



Characterization of acidic species in ethanol-soluble portion from Zhaotong lignite ethanolysis by negative-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry



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ARTICLE INFO

Article history:

Received 23 June 2014

Received in revised form 18 July 2014

Accepted 18 July 2014

Available online xxx

Keywords:

Lignite

Ethanolysis

Acidic species

Fourier transform ion cyclotron resonance mass spectrometry

Electrospray ionization

ABSTRACT

Thermal dissolution of Zhaotong lignite in ethanol was conducted in a temperature range of 230 to 350 °C for 2 h. The maximum yield of the ethanol-soluble portion (ESP) is 64.9% at 305 °C. ESP was analyzed with a negative-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS). Molecular mass of ESP ranges from 100 to 500 u with an average peak around m/z 260. According to the assignment of molecular formulae, most of the compounds detected in ESP are oxygen-containing species of types O_n and O_nN_1 ($n = 0-6$), especially O_1-O_4 class acidic species (ASs) with 1–12 double bond equivalent (DBE) values and 8–34 carbon atoms. The maximum condensation degree of aromatic clusters in the ASs is 3 (DBE = 10). The average DBE values of O_n class species are 5 or 6, suggesting that phenols, benzenepolyols, and/or benzoic acids with an aliphatic ring and alkyl chains are characteristic structures. FT-ICR MS proved to be a powerful tool for identifying soluble polar species from coal conversion.

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1. Introduction

Since conventional direct coal liquefaction (DCL) has some disadvantages, such as severe conditions and consumption of catalyst, developing new DCL processes is necessary to minimize such disadvantages. Thermal dissolution (TD) of coals to soluble portion (SP) under mild conditions is of great significance for efficient utilization of coals. Extensive investigations have been performed on TD behavior of different coals in various solvents at different temperatures. Miura et al. [1–4] examined TD of different coals in tetralin, 1-methylnaphthalene, coal-derived oil or carbol oil at 200–400 °C. Their results show that 80% of organic matter in the coals can be converted to SP after TD at 350 °C. Related investigation on TD of Shenfu subbituminous coal in 1-methylnaphthalene was also conducted and up to 56% of SP was obtained at 360 °C [5]. However, recovering such solvents is difficult because of their high boiling points and viscosities. To overcome the difficulties, solvents with low boiling points and viscosities deserve consideration for TD of coals. Low-carbon alkanols, such as methanol [6], ethanol [7], and isopropanol [8] were reported to act as hydrogen donors and

alkylation reagents during TD of coals, especially lignites. However, molecular characterization of SP from TD of coals is challenging due to its highly complex composition.

Gas chromatography/mass spectrometry (GC/MS) has been successfully applied in identification of some species in coal extracts and SP from coal conversion [9–15], but such identification is limited to relatively volatile, thermally stable, and less polar species. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) proved to be a powerful technique for molecular characterization of extremely complex samples, such as petroleum [16–20], coal liquids [21–24], pyrolysis bio-oils [25,26], and wastewater [27]. FT-ICR MS has an ultrahigh broadband mass resolution (exceeding 200,000) and mass accuracy (<1 ppm), which allows for distinct assignment of a unique elemental composition to each mass spectrum peak. In addition, electrospray ionization (ESI) allows soft ionization of polar molecules, which is useful for analyzing polar species in coal extracts [28]. Owing to the presence of large amount of oxygen-containing organic compounds in lignites, ESI is an appropriate ion source for analyzing SP in lignites and their derivatives.

In the present investigation, we focus on acidic species (ASs) in ethanol-soluble portion (ESP) from ethanolysis of Zhaotong lignite (ZL) using ESI FT-ICR MS in negative-ion mode (NIM).

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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. Experimental

2.1. Materials

ZL was collected from Zhaotong Coal Mine, Yunnan Province, China and pulverized to pass through a 200-mesh sieve (particle size of $<74 \mu\text{m}$) followed by desiccation in a vacuum at 80°C for 24 h before use. As listed in Table 1, ZL has very high oxygen content and relatively high nitrogen content. All the solvents used in the experiment were commercially purchased analytical reagents and purified by distillation prior to use.

2.2. Ethanolysis procedure

As shown in Fig. 1, 1 g of ZL and 20 mL of ethanol were put into a 100 mL stainless-steel, magnetically stirred autoclave. After replacing air with nitrogen, the autoclave was heated to a described temperature at $10^\circ\text{C}/\text{min}$ and maintained at the temperature for 2 h. Then, the autoclave was cooled to room temperature in a water bath, and the reaction mixture (RM) was taken out from the autoclave and filtrated to separate the RM into filtrate and filter cake (FC). FC was exhaustively extracted with ethanol to afford extract solution (ES) and residue. ES was incorporated with filtrate followed by distillation to afford ESP. The yield (Y_{ESP}) of ESP was calculated as the mass ratio of ESP (m_{ESP}) to ZL on a dry and ash-free basis ($m_{ZL,daf}$); i.e., $Y_{ESP} = m_{ESP}/m_{ZL,daf}$.

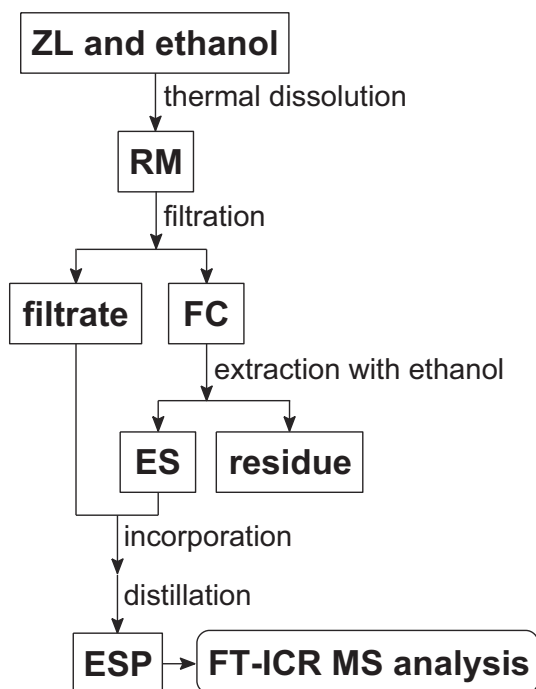


Fig. 1. Procedure for ZL ethanolysis and subsequent analysis.

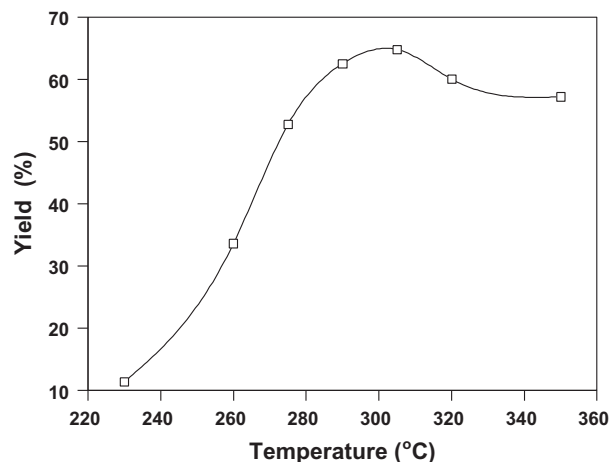


Fig. 2. Yields of ESP obtained at different temperatures.

2.3. ESI FT-ICR MS analysis

ESP obtained at 305°C was dissolved in methanol/toluene (1:3, v/v) to 0.3 mg/mL. Then 20 μL of 25% ammonia was added into the sample as the dopant to enhance the ionization efficiency followed by analysis using a Bruker apex-ultra FT-ICR MS equipped with a 9.4 T superconducting magnet. The sample solution was infused via an Apollo II ESI at 300 $\mu\text{L}/\text{h}$ with a peristaltic pump. In ESI source, the voltages at the emitter, capillary column front end, and capillary column end were set to 4.0, 4.5, and -320 kV , respectively. Ions accumulated for 0.01 s in a hexapole with -3.2 V of direct current voltage and 500 Vp-p of radio frequency (RF) amplitude. The optimized mass for Q1 is 150 u. An argon-filled hexapole collision pool was operated at 5 MHz and 700 Vp-p of RF amplitude, in which ions accumulated for 0.2 s. The data size was set to 4 M. A total of 64 scans were collected to enhance the signal/noise ratio (S/N).

2.4. FT-ICR MS data processing

The FT-ICR MS was calibrated using sodium formate and recalibrated with a known mass series, such as phenols and/or fatty acids, in the sample. For data processing Bruker software *Data Analysis* was used for peak detection and molecular formula (MF) assignment. Mass spectrum peaks with S/N greater than 6 were exported to a spreadsheet. Data analysis was performed using custom software [22].

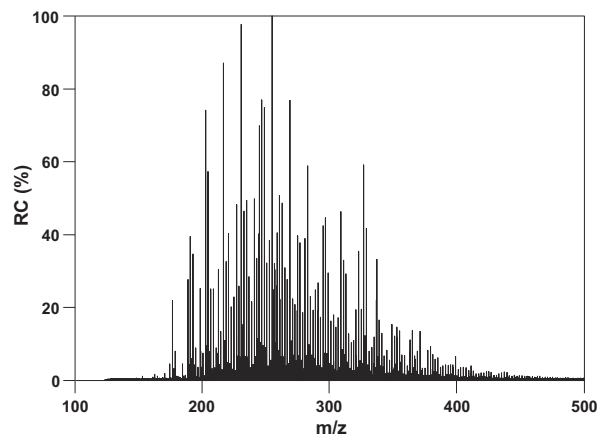


Fig. 3. Mass spectrum from FT-ICR MS analysis of ESP.

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