



Detailed compositional characterization of plastic waste pyrolysis oil by comprehensive two-dimensional gas-chromatography coupled to multiple detectors[☆]



Hilal E. Toraman, Thomas Dijkmans, Marko R. Djokic, Kevin M. Van Geem^{*}, Guy B. Marin

Ghent University, Laboratory for Chemical Technology, Technologiepark 914, 9052 Zwijnaarde, Belgium

ARTICLE INFO

Article history:

Received 2 May 2014

Received in revised form 1 July 2014

Accepted 7 July 2014

Available online 14 July 2014

Keywords:

Mixed plastic waste

Pyrolysis oil

GC × GC–FID/NCD/SCD/TOF-MS

Sulfur containing hydrocarbons

Nitrogen containing hydrocarbons

Oxygen containing hydrocarbons

ABSTRACT

The detailed compositional characterization of plastic waste pyrolysis oil was performed with comprehensive two-dimensional GC (GC × GC) coupled to four different detectors: a flame ionization detector (FID), a sulfur chemiluminescence detector (SCD), a nitrogen chemiluminescence detector (NCD) and a time of flight mass spectrometer (TOF-MS). The performances of different column combinations were assessed in normal i.e. apolar/mid-polar and reversed configurations for the GC × GC–NCD and GC × GC–SCD analyses. The information obtained from the four detectors and the use of internal standards, i.e. 3-chlorothiophene for the FID and the SCD and 2-chloropyridine for the NCD analysis, enabled the identification and quantification of the pyrolysis oil in terms of both group type and carbon number: hydrocarbon groups (n-paraffins, iso-paraffins, olefins and naphthenes, monoaromatics, naphthenoaromatics, diaromatics, naphthenodiaromatics, triaromatics, naphthenotriaromatics and tetra-aromatics), nitrogen (nitriles, pyridines, quinolines, indole, caprolactam, etc.), sulfur (thiols/sulfides, thiophenes/disulfides, benzothiophenes, dibenzothiophenes, etc.) and oxygen containing compounds (ketones, phenols, aldehydes, ethers, etc.). Quantification of trace impurities is illustrated for indole and caprolactam. The analyzed pyrolysis oil included a significant amount of nitrogen containing compounds (6.4 wt%) and to a lesser extent sulfur containing compounds (0.6 wt%). These nitrogen and sulfur containing compounds described approximately 80% of the total peak volume for respectively the NCD and SCD analysis. TOF-MS indicated the presence of the oxygen containing compounds. However only a part of the oxygen containing compounds (2.5 wt%) was identified because of their low concentrations and possible overlap with the complex hydrocarbon matrix as no selective detector or preparative separation for oxygen compounds was used.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

In 2012, about 57 million tonnes of plastics were produced in Europe, describing 20% of the total plastics production in the world [1]. Worldwide plastics production is expected to keep growing at a rate of 5% per year [2]. Together with the increase in the worldwide consumption and production of plastics an increase in the amount of plastic wastes is expected. This increasing amount of plastic wastes generates many environmental problems. Therefore the management of plastic wastes is becoming more and more essential in terms of environmental as well as energetic and political aspects

[3]. Depending on the source plastic wastes can be composed of different synthetic polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), polyamide (PA), polyvinyl chloride (PVC), etc. [4–10]. Currently there are three ways to manage plastic waste which are landfilling, incineration with or without energy recovery and recycling. Most of the plastic wastes in Europe is disposed of by landfilling (38%), incineration with energy recovery (36%) and recycling (26%) [1]. Furthermore, landfilling and incineration cannot provide a feasible solution for the disposal of plastic wastes in the long term because suitable and safe depots are expensive, and incineration increases the emission of harmful greenhouse gases such as NO_x, SO_x, CO_x, etc. Chemical recycling, specifically pyrolysis, is one of the promising ways to solve problems associated with the plastic waste disposal. This way the plastic wastes can be used as fuels or provide an alternative pathway to produce (recycled) chemicals for the petrochemical industry [4,11].

[☆] Presented at the 13th International Symposium on Hyphenated Techniques in Chromatography and Separation Technology, Bruges, Belgium, 29–31 January 2014.

^{*} Corresponding author. Tel.: +32 9 264 56 77.

E-mail address: Kevin.VanGeem@UGent.be (K.M. Van Geem).

Pyrolysis is a thermal degradation process in which polymeric materials are heated to high temperatures in order to break down their macromolecular structures into smaller molecules and to produce a wide range of hydrocarbons. These pyrolytic products can be divided into a gas fraction, a liquid fraction (pyrolysis oil) and solid residues [9,12–17]. The pyrolysis oil consists of paraffins, olefins, naphthenes, aromatics, oxygen-, sulfur- and nitrogen-containing compounds depending on the used material. The presence of nitrogen and sulfur containing compounds will necessitate further refining treatment depending on the use of the resulting oil [4,5,11]. To the authors' knowledge detailed compositional characterization of the produced plastic waste pyrolysis oil has not been attempted. Moreover, a proper methodology to determine a detailed composition of plastic waste pyrolysis oil in terms of pure hydrocarbons and sulfur, nitrogen and oxygen containing hydrocarbons is still unavailable although it is crucial for the development of efficient production processes and better assessment of upgrading strategies. GC-MS is the most widely applied technique to obtain detailed information about the composition of plastic waste pyrolysis oil [8,18–21]. However, this method has proven to be mainly applicable for the analysis of hydrocarbon compounds. The quantification of sulfur and nitrogen containing compounds using GC-MS is more difficult because of the interference with the complex hydrocarbon matrix [22–24]. To solve this problem element selective detectors such as sulfur chemiluminescence detector (SCD) [25–30] and nitrogen chemiluminescence detector (NCD) [31–33] can be used for the detection of sulfur and nitrogen containing compounds, respectively. Until now this has not been done.

Therefore in this work a combined analysis, using both selective and non-selective detectors coupled to GC × GC [34,35], is presented for the detailed characterization of plastic waste pyrolysis oil. The detectors used in this work are the flame ionization detector (FID), the sulfur chemiluminescence detector (SCD), the nitrogen chemiluminescence detector (NCD) and the time of flight mass spectrometer (TOF-MS). The influence of different column combinations was also investigated to further improve and optimize the separation of the detected compounds. The information obtained from the analysis provides an unprecedented insight into the composition of the plastic waste pyrolysis oils.

2. Materials and methods

2.1. Chemicals and standards

Analytical gases (helium, nitrogen, hydrogen, carbon dioxide and air) were provided at a minimum purity of 99.99% (Air Liquide, Belgium). 3-chlorothiophene, thiophene, benzothiophene and dibenzothiophene were purchased from Sigma-Aldrich with a minimum purity of 98%. 2-chloropyridine and hexane were purchased from Sigma-Aldrich with a minimum purity of 99%. Dichloromethane was obtained from Chem-Lab at a minimum purity of 98% while acetone was obtained from Chem-Lab at a minimum purity of 99.5%. The elemental composition of the plastic waste pyrolysis oil was obtained using Flash EA2000 (Interscience, Belgium). The device was equipped with both a TCD and an FPD detector. For the trace elemental sulfur content determination the FPD detector was used since the analyzed sample contained sulfur with a concentration lower than 5000 ppm while for carbon, hydrogen and nitrogen the TCD detector was used. The elemental composition was derived based on at least three repeat analyses of the sample. Table 1 shows the elemental composition of the analyzed plastic waste pyrolysis oil and a gas oil sample. The uncertainty on the amount of carbon, hydrogen, oxygen, nitrogen and sulfur detected with this method was within vendor specifications.

Table 1

Measured elemental composition of the plastic waste pyrolysis oil by elemental analysis (EA) and based on the GC analysis and elemental composition of a gas oil sample.

	Plastic waste pyrolysis oil (EA)	Plastic waste pyrolysis oil (GC × GC)	Gas oil
C (wt%)	88.4 ± 0.3	88.0	85.7
H (wt%)	9.6 ± 0.2	10.9	13.4
S (wt%)	0.17 ± 0.003	0.17 ^a ± 0.005	<0.9
N (wt%)	1.08 ± 0.07	1.06 ^b ± 0.05	<0.1
O (wt%)	0.99 ± 0.09	0.35	<0.1

^a Of which 0.14 wt% identified.

^b Of which 0.84 wt% identified.

2.2. Sample preparation

A plastic waste pyrolysis oil was analyzed in this study. The pyrolysis oil was produced by fast pyrolysis of a complex mixture of plastic solid wastes (PSW) which was mainly composed of polyethylene (PE), polypropylene (PP), polystyrene (PS), polyamide (PA), etc. and trace amounts of food residuals. Plastic waste fast pyrolysis has been carried out at a temperature of 430 °C and a pressure of 100 kPa. The vapor residence time was ca. 1 second. Well-chosen internal standards were added to the samples for the separate analysis on GC × GC-FID, GC × GC-SCD and GC × GC-NCD. For FID analysis the sample contained around 2.7 wt% of 3-chlorothiophene whereas the sample contained around 170 ppmw of 3-chlorothiophene and 0.75 wt% of 2-chloropyridine for SCD and NCD analysis, respectively. Because of the instability of the pyrolysis oil all samples were kept in a refrigerator at temperatures in the range of 3–5 °C.

A solid phase extraction (SPE) was applied to extract and separate nitrogen containing compounds into basic and neutral fractions and to aid with the identification of the nitrogen containing compounds [33]. The separation was done using 0.5 g silica SPE cartridges with a volume of 3 ml (Restek). The SPE column was activated using 6 ml of hexane before introducing 2 ml of sample into the SPE cartridge. The non-polar compounds (mostly hydrocarbons) were extracted from the column with 9 mL of hexane while most of the polar compounds stayed in the SPE column. Some of the nitrogen containing compounds such as benzenedicarbonitrile and benzonitriles also eluted off the column with hexane. Pyridine, quinoline, indole and benzenedicarbonitrile compound groups were extracted with 9 ml of dichloromethane whereas caprolactam was extracted with 6 ml of acetone. The obtained hexane, dichloromethane and acetone fractions were analyzed using GC × GC-TOF-MS for identification purposes only.

2.3. GC × GC-FID/SCD/NCD/TOF-MS

The GC × GC setups were built from a Thermo Scientific TRACE GC × GC (Interscience, Belgium). The columns, i.e. a typical non-polar/medium polar column set, and the modulator, i.e. a two stage cryogenic modulator (liquid CO₂), were positioned together in a single oven. The first and second columns were connected to a piece of deactivated fused silica column (Rxi Guard, 0.1 m × 0.25 mm, Restek) by means of a SilTite™ metal ferrule from SGE. Different column sets, placed in the same oven, were tested and an overview of these sets can be found in Table 2.

One setup was equipped with both an FID and an SCD detector. The second setup was equipped with an FID and an NCD detector while the third setup was equipped with both an FID and a TEMPUS TOF-MS detector (Thermo Scientific, Interscience Belgium). For the FID the H₂, air and N₂ (make-up gas) flow rates were respectively 35, 350 and 35 ml min⁻¹. The FID temperature was set at 300 °C

Download English Version:

<https://daneshyari.com/en/article/1199404>

Download Persian Version:

<https://daneshyari.com/article/1199404>

[Daneshyari.com](https://daneshyari.com)