Fuel 141 (2015) 268–274

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Identification of basic nitrogen compounds in ethanol-soluble portion from Zhaotong lignite ethanolysis by positive-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry

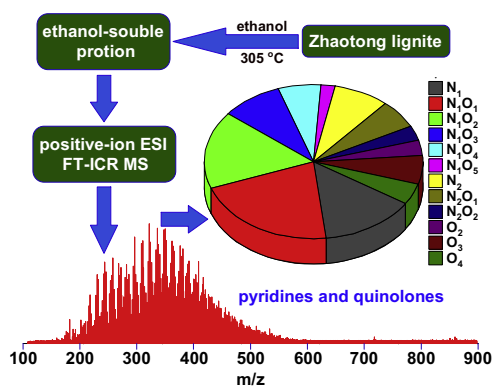
Zhan-Ku Li [a], Zhi-Min Zong [a,*], Hong-Lei Yan [a], Zhe-Hao Wei [b], Yan Li [b], Xian-Yong Wei [a]

[a] Key Laboratory of Coal Processing and Efficient Utilization, Ministry of Education, China University of Mining & Technology, Xuzhou 221116, Jiangsu, China
[b] The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99164, USA

HIGHLIGHTS

- Numerous basic species in ethanol-soluble portion from Zhaotong lignite were detected.
- N_1O_x class species with 1–12 DBE and 8–34 carbon numbers are dominant in the portion.
- Molecular mass of the detected species in the portion ranges from 100 to 600 *u*.
- Pyridines and quinolines are the main basic nitrogen species in the portion.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 9 July 2014
Received in revised form 14 October 2014
Accepted 16 October 2014
Available online 4 November 2014

Keywords:
Basic nitrogen compounds
Lignite
Ethanolysis
Fourier transform ion cyclotron resonance
Mass spectrometry
Positive-ion electrospray ionization

ABSTRACT

Ethanol-soluble portion (ESP) from Zhaotong lignite ethanolysis at 305 °C was analyzed with a positive-ion electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS). The range of molecular mass distribution is from *m/z* 100 to 600 with the center around *m/z* 330. Assignment of molecular formulae reveals that the main nitrogen-containing species with relative content of 86.4% are most probably basic nitrogen compounds (BNCs) ionized during ESI in positive-ion mode. The BNCs are N_1O_x (x = 0–5) and N_2O_y (y = 0–2) with 0–14 double bond equivalent (DBE) values and 9–39 carbon numbers. According to DBE distributions, pyridines and quinolines should be predominant BNCs in the ESP. In addition, amines (DBE < 4) were also identified in the ESP. The average DBE values are 6–8 for N_1O_x class species and 7 and 8 for N_2O_x class species, indicating that pyridines (or quinolones) and quinolines with an amino group are characteristic structures for N_1O_x and N_2O_x classes, respectively. Positive-ion ESI FT-ICR MS proved to be a powerful tool for identifying BNCs in coal-derived liquids.

1. Introduction

During coal combustion, organonitrogen compounds (ONCs) in coals are converted to NO_x, causing acid rain, photochemical smog, and greenhouse effects [1–3]. To meet environmental regulations and upgrade the quality of coal-derived oils, catalytically removing heteroatoms is necessary. Basic nitrogen compounds (BNCs) play a key role in catalyst deactivation by forming coke on the catalyst surface [4,5]. Therefore, the knowledge of BNCs occurring in coals is necessary to develop the better methods for nitrogen removal. ONCs were considered to exist mainly in the form of pyrrole

* Corresponding author. Tel.: +86 516 83885951; fax: +86 516 83884399.
E-mail address: zong_zhimin@163.com (Z.-M. Zong).

http://dx.doi.org/10.1016/j.fuel.2014.10.037
0016-2361/

Nomenclature

ACN	average carbon number
ADBE	average DBE
BNCs	basic nitrogen compounds
CHDN	catalytic hydrodenitrogenation
DBE	double bond equivalent
ESI	electrospray ionization
ESP	ethanol-soluble portion
FT-ICR MS	Fourier transform ion cyclotron resonance mass spectrometry
GC/MS	gas chromatography/mass spectrometry
HBs	hydrogen bonds
KMD	Kendrick mass defect
ONCs	organonitrogen compounds
S/N	signal-to-noise ratio
ZL	Zhaotong lignite

(neutral), pyridine (basic), and amide groups (basic) using X-ray photoelectron spectroscopy and ^{15}N nuclear magnetic resonance spectroscopy analyses [6–11]. Nevertheless, previous nondestructive analyses cannot afford detailed information on ONCs in coals at the molecular level. Obtaining detailed information on ONCs is difficult due to their low content in coals. Gas chromatography/mass spectrometry (GC/MS) has been successfully applied in identification of some soluble species from coals [12–19], but detecting less volatile and/or thermally labile species is difficult using this technology. In addition, GC/MS analysis is easily affected by complex matrix and there are only limited standard libraries for the identification of detected 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 [20–23], coal-derived liquids [24–28], pyrolysis bio-oils [29–31], and dissolved organic matter in waste water [32]. It has an ultra-high broadband mass resolving power (exceeding 200,000) and mass accuracy (<1 ppm), allowing for baseline resolution of closely spaced isobaric species as well as distinct assignment of a unique elemental composition to each mass spectral peak. If each peak of a mass spectrum obtained by FT-ICR MS is expanded to be observable, the length of the spectrum will be up to 200 m. In addition, electrospray ionization (ESI) allows soft ionization of macromolecules, which is useful for analyzing polar components in soluble portion from coals [33]. Negative-ion ESI favors the ionization of acidic species, while positive-ion ESI facilitates the formation of protonated basic species [34].

In our recent investigation [35], thermal dissolution of Zhaotong lignite (ZL) in ethanol was conducted at 230–350 °C, and maximum yield of ethanol-soluble portion (ESP) is 64.9% at 305 °C. Acidic species in the ESP obtained at 305 °C were analyzed by negative-ion ESI FT-ICR MS. In the present study, we examine BNCs by positive-ion ESI FT-ICR MS.

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 μm) followed by desiccation in a vacuum at 80 °C for 24 h before use. As listed in Table 1, ZL has relatively high nitrogen content. 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. ESI FT-ICR MS analysis

The ESP was dissolved in methanol/toluene (1:3, v/v) to 0.3 mg/mL. The sample was analyzed 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 a flow rate of 300 μL/h with a syringe pump. In ESI source, the voltages at the emitter, capillary column front end, and capillary column end were set to 3.5 kV, 4 kV, and 320 V, 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 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 radio frequency amplitude, in which ions accumulated for 0.2 s. The data size was set to 4 M. A total of 64 scans were co-added to enhance the signal-to-noise ratio (S/N).

2.3. FT-ICR MS data processing

The FT-ICR MS was calibrated using a known nitrogen-containing species homologous series. For data processing Bruker software *Data Analysis* was used for peak detection and molecular formula assignment. Mass spectral peaks with S/N greater than 6 were exported to a spreadsheet. Data analysis was performed using a custom software [25].

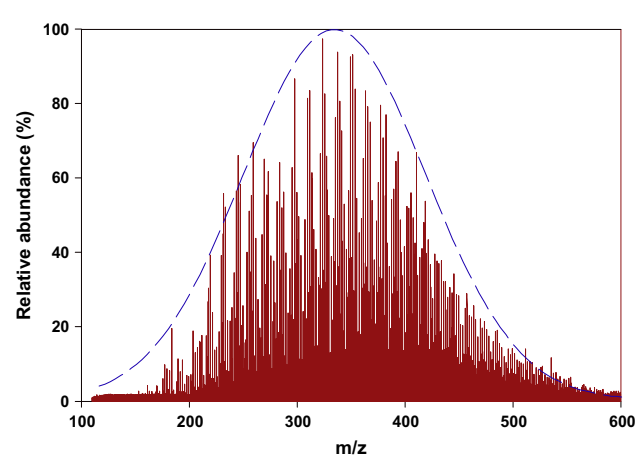


Fig. 1. Positive-ion ESI FT-ICR MS broadband spectrum of the ESP.