



Full Length Article

Characterization of a pyrolysis liquid from a German brown coal by use of negative and positive ion mode electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry and collision-induced dissociation



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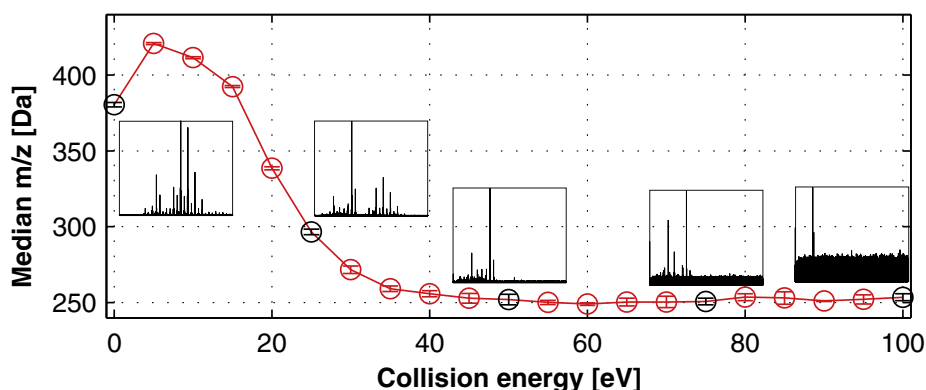
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HIGHLIGHTS

- ESI(+)/ESI(−)-FT-ICR-MS was used to analyse a pyrolysis oil from German brown coal.
- Filtering of adducts in the molecular formula lists is discussed in depth.
- Basic and acidic compounds were ionized and verified using both ESI ionization modes.
- Dealkylation and multiaromatic degradation reactions were dominant in the CID process.
- Structural building units could consist of polycyclic aromatic ketones and quinones.

GRAPHICAL ABSTRACT



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ABSTRACT

A pyrolysis oil produced by slow pyrolysis from a German brown coal was analysed using a combination of three mass spectrometric methods. Various compounds of the pyrolysis liquid sample were ionized by electrospray ionization, both in positive (ESI(+)) and negative (ESI(−)) ion mode, and analysed by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). ESI(−)-FT-ICR-MS analyses mainly exhibit oxygen- as well as sulfur-/oxygen-containing compounds in the pyrolysis oil. In contrast, ESI(+)-FT-ICR-MS analyses were dominated by nitrogen- and nitrogen-/oxygen-containing species. Structural suggestions were possible by plotting the carbon number (n_c) vs. the double bond equivalent (DBE). The assigned structures were further examined by applying ESI(−)-FT-ICR-MS with collision-induced dissociation mass spectrometry (CID-MS). The degradation of the pyrolysis oil constituents into their structural building blocks was monitored by varying the collision energy and its influence on the peak number and the median m/z . According to our results, dealkylation and decomposition processes of multiaromatic systems dominated during the CID event. Possible structural building blocks of pyrolysis oil S500 were found to be polycyclic aromatic ketones and quinones, partially bound to thiophenic structures. It was shown that the developed combination of ESI(+)- and ESI(−)-FT-ICR-MS with ESI(−)-CID-FT-ICR-MS gives the possibility to examine a complex sample, such as a pyrolysis liquid, by investigating its basic chemical backbone.

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1. Introduction

The continuous exhaustion of crude oil and natural gas forces all oil- and gas-consuming industries to find possible alternatives. Pyrolysis oils produced from coal or other organic materials are promising substances to overcome the industrial dependence on natural oil and gas. During their production process, macromolecular compounds of the introduced organic material are thermally decomposed into smaller molecules in an oxygen-free atmosphere [1–3]. Due to a great variety of chemical reactions, such as cracking, elimination, isomerization and rearrangement reactions in this process, ultra-complex product mixtures result [4]. If coal is utilized as the precursor material, the resulting liquid pyrolysates are dominated by aliphatic and aromatic compounds with a varying amount of heteroatoms (N, O, S) [5–8]. Analysing these complex mixtures in depth requires ultra-high resolving analysis techniques, such as Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). FT-ICR-MS resolves the ionized analytes according to their individual cyclotron frequencies, which themselves depend inversely on the mass-to-charge-ratios (m/z) of the ions [9]. Depending on the applied ionization technique and ionization mode, apolar, neutral and/or polar species can be analysed. For instance, electrospray ionization (ESI) provides a selective ionization for mainly polar species of petroleum related liquids [10,11]. ESI-FT-ICR-MS has been recently applied to analyse hydrocarbon mixtures, such as dissolved organic matter (DOM) [12–16], crude oil and its subfractions [17–34], oil sands and oil sand process waters [35–41], as well as shale oils [42–44], organic mixtures (e.g. pyrolysis oils) obtained from biomass [45–49] and coal [11,50–54]. Furthermore, our research group was able to demonstrate the potential of ESI(–)-FT-ICR-MS on the characterization of pyrolysis oils produced from brown coal [55,56]. In these studies, we were able to give structural suggestions for the analysed samples by applying various data evaluation and illustration concepts to the ESI-FT-ICR-MS datasets. Primarily compounds containing oxygen as well as sulfur and oxygen were detected in the oil samples. Hence, the current scientific work will build on the results published earlier.

In general, more precise structural investigations on such complex hydrocarbon mixtures are only possible if the mass spectrometry is done in tandem with a chromatographic separation technique. For instance, isomeric sample species can be separated by liquid chromatography (LC) [28,50] or gas chromatography (GC) [2,5–8,57–62] according to their behaviour on a stationary phase, usually relative to a set of reference compounds. The resulting datasets are typically very large and hence hard to process and evaluate, especially if a high-resolving mass spectrometer is combined [63]. A possible way to avoid these complex analyses is to unravel basic sample structures by means of MS with collision-induced dissociation (CID). In a CID process, functionalized molecules (precursor ion) are fragmented into various subunits (product ions) of the precursor ion by a collision event with neutral gas molecules (e.g. N_2 , Ar) [64–66]. Hence, exact structures of the precursor ions in the oil samples can be reconstructed by comprehending the fragmentation mechanism with the help of the detected mass spectra [67,68]. The application of CID-MS on organic composites was demonstrated by Amundson et al. [69] on different compounds from lignin, as well as on heavy petroleum fractions by Qian et al. [70] and Zhang et al. [71]. Employing ESI-CID-FT-ICR-MS, Qian et al. observed enhanced dealkylation, multi-core molecule decomposition and naphthenic ring-opening reactions, leading to product ions that allowed the determination of structural building blocks of the analysed petroleum fraction. Thus, an application of ESI-CID-FT-ICR-MS on pyrolysis liquids should help to reveal the structural building blocks of these coal-derived liquids (CDL's) as well.

The aim of this study is the comparative analysis of a pyrolysis oil produced from a German brown coal from Schöningen at 500 °C using ESI-FT-ICR-MS in positive and negative ion mode. ESI(–) analyses of the same samples have been conducted before by our group and results were published in two papers [55,56]. The analyses in ESI(–) mode were repeated in this study for reasons of comparability to the novel ESI(+) analyses of the liquid oil sample. Furthermore, the recent and the previous ESI(–) analyses are compared qualitatively in the current work. The comparative application of both ionization modes on the pyrolysis liquid demonstrated a domination of basic nitrogen-containing compounds in ESI(+) and acidic oxygen-containing compounds in ESI(–). Furthermore, ESI(–)-FT-ICR-MS in combination with CID was used to reveal the structural building blocks of the pyrolysis oil. Here, we demonstrate the potential of ESI(–)-CID-FT-ICR-MS to identify the skeletal structure of the analysed CDL. The development of the ESI(–)-CID analysis method is described in depth, especially the determination of the collision energy where an almost complete uncovering of the structural building blocks could be assumed. To the best of our knowledge, the deployed combination of ESI(+), ESI(–)-FT-ICR-MS and ESI(–)-CID-FT-ICR-MS represents the first application of this mass spectrometric combination for the characterization of a pyrolysis liquid from a German brown coal.

2. Materials and methods

2.1. Preparation of pyrolysis oil sample

The pyrolysis oil sample was produced by means of a fixed bed reactor in batch mode using a brown coal from Schöningen. Pulverized coal was loaded into the tubular reactor and heated by an external oven to the designated temperature of 500 °C. Pyrolysis products were trapped in two subsequent cooled traps (–18 °C). The first trap was a packed-bed and the second a solvent (tetrahydrofuran (THF)) filled trap. After each experiment the first trap was flushed with solvent to release the oil. The extract was combined with the solvent from the second trap and the solvent was separated from the oil by distillation. The pyrolysis liquid sample will be denoted as S500 during the discussion.

The sample standard solutions were prepared by weighing the pyrolysis oil into amber vials with the solvent to yield a mass concentration of $1 \text{ g} \cdot \text{L}^{-1}$. Then, the samples were sonicated for 2 min and filtered with a syringe filter (Teflon, 0.2 μm pore size). These standard solutions were further diluted with the solvent to a final concentration of $10 \text{ mg} \cdot \text{L}^{-1}$ for ESI(+)-FT-ICR-MS experiments and $100 \text{ mg} \cdot \text{L}^{-1}$ for ESI(–)- and ESI(–)-CID-FT-ICR-MS analyses. For ESI(+) analyses the solvent system consisted of 60% (v/v) acetone, 30% (v/v) isopropanol (i-PrOH) and 10% (v/v) deionized water with ammonium trifluoroacetate ($\text{NH}_4\text{COOCF}_3$, $c = 1 \text{ mmol} \cdot \text{L}^{-1}$) and for ESI(–) and ESI(–)-CID experiments solvents were 80% (v/v) methanol (MeOH), 19% (v/v) dichloromethane (DCM), 0.9% (v/v) H_2O and 0.1% (v/v) triethylamine (NET_3).

MeOH and NET_3 were purchased from VWR Chemicals as HPLC grade solvents, DCM and acetone from Merck Chemicals with a purity of 99.9% and 99.8%, respectively, i-PrOH from Carl Roth as LC-MS grade solvent (purity: 99.95%) and $\text{NH}_4\text{COOCF}_3$ from Sigma-Aldrich.

2.2. Mass spectrometry (FT-ICR-MS)

MS experiments were conducted on a 15 T solariX FT-ICR-MS from Bruker Daltonics, equipped with an ESI source and operated in positive and negative ion mode, with a scan range from

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