



Full Length Article

In-source collision activated dissociation for coal/biomass-based model compounds and structural characterization of a coal extract

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ABSTRACT

In-source collision activated dissociation (ISCAD) is an effective method to obtain molecular structure of coal and biomass and provide basic knowledge for coal/biomass conversion. Twenty two coal/biomass-based model compounds and one coal extract were studied via ISCAD to understand the relationship between collision energy and molecular structure and the application of ISCAD in the characterization of coal. Model compounds showed different fragmentation patterns with the increase of collision energy and the detailed fragmentation pathways in context of collision energies were proposed. According to the ISCAD results of coal extract, the weighted mean molecular weight (MW) and weighted mean double-bond equivalent (DBE) values of ionized coal molecules decreased over collision energy of 80 eV. The decrease of weighted mean MW and DBE were mainly caused by the cleavage of alkyl chains, bridged bonds, and minor cracking of small aromatic cores from precursor ions upon fragmentation. Therefore, the optimal ISCAD collision energy for the investigation of aromatic core structures of the coal extract should be around 80 eV.

1. Introduction

Although coal, the brother of biomass, is not considered so sustainable compared to other emerging energy sources, methodologies for the utilization of coal are still being developed in clean and green ways [1–3]. It is important to understand molecular compositions of the organic matter in coal for developing clean and green utilization processes for coal [4,5]. Products from extraction [6,7], oxidation [8,9] and liquefaction [10,11] of coal are complex mixtures containing thousands of organic species, which bring challenges to develop analytical methods for coal and coal derivatives. Mass spectrometry (MS) is a powerful tool and widely used for analyzing organic species in coals [12,13]. High-resolution MSs, such as Fourier transform ion cyclotron resonance MS (FT-ICR MS) and Orbitrap MS with powerful mass accuracy and resolution, enable the molecular level analysis of various types of complex mixtures [14–18]. High-resolution MS can acquire the unique elemental composition, which greatly advances the understanding of the mixtures' molecular compositions [19]. However, the

detailed structural information often requires additional analysis like tandem mass spectrometry (MSⁿ) [20].

Currently, collision activated dissociation (CAD), a MS method, is widely available in the majority of mass spectrometers to realize ion fragmentation [21]. Ions can be mass-selected into a collision cell, where collide with inert gas and generate product ions. The level of fragmentation can be controlled by the energy given to the precursor ions in the collision cell [22–24]. Such CAD-based MS method is named as energy-resolved mass spectrometry (ERMS), which has been used to investigate the energetics of ion fragmentation process [25,26]. During ERMS, precursor ions are fragmented with varied collision energies in a controlled fashion [22]. It allows the establishment of breakdown graphs according to the dependence of product ions yield on the collision energy. Thus ERMS can provide much more detailed information over the evolution of the product ions that allows in-depth understanding of the fragmentation pathways [27].

Other than CAD in collision cell, in-source collision activated dissociation (ISCAD) fragments all of the ionized molecules instead of only

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Nomenclature			
APCI	atmospheric-pressure chemical ionization	MS	mass spectrometry
BDE	bond dissociation energy	MS ⁿ	tandem mass spectrometry
C	carbon atom	MW	molecular weight
CAD	collision activated dissociation	N	nitrogen atom
CS ₂	carbon disulfide	NCCs	nitrogen-containing compounds
DBE	double-bond equivalent	N _x O _y	(x = 1–4 and y = 1–6) compounds include C, H, O, and N simultaneously
ERMS	energy-resolved mass spectrometry	O	oxygen atom
FT-ICR MS	Fourier transform ion cyclotron resonance MS	OCCs	oxygen-containing compounds
H	hydrogen atom	S	sulfur atom
HCCs	heteroatom-containing compounds	SCCs	sulfur-containing compounds
HCD	higher-energy collisional dissociation	TD	thermal dissolution
ISCAD	in-source collision activated dissociation	WSB	Wucaiwan subbituminous coal

the isolated ions. ISCAD was used in the investigation of aromatic core structures in low-rank coal and provided in-depth understanding on overall coal structures [28]. An ISCAD energy was employed to ensure dealkylation of alkyl aromatic compounds without significant cracking of the aromatic core structures. Albeit this approach provides useful structural information of coal, the fundamental understanding of ISCAD fragmentation in context of collision energy, which is crucial for further optimization of this approach, is still required. More specifically, the fragmentation behaviors of aromatic molecules at high collision energies need to be optimized to obtain complete dealkylation but undisturbed aromatic cores and more details in the heteroatom distributions within aromatic cores versus on alkyl chains. In this work, energy-resolved ISCAD was used to unravel the detailed fragmentation patterns of ionized model compounds and ionized molecules from a low-rank coal extract. Methodology developed for in-depth understanding of the molecular compositions and structures in coal will promote the utilization of coal in clean and green ways.

2. Materials and methods

2.1. Samples and reagents

Listed in Table 1 are the 22 commercially obtained model compounds (Aladdin, Shanghai, China) with purities higher than 97%. The 22 model compounds are divided into four classes. Arenes with and without side chains are numbered from 1 to 9. Oxygen-containing compounds (OCCs), are numbered 10–16, which can be also used as lignin-derived model compounds to study the hydrogenolysis of C–O bonds [29] and hydrodeoxygenation [30]. Sulfur-containing compounds (SCCs) and nitrogen-containing compounds (NCCs) are numbered from 17 to 22. Such heteroatom-containing compounds (HCCs) commonly exist in coal [31,32], biocrude [33], and petroleum [34].

Chromatographic pure carbon disulfide (CS₂) (99.9%, Aladdin, Shanghai, China) was used as the solvent for model compounds. Each standard solution of model compound was prepared at a final concentration of 2 mg/mL in CS₂. Wucaiwan subbituminous coal (WSB) acquired from Xinjiang, China, was used as the coal sample. Furthermore, a coal extract, the analyte, was obtained by thermal dissolution (TD) of WSB using cyclohexane (commercially obtained and purified by distillation prior to use) as solvent. The detailed experimental process was reported in our previous work [35]. The concentration of the coal extract was also prepared to 2 mg/mL in CS₂.

2.2. Instruments

CS₂ was selected as the solvent for analytes due to its widely solubility. In addition, atmospheric-pressure chemical ionization (APCI) plus CS₂ generate stable molecular ions and are suitable for the analysis of coals and model compounds [26,28,36]. MS characterization of the

model compounds and coal extract were performed using a Thermo Scientific Q-Exactive Orbitrap MS. All of the analytes (2 mg/mL) were transferred into the ion source of MS using a syringe pump at a flow rate of 10 μL/min. The positive ion mode of APCI was used and the instrumental parameters were set as follows: N₂ sheath gas 20 arbitrary unit, auxiliary gas 10 arbitrary unit, discharge voltage 4 kV, discharge current 4.00 μA, capillary temperature 275 °C, and auxiliary temperature 200 °C. In-source collision energy increased from 0 to 100 eV at 10 eV interval. Mass spectrum was collected in full-scan mode with a resolution of 140,000 and a mass scan range of *m/z* 50–750. A blank control experiment with CS₂ only is shown in Fig. S1 (Supplementary Material). Xcalibur 4.0 (Thermo Fisher Scientific, Inc., San Jose, CA) was used for acquisition and analysis of the MS data. Ion intensity was obtained based on 30 times of scan. Ions with abundances lower than 1% relative to the base peak were ignored and a mass tolerance of 3 ppm was selected. Energy-resolved fragmentation pathways of model compounds were proposed and the optimal collision energy for the analysis of coal extract was obtained.

Supplementary Figs. S1–S9 associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.fuel.2018.07.134>.

3. Results and discussion

3.1. Fragmentation reactions of model compounds

The breakdown graphs (Figs. 1–4) and proposed fragmentation pathways (Schemes 1–4) of the model compounds were discussed to reach fundamental understanding of energy-resolved ISCAD, a method to build analytical methodology for coal and biomass chemical industry.

3.1.1. Arenes

The 9 breakdown graphs for arenes in Fig. 1 show the collision energy dependence of the relative percent of total ion abundance for precursor ions and product ions. Stable precursor ions M⁺ are produced for the 9 compounds. The first 5 fused aromatic compounds (Fig. 1a–e) show predominant fragmentation reactions by the losses of hydrogen atom (H) and present high stability under the collision conditions. Besides deprotonation reaction, minor losses of carbon atom (C) sequentially to form product ions at *m/z* 115 and 103 are also observed (naphthalene in Fig. 1a). But product ions via carbon loss are not obvious in Fig. 1b–d, because the density of pair electron cloud in the tricyclic ring are more dispersed and stable compared with naphthalene [37]. Phenanthrene (Fig. 1e), an isomer of anthracene (Fig. 1d), forms more product ions at *m/z* 177, 165, and 152 with energy over 80 eV due to its weaker conjugate effect of aromatic core structure compared to anthracene [38]. In addition, sequential losses of H· and C in fluorine (Fig. 1c) and sequential losses of H·, C, and CH· in phenanthrene with the increase of energy are observed. However, different product ions,

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