



Full Length Article

Insight into the structural features of low-rank coals using comprehensive two dimensional gas chromatography/time-of-flight mass spectrometry



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ABSTRACT

Detailed characterization of organic components in low-rank coals is essential for the utilization of coals in clean, effective and value-added ways. Two kinds of low-rank coals were subjected to sequential thermal dissolution in the order of cyclohexane, acetone, and methanol to obtain six soluble portions (SPs) from the coals. Two gas chromatographic systems, gas chromatography/mass spectrometry (GC/MS) and comprehensive two dimensional gas chromatography/time-of-flight mass spectrometry (GC × GC/TOF MS), were applied to the characterization of the SPs. Compared to GC/MS, a routine analytical technique for complex mixtures, GC × GC/TOF MS improves the separating power, overcomes the co-elution, and reveals more structural details in complex mixtures like coals. Low-polar compounds like aliphatic hydrocarbons and arenes tended to be extracted by cyclohexane. High content of polar alcohols and phenols were identified in the SPs of methanol. Acetone could enrich nitrogen-containing organic compounds (NCOs) due to hydrogen bond of N–H...O between NCOs and acetone. Additionally, a series of low-concentration species including some isomers in the SPs were only identified by GC × GC/TOF MS. Distributions of various classes of compounds on the two-dimensional total ion chromatograms plot were discussed according to the separation mechanism of the two columns. Detailed analysis of biomarkers was also exhibited and discussed.

1. Introduction

Lignite and subbituminous coal are low-rank coals, which have subjected to the least metamorphic change during the coalification process [1]. Low-rank coals are regarded as inferior fuels due to their low calorific value, high ash yield, and high contents of both moisture and organic oxygen [2,3]. On the other hand, high content of organic oxygen is an important characteristic of low-rank coals, and the organic oxygen in lignite is mainly present in the form of alcohol, phenol, carboxyl, and ether groups [4]. With the coal rank increase from lignite to subbituminous coal, partial hydroxyl and methoxyl functional groups were removed from aromatic rings due to coalification [5]. The high content of organic oxygen makes low-rank coals as suitable feedstock for value-added chemicals [6,7]. To utilize low-rank coals in clean, effective and value-added ways, it is necessary to understand the molecular structure and composition of organic compounds in these coals.

As coal is a solid fuel consisting of macromolecular networks with small molecules scattered inside [8], it is difficult to obtain detailed molecular structure without separation processes to acquire soluble

compounds in advance. Non-destructive separation method like room temperature solvent extraction was applied to the separation of soluble organic matter from coal [9]. However, compounds obtained by this method only represent a portion of organic matter due to the low extraction yield. Enhancing the extraction temperature to a certain level can highly increase the extraction yield although introducing minor reactions [10,11]. Ashida and coworkers used sequential thermal dissolution (STD) to extract different coals with various solvents from 200 to 400 °C [12,13], and 80% of organic matters in coals were converted to soluble portion (SP) at 350 °C. In addition, the extraction conditions (temperature and pressure, etc.), properties of solvent (polarity and reactivity) and coal types (rank and place of origin) determine the composition distributions in extract and residual coal [14].

The enhancement of extraction yield via STD acquires enough compounds from coal. However, SP is still a complex mixture containing polar to non-polar organic species with different molecular weights [13]. To further separate and characterize compounds in SP at the molecular level, chromatography coupled with mass spectrometry has been proven as a powerful tool [15–17].

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Nomenclature

AFC _{WSB}	acetone-filter cake of WSB	MFC _{ZL}	methanol-filter cake of ZL
AFC _{ZL}	acetone-filter cake of ZL	MSP _{WSB}	methanol-soluble portion of WSB
AHs	aliphatic hydrocarbons	MSP _{ZL}	methanol-soluble portion of ZL
ASP _{WSB}	acetone-soluble portion of WSB	NCOCs	nitrogen-containing organic compounds
ASP _{ZL}	acetone-soluble portion of ZL	OCOCs	oxygen-containing organic compounds
CFC _{WSB}	cyclohexane-filter cake of WSB	OSs	other species
CFC _{ZL}	cyclohexane-filter cake of ZL	SCOCs	sulfur-containing organic compounds
CSP _{WSB}	cyclohexane-soluble portion of WSB	STD	sequential thermal dissolution
CSP _{ZL}	cyclohexane-soluble portion of ZL	SPs	soluble portions
GC/MS	gas chromatography/mass spectrometry	TICs	total ion chromatograms
GC × GC/TOF MS	comprehensive two dimensional gas chromatography/time-of-flight mass spectrometry	WSB	Wucaiwai subbituminous coal
MFC _{WSB}	methanol-filter cake of WSB	ZL	Zhaotong lignite
		1D GC	one-dimensional gas chromatography
		2D GC	comprehensive two dimensional gas chromatography

Gas chromatography/mass spectrometry (GC/MS) has been successfully applied in the determination of thermally stable, volatile and low molecular mass species in complex mixtures like coal. A series of polycyclic aromatic hydrocarbons in raw coal extracts and emissions of residential coal combustion were detected by GC/MS [18]. To characterize minor components, a silica gel-packed column was introduced to further separate and enrich thermal dissolution extracts of a coal [19]. Two organic fluorides were identified by the following GC/MS analysis. Another research reported that a silica gel-packed column combined with GC/MS was successfully used to separate and identify two phenylhopanes and two thienylhopanes [16]. Therefore, the separating power of gas chromatography can be further improved to reveal more comprehensive structural details for coal, including the minor components ignored before.

Comprehensive two dimensional gas chromatography (2D GC) consisting of two chromatographic columns with different separation mechanisms was applied to separate complex petroleum and environmental samples [20]. In general, components are separated in the first column according to volatility and by the second one depending on polarity. Compared to one-dimensional gas chromatography (1D GC), 2D GC provides greater sensitivity and higher resolution [21]. Furthermore, 2D GC can effectively reduce overlap peaks among target analytes and matrix interferences [22]. Comprehensive two dimensional gas chromatography/time-of-flight mass spectrometry (GC × GC/TOF MS) shares the same ionization mechanism with GC/MS, converting molecules into gaseous ions and preserving the properties of interest [23]. However, the TOF mass analyzer provides higher resolution and greater mass accuracy than the quadrupole mass analyzer in GC/MS. In addition, TOF mass analyzer has a favorable characteristic, good sensitivity in the full-spectrum mode, thus inducing the detection of more compounds [24]. GC × GC/TOF MS has been applied in the analysis of volatile fractions [25], bio-oil [26], pesticide [27] and petroleum [28]. Nevertheless, the application of GC × GC/TOF MS for the determination of organic species in low-rank coals has not been well studied.

In this work, two low-rank coals subjected to STD of three solvents with various polarities. The soluble compounds were separated and characterized by both GC/MS and GC × GC/TOF MS. Compounds with similar characteristics including isomers were well discriminated, which can enrich the structural knowledge of low-rank coals. The differences between two analytical methods were also discussed.

2. Materials and methods

2.1. Samples and reagents

Wucaiwai subbituminous coal (WSB) and Zhaotong lignite (ZL) were acquired from Wucaiwai Coal Mine, Xinjiang, China, and

Table 1
Proximate and ultimate analyses (wt%) of the coal samples.

Sample	Proximate analysis			Ultimate analysis (daf)				
	M _{ad}	A _d	V _{daf}	C	H	N	S	O _{diff}
WSB	15.08	17.44	46.97	72.47	5.41	1.34	0.38	20.40
ZL	21.58	20.90	53.72	66.36	4.31	1.08	0.32	27.93

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

Zhaotong Coal Mine, Yunnan, China, respectively. Table 1 shows the proximate and ultimate analyses of WSB and ZL. Coal samples were pulverized to pass through a 200 mesh sieve (< 74 μm) followed by desiccation at 80 °C for 24 h in a vacuum oven. The analytical reagents used in the experiments, including cyclohexane, acetone, and methanol, were commercially obtained and purified by distillation prior to use.

2.2. Sequential thermal dissolution

As shown in Fig. 1, 4 g WSB and 20 mL cyclohexane were put into a 100 mL stainless-steel, magnetically stirred autoclave. After replacing the air inside with nitrogen, the autoclave was heated to 300 °C and kept at the temperature for 2 h. Then the autoclave was cooled to room temperature in a water bath, and the reaction mixture was taken out from the autoclave and filtrated to acquire cyclohexane-soluble portion of WSB (CSP_{WSB}) and filter cake 1 (CFC_{WSB}). CFC_{WSB} was dried at 80 °C for 24 h in a vacuum oven and subjected to the second STD in acetone at 300 °C to afford acetone-soluble portion (ASP_{WSB}) and filter cake 2 (AFC_{WSB}). Then AFC_{WSB} was dried under the same condition and subjected to the third STD in methanol to afford methanol-soluble portion (MSP_{WSB}) and filter cake 3 (MFC_{WSB}). The same experimental procedure was applied to ZL to obtain soluble portions (CSP_{ZL}, ASP_{ZL}, MSP_{ZL}) and filter cakes (CFC_{ZL}, AFC_{ZL}, MFC_{ZL}) sequentially. The six SPs were analyzed using both GC/MS and GC × GC/TOF MS.

2.3. GC/MS

GC/MS (Model 7890/5975, Agilent Technologies, USA) used in this work was equipped with a capillary column coated with HP-5 (crosslink 5% PH ME siloxane, 30 m × 0.25 mm i.d., 0.25 μm film thickness) and a quadrupole mass analyzer, and operated in electron impact mode (70 eV). The scanning mass range was from 30 to 500 amu. The column temperature increased from 60 °C to 300 °C with a heating rate of 5 °C min⁻¹ and held at 300 °C for 10 min. Data were acquired and processed with Agilent ChemStation software.

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