



Full Length Article

Structural insights of four thermal dissolution products of Dongming lignite by using in-source collision-activated dissociation mass spectrometry

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ABSTRACT

Thermal dissolution (TD) plays an important role in obtaining soluble components from low-rank coals. Characterization of the TD product is essential for both optimization of TD conditions and in-depth understanding of molecular structures in coal that is crucial for the refining processes. In-source collision-activated dissociation (ISCAD) combined with high-resolution mass spectrometry (MS) was employed in this study to analyze four TD products of a low-rank coal obtained by using cyclohexane, acetone, methanol and ethanol as solvents. ISCAD-MS allows the evaluation of distributions of oxygen and nitrogen atoms located within aromatic cores or on alkyl chains based on the abundances of heteroatom-containing precursor ions and fragment ions. In addition, ISCAD-MS can evaluate the abundance of multi-core compounds based on the change of average double bond equivalent value upon fragmentation. These structural details advance the current understanding of the TD products at the molecular level.

1. Introduction

Economic growth and industrialization inevitably result in the rapid growth in global energy consumption. Despite the recent developments in renewable energy sources, fossil fuels will continue to be responsible for supplying 78% of total world energy for the next few decades [1]. Compared to other fossil fuels, coals have drawn a great amount of attention due to their large and widely distributed reserves [2,3]. Currently, the majority of coals are burned as fuel [2,3]. Low-rank coals such as lignite and subbituminous coal account for significant portion of coals [4]. However, high content of organic oxygen within low-rank coals limits their value in the thermoelectricity generation [5]. In addition, the presence of nitrogen and sulfur in coals brings NO_x and SO_x emissions, which cause serious environmental issues such as acid rain and photochemical smog [6,7]. In the meantime, high contents of organic oxygen and nitrogen make low-rank coals as potential feedstock for the production of valuable chemicals [8–10]. For example, coal molecules with heterocyclic or aromatic cores can be used as precursors for pharmaceutical and agrochemical industries to produce insecticides, drugs, preservatives and explosives [11–14]. Therefore, a better

understanding of the aromatic core structures in low-rank coals and other potential chemical feedstock is necessary for diversified utilization of coals [15–17].

Thermal dissolution (TD) of low-rank coals has gained attention from both academia and industry because soluble components can be obtained at a low energy cost [18,19]. However, the molecular compositions of soluble portions derived from TD using different solvents, which is crucial for the optimal industrial utilization of coals, are insufficiently reported [20–22]. Mass spectrometry (MS) has been intensively employed in the analysis of a wide range of complex mixtures due to its excellent sensitivity and resolution [23–27]. However, MS characterization of the heterocyclic and/or aromatic cores in coal TD products is scarcely reported. The aromatic core structures in coals can be either a single aromatic core with multiple attached alkyl chains (referred to as island structure) or multiple aromatic cores connected by alkyl chains (referred to as archipelago structure) [9,28,29]. The relative abundances of archipelago and island structures affect the downstream upgrading and chemical application process of coals [28,30,31].

In-source collision-activated dissociation (ISCAD) MS was employed

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Table 1
Proximate and ultimate analyses of DL (wt%).

Proximate analysis			Ultimate analysis (daf)				
M_{ad}	A_d	V_{daf}	C	H	N	S	O_{diff}
15.08	17.44	50.61	68.55	5.34	0.91	0.26	24.94

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).

in this work for the characterization of aromatic core structures in TD products. ISCAD and the similar beam-type CAD methods allow dealkylation of the ionized alkyl aromatic compounds and generate fragment ions that correspond to aromatic cores for both model compounds and compounds in complex mixtures [32–37]. ISCAD-MS allows the evaluation of distribution of heteroatoms located within aromatic cores versus on alkyl chains. In addition, ISCAD-MS provides information on the presence of archipelago and island structures in the TD products. Such structural details will provide in-depth understanding of coal TD products, which is vital for downstream refining processes.

2. Experimental

2.1. Samples and reagents

Dongming lignite (DL) was obtained from Inner Mongolia, China. DL was ground and passed through a 200 mesh sieve ($< 74 \mu\text{m}$). Coal powders were dried in a vacuum oven at $80 \text{ }^\circ\text{C}$ for 24 h and then kept in a silica desiccator for later use. Proximate and ultimate analyses of the coal sample are shown in Table 1. Cyclohexane, acetone, ethanol and methanol were purchased from Xilong Scientific Co., Shanghai, China and distilled using a rotary evaporator before use. Carbon disulfide (99%) was purchased from Sigma-Aldrich.

2.2. Thermal dissolution

4.0 g DL and 20 mL cyclohexane were introduced into a 100 mL magnetically stirred stainless-steel autoclave. The air inside the reactor was replaced by nitrogen at room temperature to an initial pressure of 3 MPa. The autoclave was then heated to $300 \text{ }^\circ\text{C}$ and kept there for 3 h. After cooling to room temperature, the reaction products were filtered to obtain a filtrate and a filter cake. The filtrate was concentrated by using the rotary evaporator to acquire soluble fraction 1 (SF1). The same procedure was performed using acetone, methanol and ethanol,

and the obtained soluble fractions were named as SF2, SF3 and SF4, respectively. The extraction yields for SF1, SF2, SF3 and SF4 were 8%, 16%, 12% and 37% of the original coal weight, respectively.

2.3. Mass spectrometry

A linear quadrupole ion trap/Orbitrap mass spectrometer (Q-Exactive, Thermal-Fisher Scientific, Waltham, USA), was used. Four soluble fractions (SF1–SF4) were dried via rotary evaporation and reconstituted in 1 mL carbon disulfide. The samples were introduced into MS through direct injection. Carbon disulfide was used as ionization reagent to generate stable molecular ions during atmospheric-pressure chemical ionization (APCI) [38]. ISCAD (100 eV) was carried out for dealkylation of the molecular ions of alkyl aromatic compounds. Both molecular ions (representing whole molecules and referred to as ions of molecules) and fragment ions (representing aromatic cores and referred to as ions of aromatic cores) obtained via ISCAD were analyzed and compared. Double bond equivalence (DBE) versus carbon number plots were constructed by using Origin software. Details of MS parameters and data processing are listed in Supporting Information.

3. Results and discussion

3.1. ISCAD for dealkylation of ionized coal compounds

To acquire the information of aromatic cores, alkyl chains attached to the aromatic cores need to be removed. Therefore, dealkylation is the prerequisite to observe the aromatic cores of alkyl aromatics in coal TD products. ISCAD was employed to perform dealkylation of the ionized cyclohexane TD product. The DBE plots of mass spectra and ISCAD mass spectra are illustrated in Fig. 1. Mass spectra of ionized cyclohexane TD product implied the existence of both highly unsaturated compounds and less unsaturated compounds (Fig. 1a). The blue rectangle in Fig. 1 indicates the theoretical location of aromatic cores in DBE plots [39]. The highly unsaturated compounds have high ratios of DBE to carbon number and are located close to the blue rectangle in the DBE plots. The less unsaturated compounds have lower ratios of DBE to carbon number and locate at far right from the blue rectangle. In contrast to the DBE plot shown in Fig. 1a, the DBE plot from ISCAD spectra of ionized cyclohexane TD product (Fig. 1b) only shows highly unsaturated ions that correspond to aromatic cores which locate inside the blue rectangle. This suggests that most of the alkyl chains were removed and mostly ions of aromatic cores were observed in ISCAD mass spectra. Same fragmentation patterns were also observed in DBE plots of mass spectra and ISCAD mass spectra of acetone, methanol and

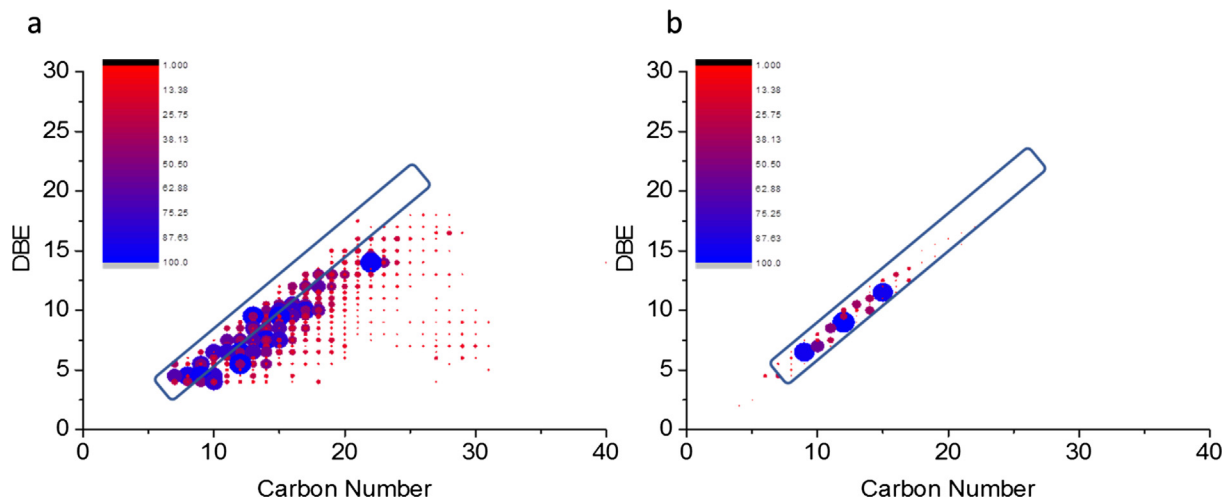


Fig. 1. DBE plots derived from mass spectra of the cyclohexane TD product and ISCAD mass spectra of the ionized cyclohexane TD product at 100 eV.

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