

Chemical elucidation of recycled plastic pyrolysis oils by means of GC×GC-PI-TOF-MS and GC-VUV

Eliane Lazzari^{a,b,c,1}, Marco Piparo^{a,b,*,2}, Charlotte Mase^{a,b,3}, Laurence Levacher^{a,b}, Pierre-Hugues Stefanuto^{c,4}, Giorgia Purcaro^{d,5}, Jean-François Focant^{c,6}, Pierre Giusti^{a,b,e,7}

^a One Tech – R&D – Downstream Processes & Polymers - TOTAL Research & Technology Gonfreville, Harfleur, France

^b International Joint Laboratory - iC2MC: Complex Matrices Molecular Characterization, TRTG, Harfleur, France

^c Organic and Biological Analytical Chemistry Group, MolSys Research Unit, University of Liège, Liège, Belgium

^d Analytical Chemistry Lab, Gembloux Agro-Bio Tech, University of Liège, Gembloux, Belgium

^e Université de Pau et des Pays de l'Adour, IPREM UMR 5254, Hélioparc, Pau 64053, France

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ABSTRACT

Detailed chemical characterization of the composition of pyrolysis oils produced from plastics is a mandatory step in understanding the recycling process. Even though the chemical composition of pyrolysis plastic waste oils shows similarities with fossil-based oils, e.g. PIONA related compounds, the relative proportions of the chemical classes are significantly different, resulting in important changes in the global properties of these fluids. In this context, an analytical method based on comprehensive two-dimensional gas chromatography (GC×GC), coupled with photoionization (PI) – time-of-flight mass spectrometry (TOF MS) was developed to obtain a detailed chemical characterization of plastic pyrolysis-oil. A group-type analysis was achieved thanks to the detection of molecular ions by soft ionization PI-TOF MS. Moreover, olefins were successfully distinguished from naphthenes by in-depth consideration of MS spectra, even though such compounds elute very close in the 2D chromatographic separation space. A part of the olefins identified by PI was further confirmed by GC coupled to vacuum ultraviolet detection (VUV) since olefins VUV spectra differ from other compounds. The overall combination of the entire set of data of this multi-modal approach was valuable in studying the pyrolyzed plastic oil composition. It was furthermore applied to monitor the efficiency of upgrading processes that were applied to the oils to remove specific contaminants such as the diolefins. This approach has the potential to support the production of plastic pyrolysis oils that could efficiently be reintroduced in the market to sustain economic circularity needs.

1. Introduction

The pyrolysis of plastics is of high industrial concern as it potentially allows converting a large amount of waste into new polymers and contributes to a circular economy [1]. In 2018, plastic production in Europe exceeded 60 million tons, of which almost 40% were used for packing and less than 25% were recycled [2]. During the pyrolysis of plastic wastes (chemical recycling), the large polymer chains break

down into chemical building blocks by thermal degradation in the absence of oxygen, generating unsorted waste streams [3]. The liquid output generated from this process can be used to obtain new monomers and, eventually, new plastic products by applying upgrading processes [1,4]. Such upgrading processes serve to eliminate specific contaminants to improve the quality of the product and avoid problems in the steam cracker unit.

Even though the chemical composition of pyrolysis plastic waste oils

* Corresponding author at: One Tech – R&D – Downstream Processes & Polymers - TOTAL Research & Technology Gonfreville, Harfleur, France.

E-mail address: marco.piparo@totalenergies.com (M. Piparo).

¹ 0000-0003-0286-4833

² 0000-0003-4404-442X

³ 0000-0001-8820-2595

⁴ 0000-0002-1224-8869

⁵ 0000-0002-8235-9409

⁶ 0000-0001-8075-2920

⁷ 0000-0002-9569-3158

shows a similar profile to traditional fossil-based hydrocarbon streams, highly complex and basically composed of PIONA-related compounds, the relative proportions of chemical classes are different. For instance, pyrolysis plastic oils contain large amounts of olefins (linear, branched) and diolefins, which make not only the detailed group-type analysis a real analytical challenge [5–7], but can cause problems in the cracking unit. It is generally known that diolefins substantially impact coke formation and fouling of the heat exchanger surfaces if those compounds are present in a certain amount in the steam cracker feedstocks [4,8]. Therefore, using recycled plastic pyrolysis oils as a potential steam cracker feedstock requires its complete characterization to adapt processes correctly.

For this purpose, the GC×GC has been applied successfully due to its significant gain in separation power, sensitivity, and selectivity compared to monodimensional GC techniques [4–6,9,10]. So far, the coupling of the GC×GC with mass spectrometry (MS) using conventional electron ionization (EI) at +70 eV is the main approach reported in the literature for recycling plastic pyrolysis oil characterization [7,11]. The use of reverse column set GC×GC coupled with different detectors has been reported by Dao Thi and co-workers [5] for the detailed characterization of plastic waste pyrolysis oil. Identification of PIONA compounds as well as α -olefins, iso-olefins, and diolefins was made by TOF MS using EI (+70 eV). A similar approach was reported by Toraman and co-workers [6] with a focus on PIONA-related compounds, particularly in the aromatics classes, without details about the olefin isomers composition.

Although GC×GC-MS allows the separation of hundreds of peaks, the identification of the compounds by EI and usage of mass spectral libraries is not straightforward, mainly due to a lack of molecular ion information. At +70 eV, molecules undergo extensive fragmentations, resulting in so-called fragmentograms that can be organized in searchable spectral libraries but also significantly reduce the intensity of parent ions. In many cases, the parent ions have non-remaining abundance at all, which makes the identification of isomer structures and alkyl series compounds, or even PIONA chemical classes ambiguous. For instance, the EI fragmentation patterns of olefins and diolefins are like those of the corresponding saturated and unsaturated mono naphthenes, respectively [5,12].

In contrast, soft ionization techniques lead to limited or no fragmentation, significantly enhancing the molecular ions signal. Among the soft ionization techniques available, photoionization (PI) employs a classic VUV light source that is capable of a soft ionization of many organic compounds [13]. The coupling of PI with MS has shown powerful abilities for the analysis of complex samples. Giri and co-workers [14] used GC×GC-PI-TOF MS for isomeric identification of hydrocarbons, particularly branched alkanes, and cycloalkanes, in petroleum base oils, based on the use of the valuable mass spectra retaining both molecular parent ion and fragmentation patterns given by PI. Recently, Zou and co-workers [15] obtained the structural composition of commercial dodecene products using the same instrumental setup. Utilizing the intensity of molecular ion and fragmentation patterns in PI, C12 olefins congeners were grouped, and the double bond location unraveled.

Additionally, to the PI advantages, recent developments in the GC-VUV field highlighted the capability of this system for PIONA compounds characterization [16–18]. Compared to MS, VUV has shown its efficiency in the differentiation of isomeric species [18]. When using a VUV detector, compound identification is handled through the unique absorbance spectra in combination with spectra library data, pseudo-absolute quantification, and interval deconvolution are also possible [19,20]. Those capabilities, tied to the fact that PIONA class compounds have different spectral signatures in VUV, have recently been used to characterize recycled plastic pyrolysis oil samples [16]. The report shows a combination of PIONA+ software and an in-house modified spectral library for the accurate identification and quantification of the PIONA-related compounds. Previously, the same authors

demonstrated, in fossil-based liquid hydrocarbon streams, that GC-VUV was more accurate at identifying and quantifying PIONA compounds when compared to standard GC-FID methods [17].

Therefore, the focus of this paper is to combine the capabilities of the GC×GC-PI-TOF MS with the potential of GC-VUV to explore the chemical classes present in recycled pyrolysis oil with the ultimate goal of verifying the efficiency of upgrading processes applied for removing specific contaminants, especially conjugated diolefins, to obtain a product that could be efficiently reintroduced in the market. Indeed, olefins and mainly conjugated diolefins are known for their gum-formation property through secondary chemical reactions, such as Diels-Alder reaction, resulting in adverse effects in the unit during the fuel and feedstock processing [21,22]. First, a reverse phase GC×GC analytical method was developed, and the characterization of recycled plastic pyrolysis oil was obtained by PI-TOF MS. A group-type analysis, focusing on the detectability of molecular ions and fragmentation patterns toward different chemical classes, allowed achieving the composition differences between untreated samples and upgraded samples, which were not visible using EI, particularly in terms of olefins and naphthenes. The characterization of the sample was extended to GC-VUV, to confirm the identification of the two samples achieved by PI. Quantitative values, particularly in terms of olefins, were also investigated. Finally, the overall combination of the entire set of data was used to unravel the recycled plastic pyrolysis oil composition and estimate the efficiency of the upgrading processes that were applied.

2. Material and methods

2.1. Samples and pyrolysis process

Two main pyrolysis oil types were evaluated in this work. The first type comprises the untreated pyrolysis oil, the liquid product obtained directly from the pyrolysis process to which no upgrades have been applied; while the second type, is the liquid hydrocarbon streams (hydrotreated pyrolysis oil – HDT) obtained from a hydrotreating process using the untreated pyrolysis oil as feedstock. The upgrading was performed by hydrogenation to decrease the amount of diolefins, avoiding problems in the following unit. The mixed plastic pyrolysis oil was supplied by TOTB (TotalEnergies OneTech, Belgium). The global composition of the mixed plastic sample used for the pyrolysis test is 99%wt in plastics and 1%wt of metals and fibrous. The plastic fraction is mainly composed of PE (83%wt) and PP (10%wt) and in less quantity of PS (2%wt), PVC (1%wt) and PET (3%wt). This mix was pyrolyzed in a pyrolysis unit at 410 °C under an inert atmosphere without additives addition.

Samples were analyzed by GC×GC-FID, GC×GC-TOF MS using EI/PI combination ion-source, and by GC-VUV. The untreated pyrolysis oil was used for analytical condition optimization because it represented the major complexity in terms of classes of compounds. All samples were injected without previous dilutions.

2.2. GC×GC analysis

2.2.1. GC×GC-FID instrumentation

GC×GC-FID experiments were carried out on an Agilent 7890B (Agilent Technologies, Wilmington, DE, U.S.A.) equipped with a split/splitless injector. Column phase setup and flow modulation conditions, as outlined in Table 1 below, were carefully optimized starting from previously reported research works [23,24].

2.2.2. GC×GC-EI/PI-TOF MS Instrumentation

The GC×GC analyses were conducted using an Agilent 7890B GC equipped with a split/splitless injector and a ZOEX ZX2 cryogenic modulator (Houston, TX, U.S.A.). The GC×GC was interfaced with a PI/EI combination ion source coupled to the TOF MS (JMS-T200GC “AccuTOF GCx-plus”, JEOL Ltd., Tokyo, Japan). PI soft ionization used a

Table 1
Conditions used on the GC×GC-FID flow modulator analysis.

Method conditions	Conventional set up	Reverse phase set up
Columns set up	DB-1 10 m x 0.18 mm × 0.18 μm (¹ D) DB-17HT 10 m x 0.25 mm × 0.15 μm (² D)	DB 17HT 30 m x 0.25 mm × 0.15 μm (¹ D) HP-1 5 m x 0.32 mm × 0.25 μm (² D)
Flow rate (He)	0.15 mL.min ⁻¹ (¹ D) 20 mL.min ⁻¹ (² D)	0.2 mL.min ⁻¹ (¹ D) 20 mL.min ⁻¹ (² D)
Oven temperature	Starting at 40 °C until 350 °C	
Detector temperature	300 °C	
Injector	0.2μL (split ratio 400) 300 °C	
Flow modulator type	Forward fill/flush (FFF) flow modulator from Agilent (Modulation period 11 s)	reverse fill/flush (RFF) flow modulator from SepSolve (Modulation period 12 s)

deuterium lamp in single-photon photoionization, with maximum energy of + 10.78 eV at 118 nm. Further technical details of the PI are described elsewhere [14]. Analytical conditions are outlined in Table 2 below. All data produced were processed using GC Image v 2.3 (Zoex Corporation, Houston, U.S.A.).

2.3. GC-VUV analysis

A VGA-101 from VUV Analytics was coupled to a GC Agilent (7890 A). A split injection (split ratio 100) of 0.5 μL was made at 280 °C. Helium was used as the carrier gas at a flow rate of 1.5 mL min⁻¹. GC program oven was set initially at 35 °C and increased to a final temperature of 350 °C (hold for 5 min) at a rate of 3 °C min⁻¹. At the interface between the VGA-101 and the GC, the transfer line was maintained at 275 °C. Flow cell temperatures were set to 275 °C and nitrogen was used as a make-up gas at a constant pressure of 0.25 psi. The detector measured the transmission of light between 125 nm and 430 nm.

Instrumental control and data processing were carried out by VUV Vision v.3.4.0. Data processing was performed using a chromatogram filter set to 125–160 nm, 140–160 nm, 170–205 nm, 170–240 nm, 200–240 nm and analyzed from 2 to 120 min in steps of 0.2 min. The background was taken from 1.4 to 1.6 min. Identification and quantification of olefins peaks were handled by the VUVAnalyze v.1.7.3 software packages using a provided VUV spectral library, which contains spectra data and its corresponding response factor for olefins. Retention Index (RI) was also considered for the peak identification, and in the GC-VUV, a RI tolerance of ± 20 can be considered without sacrificing the accuracy of the results and to minimize eventual run-to-run variations.

By VUVAnalyze automated time interval deconvolution on the full spectral range (125–430 nm) provided a quantification reported as wt% of the total class as well as specified for individual components. Additionally, since olefins were low concentration in the HDT, deconvolution features were used to avoid that overlapping signals of aromatics and

Table 2
Analytical conditions for the GC×GC-MS analysis.

Method conditions	Reverse phase set up
Columns set up	Rxi 17Sil MS 60 m x 0.25 mm × 0.25 μm (¹ D) Rxi 5 ms 1 m x 0.25 mm × 0.25 μm (² D)
Flow rate (He)	1 mL
Oven temperature	Starting at 40 °C until 350 °C (hold 2 min)
Detector temperature	Interface: 250 °C Ion source: 300 °C PI source: interface and ion source 250 °C
Mass range	From 35–450 m/z
Injector	1 μL (split ratio 50) at 280 °C
Flow modulator type	ZOEX ZX2 (Modulation period 6 s, hot jet 0.3 s)

saturated hydrocarbons could provide false olefins identification.

3. Results and discussion

3.1. Column setup combination

Due to recycled plastic pyrolysis oil's complexity, proper column selection and optimal modulator conditions are crucial to achieve efficient chromatographic resolution. Both conventional (nonpolar × polar) and reversed (polar × nonpolar) column sets were tested, and the flow modulation optimal conditions were chosen according to previous research work [23] and by measuring an untreated pyrolysis oil in a GC×GC-FID system. For the reverse phase, conditions were optimized using an RFF flow modulator against a forward fill/flush (FFF) flow modulator for the conventional setup. As recycled plastic pyrolysis oil is mainly composed of PIONA-related compounds, a structured group-type elution should be expected on the chromatogram. An optimal group type separation not only gives an easy understanding of the entire sample composition but is crucial for routine quantitative analysis, as reported hereby. Therefore, the performance and suitability of the column combinations were evaluated by an intra-classes bi-dimensional resolution and by a group-type separation of the main chemical classes in the sample. The GC×GC-FID chromatograms of the two column sets evaluated under their respective optimized conditions are shown in Fig. 1.

The conventional combination of a nonpolar DB-1 ms (100% methylpolysiloxane) at ¹D and a mid-polar DB-17HT (50% phenyl/50% dimethylpolysiloxane) at ²D, even resulting in an entire composition view of the sample, was far from optimal to achieve the desired group-type structure. Peaks belonging to the saturated chemical compounds, mainly n-paraffines, α-olefins, and di-olefins were enclosed in the bottom part of the chromatogram, and in particular, olefins are gathered eluting with neighboring diolefins and paraffin peaks.

Therefore, a reversed-phase set was evaluated with a mid-polar column DB-17HT (50% phenyl/50% dimethylpolysiloxane) in the first dimension and a nonpolar column HP-1 (5%-Phenyl-methylpolysiloxane) in the second dimension, improved the structure-ordered chromatogram of the region of interest. In particular, peaks are better distributed over the 2D space, and an improved occupation of two-dimensional space has been observed. n-paraffins, α-olefins and di-olefins, mainly coming from the PE contribution, were better separated. Furthermore, a family of compounds is now clearly visible above the n-paraffins. This latter, named polyolefines saturated hydrocarbon (POSH), mainly iso-olefins or iso-paraffins, derive from the contribution of PP in the mix of plastics as previously reported by Beccaria et al. [25]. The aromatics families were well separated from paraffins and olefins. In particular, light aromatics and benzoic acid, belonging to PVC degradation and secondary reaction with olefins during the pyrolysis processes, have been identified. Finally, styrene was detected as the compound with the highest concentration, i.e. 2 w/t%. Taking into consideration that this compound cannot be generated from the pyrolysis of polyolefins and PVC, it confirms that 2% of the initial charge was from PS as reported already by Abbas-Abadi et al. [26,27].

Considering the superior separation obtained with the reverse-phase column combination, the same set up was used in the GC×GC-TOF MS and an equally good separation was obtained using a cryogenic modulator, enabling a reliable qualitative analysis.

3.2. Qualitative screening

A qualitative evaluation of samples was performed by GC×GC-PI-TOFMS for speciation of the chemical classes of the two different types of pyrolysis oil used in this study. Fig. 2 shows a zoom of the carbon region between C10-C11 of untreated pyrolysis oil (a) and an HTD pyrolysis oil (b); identified molecular ions are listed. The zoom region and intensity scale were fixed to facilitate sample comparison and selected for lower carbon numbers, avoiding thus, large isomeric possibilities and

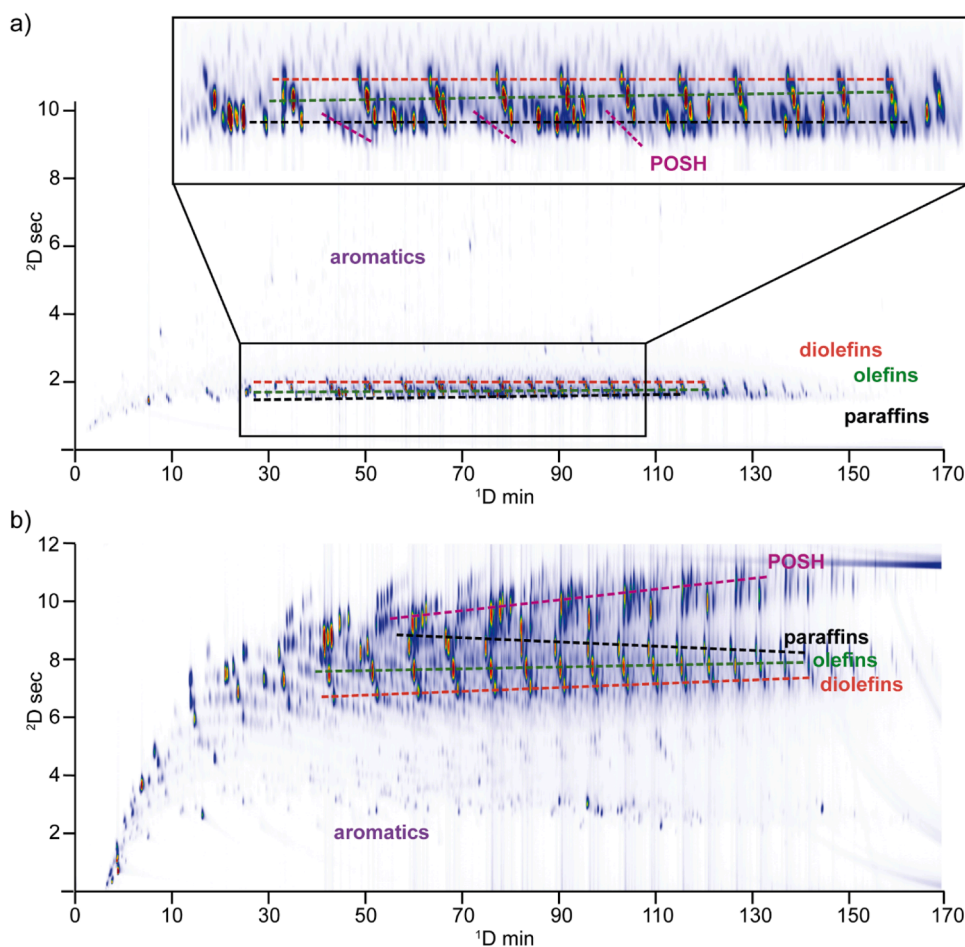


Fig. 1. GC \times GC-FID 2D chromatogram comparison between conventional (nonpolar \times polar) column set using an FFF flow modulator (a) and reverse phase (polar \times nonpolar) column set using an RFF flow modulator (b) under respective optimized conditions. The recycled plastic pyrolysis oils used for the generation of those chromatograms were untreated samples. Elution regions of paraffins, olefins, diolefins, and aromatics are highlighted.

making the group type analysis easier.

Utilizing the predominant intensity of molecular ions in PI mass spectra congeners were grouped by carbon chain length and aliphatic hydrocarbons chemical classes. The presence of the molecular ion at m/z 158, 156 and 154 allowed assigning these compounds with C10-paraffin, C10-olefins and C10-diolefins, respectively and the branching chains were positively assigned by molecular ions, at m/z 156 (C11-branched-paraffins), 154 (C11-branched-olefins) and 124 (C9-branched-diolefins). The order of branching with increasing retention time, in both dimensions, is consistent throughout the chromatogram with increasing carbon number. Slight above of n-olefins, the identified molecular ion m/z 140 reveals an elution region of C10 n-olefins or C10 naphthenes; the first high-intensity peak is easily attributed to 1-decene, for the following peaks, however, if no further molecular ion information has been taken, they possibly would be assigned as C11-branching olefins due to its elution shortly after C10 n-olefin.

Comparing samples (Fig. 2a and b), at first view, it is noted that the diolefins (assigned by the presence of molecular ion m/z 138 and m/z 124) and the branched olefins (assigned by molecular ion m/z 154) have been eliminated by the upgrading process, while more peaks have been detected in the branched paraffins and POSH elution regions (molecular ions m/z 156, 168 and 170). Regarding olefins, a decrease in the number of peaks in the region of the molecular ion m/z 140 was observed. As aforementioned, olefins and mainly diolefins are known for their gum-formation property through secondary chemical reactions, such as Diels-Alder reaction, resulting in adverse effects in the unit during the fuel and feedstock processing [21,22]. Therefore, upgrading processes

by hydrogenation was successfully applied in the raw pyrolysis oil to eliminate diolefins.

In the case of olefins, since they cannot be straightforwardly distinguished from naphthenes by their mass spectra obtained under + 70 eV, the HDT pyrolysis oil was further analyzed by PI. One of the biggest hurdles in the GC \times GC-MS characterization of plastic pyrolysis oil and its hydrogenated product by electron ionization mode (EI) is the identification of olefins in the presence of naphthene as both compounds' classes present the same molecular masses and very similar fragmentation patterns. Likewise, it happens for diolefins and naphthene with an unsaturated carbon chain. Using PI, however, those classes of compounds are distinguishable by their fragmentation patterns.

Olefins were already separated from naphthenes in recycled plastic pyrolysis oil using a GC \times GC-TOF MS with reverse phase setup [5], but in this work, the full characterization was limited to the use of EI-MS. Moreover, fragmentation patterns or congeners grouping using molecular ion information have been not displayed, moreover, since a Stabilwax was chosen for the first-dimension separation, a limit on final temperature was also imposed.

3.3. Insights on PI fragmentation patterns for PIONA compounds

In Fig. 3 is presented a comparative fragmentation of PI vs EI for compounds examples of PIONA classification (n-paraffins (a), iso-paraffins (b), olefins (c), naphthenes (d) and aromatics (e)) obtained for both: untreated and HDT pyrolysis oil. These samples were run using both ionization modes (EI and PI) to gain insight into chemical classes'

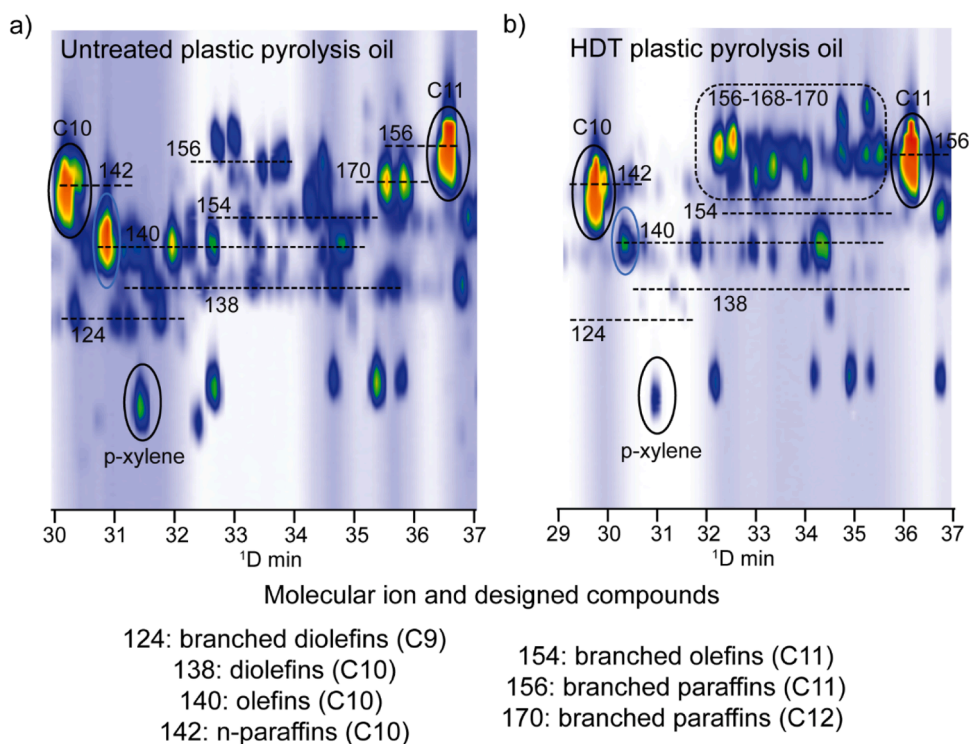


Fig. 2. Comparison between an untreated pyrolysis oil (a) and an HTD (b) in the zoom region of C10-C11 elution. Peaks are grouped under the same molecular ion achieved by PI spectra.

identity. As can be seen, under EI, most aliphatic hydrocarbons displayed similar skeleton spectra with a high intensity of fragments and a lack of molecular ion preservation. Contrary, PI greatly retained the molecular ion (M^{+*}) as the predominant ion and showed unique fragment patterns for most chemical classes.

Among PIONA compounds, the separation and identification of n-paraffins by GC×GC-MS is not a matter of concern since these compounds have remarkable retention indexes and easy-to-interpret EI mass spectra, which is not the case of iso-paraffins. The ambiguous fragmentation patterns and absence of molecular ions make the large number of isomeric possibilities in branched acyclic alkanes indistinguishable, using their fragmentation at +70 eV. Alike, PI enhanced the intensity of the molecular ion and formed characteristic fragmentation ions. The usual fragmentation pathway in monomethyl alkanes isomers is the cleavage of the C-C bond adjacent to the tertiary carbon atom [28, 29]. Accordingly, a 2-methyldecane (Fig. 3b) was revealed by the presence of the molecular ion at m/z 156 and the branching position by the peak base at m/z 112 and the peak at m/z 141, attributed to cleavages C-C bond adjacent to the tertiary carbon atom and suggesting a branched position locating between the 1st and 2nd C.

Congeners of olefins, which have the same mass weight, can also be distinguished by fragmentation patterns into PI spectra. Briefly, light olefins have the allylic cleavage as their main cleavage (the cleavage of the allylic bond which is between α -C and β -C), while vinylic cleavage (between the vinylic group and α -C) is typical in longer carbon chain olefins and, in less proportion, a γ -bond-cleavage (cleavage of the bond between β -C and γ -C) can also be observed [15,30]. Compared to EI (Fig. 3c#1), the signal of fragments m/z 111, 97, 84 in a 1-decene (assigned by the molecular ion m/z 140) was enhanced in PI mass spectra, while small fragments did not show high intensity. The relatively high intensity of the fragment m/z 97 in a 1-decene is due to the allylic cleavage, and it was useful for deducing the double bond position and assigning the compounds as α -olefins. In contrast, the fragment m/z 111 is related to the vinylic cleavage and loss of C_2H_4 . The following olefin congener (Fig. 3c#2) showed even less fragmentation than

α -olefins in the PI mass spectra; according to the olefin common fragmentation pathway, the double bond position is supposedly located between the 4th and 5th C (4-decene) due to the fragments at m/z 111 and 97 linked to the allylic and vinylic cleavage, respectively. Further PI mass spectra interpretation of olefin congeners are well detailed by Zou and co-workers [15]. In this work, the authors have explained in detail the fragmentation pathway of dodecene isomers, confirming the identity of certain dodecene isomers as well as their double bond location.

Regarding naphthenes, these compounds result in a simplified PI spectrum with a dominant intensity of molecular ion and characteristics ring fragments, m/z 68 and 82 for alkylcyclopentanes and alkylcyclohexanes, respectively. In addition, the analogs mono-, di-, tri- and tetra-methyl monocyclic alkanes can be monitored through the fragments corresponding to the C-C cleavage of the substituted alkyl chain. Giri *et al.* [14] tentatively identified a series of C24 monocyclic alkanes, checking the presence of molecular ions and peaks at m/z 82, 96, 110, 124 for mono-, di- tri-, and tetra-methyl cyclohexanes and peaks at m/z 68, 82, 96, 110 for mono-, di- tri- and tetra-methyl cycloheptanes, respectively. Therefore, the PI mass spectra in Fig. 3d were assigned to a C10 alkylcyclohexanes compound, tentatively identified by the molecular ion at m/z 140 and the even fragments at m/z 82, 96, and 110 which are due to a C4 alkyl substituted in cyclohexane ring, likely methyls or ethyls groups. Under extensive fragmentation, in contrast, monocyclic alkanes show a spectrum dominated by high intensity of fragment at m/z 69, 83 and 97, and 111 and low intensity of molecular ions. Those odd fragments have been used by Shimoyama and Yabuta [31] to assign methylcyclohexanes and cyclopentanes in sediments and more recently by Alam and co-workers [12] to assign alkyl methyl, di and tri methyl monocyclic alkanes in base oil. Although monocyclic alkanes could be readily detected using EI at +70 eV, slight differences in the fragment patterns are often considered to distinguish naphthenes from olefins in recycled plastic pyrolysis oil; naphthenes show the higher intensity of fragment m/z 83 and the molecular ion is more stable, making it usually visible in the EI spectra (see the comparison between EI spectra Fig. 3c and d). However, such differences often remain insignificant when

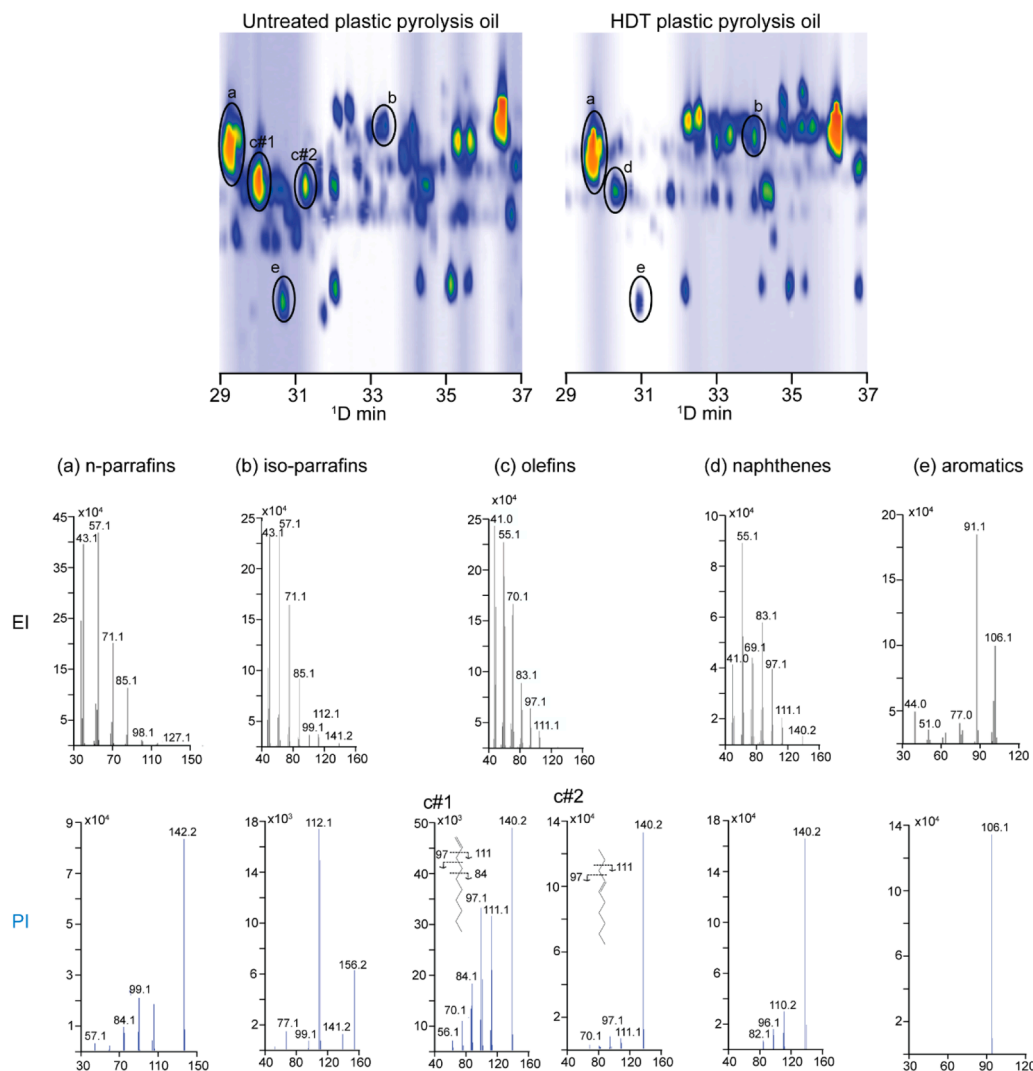


Fig. 3. Partially zoomed total ion chromatogram (TIC) of an untreated pyrolysis plastic oil and an HDT pyrolysis oil analyzed by GC×GC-EI/PI-TOF MS. Mass spectra comparison of EI vs PI for selected (a) C10 n-paraffins, (b) C11-isoparaffins, (c) and (d) C10-olefin congeners, (e) C10-naphthenes and (f) aromatics. For olefins, probable molecule structures and the breaking site are indicated.

complete separation is not achieved or longer carbon chains are targeted, making proper compound assignments difficult. On the other hand, naphthenes PI mass spectra are notably distinct from olefin ones.

Another pair of molecular isomers that can also be distinguished by PI spectra are the diolefins and naphthenes with an unsaturated carbon chain. Even though those compounds are not inside PIONA classification, their measurement in recycled plastic pyrolysis oil is of crucial importance to verify the upgrading processes' efficiency. In Fig. 1S (Support Information) is shown a comparative PI fragmentation for diolefins and naphthenes with unsaturated chains for a recycled plastic pyrolysis oil. As can be seen, the naphthenes species maintains a simplified spectrum with high intensity of the molecular ion and fragments corresponding to the ring with alkyl substitute, as in the examples of the fragments at m/z 96 and 110. Higher fragmentation is noted for diolefins due to the two double bonds, which increase the fragmentation pathways.

Aromatics spectra under hard ionization do not mismatch with other PIONA compounds thus PI fragmentation patterns have not introduced great advantages in the aromatics distinguishment compared to their EI fragmentation. Moreover, PI mass spectra often show only the molecular ion, which is also already in the EI mass spectra, as shown in Fig. 3e for the p-xylene.

Many differences were observed between the untreated and HDT

recycled plastic pyrolysis oil when PI spectra data were considered, the most notable being the spectra of the peaks in the region of the molecular ion at m/z 140, which was previously defined as olefins elution region. Fig. 4 highlights the PI spectra for each peak eluting in this region in both samples.

Initially, for untreated pyrolysis samples, PI spectra confirmed fragmentation patterns of olefins, peak #a is notable α -decene spectra, followed by peaks assigned as decene congeners, except the peak #e. However, for an HDT sample, a detailed evaluation of PI spectra revealed likely fragmentation patterns of naphthenes compounds. The simplified PI spectra with characteristics ring fragments at m/z 82, 96 and 110 were assigned as C10-alkylcyclohexane compounds. Peak #e has been also detected in the untreated pyrolysis oil and remained after upgrading processes while three other naphthenes compounds (peaks #g, #h and #i) have been enhanced. The increase of naphthene compounds in the HDT sample was expected since the upgrading processes using hydrogenation should also convert some olefins into saturated compounds, such as naphthenes.

The above insights on the structural identifications by PI spectra understanding were enough to distinguish among PIONA chemical classes, particularly in terms of olefin and naphthene classes, as proposed hereby. However, if a detailed compound identity is targeted a further in-depth PI spectra evaluation throughout the chromatogram

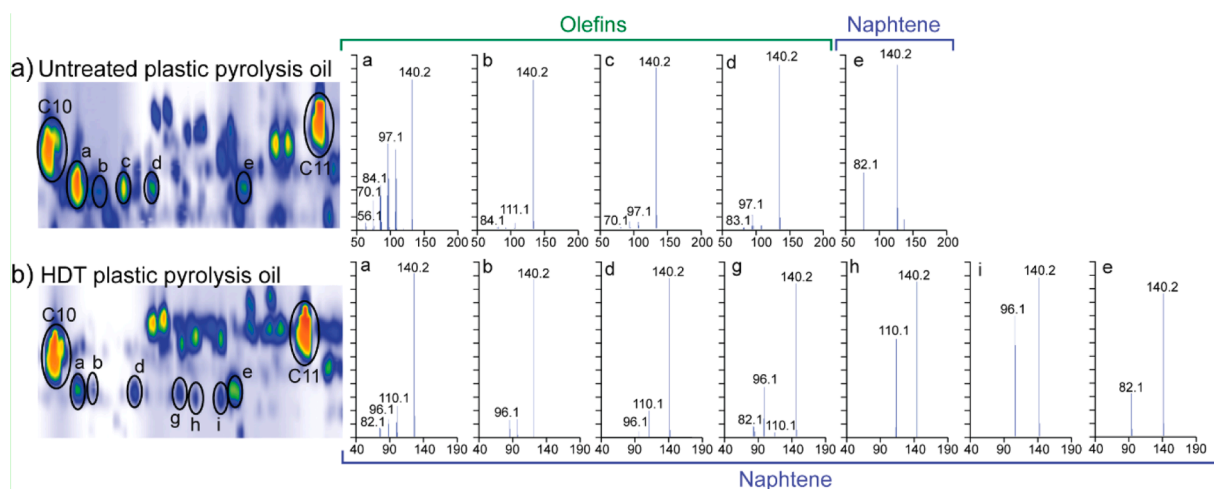


Fig. 4. PI mass spectra acquired by GC×GC-PI-MS for peak eluted in the region of molecular ion m/z 140 for the untreated and HDT samples.

will be needed, but it is out of the scope of this paper.

3.4. GC-VUV measurements

It is acknowledged that the VUV detector is a less well-established detection technique compared to mass spectrometers and flame ionization detectors. However, the focus of the GC-VUV measurement in this work was to obtain quantitative results for olefins to estimate the efficiency of the upgrading processes as well as combine information obtained using multiple techniques.

Fig. 5a shows the GC-VUV profile in a zoom region between C10 to C12 in the full spectra range 125–430 nm for both samples: untreated pyrolysis oil (blue line) and HDT sample (red line). Since compounds within the same chemical classes exhibit similar absorbance features, spectral filters (defined wavelength regions) were used to plot the relative abundance of the different chemical classes. Olefins and naphthenes show different absorption spectra making the VUV technique suitable to distinguish between analytes of both classes and confirming

the results obtained by PI spectra evaluation. For comparison purposes, two spectral filters are depicted in Fig. 5, (b) a 170–205 nm that responds preferentially to olefins compounds and a (c) 125–160 nm that responds to saturated hydrocarbons, including naphthenes. As these compounds respond at the same filter as other saturated hydrocarbons, the specific filter could not be used to naphthenes speciation. However, by applying the spectral filter from 170 to 205 nm, the decrease of olefin signals was significant in the HDT sample compared to its feedstock. For instance, the high peaks defined as α -olefins were not detected in the HDT sample. As can be seen in the reported VUV spectra the high-intensity peak assigned as C11 α -olefins show a typical olefins VUV spectrum with an absorption peak between 160 and 200 nm for the untreated sample (blue line) for the HDT (red line), otherwise, the peak show a very low intensity and the VUV spectra is not belong to olefins compounds.

Because the VUV library is not complete with all spectra for olefins, qualification and quantification can still be subject to significant error, however, GC-VUV results are still quite comparable to those from other

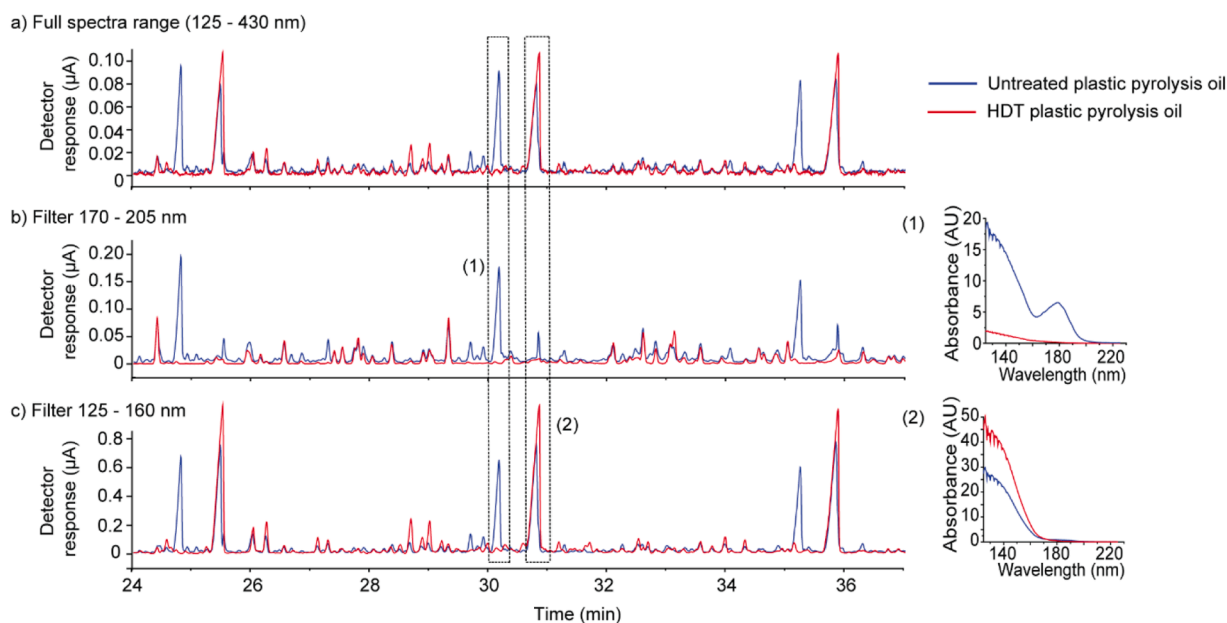


Fig. 5. (a) VUV chromatogram profile of a recycled pyrolysis plastic oil under full spectra range 125–430 nm. Zoom (C10-C12) chromatogram region with applied spectral filters of (b) 125–160 nm and (c) 170–205 nm for untreated pyrolysis oil (blue line) and HDT sample (red line). VUV spectra are also shown for high-lighted peaks.

measurements such as bromide Index analysis. It was determined 1.37 wt% of olefins in the HDT sample against 38 wt% in the untreated sample by bromide Index, while 1.3 wt% of olefins in an HDT and 36 wt% in an untreated sample were obtained using GC-VUV. For the uncertainty of the methods, the calculated RSD% was lower than 7 for both, the bromide index and GC-VUV method, which supports the comparison between results.

4. Conclusions

This study demonstrated the use of GC×GC-TOF MS with soft photoionization (PI) source in a reverse phase configuration for the qualitative screening of plastic pyrolysis oil. The fragmentation patterns observed in the current PI were successfully used for the distinguishment of the pair of isomers, olefins, and naphthenes in recycled plastic pyrolysis oil, despite the fact that such compounds were very close elutes in the 2D chromatographic separation space. A further GC-VUV methodology developed confirmed the results found by PI since PIONA compounds display different VUV spectra. The entire data setup helped in the challenge of differentiating naphthenes and olefins isomers in pyrolyzed plastic oil, as well as in its qualitative screening, and can be a good approach for tuning refinery processes to develop appropriate product quality for reintroducing in the market to sustain the economic circularity needs.

Credit authorship contribution statement

Eliane Lazzari: Methodology, Software, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Technical support, Conceptualization. **Laurence Levacher:** Software, Technical support. **Charlotte Mase:** Writing – original draft, Writing – review & editing, Technical support. **Marco Piparo:** Methodology, Investigation, Writing – review & editing, Technical support, Conceptualization, Project administration, Supervision, Resources. **Pierre-Hugues Stefanuto:** Software, Writing – review & editing, Technical support. **Giorgia Purcaro:** Methodology, Writing – review & editing, Technical support, Supervision. **Jean-François Focant:** Methodology, Writing – review & editing, Technical support, Supervision. **Pierre Giusti:** Methodology, Investigation, Writing – review & editing, Technical support, Conceptualization, Project administration, Supervision, Resources.

Declaration of Competing Interest

Authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

The data that has been used is confidential.

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Supporting Information S-1

Details on fragmentation patterns for a pair of molecular isomers, diolefins, and naphthenes with unsaturated carbon chains, using EI and PI. Fig. S1. Examples of comparative PI fragmentation patterns for diolefins and naphthenes with unsaturated carbon chain for a recycled

plastic pyrolysis oil: (a, c, e and g) are C14 and C15-diolefins, molecular ion at m/z 194 and m/z 208, respectively (b, d, f and h) are C14 and C15-naphthenes with unsaturated carbon chain, molecular ion at m/z 194 and m/z 208, respectively. Analysis has been carried out using a GC×GC-PI/EI-TOFMS with a conventional column setup.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jaap.2023.106224](https://doi.org/10.1016/j.jaap.2023.106224).

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