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Characterization of PP and PE Waste Pyrolysis Oils by Ultrahigh-Resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

Yannick Ureel, Martha L. Chacón-Patiño, Marvin Kusenberg, Ryan P. Rodgers, Maarten K. Sabbe, and Kevin M. Van Geem*

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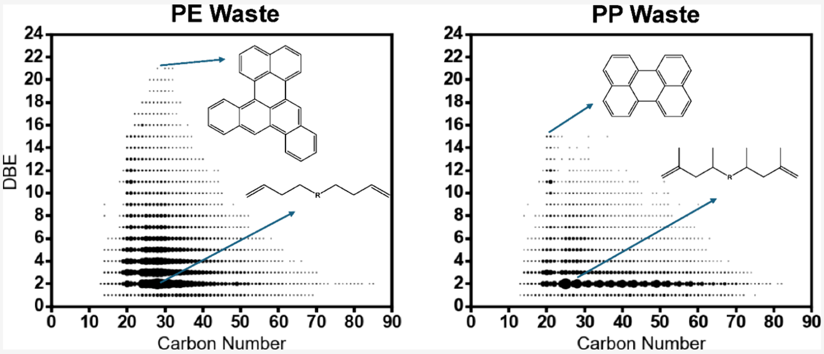

ABSTRACT: Increasing recycling rates of plastic waste is necessary to achieve a sustainable and climate-neutral chemical industry. For polyolefin waste, corresponding to 60% of plastic waste, chemical recycling via thermal pyrolysis is the most promising process. However, the hydrocarbon composition of these pyrolysis oils differs from conventional fossil-based feedstocks as they are heavier and more unsaturated. GC × GC-FID is the most prevalent characterization method for the analysis of these complex hydrocarbon mixtures but fails to discern heavy unsaturated, aromatic compounds. An up-and-coming technique to fully characterize those analytically challenging heavy fractions is ultrahigh-resolution Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) coupled with soft ionization techniques, such as atmospheric pressure photoionization and atmospheric pressure chemical ionization. In this work, FT-ICR MS has been employed to analyze both real PE and PP postconsumer waste pyrolysis oils, which allowed to provide additional insights into the pyrolysis reaction pathways of both polyolefin types. FT-ICR MS identifies heavy hydrocarbons, up to C_{85}, and discerns a wide range of complex polycyclic aromatic hydrocarbons with up to seven aromatic rings. These hepta-aromatics were not found in PP, which only revealed penta-aromatics; this complies with the reaction mechanism proposed in the literature. Moreover, the polypropylene (PP) pyrolysis oil displayed clear signs of depolymerization reactions occurring during pyrolysis, both for the formation of olefins and diolefins. Here, FT-ICR MS identified heavier, unsaturated, and highly aromatic hydrocarbons, whereas GC × GC-FID quantified saturated and less complex unsaturated components. These observations highlight the added benefit of combining GC × GC-FID and FT-ICR MS data to completely characterize plastic pyrolysis oils and understand pyrolysis reaction pathways.

1. INTRODUCTION

At present, 350 Mt/y plastics are produced worldwide and the current demand is expected to nearly double to 580 Mt/y the coming 30 years.[1] If this trend continues, plastics could be responsible for 15% of the global greenhouse gas emissions by 2050 (including scope 1, 2, and 3 emissions).[2] Therefore, the current linear plastic life cycle is both unsustainable and a threat to global warming. Plastic recycling, either mechanical or chemical, alleviates both issues and facilitates a sustainable circular plastic economy.[3] Around 42% of European plastics are mechanically recycled, whereas chemical recycling accounts for less than 1%, with most plastic waste still being incinerated or landfilled.[4] However, mechanical recycling has limitations regarding complex polymer waste mixtures, especially for polyolefins, which account for 60% of plastic waste, making chemical recycling necessary for this abundant waste stream. These polyolefin wastes, comprising a mixture of polyethylene

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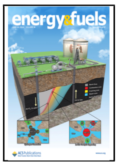


(PE) and polypropylene (PP), are currently challenging to mechanically recycle for three reasons.[5] The PE and PP fractions are nearly impossible to separate perfectly via sorting due to their similar properties (e.g., density), resulting in an inferior mechanically recycled polymer due to polymer immiscibility. Furthermore, every type of polyolefin contains different additives such as antioxidants, plasticizers, and stabilizers specifically tuned for their application.[6−8] Unfortunately, removing these additives before mechanical recycling is impossible, resulting in a complex blend of undesired additives in the recycled polymer. Last, mechanical recycling is typically performed at elevated temperatures, leading to thermomechanical degradation within the recycled polymer, which gradually diminishes mechanical properties throughout the recycling cycles. Therefore, it is essential to develop a chemical recycling option for polyolefin waste streams.[9−11]

One of the most promising processes for chemical recycling of plastic waste mixtures, especially polyolefins, is thermal or catalytic pyrolysis.[12−14] In thermal pyrolysis, the plastics are cracked into pyrolysis oils, which are then further refined downstream to plastic monomers by steam cracking or fluid catalytic cracking. It is estimated that the chemical recycling of plastics has a substantial emission reduction potential of around 1.87 tons of CO_2-equivalent per ton of recycled plastics, which is largely related to the avoided incineration.[15,16] However, large-scale industrial implementation of pyrolysis oils in the petrochemical production of polyolefins is still not developed to this day, which is mainly due to the complex composition of pyrolysis oils, which differ vastly from conventional crude oil feedstocks. The discrepancy between fossil-based feedstocks, for which large-scale industrial processes such as steam cracking are designed, and plastic waste pyrolysis oils makes it highly difficult for plant operators to predict the performance of pyrolysis oils. In fact, the value of the pyrolysis oils largely depends on their hydrocarbon composition as aromatic pyrolysis oils, for example, are typically less valuable for steam cracking plants. In fact, technical issues such as increased coke formation, which can result from higher concentrations of unsaturated compounds and aromatics, are among the main aspects that still hamper the large-scale implementation of pyrolysis oils into the petrochemical process systems. Therefore, proper characterization is the most important aspect in understanding and predicting the performance of those oils. Various analytical techniques have already been applied to analyze the composition of plastic pyrolysis oils.[17−19] One of the most powerful tools to determine the hydrocarbon composition is comprehensive two-dimensional gas chromatography (GC × GC), which can be coupled to various detectors. Detailed PIONA compositions (paraffins, isoparaffins, olefins, naphthenes, and aromatics) have been determined via GC × GC coupled to a flame ionization detector (GC × GC-FID), revealing the complexity of these hydrocarbon mixtures.[17,18,20] These analyses have shown that plastic pyrolysis oils have an increased fraction of (di)olefins and aromatics and span a wider carbon range than conventional fossil-based feedstocks.[17,20] In fact, the measured carbon range by GC × GC-FID can span up to C_{76}.[20,21] However, due to limited separation, polyaromatic components are typically not identified in detail and, therefore, lumped into groups of aromatics. Herewith, reversed-phase GC × GC-FID can be utilized by swapping the type of the first and second columns in a conventional comprehensive two-dimensional GC × GC to improve the second-dimension separation of the complex hydrocarbon matrix, improving detection of unsaturated hydrocarbons, aromatics, and heteroatomic components.[18,22] With reversed-phase GC × GC, the first dimension of separation is based on polarity, whereas the second-dimension medium polar column separates the polar compounds further. However, due to column capacities and temperature resistances of polar columns, the analytical accuracy of reversed-phase GC × GC is limited for heavy compounds up to a carbon number of around C_{26}.[22] Hence, ultrahigh-resolution mass spectrometry without prior gas chromatographic separation can be used to unravel the detailed composition of the heavy tail of pyrolysis oils, including polyaromatics, as no volatilization in the chromatographic columns is required.[23,24] Especially Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has proven efficient as it provides exceptionally high resolutions to determine the detailed molecular composition of the species present in complex mixtures.[25] The ultrahigh resolving power enabled by FT-ICR MS has its benefits for the analysis of high molecular weight compounds such as proteins[26] and ultra-complex samples like heavy crude oils,[27−29] asphaltenes, and bitumen.[30−36] For the analysis of pyrolysis oils, the use of FT-ICR-MS has been increasing over the past years, with a limited number of studies published to this day for plastic pyrolysis oils.[21,37−43] The main focus of these studies was mixed plastic waste or polyolefin mixtures, but also a polyethylene terephthalate oil has been studied.[42] Ware et al. analyzed a mixed plastic pyrolysis oil and compared its composition to those from biomass and landfill waste pyrolysis oils to understand the role of the starting material in the composition of the pyrolysis products.[21] Furthermore, in later work, the authors performed silica-gel fractionation to separate saturated, polar, and aromatic compounds for detailed identification.[39] The authors found a higher level of saturated hydrocarbons in plastic pyrolysis oils compared to the biomass and landfill waste pyrolysis oils. In another work, Hassibi et al. performed a 7-T FT-ICR MS analysis on a virgin PP pyrolysis oil to access the corresponding hydrocarbon composition and identified compounds up to C_{60}.[38] Similarly, Mase et al. investigated one mixed polyolefin pyrolysis oil with four different ionization techniques, identifying both complex hydrocarbons, oxygenates, and nitrogenates.[37] Recently, Mase et al. investigated the coupling of GC to FT-ICR MS with dopants to target the ionization of specific molecular families present in the pyrolysis oils.[41] However, no study has investigated the effect of the composition of the starting plastic material, for example, the content of PP and PE, on specific compositional trends of derived pyrolysis oils via FT-ICR MS. Moreover, the obtained results are linked with the reaction pathways occurring in thermal pyrolysis of polyolefin waste. This is crucial information to gain an understanding of the pyrolysis process itself and to be able to select the best processing methods depending on the waste composition.

The work herein presents the composition of two different plastic pyrolysis oils analyzed in detail by FT-ICR MS. These plastic pyrolysis oils stem from two sorted postconsumer waste samples either consisting mainly of PE and PP and have been previously characterized by GC × GC-FID.[20] Ultrahigh resolution 21-T FT-ICR MS coupled with positive-ion atmospheric pressure photoionization [(+)APPI] is used to determine the exact molecular mass for thousands of ions, which get assigned unique molecular formulas based on mass

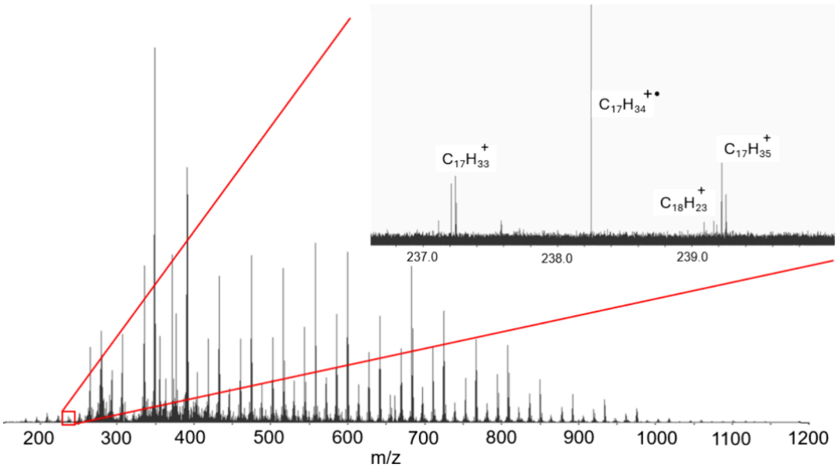


Figure 1. Raw mass spectrum of the PE waste pyrolysis oil obtained by (+)APPI FT-ICR MS and enlargement of 237−239 nominal mass.

accuracy.[44] (+)APPI is excellent for identifying the hydrocarbon matrix as it provides more uniform ionization than other ion sources, such as electrospray ionization.[25,45−47] Moreover, APPI ionization has been demonstrated to be suitable for the characterization of olefin model compounds, showing no indication of decomposition or rearrangement during the ionization process.[48,49] However, (+)APPI is not well suited for the ionization of hydrocarbons with lower aromaticity. Therefore, atmospheric pressure chemical ionization [(+)APCI] is also used. The combination of the quantitative GC × GC-FID and qualitative FT-ICR MS is shown to complement one another, providing a comprehensive view of the molecular composition of plastic pyrolysis oils. Thus, this work aims to highlight the application of FT-ICR MS for the identification of complex hydrocarbons in plastic pyrolysis oils and link this knowledge to the pyrolysis mechanism. Due to the record-high resolution of the applied FT-ICR MS, we could identify the molecular composition of the heavy fraction (C_{13+}) of the pyrolysis oils, which allowed us to discern the molecular composition of PE and PP pyrolysis oils at an unprecedented level of detail and provide additional insights in the pyrolysis mechanism.

2. MATERIALS AND METHODOLOGY

2.1. Materials. Two different sorted postconsumer plastic waste blends were obtained from the recycling company Ecoo (Belgium). These blends are a PP blend predominantly consisting of rigid PP and a PE film mixture. The two sorted postconsumer plastic waste fractions were pyrolyzed in earlier work, where more information on their origin and production process can be found.[20] These blends are representative products of the current state-of-the-art plastic waste sorting and separation schemes in Europe as they went through the real-life preprocessing steps, including shredding, washing, drying, and sorting, among others. Both polyolefin blends contain traces of other (polyolefin) polymers due to imperfect sorting and (in)organic residue accumulated during the usage of these plastics.

Both plastic blends have been thermally pyrolyzed in a pilot-scale pyrolysis unit as reported in detail by Kusenberg et al.[20] The pyrolysis was carried out in a heated continuously stirred tank reactor (CSTR) at a constant feeding rate of 1 kg/h and at 450 °C and atmospheric pressure. Further details on the pilot-scale pyrolysis unit can be found in the literature.[20]

The PE and PP pyrolysis oils are of waxy quality with melting points of around 80 °C and have been previously characterized by CHNS/O elemental analysis and normal-phase comprehensive two-dimensional GC × GC-FID.[20]

2.2. 21-T FT-ICR MS. Before the analysis, the plastic pyrolysis oils were dissolved in a 1:1-volumetric ratio toluene:methanol solution at a 50 μg/mL concentration. Methanol was required to fully dissolve polar species (O-containing compounds) present in the postconsumer plastic pyrolysis oil and ensure a proper operation of the ion sources that were used for FT-ICR MS. A Thermo-Fisher Ion Max APPI source (Thermo-Fisher Scientific, Inc., San Jose, CA, U.S.A.) was operated with a vaporizer temperature of 350 °C. N_2 sheath gas was used at 3.44 bar, and N_2 auxiliary gas (32 mL min^{-1}) helped prevent sample oxidation. Gas-phase neutrals were photoionized by a 10 eV (120 nm) ultraviolet krypton lamp (Syagen Technology, Inc., Tustin, CA, U.S.A.). Ions were analyzed with a custom-built 21-T FT-ICR mass spectrometer.[44] For analysis, 2×10^6 charges were accumulated for ~1−5 ms in an external multipole ion trap equipped with automatic gain control (AGC).[50] Ion depletion, a method for mass filtering or gas-phase depletion of contaminant ions, was employed to enhance the signal-to-noise ratio by dampening the abundance of species with a mass-to-charge ratio (m/z) between 306 and 334 Da due to an unknown impurity in the samples as will be discussed further in Section 3.[51] Ions were transferred to the ICR cell as a function of m/z and then excited to a m/z-dependent radius to maximize the dynamic range and number of detected peaks. Excitation and detection were performed on the same pair of electrodes of the dynamically harmonized ICR, operated with 6 V trapping potential. Time-domain transients of 3.2 s were acquired with Predator Software, and 100 time-domain transients were averaged for all the samples. Spectra were internally calibrated from an extended homologous alkylation series of high relative abundance before peak detection (>6σ baseline root-mean-square (RMS) noise) and automated elemental composition assignment. These homologous series included but were not limited to the series with DBEs of 0, 1, 2, and 4 as these span a wide mass range. PetroOrg software assisted molecular formula calculation and data visualization in plots of double bond equivalent (DBE) vs carbon number. The DBE is defined by eq 1 and represents the number of double bonds and cyclic rings for hydrocarbons, with C denoting the number of carbon atoms and H the number of hydrogen atoms.

$$\mathrm{DBE} = C - \frac{H}{2} + 1 \tag{1}$$

Only molecular formulas with an error below ~0.10 ppm were kept for data interpretation. In addition to APPI, (+)APCI was carried out with a vaporizer temperature of 325 °C, a corona discharge of 4.5 mA, and sample dissolution in a mixture of toluene/methanol/heptane (5/5/1). The results of (+)APCI are presented in the Supporting Information (Section S2).

3. RESULTS AND DISCUSSION

3.1. (+)APPI FT-ICR MS. The obtained raw mass spectra of the PE pyrolysis oil are presented in Figure 1. FT-ICR MS provides the exact mass with ultrahigh accuracy, which allows to identify their molecular formula. Hydrocarbons (HCs) reveal the highest relative abundance of the compounds that were identified within both pyrolysis oils by (+)APPI FT-ICR MS, corresponding to 82.6 and 73.0% in relative abundance for the waste PE oil and PP oil, respectively, as shown in Figure 2.

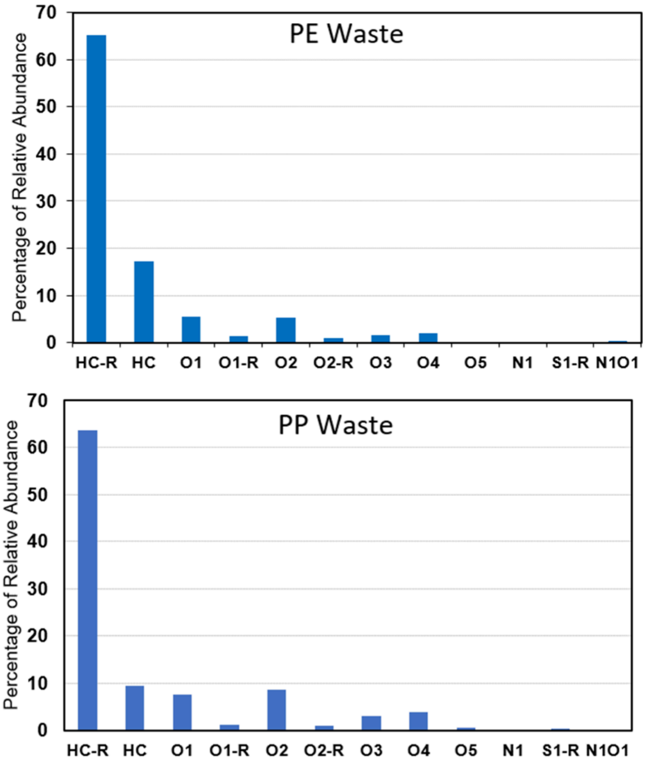


Figure 2. Class distribution with the percentage of relative abundances depicting hydrocarbons (HCs); radical ions denoted by (R).

The rest of the identified compounds are mainly oxygenates and a very small share of nitrogen- and sulfur-containing species, which account for less than 0.3% of the total ion abundance. The scope of this work is to discuss the benefit of FT-ICR MS for the identification of complex hydrocarbons in plastic pyrolysis oils and link this knowledge to the pyrolysis mechanism. Therefore, the composition of the oxygenates is not discussed here.

Analysis by (+)APPI FT-ICR MS provides a compositional coverage of the molecular complexity of the heavy hydrocarbons in both pyrolysis oils than GC × GC. It should be noted that hydrocarbons with a molecular weight below 180 Da (corresponding to C_1−C_{12}) were not detected, given the transfer ion conditions in the 21T FT-ICR mass spectrometer.[44] Of all peaks detected by (+)APPI FT-ICR MS, ∼ 98% of the abundance was assigned with a root mean squared error (RMSE) between the theoretical and experimental mass of 0.033 ppm. The exceptionally low RMSE and high assignment rate demonstrate the suitability of (+)APPI FT-ICR MS for the analysis of these complex hydrocarbon mixtures and the accuracy of the processing of the experimental data. The detailed error distributions on the mass assignment for both pyrolysis oils can be found in the Supporting Information in Figures S1 and S2.

Figure 3 displays the DBE versus carbon number plot of the hydrocarbons detected by FT-ICR MS for both the PE and PP waste pyrolysis oils. The area of the dots represents the relative abundance of each molecular formula, which is normalized within each plot. The figures display the detected hydrocarbon ions with an odd electron number (corresponding to radical ions) and even electron number (protonated molecules) in both feeds. With (+)APPI, the dominant hydrocarbon species are odd-electron ions, which corresponds to 87% in PP and 79% in PE. The elevated relative abundance of radical cations is due to the mechanism of the ionization method, which predominantly produces radicals. The share of radical ions and even-electron ions is also sample-dependent, where the dominance of radical cations is indicative of low proton affinities of the gas phase species.[36]

Figure 3 reveals a dip in relative abundance between C_{21} and C_{24} resulting from the mass filter required to optimize the signal-to-noise ratio of the ions of interest and decrease that of common contaminant peaks detected in APPI, as previously mentioned in Section 2. A potential contaminant in this *m*/*z* range is a highly abundant peak with a mass of around 322 Da, which causes significant ion suppression. The analysis by FT-ICR MS provides a better perspective on the complexity of the hydrocarbons in the heavy tail of the oils, which is highly difficult to analyze using GC × GC. Heavy hydrocarbons have been detected up to C_{82} for PP and C_{85} for PE. Moreover, the detected hydrocarbons are heavier than those reported in previous works, which typically reached carbon numbers of C_{60}−C_{70},[37,38] which is likely due to the superior performance of the 21-T FT-ICR mass spectrometer. Moreover, the results revealed a wide range of DBEs compared to conventional hydrocarbon feeds, which highlights the complexity of the unsaturated hydrocarbons. Specifically, compounds are detected at DBEs ranging from 1 to 15 for PP and 1 to 21 for PE.

The radical cations featured a much wider range in both carbon number and DBE than the protonated species. The most abundant molecular formulas have a DBE of 2 and odd-electron configurations and likely correspond to diolefins, which are discussed later. For the even-electron ions, the dominant DBE is 3, which could correspond to triolefins or cyclic diolefins. This difference between odd- and even-electron configurations in plastic pyrolysis oils has also been observed by Mase et al., who observed a peak of odd-electron configurations at a DBE of 2 and even-electron ions at a DBE of 3.[37]

Table 1 presents the molecular classes that correspond to prevalent DBE numbers along with a tentative molecular structure for a better understanding of the compounds that were detected. The lowest DBE, 0, comprises fully saturated hydrocarbons, which are paraffins. Only a limited amount of paraffins is detected by (+)APPI FT-ICR MS, as this ionization method targets unsaturated and aromatic hydrocarbons and is less selective toward saturated species.[52] Generally, (+)APCI facilitates the ionization of saturated hydrocarbons. However, in this work, only hydrocarbon ions with a DBE higher than 3 were observed in APCI (see the Supporting Information, Section S2), likely because of the use of both methanol and toluene as solvents to fully dissolve the samples and avoid aggregation during ionization. These findings suggest that the ionization of saturated hydrocarbons in plastic pyrolysis oils via (+)APCI is suppressed by combining both polar and apolar

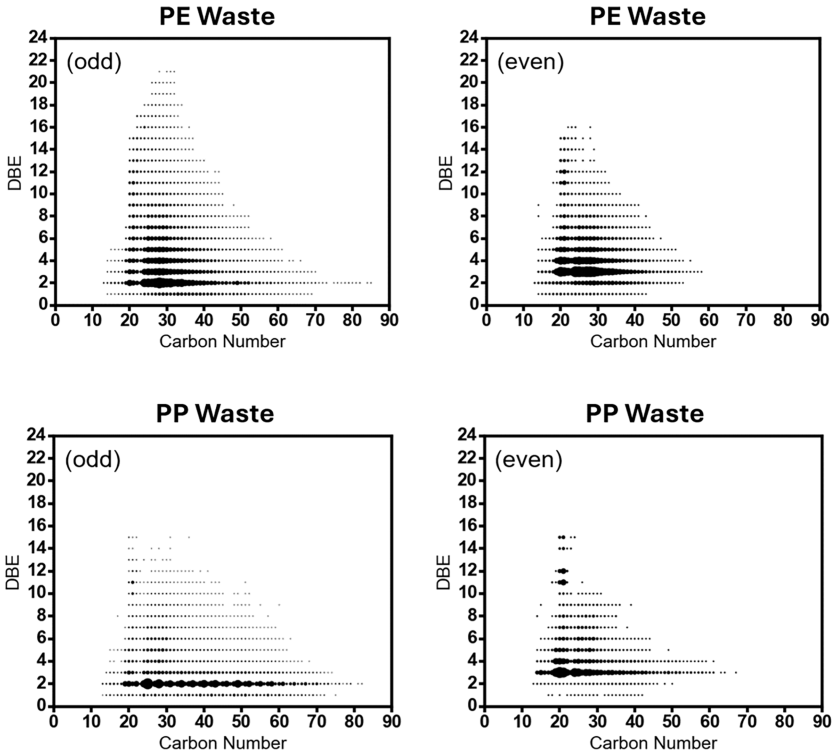


Figure 3. Carbon number vs DBE plot for the hydrocarbons in PE (top) and PP (bottom) waste pyrolysis oil with odd-electron ions (left) and even-electron ions (right) for (+)APPI FT-ICR MS. The area of the dots is proportional to the relative abundance of the respective molecular formula.

solvents. A DBE of 1 could correspond to two molecular classes, namely, olefins and cycloalkanes. From GC × GC-FID, it is known that olefins are dominant in the plastic pyrolysis oils, especially for PP, making it likely that olefins are the dominant class for a DBE of 1. Next, diolefins, alkynes, cycloalkenes, and dicycloalkanes are represented by a DBE of 2. For PP, diolefins are definitely the prevalent compound family as found by GC × GC-FID, while for the PE pyrolysis oil, both classes are presented as 4.3 wt % diolefins and 11.6 wt % naphthenes (cycloalkanes and cycloalkenes).[20] Alkynes are not expected to be present in plastic pyrolysis oils as they require hydrogen abstraction of a double bond followed by a C−H β-scission. However, hydrogen abstraction on the double bond results in an intermediate radical, which is 102 kJ mol^{-1} more unstable in the gas phase than when the neighboring carbon atom would be a radical.[53] The absence of alkynes in plastic pyrolysis oils has been confirmed by Fourier-transform infrared spectroscopy.[54]

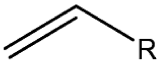
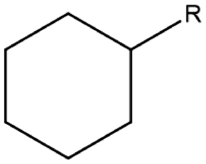
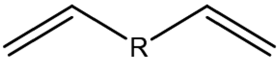
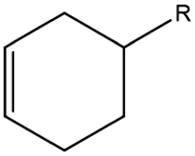
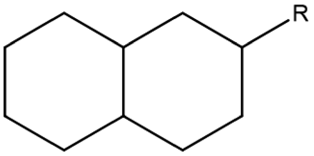
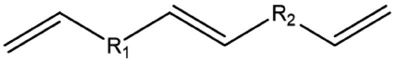
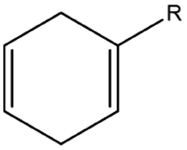
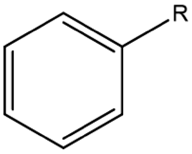
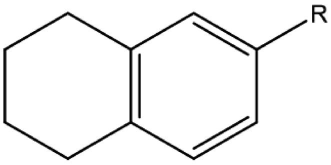
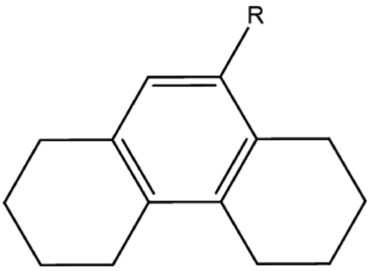
The next DBE of 3 consists of triolefins, cycloalkadienes, or three naphthenic cycles. Again, PP is less likely to contain a significant fraction of cycloalkadienes and three naphthenic cycles due to the suppressed rate of cyclization reactions, while for PE, no definitive conclusion can be made.[20] The existence of triolefins in plastic pyrolysis oils has not been shown by GC × GC-FID analysis as either their concentration is below the limit of detection or they have been misidentified. This demonstrates the power of (+)APPI FT-ICR MS in elucidating the complexity of the unsaturated hydrocarbons.

Potential triolefins can be produced when the polymer chain is branched, as indicated by Figure 4. These polymer side chains exist within most polymers either as a defect (in a limited amount) or by design (for low-density polyethylene or linear low-density polyethylene).[55] The tertiary radical (a) serves as the reactant for the subsequent β-scission, resulting in the removal of the polymer side chain. The tertiary radical is considerably more stable than its secondary counterpart, resulting in an elevated concentration of these species.[53] Especially within polyethylene, this effect will be pronounced because of its linear nature; nevertheless, in polypropylene, this tertiary radical is also further stabilized by inductive stabilization of the long side chain. This results in the production of (b) a polymer chain with an unsaturated bond in the middle of the structure. Subsequently, when the polymer further depolymerizes via the same process of intermolecular hydrogen abstraction and β-scission, instead of a regular diolefin, a triolefin (c) is produced. Besides depolymerization, structure (b) could form resonance-stabilized radicals with a hydrogen abstraction on the carbon atoms in positions R_1 and R_2. These resonance-stabilized radicals can form triolefins with internal double bonds instead of end-chain double bonds after a C−H β-scission.

At a DBE of 4, monoaromatics, various combinations of (un)saturated naphthenes, and tetra-olefins are the potential molecular classes, where the monoaromatics are expected to be the dominant fraction in both pyrolysis oils as observed by GC-analysis.[12] For DBEs of 5 and 6, naphthenoaromatics and dinaphthenoaromatics are respectively the most commonly expected structures, in addition to a wide range of more complex combinations of aromatic, cyclic, and unsaturated groups.

The relative abundances detected for the PE and PP waste pyrolysis oils show three clear differences (Figure 3). The first difference is the presence of more complex polyaromatics, indicated by 11 species with a DBE higher than 20 in the PE waste pyrolysis oil compared to the corresponding PP fraction. The tendency of PE to form more aromatics upon thermal

Table 1. Illustrative Hydrocarbon Structures for Different Double Bond Equivalent (DBE) Values

DBE	Molecular structure
1	 *olefins*  *cycloalkanes*
2	 *diolefins*  *cycloalkenes*  *dicycloalkanes*
3	 *triolefins*  *cycloalkadienes*
4	 *mono-aromatics*
5	 *naphthenoaromatics*
6	 *dinaphthenoaromatics*

pyrolysis is a well-known behavior in the literature. These aromatics are, according to the literature, formed via a cyclization reaction of olefins and diolefins, leading to the formation of naphthenes (i.e., via Diels–Alder reactions), which react further to form aromatics.[56] In turn, these aromatics form more complex polyaromatic structures (coke precursors), leading to pyrolytic coke formation.[57−59] The pyrolysis of PP results in the formation of more branched hydrocarbons, such as iso-olefins as quantified by various GC analyses.[12] These branched compounds sterically hinder the

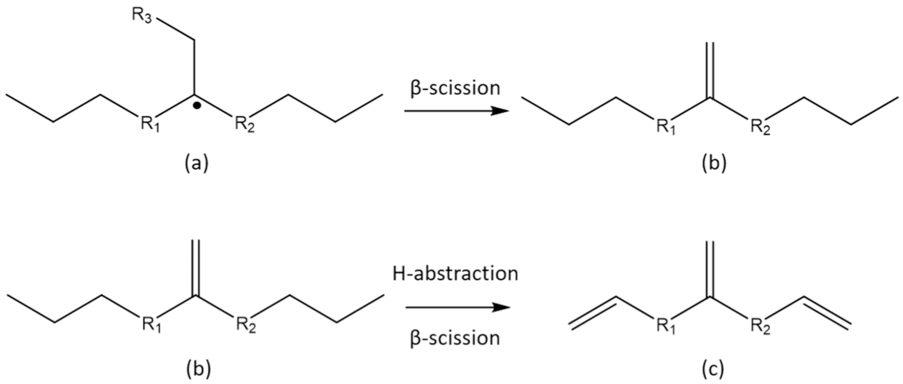


Figure 4. Illustrative reaction mechanism for the formation of triolefins during thermal pyrolysis of polyolefins.

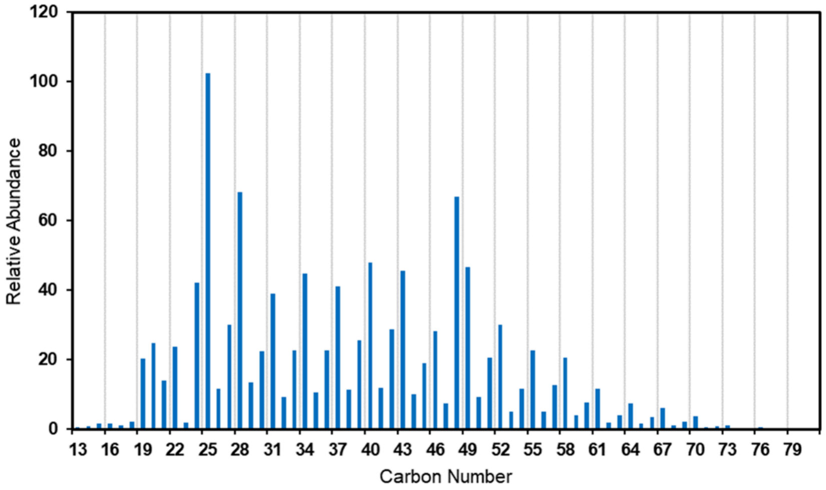


Figure 5. Relative abundance at different carbon numbers of even- and odd-electron ion hydrocarbons.

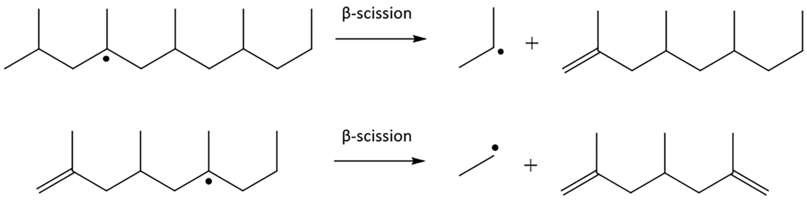


Figure 6. Illustrative reaction mechanism for the formation of iso-olefins and diolefins in PP pyrolysis.

cyclization reaction between olefins and diolefins, suppressing the formation of naphthenes and aromatics.

The second difference between both hydrocarbon mixtures is the variation in abundance across different DBEs. For the postconsumer waste PE oil, the highest abundance is observed for the homologous series with a DBE of 2 (diolefins and cycloalkenes), with more uniform abundances across the other DBEs. In contrast, for PP, a prominent peak in abundance is found for the DBE of 2, whereas all other DBEs were found to be present at a much lower extent. As previously mentioned, PE pyrolysis oils contain more aromatics and naphthenes, resulting in an elevated presence of species with a DBE of minimally 2.[20,60] Additionally, PP pyrolysis is known to give rise to a significant fraction of diolefins due to the higher share of tertiary carbon atoms compared to PE. These tertiary radicals are more stable than their secondary counterparts, resulting in more cracking reactions. These diolefins comprise 19.5 wt % PP waste pyrolysis oil according to GC × GC-FID, resulting in a peak at a DBE of 2 for this pyrolysis oil.[20] This observation confirms the substantial difference in the pyrolysis chemistry of PP and PE. The fact that PP pyrolysis leads to mainly branched olefins and diolefins, which are then less likely to react further toward cyclic products via Diels–Alder reactions due to steric hindrance, is confirmed by the significantly lower distribution of DBE compared to PE.[61,62]

A last difference between both postconsumer polyolefin pyrolysis oils is the share of depolymerization during thermal pyrolysis. The olefins and diolefins in PP waste pyrolysis oil show a clear trend with carbon number, where a high abundance is observed with repeating units of three carbons as illustrated in Figure 5. This is clearly an effect of PP depolymerizing into oligomers of propylene. This trend in carbon number is a consequence of the stability of a more stable tertiary radical in PP pyrolysis (as indicated in Figure 6) compared to a less stable secondary radical in PE, making it a less favorable pathway for the latter and leading to a more random decomposition of the PE polymer chain.[55,63] The effect is well known for the formation of olefins and is known to result in propylene oligomers being C_3, C_6, C_9, ..., C_{3n}. However, with FT-ICR MS, this effect is also detected for diolefins, which to the best of our knowledge, has not been explained before on a mechanistic level. The increased abundance observed for diolefins displays the same pattern of repeating units of three carbon atoms but with a shift in carbon number being C_{22}, C_{25}, C_{28}, ..., C_{3n-2}. The shift in peaks for the carbon number between olefins and diolefins results from the further depolymerization by β-scissions of the formed iso-olefins, as illustrated in Figure 6. Due to the scission reaction, an ethyl radical is produced, which can dehydrogenate with ethylene formation; this produces an α,ω-diolefin with a chain length two carbon atoms shorter than the original olefin. This reaction mechanism for PP pyrolysis explains the clear trend in carbon number for both olefins and diolefins.

One advantage of FT-ICR MS compared to GC × GC-FID is that very heavy complex aromatic structures can be identified. For the PE waste pyrolysis oil, the most unsaturated compound observed was $C_{28}H_{16}$, which is most likely a hepta-aromatic compound such as dibenzoperylene, for which the tentative molecular structure is provided in Figure 7. It should be stressed that this molecular structure is a potential structure of the compound observed and the exact connection of the aromatic rings can differ, as mass spectrometry allows to identify the molecular formula but not its structure. However, $C_{28}H_{16}$ is definitely a complex aromatic and coke precursor formed during PE waste pyrolysis. Other FT-ICR MS studies with plastic pyrolysis oils identified similar PAHs, with the most complex structures corresponding to hepta-aromatics.[37,39] This is remarkable as those plastic pyrolysis oils stem from different sources either being a mix of PE and PP or a complex blend of postconsumer waste. This indicates that polyaromatics ranging from octa-aromatics and onward end up in the solid char phase and will not be present in the liquid pyrolysis oils. Ware et al. investigated a complex blend of postconsumer waste with unknown composition and observed heavier PAHs than the polyolefin oils characterized in this work. They observed hepta-aromatics with up to 50 carbon atoms, while here the heaviest carbon number was 33.[39] This is likely due to the presence of a large share of aromatic polymers such as PET or PS in the pyrolyzed plastics of Ware et al.

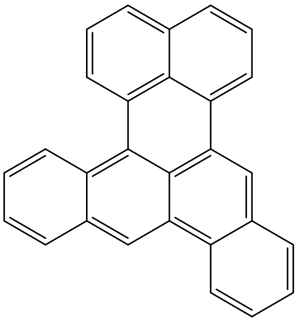


Figure 7. Molecular structure of dibenzoperylene ($C_{28}H_{16}$).

FT-ICR MS allows differentiation between hydrocarbons with varying DBE, as displayed in Figure 3. Here, a peak in relative abundance at a DBE of 11−12 and a carbon number of 21 is found in both the PE and PP waste pyrolysis oils. While the increase in relative abundance is not exaggerated, this discontinuity is unexpected within the plastic pyrolysis oils as, normally, a Gaussian-like distribution is expected. This shows the benefit of FT-ICR MS in identifying detailed patterns in the plastic pyrolysis oils. Three hypotheses can be formulated to explain the origin of this peak. First, it might be due to an increased ionization efficiency of these specific compounds, but this is unlikely as the peak does not vary in carbon number. If these compounds were easier to ionize, adding a methyl substituent would change little the ionization efficiency, resulting in an increased abundance at carbon number of, for instance, 22, which is not observed. Second, the increased thermodynamic stability of these compounds might increase the selectivity toward these species upon thermal pyrolysis. Last, these molecules can stem from polymer additives or contaminants breaking down during pyrolysis. However, further investigation is required to elucidate the exact cause of this increased fraction.

The DBE vs carbon number plot of Figure 3 displays a pyramid-like shape for the detected hydrocarbons. At high DBE and high carbon numbers, no compounds are observed in the plastic pyrolysis oil as the melting point of the compounds is reached. Therefore, these species remain in the thermal pyrolysis oil's solid residue (char). The hydrocarbons in the pyrolysis oil show a clear trend as the highest carbon number detected for a given DBE value decreases with increasing DBE. This pyramid shape in hydrocarbon composition is similar to the DBE vs carbon number plot for fossil sources such as heavy crude oils or asphaltenes, as found in the literature.[45,64] However, these crude oils predominantly consist of aromatics and contain nearly no olefins as opposed to pyrolysis oils.

3.2. Complementarity of FT-ICR MS and GC × GC-FID.

One of the most used analytical methods for determining the composition of complex hydrocarbon mixtures is GC × GC-FID. The results of the GC × GC-FID analysis were previously presented by Kusenberg et al., and they are briefly discussed here.[20] Further information on the GC × GC-FID analysis and a detailed PIONA analysis can be found in the Supporting Information. The studied PE and PP waste pyrolysis oils spanned a wide range between C_5 and C_{76} by normal-phase GC × GC-FID analysis.

These observations comply with trends found in the literature as PE pyrolysis oils consist primarily of *n*-paraffins and α-olefins, while PP pyrolysis oils consist of iso-olefins and branched diolefins, with a limited share of naphthenes and aromatics (see Table 2). As PE is a linear polymer, it predominantly depolymerizes into linear products, while the branched PP correspondingly results in more branched iso-olefins and diolefins. GC × GC-FID spectra typically allow excellent differentiation up to C_{15}, after which separating the complex mixture of linear and branched paraffins and (di)olefins and naphthenes becomes increasingly challenging. Furthermore, GC × GC methods and column combinations

Table 2. PIONA Analysis of PE and PP Waste Pyrolysis Oils Obtained by GC × GC-FID[20]

	PE waste pyrolysis oil	PP waste pyrolysis oil
n-paraffins	34.4	3.1
isoparaffins	6.5	4.7
α-olefins	25.5	6.0
iso-olefins	13.8	62.7
diolefins	4.3	19.5
naphthenes	11.6	3.0
aromatics	3.9	1.0

must be selected to focus on a particular aspect of the composition. While it is crucial to separate aliphatic components to analyze polyolefin pyrolysis oils properly, cyclics are typically less well separated when using a typical nonpolar × polar combination. While separation of complex aromatics is theoretically possible using GC × GC, there is always a trade-off between the respective analytical capacities of the different selected GC columns and their combination for the different hydrocarbon compound families. For instance, in previous work, aromatics were only identified up to diaromatics with GC × GC-FID.[20] Notably, while high-temperature columns increase the observed carbon number range up to C_{76}, it is challenging to elute components with even higher boiling points (>400 °C), and especially, the very heavy tail of such pyrolysis oils is difficult to characterize without the extensive use of lumping or even without cutting off a portion of the heavy tail when it is outside the temperature limit of the utilized columns. Hence, GC × GC-FID is ideal for the detailed analysis of (heavy) distilled fractions of pyrolysis oils, including detailed quantification of aliphatic components up to a final boiling point of around 400 °C, and indeed limited for crude pyrolysis oils, which are in a waxy solid state at room temperatures. This is even more the case for reversed-phase GC × GC, which, on the one hand, shows a superior second-dimension separation of saturated and unsaturated hydrocarbons and even heteroatomic components but, on the other hand, is even more limited toward very heavy-boiling hydrocarbon mixtures due to the lower thermal stability of polar first-dimension columns such as Megawax or Stabilwax.[17,18,22] These columns can be operated up to 260−300 °C, corresponding to the boiling point of heptadecane (303 °C).[65] Hence, these polar columns are not applicable to investigate the heavy fraction of pyrolysis oils above C_{17}, as reported by Toraman et al.[17] To design effective post-treatment techniques of pyrolysis oils to close the gap toward industrial steam crackers, this last element of uncertainty, i.e., the detailed composition of the heaviest boiling fractions, needs to be unraveled.

At this point, it is clear that both FT-ICR MS and GC × GC-FID yield valuable information for analyzing plastic pyrolysis oils, however, with vastly different focus points and strengths. Figure 8 displays the results of GC × GC-FID and (+)APPI FT-ICR MS for both postconsumer waste pyrolysis oils. The area of the dots is proportional to the abundance of the detected molecular class with the abundance scaled to 100 to improve the comparability of both data sets. It is clear that both techniques investigate different areas of the hydrocarbon composition. GC × GC-FID is excellent for obtaining a detailed molecular composition of low carbon numbers (C_5−C_{20}). Furthermore, GC × GC-FID allows to elute heavy components even up to C_{76} for the PP pyrolysis oil. However, it becomes challenging to discern between different molecular classes such as paraffins, olefins, and naphthenes for those compounds. Furthermore, detailed identification of different classes of aromatics remains somewhat vague, leading to lumped groups.

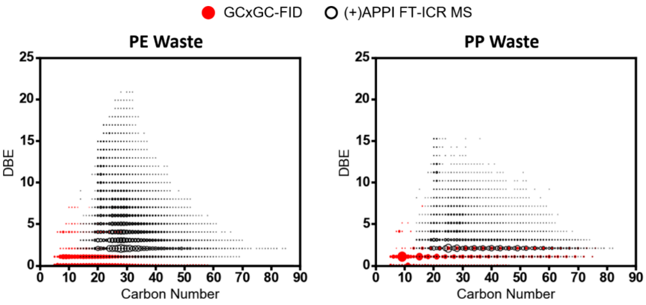


Figure 8. Carbon number vs DBE plot for the PE waste pyrolysis oil (left) and PP waste pyrolysis oil (right) for GC × GC-FID (red) and (+)APPI FT-ICR MS (black). The area of the dots is proportional to the abundance of the respective molecular formula for FT-ICR MS and GC × GC-FID.

On the other hand, FT-ICR MS allows the identification of heavier fractions up to C_{85} but fails to detect light compounds (<C_{13}), given the ion transfer conditions of the used instrument. Therefore, GC × GC-FID is excellent for detecting saturated components, while (+)APPI FT-ICR MS is more sensitive to unsaturated and highly aromatic hydrocarbons.[66] In fact, FT-ICR MS allows to differentiate between the different complex unsaturated hydrocarbons and can identify the molecular formula of PAHs, which is a clear advancement of the state of the art in terms of pyrolysis oil characterization. With FT-ICR MS, complex aromatics have been observed up to hepta-aromatics, whereas GC × GC-FID has only identified diaromatics at most. This is caused by two effects, namely, the higher limit of detection in GC × GC-FID for those very complex polyaromatic structures compared to FT-ICR MS and the high boiling point of polyaromatics such as hepta-aromatics, which are more challenging to elute through GC columns commercially available. Especially for high molecular weights, FT-ICR MS surmounts the capability of GC × GC-FID in differentiating between different DBEs. The last difference is that GC × GC-FID is a quantitative method, while FT-ICR MS is at best a semiquantitative approach, allowing one to identify trends in abundance between different species. This semiquantitative nature of (+)APPI FT-ICR MS is demonstrated by its selectivity toward the ionization of aromatic and unsaturated compounds, while paraffins are more difficult to ionize and hence detect. Furthermore, from the FT-ICR MS results in Figure 8, one would claim that most of the compounds detected in both PE and PP pyrolysis oils are compounds with a DBE of 2 (diolefins, cycloalkenes, or dicycloalkanes). However, the quantitative GC × GC-FID data shed light on this as olefins and paraffins are found to be more prevalent. Ideally, one would be able to integrate the results of both methodologies to acquire a complete image of the plastic pyrolysis oils and the quantities of all compounds. However, due to the different ionization selectivities of different hydrocarbons depending on their functionality and size, FT-ICR MS is only semiquantitative. As there is only a limited overlap between FT-ICR MS and GC × GC-FID, it is currently impossible to discern the ionization selectivities of FT-ICR MS to allow full quantification based on both methods.

It is clear that both analytical methodologies have their advantages and disadvantages. GC × GC-FID is one of the workhorses in petrochemistry and provides essential information such as PIONA composition and a detailed hydrocarbon composition up to C_{20}, after which it increasingly relies on lumping components into groups. However, plastic pyrolysis oils pose a challenge as they contain high molecular weight compounds and a complex mixture of unsaturated (aromatic) hydrocarbons that are difficult to discern with GC × GC-FID. Here, (+)APPI FT-ICR MS is a perfect alternative for these challenges as it focuses on heavy species (C_{13}−C_{85} in this work) and allows to differentiate between complex aromatic molecular formulas. However, FT-ICR MS requires a proper GC × GC-FID analysis to put results into perspective as mass spectrometry cannot quantify components and fails to detect low molecular weight components (based on the configuration of the FT-ICR mass spectrometer). In essence, both analytical methods are perfectly complementary in the sense of both carbon number (low for GC × GC-FID and high for FT-ICR MS) and DBE (paraffin detection for GC × GC-FID and complex aromatics for FT-ICR MS) for plastic pyrolysis oils. Despite the benefits of combining GC × GC-FID and FT-ICR MS, there are still questions unaddressed by the combination of both techniques. One of these is the overlap between naphthenes and olefins in both techniques requiring additional analytical approaches to resolve this. A potential solution for this can be the use of a GC and a vacuum ultraviolet detector, which can quantify both olefins and naphthenes.[67,68] Nevertheless, it can be stated that a combination of both is needed to unravel the complex composition of real waste pyrolysis oils, which is an essential prerequisite for the design of upgrading techniques to improve the suitability in subsequent (petro-)chemical processes such as steam cracking.

4. CONCLUSIONS

Both postconsumer PE and PP pyrolysis oils have been analyzed by (+)APPI FT-ICR MS, and the observed trends were related to the pyrolysis mechanism. In this work, molecules up to C_{85} have been observed in real postconsumer plastic waste pyrolysis oils using FT-ICR MS, enabling the distinction between complex aromatics and triolefins. With FT-ICR MS, an increased fraction of PAH was observed in the PE waste, where even compounds with seven aromatic rings were found. These results comply with previous results of different pyrolysis oils where the most complex PAHs were hepta-aromatics, making it likely that all octa-aromatics are in the solid phase. These results complemented previous analyses by GC × GC-FID on the increased fraction of aromatics in PE pyrolysis oils compared to PP. It was found that besides the increased fraction of aromatics in PE, the aromatics were also of more complex nature than with PP oils. This was caused by the branched PP chain, which inhibits cyclization reactions due to steric hindrance. With PP pyrolysis oils, a depolymerization pattern is observed for both olefins and diolefins. The advantage of FT-ICR MS is that it can differentiate between various DBEs. Hence, the reaction mechanism for diolefin formation and the depolymerization trends for diolefins could be observed in more detail compared to the current state of the art. The combined analysis by GC × GC-FID and (+)APPI FT-ICR MS enables an improved characterization of the hydrocarbons in the plastic pyrolysis oil and, hence, a more in-depth understanding of these new synthetic petrochemical feedstocks. The enhanced understanding and characterization of these valuable waste feedstocks will facilitate their incorporation into the existing chemical industry as a renewable carbon source.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.4c01954.

S1: error distribution mass-assignment (+)APPI FT-ICR MS; S2: (+)APCI FT-ICR MS; S3: elemental composition; S4: detailed PIONA pyrolysis oils (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Kevin M. Van Geem − *Laboratory for Chemical Technology, Department of Materials, Textiles and Chemical Engineering, Ghent University, Gent 9052, Belgium;* orcid.org/0000-0003-4191-4960; Email: Kevin.VanGeem@UGent.be

Authors

Yannick Ureel − *Laboratory for Chemical Technology, Department of Materials, Textiles and Chemical Engineering, Ghent University, Gent 9052, Belgium;* orcid.org/0000-0001-6883-320X

Martha L. Chacón-Patiño − *Ion Cyclotron Resonance Program, National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310, United States; International Joint Laboratory for Complex Matrices Molecular Characterization, iC2MC, TRTG, Harfleur 76700, France;* orcid.org/0000-0002-7273-5343

Marvin Kusenberg − *Laboratory for Chemical Technology, Department of Materials, Textiles and Chemical Engineering, Ghent University, Gent 9052, Belgium;* orcid.org/0000-0002-3733-3293

Ryan P. Rodgers − *Ion Cyclotron Resonance Program, National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310, United States; International Joint Laboratory for Complex Matrices Molecular Characterization, iC2MC, TRTG, Harfleur 76700, France; Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 32308, United States;* orcid.org/0000-0003-1302-2850

Maarten K. Sabbe − *Laboratory for Chemical Technology, Department of Materials, Textiles and Chemical Engineering, Ghent University, Gent 9052, Belgium;* orcid.org/0000-0003-4824-2407

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.energyfuels.4c01954

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) IEAThe Future of Petrochemicals; IEA: Paris, 2018. https://www.iea.org/reports/the-future-of-petrochemicals.

(2) *The New Plastics Economy: Rethinking the future of plastics; World Economic Forum*; Ellen MacArthur Foundation and McKinsey & Company, 2016.

(3) Van Geem, K. M. Plastic waste recycling is gaining momentum. *Science* **2023**, *381* (6658), 607−608.

(4) *Plastics - The Facts 2020*; Plastics Europe, 2020.

(5) Ragaert, K.; Delva, L.; Van Geem, K.Mechanical and chemical recycling of solid plastic waste. In *Waste Management*; Elsevier Ltd: 2017; Vol. *69*, pp 24−58.

(6) Marturano, V.; Cerruti, P.; Ambrogi, V. Polymer additives. *Phys. Sci. Rev.* **2017**, *2* (6), No. 20160130.

(7) Pelzl, B.; Wolf, R.; Kaul, B. L. *Plastics, Additives*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2018.

(8) Ügdüler, S.; Van Geem, K. M.; Roosen, M.; Delbeke, E. I. P.; De Meester, S. Challenges and opportunities of solvent-based additive extraction methods for plastic recycling. *Waste Management* **2020**, *104*, 148−182.

(9) Beyler, C. L.; Hirschler, M. M.*Thermal decomposition of polymers*; National Fire Protection Association: Quincy, MA, 2002.

(10) Jung, S.-H.; Cho, M.-H.; Kang, B.-S.; Kim, J.-S. Pyrolysis of a fraction of waste polypropylene and polyethylene for the recovery of BTX aromatics using a fluidized bed reactor. *Fuel Process. Technol.* **2010**, *91* (3), 277−284.

(11) Encinar, J. M.; González, J. F. Pyrolysis of synthetic polymers and plastic wastes. Kinetic study. *Fuel Process. Technol.* **2008**, *89* (7), 678−686.

(12) Abbas-Abadi, M. S.; Ureel, Y.; Eschenbacher, A.; Vermeire, F. H.; Varghese, R. J.; Oenema, J.; Stefanidis, G. D.; Van Geem, K. M. Challenges and opportunities of light olefin production via thermal and catalytic pyrolysis of end-of-life polyolefins: Towards full recyclability. *Prog. Energy Combust. Sci.* **2023**, *96*, No. 101046.

(13) Donaj, P. J.; Kaminsky, W.; Buzeto, F.; Yang, W. Pyrolysis of polyolefins for increasing the yield of monomers' recovery. *Waste Management* **2012**, *32* (5), 840−846.

(14) Hussein, Z. A.; Shakor, Z. M.; Alzuhairi, M.; Al-Sheikh, F. Thermal and catalytic cracking of plastic waste: a review. *Int. J. Environ. Anal. Chem.* **2021**, 5920−5937.

(15) Containers, Packaging, and Non-Durable Good. *Documentation for greenhouse gas emission and energy factors used in the waste reduction model (WARM)*; U.S. Environmental Protection Agency - Office of Resource Conservation and Recovery, 2016.

(16) Dogu, O.; Pelucchi, M.; Van de Vijver, R.; Van Steenberge, P. H. M.; D'Hooge, D. R.; Cuoci, A.; Mehl, M.; Frassoldati, A.; Faravelli, T.; Van Geem, K. M. The chemistry of chemical recycling of solid plastic waste via pyrolysis and gasification: State-of-the-art, challenges, and future directions. In *Prog. Energy Combust. Sci.*; Elsevier Ltd: 2021; Vol. *84*, pp 100901−100901.

(17) Toraman, H. E.; Dijkmans, T.; Djokic, M. R.; Van Geem, K. M.; Marin, G. B. Detailed compositional characterization of plastic waste pyrolysis oil by comprehensive two-dimensional gas-chromatography coupled to multiple detectors. *Journal of Chromatography A* **2014**, *1359*, 237−246.

(18) Dao Thi, H.; Djokic, M. R.; Van Geem, K. M. Detailed Group-Type Characterization of Plastic-Waste Pyrolysis Oils: By Comprehensive Two-Dimensional Gas Chromatography Including Linear, Branched, and Di-Olefins. *Separations* **2021**, *8* (7), 103.

(19) Zhang, Y.; Ji, G.; Chen, C.; Wang, Y.; Wang, W.; Li, A. Liquid oils produced from pyrolysis of plastic wastes with heat carrier in rotary kiln. *Fuel Process. Technol.* **2020**, *206*, No. 106455.

(20) Kusenberg, M.; Zayoud, A.; Roosen, M.; Thi, H. D.; Abbas-Abadi, M. S.; Eschenbacher, A.; Kresovic, U.; De Meester, S.; Van Geem, K. M. A comprehensive experimental investigation of plastic waste pyrolysis oil quality and its dependence on the plastic waste composition. *Fuel Process. Technol.* **2022**, *227*, No. 107090.

(21) Ware, R. L.; Rowland, S. M.; Rodgers, R. P.; Marshall, A. G. Advanced Chemical Characterization of Pyrolysis Oils from Landfill Waste, Recycled Plastics, and Forestry Residue. *Energy Fuels* **2017**, *31* (8), 8210−8216.

(22) Ristic, N. D.; Djokic, M. R.; Konist, A.; Van Geem, K. M.; Marin, G. B. Quantitative compositional analysis of Estonian shale oil using comprehensive two dimensional gas chromatography. *Fuel processing technology* **2017**, *167*, 241−249.

(23) Shaw, J. B.; Lin, T.-Y.; Leach, F. E., III; Tolmachev, A. V.; Tolić, N.; Robinson, E. W.; Koppenaal, D. W.; Paša-Tolić, L. 21 Tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometer Greatly Expands Mass Spectrometry Toolbox. *J. Am. Soc. Mass Spectrom.* **2016**, *27* (12), 1929−1936.

(24) Niyonsaba, E.; Manheim, J. M.; Yerabolu, R.; Kenttämaa, H. I. Recent Advances in Petroleum Analysis by Mass Spectrometry. *Anal. Chem.* **2019**, *91* (1), 156−177.

(25) Cho, Y.; Ahmed, A.; Islam, A.; Kim, S. Developments in FT-ICR MS instrumentation, ionization techniques, and data interpretation methods for petroleomics. *Mass Spectrom. Rev.* **2015**, *34* (2), 248−263. (acccessed 2023/11/21)

(26) Spraggins, J. M.; Rizzo, D. G.; Moore, J. L.; Rose, K. L.; Hammer, N. D.; Skaar, E. P.; Caprioli, R. M. MALDI FTICR IMS of intact proteins: using mass accuracy to link protein images with proteomics data. *J. Am. Soc. Mass Spectrom.* **2015**, *26* (6), 974−985.

(27) Zhu, Y.; Zheng, H.; Tian, F.; Wang, Y.; Huang, C.; Dan, Y.; Yang, T.; Du, N.; Zhou, Q.; Li, D. Characterization of nitrogen-containing compounds in coal tar and its subfractions by comprehensive two-dimensional GC × GC-TOF and ESI FT-ICR mass spectrometry based on new separation method. *Fuel Process. Technol.* **2022**, *227*, No. 107125.

(28) Liu, M.; Zhao, D.-Z.; Zhang, L.-Z.; Zhao, S.-Q. Stepwise structural characterization of hydrocarbon compounds and polar components during atmospheric residue hydrotreatment. *Fuel Process. Technol.* **2017**, *158*, 238−246.

(29) Guillemant, J.; Berlioz-Barbier, A.; Chainet, F.; de Oliveira, L. P.; Lacoue-Nègre, M.; Joly, J.-F.; Duponchel, L. Sulfur compounds characterization using FT-ICR MS: Towards a better comprehension of vacuum gas oils hydrodesulfurization process. *Fuel Process. Technol.* **2020**, *210*, No. 106529.

(30) Rodgers, R. P.; Marshall, A. G.Petroleomics: Advanced characterization of petroleum-derived materials by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). In *Asphaltenes, heavy oils, and petroleomics*; Springer: New York, NY 2007; pp 63−93.

(31) Chacón-Patiño, M. L.; Rowland, S. M.; Rodgers, R. P. Advances in asphaltene petroleomics. part 1: asphaltenes are composed of abundant island and archipelago structural motifs. *Energy Fuels* **2017**, *31* (12), 13509−13518.

(32) Chacón-Patiño, M. L.; Rowland, S. M.; Rodgers, R. P. Advances in asphaltene petroleomics. Part 2: selective separation method that reveals fractions enriched in island and archipelago structural motifs by mass spectrometry. *Energy Fuels* **2018**, *32* (1), 314−328.

(33) Chacón-Patiño, M. L.; Rowland, S. M.; Rodgers, R. P. Advances in asphaltene petroleomics. Part 3. Dominance of island or archipelago structural motif is sample dependent. *Energy Fuels* **2018**, *32* (9), 9106−9120.

(34) Marshall, A. G.; Rodgers, R. P. Petroleomics: The Next Grand Challenge for Chemical Analysis. *Acc. Chem. Res.* **2004**, *37* (1), 53−59.

(35) Chacón-Patiño, M. L.; Gray, M. R.; Rüger, C.; Smith, D. F.; Glattke, T. J.; Niles, S. F.; Neumann, A.; Weisbrod, C. R.; Yen, A.; McKenna, A. M.; et al. Lessons Learned from a Decade-Long Assessment of Asphaltenes by Ultrahigh-Resolution Mass Spectrometry and Implications for Complex Mixture Analysis. *Energy Fuels* **2021**, *35* (20), 16335−16376.

(36) Chacón-Patiño, M. L.; Smith, D. F.; Hendrickson, C. L.; Marshall, A. G.; Rodgers, R. P. Advances in Asphaltene Petroleomics. Part 4. Compositional Trends of Solubility Subfractions Reveal that Polyfunctional Oxygen-Containing Compounds Drive Asphaltene Chemistry. *Energy Fuels* **2020**, *34* (3), 3013−3030.

(37) Mase, C.; Maillard, J. F.; Paupy, B.; Farenc, M.; Adam, C.; Hubert-Roux, M.; Afonso, C.; Giusti, P. Molecular Characterization of a Mixed Plastic Pyrolysis Oil from Municipal Wastes by Direct Infusion Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* **2021**, *35* (18), 14828−14837.

(38) Hassibi, N.; Quiring, Y.; Carré, V.; Aubriet, F.; Vernex-Loset, L.; Mauviel, G.; Burklé-Vitzthum, V. Analysis and control of products obtained from pyrolysis of polypropylene using a reflux semi-batch reactor and GC-MS/FID and FT-ICR MS. *Journal of Analytical and Applied Pyrolysis* **2023**, *169*, No. 105826.

(39) Ware, R. L.; Rowland, S. M.; Lu, J.; Rodgers, R. P.; Marshall, A. G. Compositional and Structural Analysis of Silica Gel Fractions from Municipal Waste Pyrolysis Oils. *Energy Fuels* **2018**, *32* (7), 7752−7761.

(40) Mase, C.; Maillard, J. F.; Paupy, B.; Hubert-Roux, M.; Afonso, C.; Giusti, P. Speciation and Semiquantification of Nitrogen-Containing Species in Complex Mixtures: Application to Plastic Pyrolysis Oil. *ACS Omega* **2022**, *7* (23), 19428−19436.

(41) Mase, C.; Maillard, J. F.; Piparo, M.; Friederici, L.; Rüger, C. P.; Marceau, S.; Paupy, B.; Hubert-Roux, M.; Afonso, C.; Giusti, P. GC-FTICR mass spectrometry with dopant assisted atmospheric pressure photoionization: application to the characterization of plastic pyrolysis oil. *Analyst* **2023**, *148* (20), 5221−5232.

(42) Dhahak, A.; Carre, V.; Aubriet, F.; Mauviel, G.; Burkle-Vitzthum, V. Analysis of Products Obtained from Slow Pyrolysis of Poly(ethylene terephthalate) by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Coupled to Electrospray Ionization (ESI) and Laser Desorption Ionization (LDI). *Ind. Eng. Chem. Res.* **2020**, *59* (4), 1495−1504.

(43) Lazzari, E.; Piparo, M.; Mase, C.; Levacher, L.; Stefanuto, P.-H.; Purcaro, G.; Focant, J.-F.; Giusti, P. Chemical elucidation of recycled plastic pyrolysis oils by means of GC × GC-PI-TOF-MS and GC-VUV. *Journal of Analytical and Applied Pyrolysis* **2023**, *176*, No. 106224.

(44) Smith, D. F.; Podgorski, D. C.; Rodgers, R. P.; Blakney, G. T.; Hendrickson, C. L. 21 T FT-ICR Mass Spectrometer for Ultrahigh-Resolution Analysis of Complex Organic Mixtures. *Anal. Chem.* **2018**, *90* (3), 2041−2047.

(45) Rodgers, R. P.; Mapolelo, M. M.; Robbins, W. K.; Chacón-Patiño, M. L.; Putman, J. C.; Niles, S. F.; Rowland, S. M.; Marshall, A. G. Combating selective ionization in the high resolution mass spectral characterization of complex mixtures. *Faraday Discuss.* **2019**, *218*, 29−51.

(46) Barrow, M. P.; Peru, K. M.; Headley, J. V. An Added Dimension: GC Atmospheric Pressure Chemical Ionization FTICR MS and the Athabasca Oil Sands. *Anal. Chem.* **2014**, *86* (16), 8281−8288.

(47) Olcese, R.; Carré, V.; Aubriet, F.; Dufour, A. Selectivity of Bio-oils Catalytic Hydrotreatment Assessed by Petroleomic and GC*GC/MS-FID Analysis. *Energy Fuels* **2013**, *27* (4), 2135−2145.

(48) Lee, S.; Palacio Lozano, D. C.; Jones, H. E.; Shin, K.; Barrow, M. P. Characterization of Mineral and Synthetic Base Oils by Gas Chromatography−Mass Spectrometry and Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* **2022**, *36* (22), 13518−13525.

(49) Dimitrov, P.; Emert, J.; Hua, J.; Keki, S.; Faust, R. Mechanism of Isomerization in the Cationic Polymerization of Isobutylene. *Macromolecules* **2011**, *44* (7), 1831−1840.

(50) Chacón-Patiño, M. L.; Moulian, R.; Barrère-Mangote, C.; Putman, J. C.; Weisbrod, C. R.; Blakney, G. T.; Bouyssiere, B.; Rodgers, R. P.; Giusti, P. Compositional Trends for Total Vanadium Content and Vanadyl Porphyrins in Gel Permeation Chromatography Fractions Reveal Correlations between Asphaltene Aggregation and Ion Production Efficiency in Atmospheric Pressure Photoionization. *Energy Fuels* **2020**, *34* (12), 16158−16172.

(51) Nisson, D. M.; Walters, C. C.; Chacón-Patiño, M. L.; Weisbrod, C. R.; Kieft, T. L.; Sherwood Lollar, B.; Warr, O.; Castillo, J.; Perl, S. M.; Cason, E. D.; et al. Radiolytically reworked Archean organic matter in a habitable deep ancient high-temperature brine. *Nat. Commun.* **2023**, *14* (1), 6163.

(52) Purcell, J. M.; Rodgers, R. P.; Hendrickson, C. L.; Marshall, A. G. Speciation of nitrogen containing aromatics by atmospheric pressure photoionization or electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *J. Am. Soc. Mass Spectrom.* **2007**, *18* (7), 1265−1273.

(53) Sabbe, M. K.; Saeys, M.; Reyniers, M.-F.; Marin, G. B.; Van Speybroeck, V.; Waroquier, M. Group additive values for the gas phase standard enthalpy of formation of hydrocarbons and hydrocarbon radicals. *J. Phys. Chem. A* **2005**, *109* (33), 7466−7480.

(54) Miandad, R.; Barakat, M. A.; Rehan, M.; Aburiazaiza, A. S.; Ismail, I. M. I.; Nizami, A. S. Plastic waste to liquid oil through catalytic pyrolysis using natural and synthetic zeolite catalysts. *Waste Management* **2017**, *69*, 66−78.

(55) Abbas-Abadi, M. S.; Zayoud, A.; Kusenberg, M.; Roosen, M.; Vermeire, F.; Yazdani, P.; Van Waeyenberg, J.; Eschenbacher, A.; Hernandez, F. J. A.; Kuzmanović, M.; et al. Thermochemical recycling of end-of-life and virgin HDPE: A pilot-scale study. *Journal of Analytical and Applied Pyrolysis* **2022**, *166*, No. 105614.

(56) Quintana-Solórzano, R.; Thybaut, J. W.; Marin, G. B.; Lødeng, R.; Holmen, A. Single-Event MicroKinetics for coke formation in catalytic cracking. *Catal. Today* **2005**, *107−108*, 619−629.

(57) Kopinke, F. D.; Zimmermann, G.; Reyniers, G. C.; Froment, G. F. Relative rates of coke formation from hydrocarbons in steam cracking of naphtha. 2. Paraffins, naphthenes, mono-, di-, and cycloolefins, and acetylenes. *Ind. Eng. Chem. Res.* **1993**, *32* (1), 56−61.

(58) Kopinke, F. D.; Zimmermann, G.; Reyniers, G. C.; Froment, G. F. Relative rates of coke formation from hydrocarbons in steam cracking of naphtha. 3. Aromatic hydrocarbons. *Ind. Eng. Chem. Res.* **1993**, *32* (11), 2620−2625.

(59) Reyniers, G. C.; Froment, G. F.; Kopinke, F.-D.; Zimmermann, G. Coke Formation in the Thermal Cracking of Hydrocarbons. 4. Modeling of Coke Formation in Naphtha Cracking. *Ind. Eng. Chem. Res.* **1994**, *33* (11), 2584−2590.

(60) Kusenberg, M.; Roosen, M.; Zayoud, A.; Djokic, M. R.; Dao Thi, H.; De Meester, S.; Ragaert, K.; Kresovic, U.; Van Geem, K. M. Assessing the feasibility of chemical recycling via steam cracking of untreated plastic waste pyrolysis oils: Feedstock impurities, product yields and coke formation. *Waste Manage.* **2022**, *141*, 104−114.

(61) Williams, P. T.; Williams, E. A. Interaction of Plastics in Mixed-Plastics Pyrolysis. *Energy Fuels* **1999**, *13* (1), 188−196.

(62) Zhou, X.; Broadbelt, L. J.; Vinu, R. Mechanistic Understanding of Thermochemical Conversion of Polymers and Lignocellulosic Biomass. *Advances in Chemical Engineering* **2016**, *49*, 95−198.

(63) Levine, S. E.; Broadbelt, L. J. Detailed mechanistic modeling of high-density polyethylene pyrolysis: Low molecular weight product evolution. *Polym. Degrad. Stab.* **2009**, *94* (5), 810−822.

(64) Abdul Jameel, A. G.; Khateeb, A.; Elbaz, A. M.; Emwas, A.-H.; Zhang, W.; Roberts, W. L.; Sarathy, S. M. Characterization of deasphalted heavy fuel oil using APPI (+) FT-ICR mass spectrometry and NMR spectroscopy. *Fuel* **2019**, *253*, 950−963.

(65) Lewis, R. A. *Hawley's condensed chemical dictionary*; John Wiley & Sons, 2016.

(66) Cho, Y.; Na, J.-G.; Nho, N.-S.; Kim, S.; Kim, S. Application of Saturates, Aromatics, Resins, and Asphaltenes Crude Oil Fractionation for Detailed Chemical Characterization of Heavy Crude Oils by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Equipped with Atmospheric Pressure Photoionization. *Energy Fuels* **2012**, *26* (5), 2558−2565.

(67) Dunkle, M. N.; Pijcke, P.; Winniford, W. L.; Ruitenbeek, M.; Bellos, G. Method development and evaluation of pyrolysis oils from mixed waste plastic by GC-VUV. *Journal of Chromatography A* **2021**, *1637*, No. 461837.

(68) Dunkle, M. N.; Benedetti, C.; Pijcke, P.; van Belzen, R.; Boekwa, M.; Mitsios, M.; Ruitenbeek, M.; Bellos, G. Comparing different methods for olefin quantification in pygas and plastic pyrolysis oils: Gas chromatography-vacuum ultraviolet detection

versus comprehensive gas chromatography versus bromine number titration. *Journal of Chromatography A* **2024**, *1713*, No. 464569.