigh resolving power (>300,000) and mass accuracy (<1 ppm), has been widely used to characterize oxygen- and nitrogen-containing compounds in complex mixtures, such as petroleum [19–21], coal-derived liquids [22–27], and bio-oils [28,29]. Rathsack et al. [23] investigated molecular composition of the liquid products from pyrolysis of a German lignite using electrospray ionization (ESI) FT-ICR MS. Their results exhibit that compounds detected are dominated by O_x ($x = 1\text{--}12$) species and possible structures were proposed based on double bond equivalent (DBE, i.e., rings plus double bonds). Shi et al. [25–27] used ESI FT-ICR MS to analyze a middle-temperature coal tar. They only focused on N_1 species for neutral nitrogen compounds (NNCs). In our recent investigations [2,30], ZL was subjected to ethanolysis at 230–350 °C and the resulting ethanol-soluble portion (ESP) obtained at 305 °C with the highest yield of 64.9% was analyzed using ESI FT-ICR MS both in negative- and positive-ion modes for identifying oxygen-containing species and basic nitrogen compounds, respectively. However, NNCS in the ESP were paid less attention.

In this paper, several direct techniques, including solid-state ^{13}C NMR, XPS, FTIR, and TG, were used to characterize the chemical structures of ZL. In addition, NNCS in the ESP were identified by ESI FT-ICR MS analysis. The purpose of this study is to gain a detailed understanding of the chemical structures of ZL. Moreover, this study is also necessary for further work—developing efficient conversion processes of coals, especially ZL.

2. Experimental

2.1. Materials

ZL was pulverized to pass through a 200-mesh sieve (particle size of <74 μm) followed by desiccation in a vacuum at 80 °C for 24 h before use. Table 1 lists the proximate and ultimate analyses of ZL. All the solvents used in the experiment were commercially purchased analytical reagents and purified by distillation prior to use.

Table 1
Proximate and ultimate analyses (wt%) of ZL.

Proximate analysis			Ultimate analysis (daf)				$S_{t,d}$
M_{ad}	A_d	VM_{daf}	C	H	N	O^a	
11.6	21.0	53.6	52.5	3.3	1.0	>41.8	1.4

daf: dry and ash-free base; M_{ad} : moisture (air dried base); A_d : ash (dry base, i.e., moisture-free base); VM_{daf} : volatile matter (dry and ash-free base); $S_{t,d}$: total sulfur (dry base).

^a By difference.

2.2. Solid-state ^{13}C NMR, XPS, FTIR, and TG analyses of ZL

Solid-state ^{13}C NMR analysis of ZL was performed on a Bruker Avance III spectrometer, which was equipped with a 4 mm cross-polarization magic angle spinning double-resonance prob head and operated at a ^{13}C frequency of 100.63 MHz at room temperature. ZL (ca. 0.2 g) was packed into a 5 mm diameter zirconia rotor with spun at 14 kHz. The spectral width, recycle delay time, and contact time were set to 10 kHz, 0.5 s, and 1 ms, respectively.

The surface elemental composition of ZL was determined by a Thermo Fisher ESCALAB 250Xi XPS, which was equipped with a monochromatic Al $K\alpha$ X-ray source and operated at 150 W. The spectra were taken in the fixed analyzer transmission mode.

Functional groups of ZL were measured with a Nicolet Magna IR-560 FTIR spectrometer using KBr pellet technique. The spectrum was recorded from 4000 to 400 cm^{-1} at a resolution of 8 cm^{-1} and compiled from 64 scans.

The pyrolysis behavior of ZL was examined using a Mettler Toledo TGA/SDTA851° TG analyzer. About 15 mg of ZL was placed in a ceramic crucible and heated from room temperature to 110 °C at a heating rate of 10 °C/min and kept at the temperature for 0.5 h to remove moisture, then from 110 to 900 °C at a heating rate of 10 °C/min using argon as carrier gas at a constant flow rate of 60 mL/min.

2.3. Procedure for ZL ethanolysis and subsequent ESI FT-ICR MS analysis

ZL ethanolysis was conducted as described in Fig. S1 in the Supporting information and our recent investigation [2]. ESP obtained from ZL ethanolysis at 305 °C was analyzed using a Apollo II ESI source in negative-ion mode coupled with a Bruker apex-ultra FT-ICR MS equipped with a 9.4 T superconducting magnet. The analytical method was reported in our recent investigation [2].

2.4. Data processing

Curve fitting of the solid-state ^{13}C NMR and differential TG (DTG) was performed using PeakFit software to obtain the

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