Analysis of pyrolysis liquids from scrap tires using comprehensive gas chromatography–mass spectrometry and unsupervised learning

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ABSTRACT

During the pyrolysis of scrap tires a complex mixtures of organic compounds is liberated and can be condensed as liquid product. In this study comprehensive gas chromatography–mass spectrometry (GC×GC–MS) and headspace gas chromatography (HS-GC) are used to unravel the complex nature of pyrolysis liquids from scrap tires produced by means of an inductively heated batch reactor. Two strategies were employed. On the one hand a set of reference compounds was used for quantification, on the other hand unsupervised learning (*c*-means clustering) was used to deduce compound classes and assignment of compound class structural features from MS data. The clustering finally allowed the evaluation of the influence of time and heating rate on observable peak areas. It could be shown, that peak area of saturated and partially unsaturated (hydroaromatic) compounds decreased during the time course of experiments and with increasing heating rate, whereas aromatic compounds increased during the course and were favorably liberated at high heating rates.

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1. Introduction

Approximately 1.4. . .1.5 billion new tires, which correspond to 17 million tonnes, are produced every year [1–3]. The same amount is expected to end up as waste tires every year, which nowadays are mainly subjected to material recycling and energetic utilization [3]. Apart from these possibilities, the recycling of scrap tires using pyrolysis as thermochemical conversion route may be useful for the production of valuable organic commodity chemicals, which can be fed into existing petrochemical infrastructure, and reducing waste streams at the same time. In the light of a shortage of fossil resources like crude oil or natural gas during the next decades, new feedstocks for petrochemical processes need to be found. Several concepts have been proposed and are part of current research. It is expected, that coal will revive as a feedstock for chemical industry, but also other carbon based resources like biomass or wastes like waste tires may play an important role in the future and lead to an industry with a diversified feedstock base.

The pyrolysis of tires produces solid, liquid and gaseous products. The liquids from tire pyrolysis, commonly referred to as oil or tar, are a complex mixture of a variety of organic molecules. Several authors reported that pyrolysis oils from tires are mainly composed of aromatic and aliphatic hydrocarbons with nitrogen, sulfur and oxygenated species present [4–8] and findings have been summarized in recent reviews [4,2,1]. Pyrolysis oils may be used as fuel after blending or as feedstock for the production of commodity chemicals after downstream processing.

Pyrolysis oils are very complex mixtures of organic compounds and hence very high resolving analytical methods are needed to unravel their composition. Among the analytical methods used gas chromatography mass spectrometry (GC–MS) is the most powerful technique since individual compounds can be identified and quantified. Comprehensive gas chromatography (GC×GC) is an advanced technique, that makes use of two GC columns in one run [9–12]. An usually first long column is connected to a second shorter column through a modulator. The modulator traps the compounds eluting from the first column for specified periods of time in the

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range from 2 to 10 s and finally releases the fractions into the second column. Virtually coeluting compounds in the first dimension are separated by the second column with a different selectivity. Most of the experimental setups use an apolar column in the first dimension and a polar column in the second dimension, hence compounds will be separated on the first column according to their boiling point and on the second column according to their polarity. The eluting compounds may be detected using a flame ionization detector (FID) or a mass spectrometer (MS). The latter enables the identification of the separated compounds by their characteristic mass spectra. The great advantage of GC×GC compared to one-dimensional GC is the increased peak capacity, which makes this technique the method of choice for very complex samples like pyrolysis oils.

If complex samples are analyzed by GC×GC–MS, resulting datasets are large and the number of observed peaks in pyrolysis oils amounts in the range of several hundred to more than thousand. Manual identification of compounds is not feasible and alternative strategies for data interpretation need to be found. One approach is the classification of the observed peaks into compound classes. Due to the structured appearance of GC×GC chromatograms elution areas can be defined and used for classification, but since the elution areas may overlap and in most cases a MS is used for detection this additional dimension should be used for classification too. Clustering of the mass spectra of the observed compounds into classes of compounds with similar molecular structure can be conducted by chemometric approaches in an unsupervised or supervised manner [13–18]. After a clustering has been conducted, a lower number of variables is obtained, e.g. summed peak areas of the compound classes, whose interpretation regarding the experiments under study should be easier to the analyst than the comparison of a large number of peaks.

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 [19]. In this publication we report concentration changes of selected analytes in pyrolysis oil samples using GC×GC–MS and the deduction of compound class specific measures by unsupervised learning.

2. Material and methods

2.1. Pyrolysis liquids

Heat introduction during pyrolysis has been performed using inductive heating. Even though inductive heating is a wide spread technology, i.e. in metal hardening, it has rarely been used to heat pyrolysis reactors. To our knowledge these operations used indirect heating of the metallic reactor wall. The novelty of our approach lays within the introduction of heat via induction of current into the wire content of the tire particles, which are subsequently heated by occurrence of Joules loss effect.

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, one in the tire particle bed, one before removal of condensable vapour components and an additional one after condensation of vapour components (permanent gas exiting the cyclone). Their positions are shown in the process diagram in the supplementary documents.

Thousand grams 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) have been collected at the bottom of the cyclone in 50 mL glass tubes.

2.2. Samples and reference compounds

Pyrolysis oils were weighted into reaction vessels and diluted with hexane to yield a mass concentration of oil of 10 g/L. The samples were shaken at 20 °C and 800 min^{-1} for 15 min in a Vortex Shaker and centrifuged for 10 min at 10,000 G. Supernatant solution was separated from the undissolved pellet and an aliquot of 100 μL was diluted by a factor of 10 with hexane in amber vials. In addition, selected samples were used without dilution with a concentration 10 g/L. The centrifugation residue was discarded. Reference compound solutions were prepared by weighing of reference compounds in volumetric flasks and solution in hexane. All reference compounds were purchased from Sigma Aldrich either as analytical standard or highest purity available.

2.3. Comprehensive gas chromatography

Comprehensive gas chromatography was carried out using a Pegasus 4D System from Leco, equipped with an Agilent 7890 GC and a liquid nitrogen cryogenic modulator. All analyses were conducted using a column setup consisting of a nonpolar column in the first dimension and a medium polar column in the second dimension. The setup consisted of a SLB-5MS (Supelco) (L = 30 m, d_c = 0.25 mm, d_f = 0.25 μm) and a Rxi-17SilMS (Restek) (L = 1.5 m, d_c = 0.15 mm, d_f = 0.15 μm). The injection volume was 1 μL. The injector was operated in split mode with a split of 1:25 and maintained at 280 °C. The primary oven was programmed from an initial temperature of 40 °C to a final temperature of 300 °C with an initial hold time of 5 min, a program rate of 8 °C min^{-1} and a final hold time of 10 min. The second dimension oven was programmed 10 °C and the modulator 60 °C higher. The modulation period was set at 3 s. The mass spectrometer was operated in electron ionization mode with 70 eV and a detector voltage of 1400 V.

The acquired chromatograms were processed using Lecos ChromaTOF Software. Peaklists were exported in ASCII format and imported into MATLAB 2013b for further processing using in house scripts. For qualitative evaluation of mass spectra a signal-to-noise (s/n) threshold of 10 was set. Data used for classification procedures comprised of peaks with s/n>25, since lower threshold values hampered the performance of the classification algorithms. The peaklists contained all relevant information, e.g. retention time, area and mass spectra.

2.4. Headspace gas chromatography

Gas chromatographic determination of volatile sample components, which could not be analyzed by the GC×GC method described above due to the presence of the solvent hexane in the corresponding chromatogram section, was conducted by headspace-GC (HS-GC). 10 mg of the samples were weighed in 10 mL headspace vials and dissolved in 500 μL DMSO.

For analysis the vials were conditioned in an Agilent 7694E headspace sampler at 80 °C for 30 min and injected into a split/splitless injector using a split ratio of 1:10 at 250 °C. The