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Analysis of high molecular weight compounds in pyrolysis liquids from scrap tires using Fourier transform ion cyclotron resonance mass spectrometry

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ABSTRACT

Liquids from the pyrolysis of scrap tires are known to be mixtures of a huge variety of organic molecules ranging from low to high boiling compounds. While the low to medium boiling fraction has been investigated using gas chromatography, virtually no information exists regarding high molecular weight compounds. Although size exclusion chromatography has been used to prove their existence no structural information has been obtained yet. In this study Fourier-transform ion-cyclotron-resonance mass-spectrometry (FT-ICR-MS) using laser desorption ionization (LDI) was applied to analyze the high molecular weight fraction of pyrolysis liquids from a fixed bed reactor. Samples were prepared as graphite slurry on conventional steel target plates and mass spectra were compared to those obtained from preparations without graphite. The influence of the graphite to sample ratio and the impact of laser fluence were examined. Using graphite as support during laser desorption increased the spot capacity and enabled the acquisition of a multitude of scans which significantly increased S/N ratios and led to the identification of a range of hydrocarbon and heteroatomic molecular formulas. Molecular formulas of highly unsaturated hydrocarbon compounds with 35–70 carbon atoms and compounds of the type $C_cH_hO_oN_nS_s$ with $o = 0,\ldots,2$, $n = 0,\ldots,1$ and $s = 0,\ldots,1$ could be identified.

1. Introduction

Pyrolysis oils from tires have been characterized by many analytical techniques, such as infrared spectroscopy, size exclusion chromatography, nuclear magnetic resonance spectroscopy and gas chromatography mass spectrometry (GC–MS). Among the methods used, GC–MS is the most powerful technique allowing for the simultaneous identification and quantification of small molecules. Several authors reported that scrap tire pyrolysis oils are mainly composed of aromatic and aliphatic hydrocarbons with nitrogen, sulfur and oxygenated compounds present [1–4] which has been summarized in a recent review [5]. Pyrolysis oils are very complex mixtures of organic compounds necessitating very high resolving analytical methods.

During pyrolysis a variety of decomposition reactions takes place, which are thought to involve radical reaction pathways [5]. Depending on the feedstock used, pyrolysis oils from scrap tires contain a variety of unsaturated compounds like alkenes, isoprene, dipentene, butadiene or styrene [1]. Molecules of higher masses, which would not be amenable to GC analysis, might be formed from these compounds right after their generation during pyrolysis in the reactor or after condensation. Kyari et al. [1] characterized pyrolysis oils derived from different tire brands with size exclusion chromatography and found compounds with molecular weights above 200 Da and even greater than 500 Da. This class of compounds may preferably be analyzed by direct mass spectrometry.

MALDI is rarely used for the analysis of small molecules (m/z<1500), since the matrix ions interfere with the analytes [6]. However, small analytes can be ionized without a matrix. In this

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case either the sample itself is capable of absorbing the laser energy or the support is responsible for absorbing the laser energy and transferring it to the analytes. Various approaches have been presented in the literature for matrix-free laser desorption ionization (LDI), e.g., coating the analyte onto fine, mostly inorganic powders or placing the analytes onto custom-built surfaces [7,8]. Graphite has also been used in form of powder or plates for the analysis of a variety of analytes ranging from small organic molecules to polymers as well as biomolecules and is considered as a photon absorbing and energy transferring material. When glycerol is added to the preparation it acts as a proton source [9]. Graphite dispersed in glycerol has been used as a support for LDI of peptides and proteins [10,11]. Samples structurally comparable to pyrolysis oils were examined in a study of the photooxidation of triterpenes using graphite-assisted LDI [12,13]. Coal tar oil and crude oil samples, which are comparable to pyrolysis oils from tires, have been analyzed by LDI after preparation directly on a target or from planar chromatography plates [14–16].

This report is part of a study aiming at comprehensively characterizing pyrolysis liquids from tires, using comprehensive gas chromatography–mass spectrometry (GC × GC–MS) and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) as complementary techniques. GC × GC–MS is used to investigate low to medium boiling point and apolar compounds, whereas FT-ICR-MS is used for apolar or polar compounds with molecular masses above 250 Da. In this publication we report the results from FT-ICR-MS of crude pyrolysis oil samples acquired using graphite supported sample preparation. The results are compared to findings from measurements without graphite support.

2. Materials and methods

2.1. Pyrolysis liquids

Heat introduction during pyrolysis was perfomed using inductive heating, which is a novel concept and not state of the art. The experimental set-up consists of a medium frequency generator (MFG) with an output power of max. 10 kW at 77 kHz frequency. The electrical energy is fed into a water-cooled copper coil of 250 mm height and 200 mm diameter, that surrounds a ceramic tubular reactor of 500 mm height and 175 mm inner diameter and 195 mm outer diameter, respectively. The reactor set-up model IT-KHS-175-250-10.0 has been designed and built by Linn HighTherm GmbH (Eschenfelden, Germany). The gaseous product is fed into a water cooled condenser and separation of condensed and gaseous phase is achieved via a cyclone. Temperature has been continuously logged using 3 NiCrNi-thermocouples.

1000 g of scrap tire material of less than 100 mm max. size and initial wire content of 2–4% (w/w) have been fed into the tubular reactor and have been exposed to magnetic fields with MFG output power of 6 kW for 100 min. Nitrogen was used as atmosphere and samples of the condensable fraction (liquid oil) has been collected at the bottom of the cyclone in 50 ml glass tubes.

2.2. Fourier transform ion cyclotron resonance mass spectrometry

Two different pyrolysis oil sample preparations were employed. The *graphite free* or *solo* samples were prepared by diluting 10 μL of the crude scrap tire pyrolysis oil sample with 20 μL of a 1:1 mixture of toluene and chloroform. The resulting solution was applied to a polished steel target and air-dried. *Graphite supported* samples were prepared by producing a slurry from 20 mg high purity graphite, 10 μL pyrolysis oil and 200 μL of a 1:1 mixture of toluene and chloroform. This slurry was applied to a polished steel target and dried in air.

All mass spectra were recorded on a Bruker 15 T FT-ICR-MS, in negative ion mode. The spectrometer is equipped with an atmospheric pressure electrospray ionization source (AP-ESI) and a source for matrix assisted laser desorption ionization (MALDI) using the Smartbeam II laser (frequency tripled Nd:Y laser, λ = 355 nm, 3 ns pulse duration, 500 μJ pulse energy). All measurements were carried out using gated trapping, where the ICR-cell is filled multiple times to generate a higher ion count. The measurement parameters were 4 ICR-cell fills per scan and 20 laser shots per ICR-cell fill. Samples prepared without graphite were measured with minimum laser focus, whereas samples prepared with graphite were measured with medium laser focus. The laser peak fluence was calculated to be 44.1 J/cm^2 for minimum focus and 1.8 J/cm^2 for medium focus at 100% laser power. The laser fluence was varied from signal onset to a value when the signal intensity of the carbon clusters surpassed the signal intensity of the analytes.

Internal calibration was achieved by employing a two step process. First the sample was spiked with polyethylene glycol (PEG), measured and internally calibrated using the known masses of PEG. A custom list of unambigiously identified compounds, which were present in all samples, was compiled and used to calibrate all other pyrolysis oil measurements. In the case where carbon clusters were present, the known masses of single negatively charged carbon clusters were used for internal calibration.

All spectra were processed using the same constraints for peak picking and sum formula determination. Peaks were detected when their S/N ratio exceeded 10. Sum formulas were assigned when a peak was twice as intense than the average baseline signal and the m/z peak had a maximum deviation of 0.35 ppm. The solvents used were toluene Uvasolv and chloroforme LiChrosolv from Merck KGaA, the high purity graphite was purchased from VWR and the purity of caesium iodide for external calibration was 99.999% trace metal basis from Sigma–Aldrich.

Peaklists were exported as comma separated ASCII files and imported in Matlab for further processing using in-house-scripts. In dependence on the number of nitrogen atoms and the mass of the observed ions, odd electron (OE) and even electron (EE) ions were identified and molecular formulas were optionally modified by addition of an hydrogen atom. Carbon clusters were excluded from peaklists when numbers of observed formulas were evaluated.

2.3. Scanning electron microscope

Scanning electron microscope (SEM) imaging was performed on a Quanta 250 FEG instrument from FEI. MALDI target plates with graphite-sample spots were placed in the vacuum chamber without further treatment. Images were acquired in secondary electron (SE) mode using 20 kV acceleration voltage at magnifications between 50 and 10,000.

3. Results and discussion

3.1. Sample spot topography and graphite particle morphology

The preparation of sample spots on the MALDI target plate as described in Section 2.2 yielded uniform spots of a layer of graphite and sample components. Sample spots were investigated with SEM after exposure to the vacuum in the MALDI source and with and without application of laser shots. In Fig. 1A the circular expansion zone of the graphite slurry can be seen at a magnification of 50× with the steel plate visible in the lower right corner. The graphite particles form a uniform layer with no obvious gradient of particle sizes or obstacles, except a visible circular deepening in the target plate caused by the cut surrounding the designated spot area. From