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Research article

Characterization of soluble portions from thermal dissolution of Zhaotong lignite in cyclohexane and methanol

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ABSTRACT

Thermal dissolution of Zhaotong lignite in cyclohexane and methanol was conducted at 300 °C for 2 h. The yields of the resulting cyclohexane- and methanol-soluble portions (CHSP and MSP) are 10.1% and 24.3%, respectively. CHSP and MSP were analyzed with a gas chromatograph/mass spectrometer (GC/MS) and negative-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometer (FTICRMS). According to analysis with GC/MS, the compounds detected in CHSP and MSP can be classified into alkanes, alkenes, arenes, arenols, anisols, ketones, esters, nitrogen-containing compounds, and sulfur-containing compounds. The most abundant group components in CHSP and MSP are arenols and arenes, respectively. The analysis with FTICRMS shows that O_n ($n = 1$–6) class species with double bond equivalent (DBE) values of 1–15 are the main acidic compounds in both CHSP and MSP, and the predominant class species in CHSP and MSP are O_2 and O_3 class species, respectively. Arenepolyols and aromatic carboxylic acids with 1–3 rings account for most of the O_n class species based on DBE distributions. In addition, fatty acids are also present in CHSP and MSP. Combination of GC/MS and FTICRMS can provide detailed composition information on coal-derived liquids at the molecular level.

1. Introduction

Lignites are abundant coal resources, but their direct commercial utilization is not suitable due to the high moisture content and low calorific value [1]. On the other hand, high amount of volatiles and high oxygen content make lignites possible to be converted into liquid fuels or chemicals. As one of the efficient conversion approaches, thermal dissolution of lignites has been widely investigated [2]. Many organic solvents, including high-boiling-point solvents (e.g., tetralin [3,4], 1-methylnaphthalene [5–7], and crude methylnaphthalene oil [7,8]) and low-boiling-point solvents (e.g., cyclohexane [9], methanol [10,11], and ethanol [11]), were used for thermal dissolution of lignites. In recent years, increasing attention has been paid to low-boiling-point solvents for thermally dissolving lignites owing to their easy recoverability. Cyclohexane was reported to be effective for thermally extracting inherent components in lignites [9]. More soluble portion can be obtained from thermal dissolution of lignites in methanol via methanolysis [10]. However, the full understanding of molecular compositions of the resulting soluble portions is still insufficient and comparison of soluble portions from thermal dissolution of lignites in cyclohexane and methanol was scarcely reported.

Gas chromatograph/mass spectrometer (GC/MS) is an effective tool for analyzing soluble portions from coals [12], while it is usually limited to identifying relatively volatile, thermally stable, and less poplar species. Recently, Fourier transformation ion cyclotron resonance mass spectrometer (FTICRMS) has been successfully applied to molecular characterization of extremely complex mixtures, such as petroleum [13–15], bio-oils [16–18], coal-derived liquids [19–21], and dissolved organic matter in waste water [22,23]. With ultrahigh mass resolving power and mass accuracy (<1 ppm), FTICRMS can achieve baseline resolution of closely spaced isobaric species and distinct assignment of a unique elemental composition to each mass spectral peak. Electrospray ionization (ESI) coupled to FTICRMS proved to be powerful for identifying polar species. Therefore, combination of GC/MS and ESI FTICRMS could provide a good understanding of soluble portions from lignites.

In the present paper, Zhaotong lignite (ZL) was subjected to thermal dissolution in cyclohexane and methanol at 300 °C to afford cyclohexane- and methanol-soluble portions (CHSP and MSP). CHSP and MSP were analyzed with a GC/MS and negative-ion ESI FTICRMS to gain a full understanding of the soluble portions.

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

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

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

[a] 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).
[b] By difference.

<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, which were obtained by GB/T 212-2008 and Elementar Vario Macro, respectively. All the solvents used in the experiments are commercially purchased analytical reagents and were purified by distillation prior to use.

2.2. Thermal dissolution procedure

About 1 g ZL and 20 mL solvent (cyclohexane or methanol) were placed into a 100 mL magnetically stirred autoclave. After replacing air with N_2, the autoclave was heated to 300 °C at 10 $°C \cdot min^{-1}$ and maintained at that temperature for 2 h. Then, the autoclave was cooled to ambient temperature in a water bath, and the reaction mixture was taken out from the autoclave and separated into filtrate and filter cake by filtration. The filter cake was exhaustively extracted with acetone to obtain extract solution and residue (R_{CH} or R_M). The extract solution was merged with the filtrate followed by distillation to obtain CHSP or MSP. The yield (Y_{CHSP} or Y_{MSP}) of each soluble portion (i.e., CHSP or MSP) was calculated as the mass ratio of the sample (m_{CHSP} or m_{MSP}) to ZL on a dry and ash-free basis ($m_{ZL,daf}$); i.e., $Y_{CHSP} = m_{CHSP}/m_{ZL,daf}$ and $Y_{MSP} = m_{MSP}/m_{ZL,daf}$.

2.3. Characterization

The pyrolysis behaviors of ZL and its residues were examined with a Mettler Toledo TGA/SDTA851° thermogravimetric analyzer according to a previous study [24]. Before thermogravimetric analysis, 2 kinds of calibrations (including mass and temperature calibrations) were conducted. The mass was calibrated using a standard reference weight with an uncertainty of 1 μg. Curie point magnetic method, i.e., alumel ($T_{Cur} = 427.4$ K) and perkalloy® ($T_{Cur} = 669.2$ K), was used for temperature calibration. Each sample was characterized with the thermogravimetric analyzer 3 times and the thermogravimetric curves are nearly coincident.

CHSP and MSP were analyzed with an Agilent 7890/5975 GC/MS, which is equipped with a HP-5ms capillary column (60 m length, 0.25 mm inner diameter, 0.25 μm film thickness) and a quadrupole analyzer with a m/z range from 33 to 500 and operated in electron impact (70 eV) mode. The column temperature was programmed from 60 to 300 °C at 5 $°C \cdot min^{-1}$ and held at that temperature for 5 min. Data acquired were processed using MSD ChemStation software. The compounds were identified by deconvolution and subsequent computer comparison with NIST11 library and artificial check for each resolved peak according to fragment ions. Pentadecane, 1-pentacosene, *o*-xylene, naphthalene, phenol, *o*-cresol, anisol, methyl stearate, carbazole, and thiophene were used as external standards for quantitative analysis of corresponding or similar species. In addition, CHSP and MSP were characterized using an Apollo II ESI source in negative-ion mode coupled with a 9.4T Bruker apex-ultra FTICRMS. The calibration and analytical method was reported in our recent investigation [25]. Each sample was analyzed with the GC/MS and FTICRMS at least 3 times and the resulting total ion chromatograms and mass spectra are almost consistent.

3. Results and discussion

3.1. Analysis of ZL and its residues with thermogravimetric analyzer and yields of CHSP and MSP

The expanded uncertainties for weight and temperature are estimated to 10 μg and 0.1 °C, respectively. As Fig. 1 displays, the pyrolysis rate of ZL first slightly increased with raising temperature and then remarkably increased at temperatures higher than 330 °C. For the residues, high pyrolysis rates shift to higher temperatures. From the thermogravimetric curves, it is obvious that the mass loss of R_M is much less than that of R_{CH} at the entire temperature range. The result suggests that more organic matter was released from ZL during thermal dissolution in methanol than in cyclohexane. As expected, the yield of MSP (24.3%) is significantly higher than that of CHSP (10.1%). The low CHSP yield could be ascribed to that cyclohexane is effective for thermally extracting inherent components in ZL without obviously cleaving the covalent bonds, while methanol was involved in the thermal dissolution process, i.e., methanolysis proceeded, leading to the high MSP yield [9,10].

3.2. Volatile and less polar species in CHSP and MSP analyzed with GC/MS

As shown in Figs. S1 and S2 and Tables S1–S10, in total, 196 organic compounds were detected with GC/MS, and 105 and 130 organic compounds were detected in CHSP and MSP, respectively, which can be classified into alkanes, alkenes, arenes, arenols, anisols, ketones, esters, nitrogen-containing compounds (NCCs), sulfur-containing compounds (SCCs), and others.

Expanded uncertainties were obtained and provided in Tables S1–S10. As Fig. 2 exhibits, hydrocarbons and arenols are predominant GC/MS-detectable group components in both CHSP and MSP. Among the hydrocarbons, alkanes and arenes are the most abundant in CHSP and MSP, respectively. Alkanes are a kind of important biomarker [26,27]. Generally, the temperature for cleaving C_{alk}—C_{alk} or C_{alk}—O bonds to form alkanes is higher than 300 °C [28]. The alkanes are probably from thermal desorption of adsorbed hydrocarbons trapped in the macromolecular skeleton or decarboxylation of alkanoic acids [29,30]. The yields (Fig. 2) and distributions (Fig. 3) of alkanes in CHSP and MSP are almost the same. The identified *n*-alkanes in both CHSP and MSP exhibit a bimodal distribution ranging from C_{13} to C_{30} with a maximum at C_{15} and C_{26}, respectively, suggesting that both low and high plants contribute to the formation of ZL [31]. In addition, isoprenoid alkanes, including nor-pristane, pristane, and phytane, were detected in CHSP and MSP. The pristane/phytane ratio can reflect the depositional environment of sediments. The pristane advantage (Fig. 3) implies dysaerobic conditions during early diagenesis of ZL [27], which is quite different from

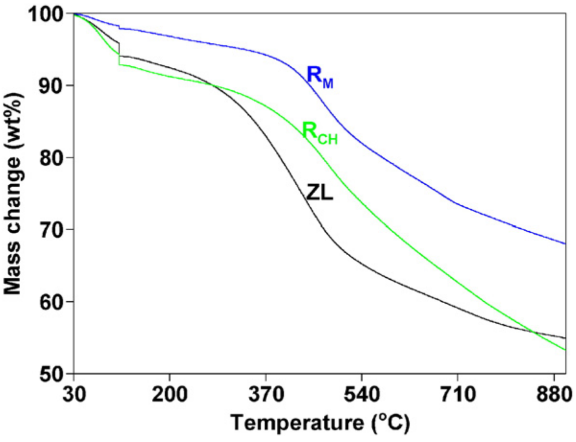

Fig. 1. Thermogravimetric curves of ZL and its residues.