Fuel 174 (2016) 287–295

Contents lists available at ScienceDirect

Fuel

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

Insight into the chemical complexity of ethanolysis products from extraction residue of Zhaotong lignite

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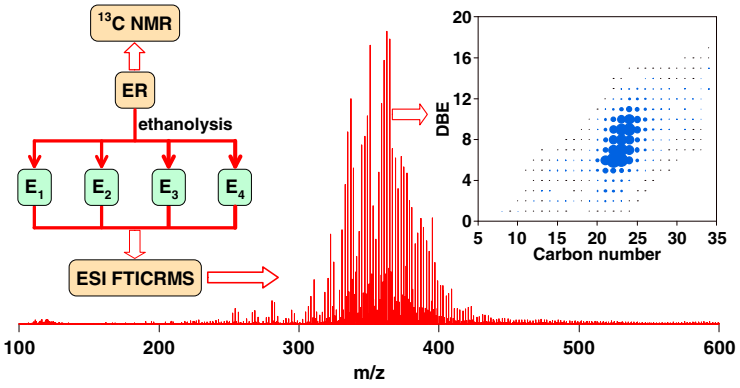
HIGHLIGHTS

- Each aromatic cluster in ethanolyzed residue (ER) from Zhaotong lignite contains one or two rings on average.
- The total yield of soluble portions (E_1–E_4) from the ER ethanolysis with NaOH is up to 70.7%.
- Numerous oxygen-/nitrogen-containing compounds were detected in E_1–E_4 with FTICRMS.
- The most abundant class species in E_1–E_4 are O_2, O_2, O_3, and O_4, respectively.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 September 2015
Received in revised form 7 December 2015
Accepted 1 February 2016
Available online 08 February 2016

Keywords:
Lignite
Solid-state ^{13}C NMR
Ethanolysis
FTICRMS
Electrospray ionization

ABSTRACT

Ethanolysis of an ethanolyzed residue (ER) from Zhaotong lignite with NaOH was conducted to afford extracts 1–4 (E_1–E_4). The yields of E_1–E_4 are 47.1%, 10.6%, 3.0%, and 10.0%, respectively. All the extracts were analyzed with a negative-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometer (ESI FTICRMS). In addition, carbon skeleton structures in the ER were determined using a solid-state ^{13}C nuclear magnetic resonance spectrometer. The results suggest that the carbon types in the ER mainly consist of aliphatic (52.3%) and aromatic (42.0%) carbons. **C**H_3– and –**C**H_2– are the major aliphatic carbons. Each aromatic cluster contains one or two aromatic rings on average. According to analysis with FTICRMS, thousands of compounds were detected in the extracts, mainly being oxygen-containing (O_x, x = 1–8) class species with double bond equivalent (DBE) values of 1–18 and carbon numbers of 7–37. The most abundant class species in E_1–E_4 are O_2, O_2, O_3, and O_4, respectively. E_4 contains low relative contents of O_2–O_3 class species but high relative contents of O_4–O_6 class species. The identified O_x class species are mainly ascribed to fatty acids, areneols, and arenecarboxylic acids. Furthermore, nitrogen-containing multiheteroatomic (N_1O_x and N_2O_x, x = 1–8) class species with DBE values of 3–17 and carbon numbers of 13–34 were also identified in the extracts.

1. Introduction

As a relatively new method, thermal dissolution has been extensively investigated for coal conversion [1–9]. Among all the solvents used for thermal dissolution, low-carbon alkanols, such as methanol [5–7,9], ethanol [5,7], and isopropanol [7,8] have great potentials due to their low toxicity and boiling points, alkylation, and hydrogen-donating ability. Ethanol was reported to be much more effective for thermally dissolving coals than methanol [5,7]. However, molecular-level characterization of the resulting soluble portion from thermal dissolution of coals still faces huge

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http://dx.doi.org/10.1016/j.fuel.2016.02.001
0016-2361/

Nomenclature

CDS	carbon disulfide
CDSIEP	CDS-inextractable portion
DBE	double bond equivalent
DCM	dichloromethane
DCMIEP	DCM-inextractable portion
ER	ethanolyzed residue from Zhaotong lignite
ESI	electrospray ionization
FTICRMS	Fourier transform ion cyclotron resonance mass spectrometry
SS ^{13}C NMRS	solid-state ^{13}C nuclear magnetic resonance spectrometry
PE	petroleum ether
PEIEP	PE-inextractable portion

challenges. The challenges are largely ascribed to the extremely complex molecular composition and the lack of appropriate separation and analytical approaches.

It is common to understand structural information on coal-derived liquids with direct techniques, such as elemental analysis [5], Fourier transform infrared spectrometry [6], and solid-state ^{13}C nuclear magnetic resonance spectrometry (SS ^{13}C NMRS) [10]. Analyses with such methods can usually obtain limited information on elemental composition, functional groups, and carbon types in coal-derived liquids. Although gas chromatography/mass spectrometry can identify some compounds, it is unable to determine nonvolatile, thermally labile, and strongly polar species. Moreover, overlap of chromatographic peaks of various species is inevitable due to the complexity of coal-derived liquids.

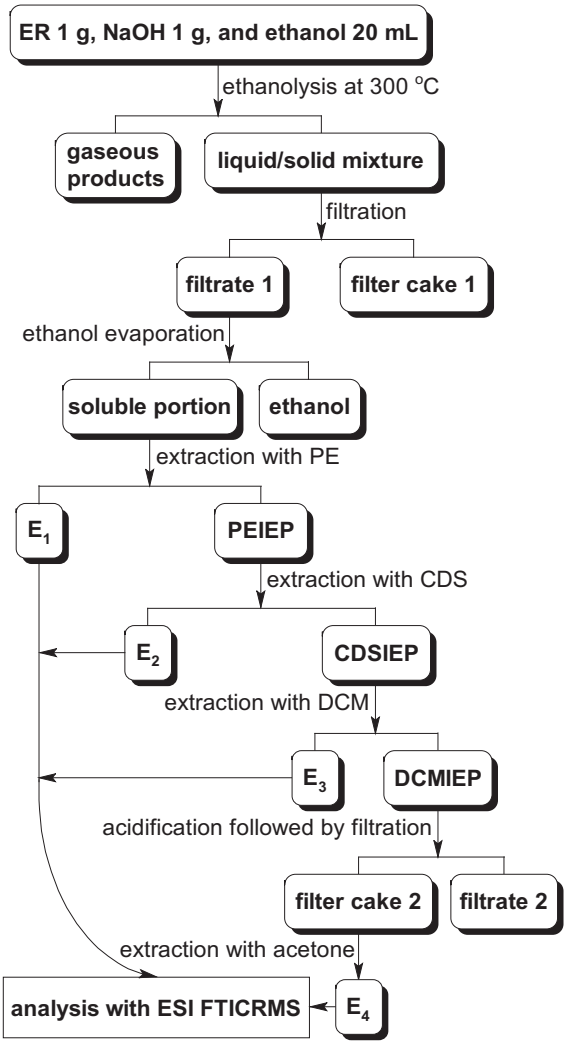

Fig. 1. Procedure for the ER ethanolysis, subsequent treatments and analysis.

Recently, Fourier transform ion cyclotron resonance mass spectrometer (FTICRMS) has achieved success in analyzing petroleum and generating a new field of "petroleomics" [11–15], and also been widely applied to analyze other complex mixtures, such as bio-oils [16–18], coal-derived liquids [19,20], and other soluble organic species [21,22]. With FTICRMS, the m/z values of ions are determined by observing the cyclotron frequency of ions subjected to a high magnetic field. Cyclotron rotation is driven by the Lorentz force exerted on an ion of mass and charge moving in a static magnetic field [23,24]. FTICRMS possesses an ultrahigh broadband mass resolution of >300,000 and sub-ppm mass accuracy, both of which are required for analyzing complex samples. In addition, as a soft ionization source, electrospray ionization (ESI) can selectively ionize polar components in coal-derived liquids. In our recent investigation [25], ethanolysis of Zhaotong lignite was performed and the resulting ethanol-soluble portion was analyzed with a 9.4 T ESI FTICRMS.

In the present paper, ethanolyzed residue (ER) from Zhaotong lignite was subjected to ethanolysis in the presence of NaOH to afford extracts 1–4 (E_1–E_4). The ER was analyzed by SS ^{13}C NMRS and all the extracts were characterized with the ESI FTICRMS to gain insight into the chemical complexity of the soluble portion from the ER ethanolysis.

2. Experimental

2.1. Materials

The ER was derived from Zhaotong lignite via ethanolysis, as reported in our recent investigation [25] and shown in Fig. S1 of the Supporting information. The proximate and ultimate analyses of the lignite were described elsewhere [25,26]. NaOH, HCl,

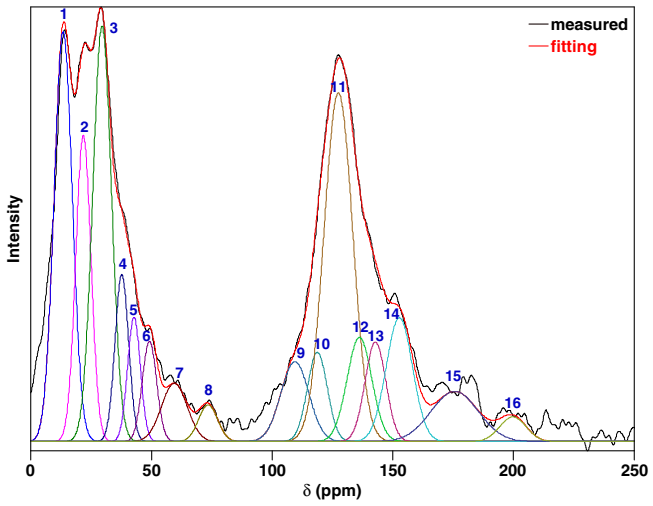

Fig. 2. SS ^{13}C NMR spectrum and its fitting curves of the ER.