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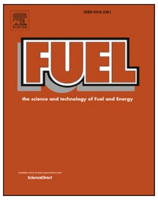

Full Length Article

A comparative study of aromatic content in pyrolysis oils from waste plastics and tires: Assessing common refinery methods

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ABSTRACT

The conversion of waste plastics and tires via pyrolysis to pyrolysis oil represents one of the most promising ways of chemical recycling. Determining aromatics in pyrolysis oils from these feedstocks is crucial for their utilization as both petrochemicals and fuels. In this study, we compared three standard methods commonly available in refinery laboratories (ASTM D1319 – FIA, EN12916 – HPLC-RI, ASTM D8396 – GC × GC-FID) for analyzing aromatic content across a wide range of waste plastic pyrolysis oils, their middle distillate fractions, and hydrotreated products. Using model compounds, we explained most of the observed differences in aromatic content determined by these methods. HPLC-RI and FIA resulted in significant errors. For instance, the FIA reports some dienes and heterocompounds as aromatics. The results from HPLC-RI showed that monoaromatics are overestimated, while polyaromatics are underestimated. Among the tested methods, GC × GC-FID provided the most reliable results.

1. Introduction

Plastic waste recycling represents one of our society's main challenges transitioning from a linear to a circular economy. Although there are several options for the chemical recycling of plastics and tires, thermochemical processes utilizing pyrolysis to produce pyrolysis oil are the most common [1]. After appropriate upgrading, the oils made from polyolefin plastics could be used as feedstock for steam cracking, production of basic petrochemicals, or transportation fuel components [1,2]. However, pyrolysis oils made from actual post-consumer plastic waste contain significant impurities, mainly in hetero-compounds, which limit their processing via steam cracking [3]. Besides heteroatom content, the high amounts of olefins and aromatics, responsible for increased coke formation during steam cracking, are typically present in pyrolysis oil from plastics [3]. Before direct valorization of the pyrolysis oils for both the steam cracking process or fuels utilization, heteroatoms (halogens, nitrogen, oxygen, and sulfur), olefins, and aromatics need to be reduced by hydrotreatment, which represents the most effective process [2]. A slightly particular case, but one associated with the same problems, describes the pyrolysis of scrap tires, promising especially from the perspective of petrochemicals (aromatics) or, at least, fuels production [4].

The determination of heteroatoms in waste plastic pyrolysis oils (further WPPO) can be accomplished using standard methods commonly employed for analyzing crude oil samples, e.g., ASTM D5453, D4629, and D7359 for sulfur, nitrogen, and chlorine, respectively. These methods are part of the guidelines for WPPO characterization prepared by Lummus Technology [5]. On the other hand, hydrocarbon composition analysis is considerably more intricate, primarily due to the high content of olefins [3,6], almost absent in fossil fuels. WPPOs usually represent a complex mixture of thousands of compounds with a broad distillation range, often containing heavy fractions boiling above 360 °C [7,8]. Thus, the applicability of single-column GC analysis is minimal. The initial analytical method dedicated to this analysis is GC with a vacuum ultraviolet detector (VUV), recently standardized as ASTM D8519 in July 2023 [9]. Although GC-VUV offers fast data processing and only little input from the user, it still represents a relatively new method, commercially available since 2014 [10]; the instrument is quite expensive, making it rare in laboratories. This study thus focuses on determining aromatic content using standard methods available in fuel laboratories.

As mentioned earlier, understanding the aromatic content of WPPOs

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is important for the steam cracking process and for the production of transportation fuel components [11,12]. ASTM D1655 [13] specifies that kerosene aviation fuel is limited to a maximum total aromatic content of 25 vol% (determined by ASTM D1319) or to 26.5 vol% (determined by ASTM D6379). Monitoring the aromatics content is crucial because of kerosene fuel's combustion characteristics and heat value. A higher aromatic content is responsible for lower heat value and smoke point, leading to increased soot formation during combustion [14]. The EU does not limit the total aromatic content in diesel fuel (according to EN590 [15]); however, aromatics significantly negatively affect the cetane number and cetane index, a crucial parameter of diesel fuel. Typically, the total aromatic content of diesel fuel is not higher than 35 vol%, which is also the limit for total aromatic content in the United States, according to ASTM D975 [16]. To comply with EU regulations, diesel fuel must have a polyaromatic content (aromatics containing two or more aromatic rings in a molecule) lower than 8 wt% (determined by EN 12916) mainly due to elimination of the production of particulate matter and ppolyaromatic hydrocarbon emissions during combustion.

Fluorescent Indication Analysis (FIA), also known as ASTM D1319, is a commonly used method for determining aromatics in samples with a boiling point of up to 315 °C [17]. The FIA method involves displacement chromatography on a long, thin silica gel column. The indicator dye allows visible identification of the boundaries between aromatic, olefinic, and saturate zones under ultraviolet light. The determination of respective groups is then based on the length of each zone. One of the significant limitations of this method is its low productivity due to the time-consuming analysis. Furthermore, the standard states that dienes can be identified as either olefins or aromatics [17], which could be a significant limitation in determining the aromatic content of WPPO.

The HPLC-RI method, known as ASTM D6379 [18] for kerosene, D6591 [18] for diesel, and EN12916 [19] for middle distillates, offers a more efficient alternative to the FIA method. This method separates the sample into saturated, mono-, di- and triaromatic hydrocarbon groups using a polar column (usually containing –NH_2 and/or –CN groups) with *n*-heptane as the mobile phase. A differential refractive index (RI) detector quantifies aromatic groups using a specific set of standard compounds for each group. Although the issue of varying responses of different aromatic molecules when using an RI detector has been well-known since the 90 s [20], this method is still the most widely used to determine aromatics in middle distillates.

In addition to the analytical methods required by product specification standards, several alternative standardized methods are available for determining aromatics in WPPO. An alternative approach to HPLC-RI is supercritical flow chromatography (SFC) [21], standardized as ASTM D5186 [22] for diesel and D8305 [23] for kerosene. In SFC, supercritical CO_2 is used as a mobile phase, allowing a flame ionization detector (FID) that consistently responds to different hydrocarbon structures.

The mass spectrometry method commonly coupled to gas chromatography is standardized as ASTM D2425 [24]. After sample fractionation into saturated and aromatic fractions using column liquid chromatography, eleven hydrocarbon groups can be determined, including alkylbenzenes, cycloaromatics, naphthalenes, and triaromatics. However, this method requires the olefin content to be <2 vol %, which is highly limiting for samples derived from plastic waste.

Comprehensive two-dimensional gas chromatography (GC × GC) is widely employed in refinery laboratories. It is considered one of the best, most available, and commonly used methods for hydrocarbon group-type analysis of complex samples such as pyrolysis oils [6,25–27]. GC × GC-FID was standardized as ASTM D8396 in 2022 and is a strong candidate to supersede the previously mentioned methods for middle distillate analysis. Besides offering a more detailed characterization of the sample compared to standard procedures, it is also more efficient. Preliminary results from an ongoing inter-laboratory study of the ASTM method indicate that the determination of aromatics exhibits good reproducibility.

Previous studies have shown that the above-mentioned methods provide consistent findings for the determination of aromatic content in both crude oil samples and biofuels. Striebich et al. [28] compared ASTM D6379 (HPLC-RI) and ASTM D2425 (GC–MS) methods with GC × GC-FID for a wide range of petroleum-based and sustainable aviation fuels. An extensive inter-laboratory comparison of ASTM D6379 (HPLC-RI), ASTM D5186 (SFC), ASTM D8267 (GC-VUV), and GC × GC-FID with ASTM D1319 (FIA) was conducted by Gonzalez et al. [29] in 2020 for 12 different jet fuels with varying aromatic contents. The authors found that all methods can substitute the ASTM D1319 method for aromatics determination in jet fuel as they provide very close results.

Accurately determining aromatic content in crude and hydrotreated pyrolysis oils and fractions obtained by distillation is essential for their subsequent application. However, WPPOs exhibit notable differences in chemical composition compared to previously tested crude oil samples and alternative fuels. WPPOs contain a significant amount of heterocompounds, olefins (up to 50 wt%), and aromatics. For the first time, this study extensively compares the standard methods for aromatics determination commonly available in refinery laboratories, such as FIA, and HPLC-RI, with the widely used GC × GC-FID method for analyzing WPPO. A diverse range of pyrolysis oils derived from the conversion of plastic waste and waste tires, both before and after hydrotreatment with varying aromatic content, was utilized in this study. The suitability of these methods for analyzing WPPOs was validated using model compounds.

2. Experimental

2.1. Model compounds, plastic oils, and their fractions

The list of tested model compounds, covering all various structures of aromatic molecules of a wide range of molecular weight and various possible interferences, is shown in the supporting material **Table S1**. Pyrolysis oils from polyolefin plastics (waste polyethylene packaging films and a mixture of waste polyethylene packaging films and polypropylene food containers, further called cups) were prepared by pilot scale pyrolysis with a flow of ~200 kg/h by ENRESS company (Czech Republic). Scrap tires were pyrolyzed in a batch reactor from Hedwiga Group (Czech Republic). The pyrolysis oils were hydrotreated using a laboratory-scale hydrotreatment setup made by CACTU Solutions (https://www.cactu.eu, UCT Prague). The hydrotreatment was conducted under various conditions (refer to samples overview in **Tables S4 and S5**) using a commercial sulfided catalyst. Please refer to our previous publication [30] for further details about the hydrotreatment process. The samples hydrotreated at the most severe conditions (temperature 330 and 360 °C) were characterized by a minimal content of potential interferents. Specifically, sulfur and nitrogen contents were < 100 mg/kg, and a minimum of olefins was present (iodine value < 3 g I_2/100 g). The results for these samples were compared in separate graphs. The following designation was used for the samples: F = films (PE), CF = waste cups (PP) and films (PE), T = scrap tires.

Fractional distillation of crude and hydrotreated pyrolysis oils was carried out using the Fischer HMS 500 automatic distillation apparatus. Naphtha fraction (<150 °C) was distilled at atmospheric pressure, kerosene (150 – 250 °C) at 5.33 kPa, and atmospheric gas oil (250 – 360 °C) at 13 Pa. At each step, the temperature in the distillation flask did not exceed 250 °C; therefore, the sample's cracking was avoided.

2.2. Analytical methods for the aromatic content determination

2.2.1. Fluorescence indicator adsorption (FIA)

The Fluorescence Indicator Adsorption (FIA) based on displacement chromatography was carried out according to the ASTM D1319 standard. The apparatus from Normalab Analysis was used for the measurement. Silica gel 60 (0.040–0.063 mm) activated at 180 °C for 8 h supplied by Merck and FIA indicator dyed gel supplied by UOP, LLC, a

Honeywell Company (UOP PROD #80675–204, LOT #30000000784) were used for analysis. Analysis of each sample (kerosene samples and pyrolysis oils with FBP < 270 °C, see **Table S6**) was performed in duplicate; for each analysis, at least four results readings were made. The gas oil samples and other pyrolysis oils tested were not analyzed using the FIA method as the respective standard specifies applicability for samples that distill below 315 °C. For more details, see the standard method. The recalculation of aromatic content from vol.% to wt.% was performed by Equation **(1)**.

$$FIA-Ar(\mathrm{wt.\%}) = \frac{\mathrm{FIA-Ar\,(vol.\%)} \times \rho_{AVG-Ar}}{\rho_{sample}} \tag{1}$$

Where FIA-Ar (wt.%) is calculated aromatic content in wt.%, FIA-Ar (vol.%) is measured aromatic content in vol.%, $\rho_{\mathrm{AVG\text{-}Ar}}$ is the density of the average aromatic molecule present in the respective sample (refer to details in the captions of **Table S4 and S6**), and ρ_{sample} is the density of the respective sample.

As mentioned, the ASTM D1319 standard specifies that dienes can be determined as either olefins or aromatics. Thus, before analyzing neat samples, the determination of the most common dienes present in pyrolysis oils was validated by spiking the kerosene fraction of hydrotreated pyrolysis oil obtained at 360 °C and 10 MPa with 10 vol% of dienes. The following representatives of the main diene groups were tested: (i) α,ω-diene (octa-1,7-diene), and branched conjugated diene (2,5-dimethylhexa-2,4-diene) typically present in polyolefinic pyrolysis oils – used for spiking the hydrotreated oil from waste polyolefin films (kerosene F3), and (ii) non-conjugated cyclic diene molecule typical product from tires pyrolysis (D-limonene) and a conjugated cyclic diene (α-terpinene) present in scrap tires pyrolysis oil – used for spiking the hydrotreated oil from scrap tires (kerosene T6).

2.2.2. GC × GC-FID

GC × GC-FID analysis of all studied samples was conducted following the ASTM D8396 standard. LECO's QuadJet SD consisted of an Agilent 8890 GC (Santa Clara, CA) with a non-moving quad-jet dual-stage modulator (LECO Corporation, St. Joseph, MI), liquid nitrogen cooling, UHP He carrier gas, mid-polar primary column DB-17 ms (29.5 m × 0.25 mm × 0.25 μm), and 1 m nonpolar secondary column DB-1 HT (1 m × 0.25 mm × 0.10 μm). Both columns were provided by Agilent (Santa Clara, CA). FID and inlet temperatures were set at 300 and 285 °C, respectively. Due to their higher final boiling points, the FID and inlet temperatures were set to 320 °C for gas oil and PO samples. The oven temperature program started at 40 °C (hold time 3 min) and ended at 285 °C (hold time 1 min) with a temperature ramp rate of 3 °C/min. The secondary oven and modulator temperature offsets were 35 and 20 °C, respectively. The modulation period was set to 1.7 s with a hot pulse duration of 0.28 s. The injection volume was 0.1 μL with a 200:1 split ratio. FID data were collected at an acquisition rate of 200 Hz. GC × GC-FID classification utilizing ChromaTOF software (version 5.52.70.0) has been described in detail in a previous publication [31]. To eliminate differences in various hydrocarbon groups present, the FID peak area was corrected using the response calculated based on the effective carbon number approach [32].

2.2.3. HPLC-RI

Following the EN 12916 standard, the HPLC-RI method was also used to analyze all studied samples. HPLC system from Shimadzu was equipped with a series of two Agilent columns – Zorbax NH_2 5 μm, 4.6 × 150 mm and Zorbax SB-CN 5 μm, 4.6 × 150 mm in respective order. A sample, diluted in *n*-heptane to a concentration of 0.05–0.1 g/mL, was injected into the system using a valve equipped with a 10 μL loop. The analysis was carried out at constant flow (1 mL/min) of *n*-heptan. A mixture of o–xylene, fluorene, and phenanthrene in the concentration range specified by EN 12916 was used to calibrate the response of monoaromatic, diaromatic, and triaromatic compounds, respectively. The results for diaromatic content from HPLC in all graphs were obtained using the response of fluorene, i.e., as suggested by EN12916. The results obtained when 1-methylnaphthalene would be used as a standard (required for diaromatics quantification by ASTM D6379 and D6591) are shown in **Table S4** in supporting material. The response of more than 80 individual model compounds was measured at the same analysis conditions after dissolving the respective compound in *n*-heptane (0.005–0.01 g/mL).

2.2.4. Content of saturated compounds

The content of saturated compounds in gas oil samples was determined after unsaturated compounds adsorption over Ag-SiO_2. Silica gel 60 (particle size 0.063–0.2 mm) for column chromatography (Merck) was modified by $AgNO_3$ according to the procedure published elsewhere [33]. Saturated compounds from deep hydrotreated gas oil fraction of pyrolysis oil were isolated from the sample (0.12 g) by elution at ambient temperature using 48 mL of mobile phase – *n*-pentane (p.a.; Penta Chemicals) over 10 g of Ag-SiO_2 (bottom) and 2 g of Al_2O_3 (upper) part of the column. Using a rotary evaporator, the mobile phase was gently evaporated from the isolated fraction. The complete evaporation of *n*-pentane was checked, and there was no change in the flask containing saturates fraction mass when left to stand open in the lab overnight. More details about the method can be found in the respective paper [33]. After deep hydrotreatment, gas oils contain only traces of olefins and heteroatoms. Therefore, when the saturates amount is known, the rest of the sample corresponds to the total aromatics content.

3. Results and discussion

3.1. Method validation by pure compounds

3.1.1. FIA – model compounds spiking

The ASTM D1319 method specifies that the following compounds: "monocyclic and polycyclic aromatics, plus aromatic olefins, some dienes, compounds containing sulfur and nitrogen, or higher boiling oxygenated compounds" are determined as aromatics. Dienes are known to be present in pyrolysis oils from plastics and tires. For instance, α,ω-dienes are present in olefinic oils [6], and limonene is typically the most abundant olefin in pyrolysis oil from tires [34]. Hence, prior to analyzing the aforementioned samples, 10 vol% of model diene compounds were introduced into the hydrotreated kerosene samples of respective pyrolysis oils. These model compounds were selected to be representative of the respective crude pyrolysis oil. Specifically, we included octa-1,7-diene and 2,5–dimethylhexa-2,4-diene (typical for polyolefins oils), as well as D-limonene and α-terpinene (commonly found in scrap tires oils).

The measurements revealed that adding 10 vol% of all tested dienes to the hydrotreated kerosene sample resulted in an insignificant change in the length of the olefinic yellow band, easily distinguishable. In contrast to the standard sample measurement, the starting point of the aromatic band cannot be clearly identified, lacking a distinct, intense blue color line. Instead, a colorless tail of the olefinic band gradually transitions to a blue color (see **Figure S1**). Consequently, the most typical dienes present in pyrolysis oils cannot be classified as olefins by FIA and are considered aromatics (**Table S2**). For more details about neat sample analysis using the FIA method, see sections 3.2 and 3.4**.**

3.1.2. HPLC-RI – Individual compounds elution and response

The non-uniform response of different aromatic molecules on differential refractive index detectors has been known for decades [20]. However, if ever published, solid response data for individual molecules are difficult to find. Furthermore, the most abundant aromatic structures present in pyrolysis oils, such as α-methylstyrene, cumene, and cymenes (**Table S3**), characterized by isopropyl substituent, are not as commonly found in petroleum samples. Additionally, in petroleum samples, the distribution of aromatic molecules is usually more uniform (see

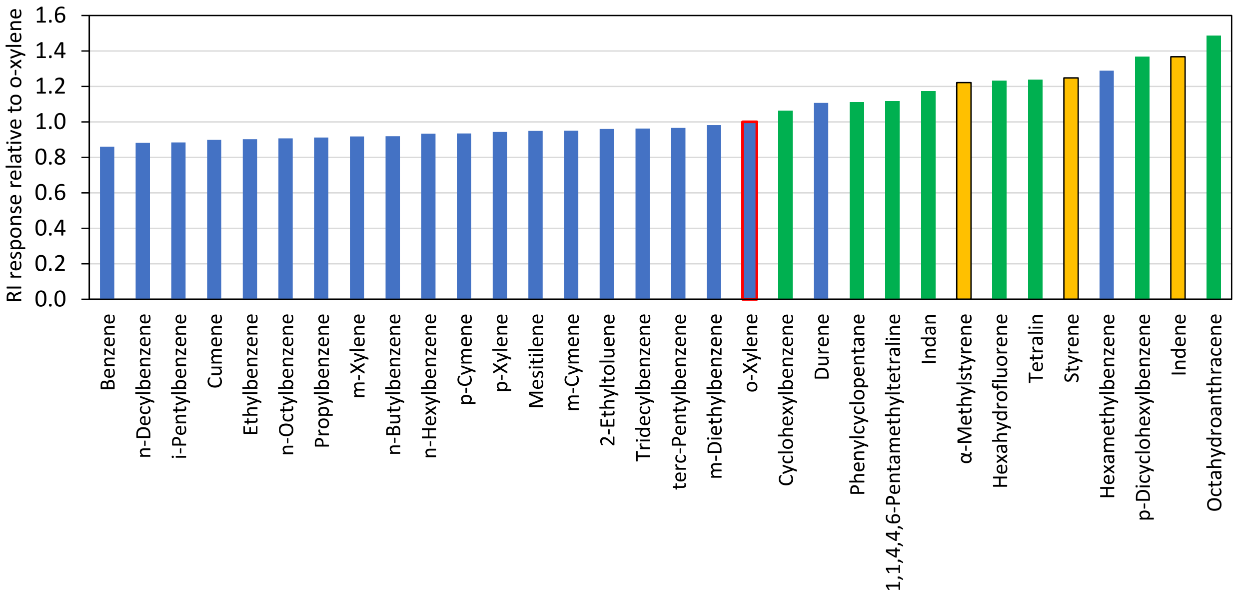

Fig. 1. Response of monoaromatic compounds relative to o-xylene (shown as a blue bar with a red boundary, the standard for monoaromatics determination by EN 12916, ASTM D6379, and D6591) on RI detector. Different structures are shown in different colors: alkylbenzenes (blue), cycloaromatics (green), and monoaromatics with olefinic substituent (yellow). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

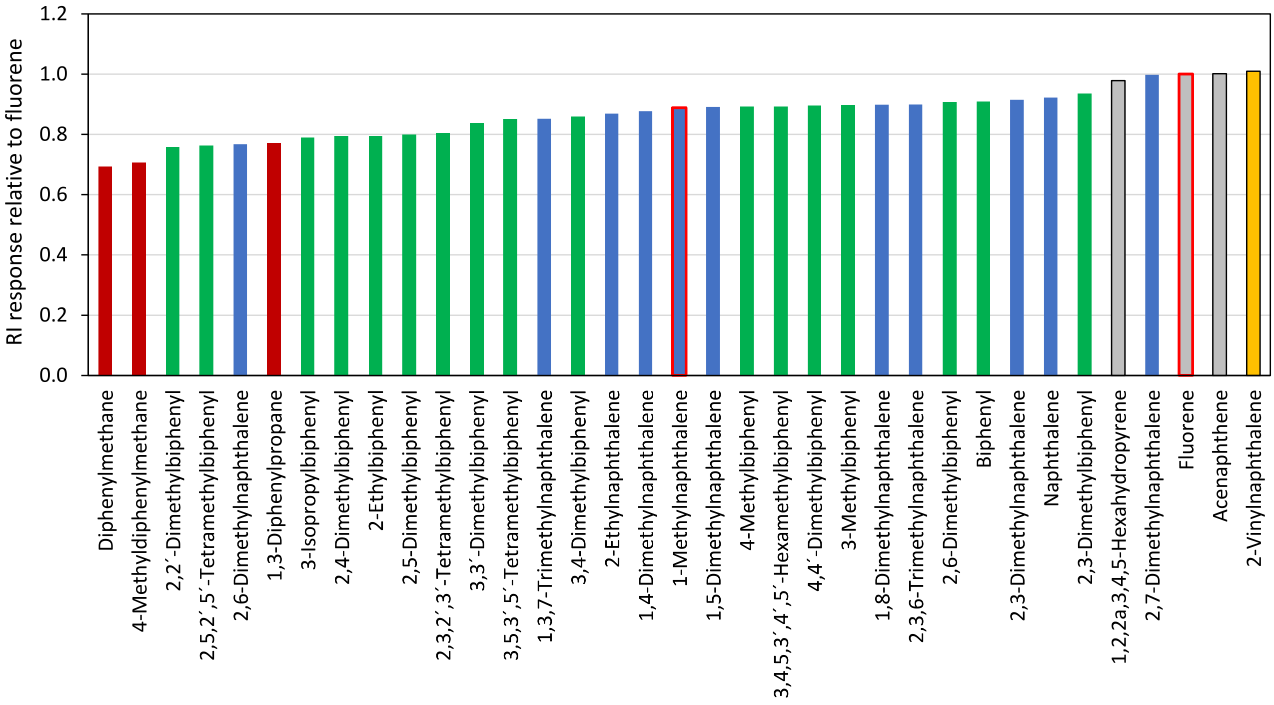

Fig. 2. Response of diaromatic compounds relative to fluorene (shown as a grey bar with a red boundary, the standard for diaromatics according to EN 12916) on the RI detector. Different structures are shown in different colors:1-methylnaphthalene (blue with a red boundary, the standard for diaromatics according to ASTMs D6379 and D6591), naphthalenes (blue), diaromatics with olefinic substituent (yellow), polycyclic structures containing two aromatic rings and simultaneously saturated naphthenic ring (grey), biphenyls (green), two aromatic rings separated by one or more carbon atoms (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table S3). To illustrate the differences in response values, we extensively screened the response of almost 80 aromatic molecules, along with possible interfering olefins and hetero-compounds present in pyrolysis oils.

o-Xylene is a standard for constructing calibration curves for monoaromatics determination in middle distillates using the main relevant standard methods employing HPLC-RI (EN 12916, ASTMs D6379, and D6591). Except for indene, an extreme example of monoaromatic olefin structure, all analyzed monoaromatics eluted within the retention time frame used for monoaromatic peak integration (Figure S2). A notable correlation was observed between the monoaromatic structure (polarity) and retention time. Specifically, the longer the aromatic alkyl substituent, the lower its retention time. On the other hand, the number of condensed cycloalkanic rings in the molecule and the presence of a

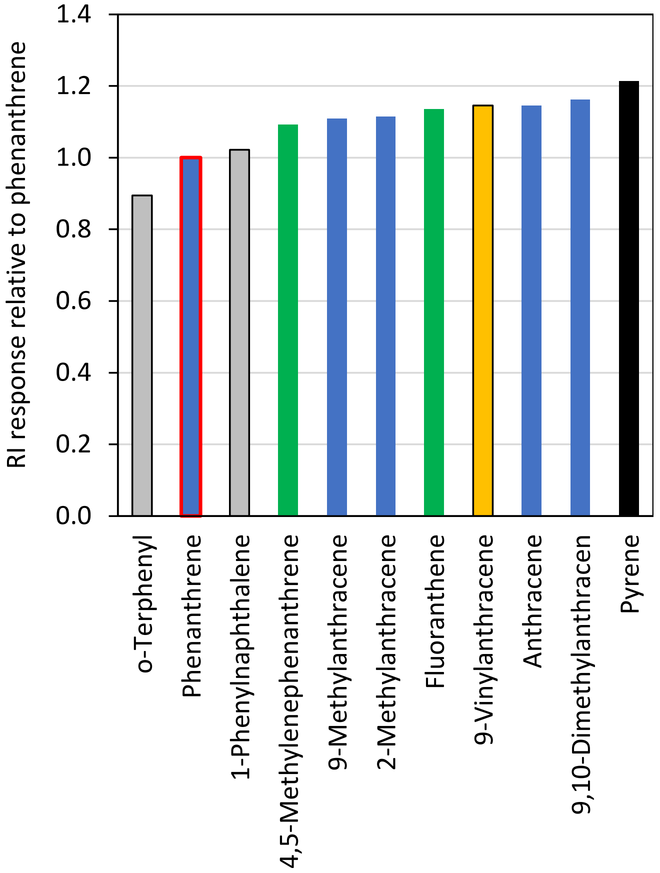

Fig. 3. Response of tri + aromatic compounds relative to phenanthrene (shown as a blue bar with a red boundary, the standard for triaromatics according to EN 12916 and ASTM D6591) on RI detector. Different structures are shown in different colors: triaromatics with olefinic substituent (yellow), polycyclic structures containing three aromatic rings and simultaneously saturated naphthenic ring (green), three condensed aromatic rings (blue), triaromatics containing partially or completely non-condensed rings (grey), tetraaroamatic compound (black). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

double bond in alkyl chain increased the retention time.

The response for alkylated benzenes was relatively uniform (Fig. 1), fluctuating between 86 % and 100 % of the o-xylene response, except for tetra and more methylated benzenes. Unfortunately, we could not identify any correlation between the alkylbenzene structure and the response. It is noteworthy that tetra and more methylated benzenes differ significantly from other alkylbenzenes in terms of melting point (e.g., the melting point of durene is 79 °C). The most notable effect of the structure on the response was the significantly higher response of cycloaromatics and aromatic olefins compared to alkylbenzenes. In general, the response of the molecule increases with an increase in (i) the number of aromatic ring substituents (above 4), (ii) the number of cycloalkane rings, or (iii) the presence of an olefinic double bond.

To determine diaromatics using HPLC-RI, all three methods (EN 12916, ASTMs D6379, and D6591) employed a 1-methylnaphthalene standard for calibration curve construction. However, in 2006, EN 12916 was modified for B7 diesel analysis, and fluorene replaced 1–methylnaphthalene. The change to fluorene was explained in EN 12916:2006 as a measure "to minimize the bias on diaromatics content between the former and a new version of the method." Regarding the elution of tested model compounds, only two biphenyl compounds (2,2́-dimethyl- and 2,5,2′,5́-tetramethylbiphenyl) eluted largely out of the retention time frame used for diaromatic peak integration (refer to Figure S3).

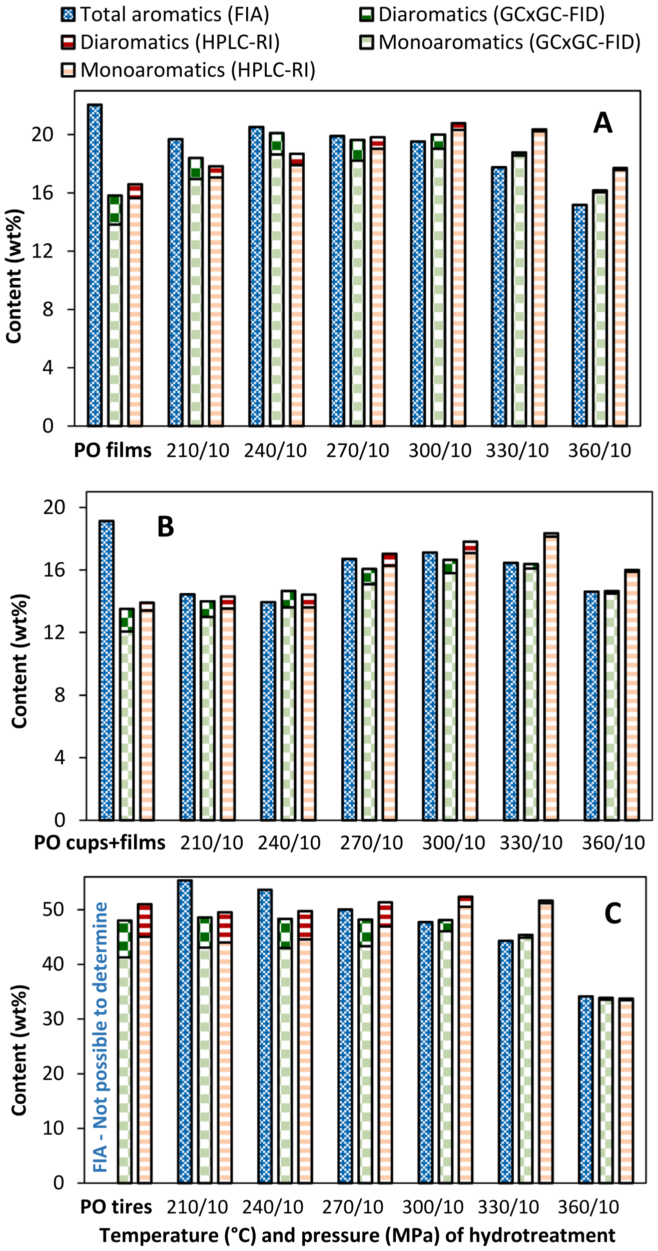

Fig. 4. Aromatic content determined by the studied methods in the kerosene fraction (b.p. 150–250 °C) of the pyrolysis oil or its products after hydrotreatment at different conditions. (**A**) – Samples from waste films (PE), (**B**) – Samples from waste cups (PP) and films (PE), (**C**) – Samples from scrap tires.

As clearly evident from Fig. 2, almost all analyzed compounds exhibit responses lower than fluorene, potentially leading to a significant underestimation of the diaromatic content in neat samples. The response of naphthalenes and biphenyls (prominent representatives of the diaromatic group) spans a broad range, from 76 to 100 %. Unfortunately, we could not identify any clear correlation between the position of alkyl groups on naphthalene and biphenyl and the response. One trend that could be deduced from the results is that diaromatics with aromatic rings separated by one or more carbon atoms have significantly lower responses than other structures. The diaromatics with the most similar structures to fluorene, i.e., diaromatics containing a cycloalkane ring, show the most similar response to the used standard for quantification.

Based on the results, 1-methylnaphthalene is likely a more suitable standard for quantifying the diaromatic content using HPLC-RI. This

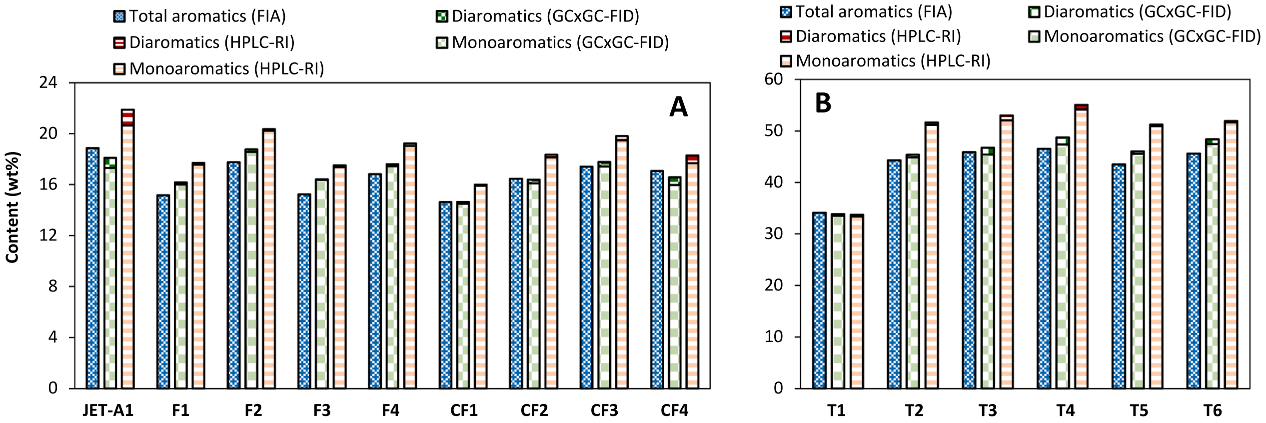

Fig. 5. Aromatic content determined by the studied methods in fossil JET-A1 kerosene and the plastic oil's kerosene fraction (b.p. 150–250 °C) after deep hydrotreatment. (**A**) – Samples from waste polyolefinic plastic oils, F = films (PE), CF = waste cups (PP) and films (PE). (**B**) –Samples from scrap tires (T). For more information about the samples, see **Table S4**.

assertion is further supported by the fact that the naphthalene structures represent the most abundant diaromatics in all kerosene samples (**Table S4**). In gas oil samples, biphenyls have a significantly higher presence than naphthalenes (**Table S5**). While the majority of diaromatic molecules fall into the group of naphthalenes and biphenyls, in gas oils from polyolefins, 1,3-diphenylpropane (eluting in biphenyls region) represents by far the most abundant diaromatic compound, constituting up to 35 % of all diaromatics in gas oil from cups and films (1.8 and 2.8 wt% of 1,3-diphenylpropane is present in gas oils from films and a mixture of cups and films, respectively).

Triaromatic molecules are exclusively present in diesel fuel and gas oil samples, typically at relatively low concentrations (<5 wt%). The response of various triaromatics relative to phenanthrene (the standard for determining triaromatics using EN 12916 and ASTM D6591) is depicted in Fig. 3**.** As observed, most of the analyzed compounds exhibit a response higher than phenanthrene, which could theoretically significantly overestimate the triaromatic content in the neat sample. A more significant concern than differences in the response for a low abundant compound group (at least for our method configuration) is the elution of triaromatics with non-condensed rings and 9-vinylantracene in the retention time frame designated for diaromatic peak integration (refer to **Figure S4**).

Crude pyrolysis oils from plastics and tires may contain many non-aromatic compounds that could elute in the aromatic region, such as unsaturated hydrocarbons and hetero-compounds. The analysis of selected unsaturated compounds demonstrated that the most abundant olefins in pyrolysis oils elute earlier than most monoaromatics. Despite the relatively limited scope of analyzed unsaturated compounds, it seems highly probable that only alkynes (probably not present in pyrolysis oils) could affect the monoaromatic determination in our method configuration. Among the most abundant heteroatom compounds identified in pyrolysis oils (thiophenes, benzonitrile, benzothiazole, cyclopentanone, and phenol), only thiophenes (abundant in tires pyrolysis oil [35]) can affect the aromatics content determination. For the summary of these results, see **Figure S5**. Thiophenes would also be the main heterocompound group that can affect aromatics determination by GC × GC.

3.1.3. Content of aromatics in kerosenes (150–250 °C) from pyrolysis oils

The effect of hydrotreatment on the aromatic content of kerosene samples from different origins determined by all studied methods (FIA, HPLC-RI, and GC × GC) is summarized in Fig. 4. For the WPPO from polyolefins, even a slight increase in aromatics content with increasing hydrotreatment temperature was observed. This observation can be attributed to heteroatom removal from the main heterocompounds (benzonitrile, 1,2-benzenedicarbonitrile, and benzenebutanenitrile) present in kerosene fraction of studied pyrolysis oils from polyolefins. The aromatics hydrogenation prevailed in their creation at hydrotreatment conditions of 360 °C and 10 MPa. Likewise, as we have already published in a previous study [29], the first significant decrease in aromatic content was thus determined at 360 °C and 10 MPa for kerosenes from tires. Up to this condition, the conversion of diaromatics into monoaromatics was mostly observed, with no significant change in total aromatic content.

The main difference was observed in the results obtained from the FIA method for kerosene from crude pyrolysis oils when comparing the methods. In the previous section, which analyzes model dienes, we demonstrated that the main diene structures present in pyrolysis oils can be determined as aromatics. Alongside dienes, hetero-compounds in kerosenes from crude pyrolysis oils can be considered the primary factor leading to a significantly higher aromatic content in these samples (Fig. 4 **A** and **B**). The difference in aromatic content determined by the FIA method compared to the other two methods was ~ 40 % for the kerosene from polyolefins. For the kerosene fraction of crude tires pyrolysis oil, the aromatic content cannot be reliably determined by FIA (Fig. 4 **C**).

Based on the tires pyrolysis mechanism [36] and the olefins determination in our previous study [30], the amount of olefins in the kerosene fraction from tires oil is very high due to the presence of limonene and other dienes in this fraction. Our previous study determined the iodine value of 91 g I_2/100 g of sample, corresponding to ~ 39 wt% of olefins [30]. The content of the most common diene pyrolysis products (like limonene) was too high to identify the start of the blue color band of aromatics (the same phenomenon observed for kerosene spiked by diene, see **Figure S1**). If the end of the yellow band (olefins) were considered as the start of the aromatic band, it would result in an enormous overestimation of aromatic content (>75 vol% – FIA vs. ~ 50 wt% – GC × GC) and very low (<20 vol%) olefins content. Besides crude samples, the FIA method reported the highest aromatic content among the tested methods for less hydrotreated tire samples (from conditions 210 and 240 °C at 10 MPa) containing higher amounts of olefins [30]. Another issue in low hydrotreated kerosenes, especially those made from tires, is the high content of hetero-compounds, such as ~1 wt% of sulfur and ~1 wt% of nitrogen present in crude tire oil kerosene [30]. On the other hand, for most samples, the FIA method provides results very close to the GC × GC method (relative difference usually much less than 5 %), which is in good agreement with the previous study analyzing fossil aviation kerosenes and identifying that GC × GC can provide very reliable results [29].

For most of the kerosenes hydrotreated at a temperature above 270 °C, HPLC provided by more than 5 % higher results for monoaromatics than the GC × GC method. However, a much higher difference

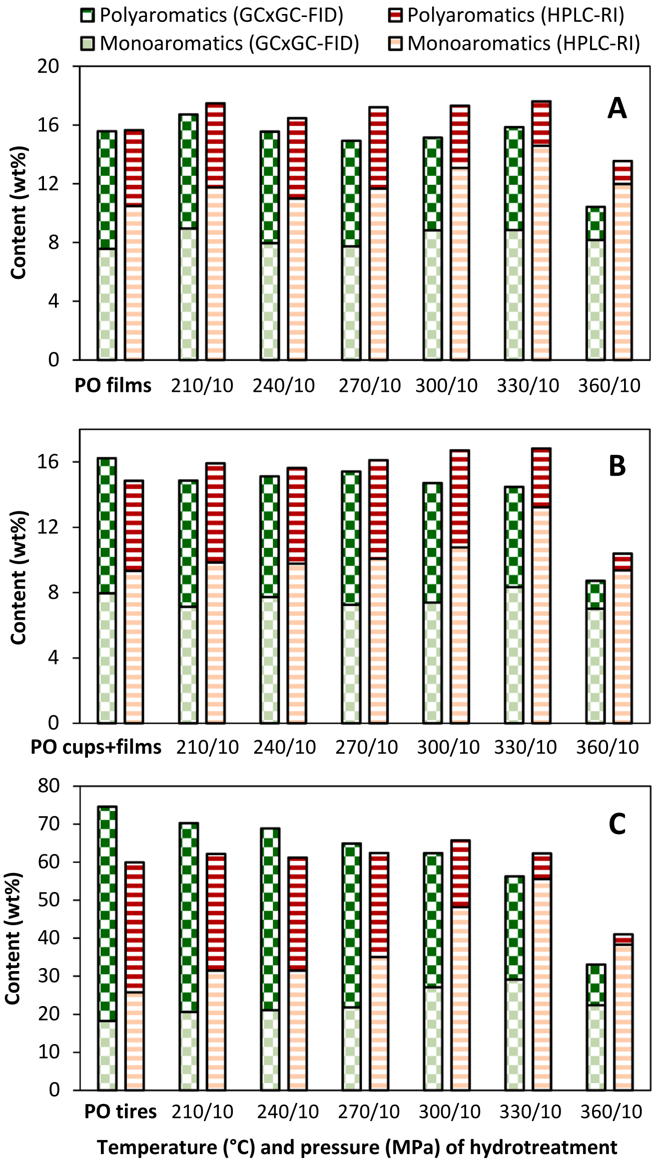

Fig. 6. Aromatic content determined by the studied methods in the gas oil fraction (b.p. 250–360 °C) of the plastic oil or its products after hydrotreatment at different conditions. (**A**) – Samples from waste films (PE), (**B**) – Samples from waste cups (PP) and films (PE), (**C**) – Samples from scrap tires.

was observed for diaromatics content. Since relatively low diaromatic content (<1 wt%) was determined for most samples, this observation can be partially attributed to the slightly worse repeatability of low-value measurements using HPLC (see RSD in **Table S4**). In the results for four pyrolysis oils from tires (feedstock, 210/10, 270/10, and 300/10), where aromatics content was above 2 wt%, we can see significantly lower (by more than 10 %) diaromatic content determined by HPLC compared to GC × GC. As observed in section 3.1.2, the reason could be partially due to using an inappropriate standard for diaromatics determination by HPLC-RI according to EN 12916. When we recalculated the results for diaromatics from HPLC-RI using the response of 1-methylnaphthalene, specified as standard in ASTM D6379, the results for these samples were in perfect correlation with those from GC × GC (relative difference < 2 %). For the other two samples, this recalculation resulted in more than 10 % lower results from GC × GC than HPLC (**Table S4**). It is thus clear that different samples would require different standards for HPLC-RI to determine aromatic content in better agreement with the other two tested methods.

After deep hydrotreatment, when the samples contained almost no olefins and heteroatoms and a minimal content of diaromatics, very comparable results (with relative difference <5 %) were obtained using FIA and GC × GC method for most of the tested samples (Fig. 5). For most of the samples, the highest aromatic content was determined by HPLC-RI, which mainly differed by more than 10 % from the results of the other two methods. These differences can be attributed to the response of the present aromatic molecules on the RI detector. Considering the aromatic content in the studied samples and specified limits for kerosene aviation fuel (ASTM D1655), it can be concluded that all methods can reliably assess the fulfillment of the specified aromatic content in aviation fuels. One should still consider the problems of the FIA method for crude pyrolysis oils mentioned above.

3.1.4. *Content of aromatics in gas oils (distillation cut 250–360 °C) from pyrolysis oils*

The impact of hydrotreatment on aromatic content in gas oil samples from various sources, as determined by HPLC-RI and GC × GC-FID, is summarized in Fig. 6. Similar trends to those seen for kerosene samples were observed. The most significant hydrogenation of aromatics occurred at 360 °C and 10 MPa. Up to this condition, the conversion of triaromatics and partially diaromatics into monoaromatics, with an insignificant change in total aromatic content, was mostly observed (**Table S5**). Regarding the trend in total aromatic content of gas oil fraction in relation to the hydrotreating temperature, both methods provided comparable results characterized by a steep decrease in aromatic content for samples from conditions of 360 °C and 10 MPa. For crude tires pyrolysis oil and its less hydrotreated products (up to 240 °C and 10 MPa), the determined aromatic content by GC × GC was by more than 10 %rel. higher than that from HPLC.

Although the total aromatic content for most of the samples determined by GC × GC and HPLC was quite comparable, a substantial difference was observed for monoaromatic and polyaromatic content (compounds with two or more aromatic cycles) monitored by EN 590 in diesel fuel. Upon closely examining the detailed result in **Table S5**, significant differences are evident in all aromatic groups. In studied gas oils, monoaromatics were predominantly present as cycloaromatic compounds, and alkylbenzenes constituted only a small fraction. Considering the identified differences in monoaromatic molecules' response (i.e., cycloaromatics have a higher response than alkylbenzenes; see Fig. 1), it is highly probable and trends for monoaromatic and cycloaromatic shown in Fig. 7**A** only confirm the fact that the results for monoaromatics in gas oils by HPLC-RI are significantly overestimated.

Concerning polyaromatics, GC × GC reported more (30–100 %) polyaromatics than HPLC in the gas oils from polyolefins and tire oils hydrotreated at milder conditions (temperature equal to or less than 300 °C) (Fig. 6 and **Table S5**). In the case of gas oils from polyolefins, the primary known problematic and the most abundant diaromatic compound was 1,3–diphenylpropane, characterized by only 77 % of the fluorene response (already discussed in section 3.1.2**)**. For all deep hydrotreated (temperature above 300 °C) gas oils from tires, 2–6 times more polyaromatics were determined by GC × GC compared to HPLC (Fig. 8 and **Table S5**). This observation and data for diaromatic content in gas oils from tires shown in Fig. 7**B** suggests that the inappropriate standard by EN 12916 (fluorene) is not the only reason for observed differences.

Deep hydrotreated gas oil samples (i.e., almost olefin- and heteroatom-free) were utilized **to determine which method yields results closest to the real aromatic content values**. The saturated fraction, isolated after the adsorption of unsaturated compounds over silica modified by silver nitrate, was weighed. Then, the content of aromatics corresponds to 100 minus the content of saturates in wt.%.

The GC × GC analysis confirmed the absence of aromatics in the isolated fraction of saturates and *n*-pentane, which was used as the mobile phase in the adsorption step. Due to the low boiling point of *n*–pentane and the gentle evaporation process, none of the gas oil

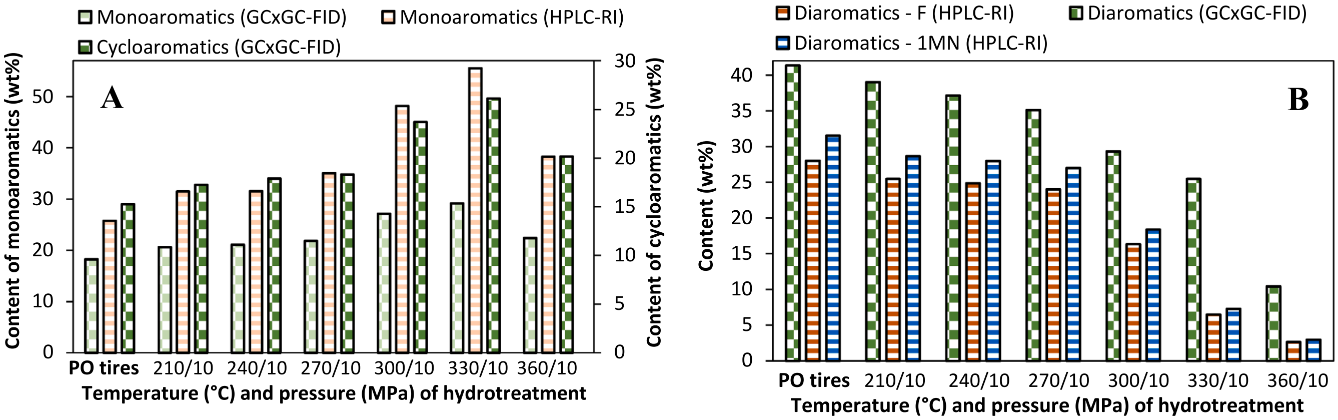

Fig. 7. Aromatic content in gas oil fraction (b.p. 250–360 °C) from tires and its products after hydrotreatment at different conditions. (**A**) – Monoaromatic content, effect of cycloaromatic content on determination by HPLC-RI. (**B**) – Diaromatic content, effect of the use of different standard on determination by HPLC-RI, F = fluorene (EN 12916), 1MN = 1-methylnaphthalene (ASTM D6591).

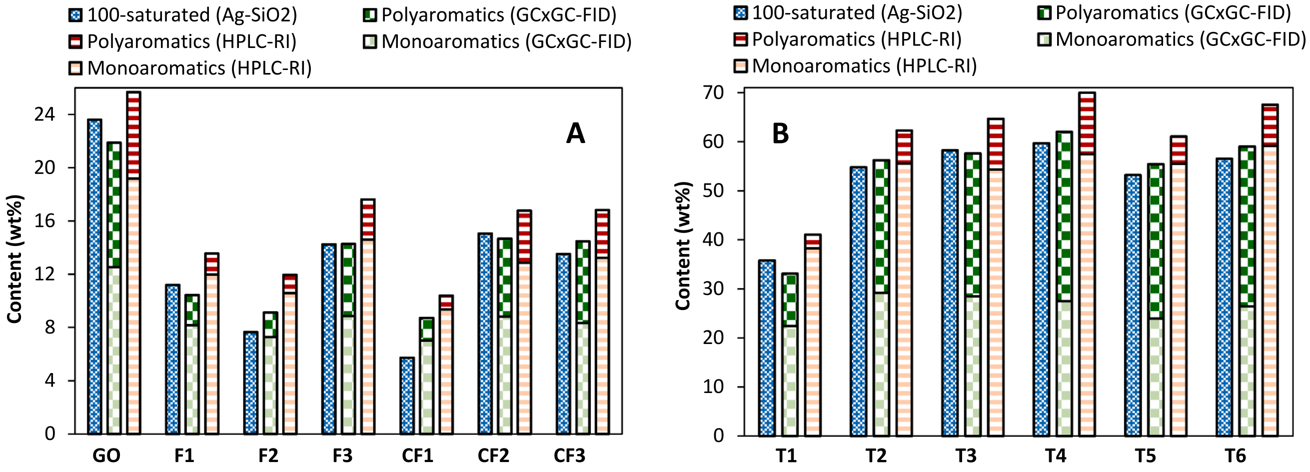

Fig. 8. Aromatic content determined by the studied methods in petroleum gas oil (GO) and gas oil fractions (b.p. 250–360 °C) of the pyrolysis oils after deep hydrotreatment. (**A**) – Samples from waste polyolefins, F = films (PE), CF = waste cups (PP) and films (PE). (**B**) – Samples from scrap tires (T). For more information about the sample designation, see Table S5.

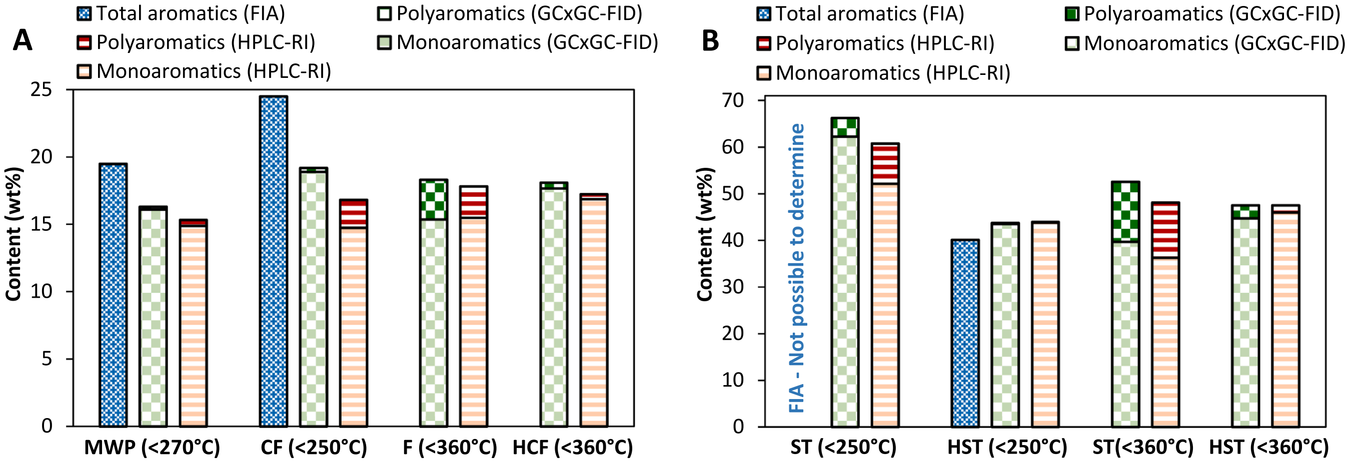

Fig. 9. Aromatic content determined by the studied methods in the samples of plastic oils and its hydrotreated (H) product at 360 °C and 10 MPa. (**A**) – Pyrolysis oils from polyolefins from different feedstocks, MWP = mixed waste plastics, CF = mixture of waste cups (PP) and films (PE), F = films (PE), HCF = hydrotreated sample from CF. (**B**) – Pyrolysis oils from scrap tires (ST), HST = hydrotreated scrap tire oil. The value in the brackets represents the final boiling point of the MWP sample; for the rest of the samples, this value represents the distillation cut used for sample preparation by distillation.

analytes evaporated. In the samples depicted in Fig. 8**,** where minimal content of heteroatoms (sulfur and nitrogen content < 100 mg/kg) and olefins (IV < 3 gI$_2$/100 g) are present, the remaining sample after saturates isolation can be considered as a reference value of aromatics. Despite the potential measurement error of up to ± 2 wt% associated with low sample size, it is evident that GC × GC can be considered to provide results for aromatics much closer to reality than HPLC-RI. For seven samples of gas oils tested, the results from GC × GC differ by less than 5 rel.% from this reference method (Fig. 8**A**). For deeply refined gas oils from tires with the worst quality (samples T4, T5, and T6, Fig. 8**B**), GC × GC reports a slightly higher aromatic content than is likely to be accurate. The analysis of the saturated fraction of these samples by GC × GC–MS showed that mostly tetracycloalkanes eluting in the monoaromatic region are responsible for the higher results of aromatic content (refer to **Figure S6**). Nevertheless, the overestimation by GC × GC is much lower than by HPLC, mainly due to the uniform response of FID compared to the RI detector. Moreover, the 2D separation in the case of GC × GC allowed us to eliminate the small differences in the response of FID by applying the effective carbon number approach.

3.1.5. *Content of aromatics in neat pyrolysis oils*

In contrast to middle distillate fractions discussed in previous sections, neat pyrolysis oils also contain a naphtha fraction (in terms of aromatics, significantly more BTXE compounds are present). Nevertheless, the differences between the results from different methods followed a pattern quite similar to that observed for middle distillates.

FIA method, suitable only for samples with a final boiling point below 315 °C, reported the highest results for crude WPPOs (MWP and CF) (Fig. 9**A**), mostly due to reporting most of the dienes and hetero-compounds as aromatics. As with the kerosene fraction and crude pyrolysis oil from tires, the aromatic content cannot be reliably determined (Fig. 9**B**). Thus, the only suitable application of the FIA method could be to analyze the hydrotreated pyrolysis oils with lower-end boiling point and without heteroatoms and olefins.

Except for one sample, HPLC-RI reported the lowest aromatic content among all methods (Fig. 9), consistently by less than 10 % lower than GC × GC. Significant differences from GC × GC were observed for all aromatic groups (**Table S6**). The variation in response of different aromatic molecules on the RI detector (see section 3.1.2) is highly likely responsible for this observation. The most similar results of aromatic content to those from GC × GC were observed for deep hydrotreated products from tires with boiling points up to 250 and 360 °C (HST $<$ 250 °C and HST $<$ 360 °C). Due to the uniform response of the FID detector to hydrocarbons and very good separation of the aromatics from non-aromatics in reversed-phase column configuration, GC × GC-FID appears to be the most suitable method for aromatics determination in pyrolysis oils.

4. Conclusions

Three standard methods commonly used in refineries for determining aromatic content were compared in analyzing crude and hydrotreated pyrolysis oils from waste plastics and tires. The FIA method (ASTM D1319) is the most time-consuming and suitable only for oils with a final boiling point under 315 °C. It is also the most erroneous method because it reports most dienes and hetero-compounds as aromatics. HPLC-RI (EN 12916) is sensitive to the distribution of aromatic molecules in the sample, owing to differences in the response of individual aromatic molecules. Due to the high content of cycloaromatics in gas oils from tires, monoaromatic content by HPLC-RI in these samples is significantly overreported compared to GC × GC-FID. The most challenging aspect is the determination of diaromatics and triaromatics, whose content can be significantly underreported than that determined by GC × GC-FID. Therefore, although HPLC represents a much faster method than GC × GC, this limitation must be considered. When focusing on meeting the limits for polyaromatics in diesel fuel (according to EN 590) or monitoring aromatics removal during hydrotreatment, GC × GC-FID should be the preferable choice. Although GC × GC analysis is more time-consuming than HPLC, it provides much more information about the sample, and the results for aromatic content are much more reliable and closer to reality. The findings of this paper will be valuable for researchers and industrial companies involved in waste plastics and tires recycling. It guides the selection of the right analytical tool for the reliable and accurate monitoring of aromatic content in pyrolysis oils from waste plastics and tires.

CRediT authorship contribution statement

Miloš Auersvald: Writing – original draft, Visualization, Project administration, Methodology, Investigation, Formal analysis, Conceptualization. **Michal Šiman:** Investigation. **Eliška Lyko Vachková:** Writing – review & editing, Investigation. **Jiří Kroufek:** Writing – review & editing, Methodology. **Petr Straka:** Writing – review & editing, Supervision, Methodology, Investigation, Funding acquisition. **Genesis Barzallo:** Writing – review & editing, Investigation, Data curation. **Petr Vozka:** Writing – review & editing, Supervision, Methodology, Investigation, Funding acquisition.

Declaration of competing interest

The 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

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2024.131714.

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