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Research Paper

Advancing circular plastics: hydrotreatment of pyrolysis oils for high-yield ethylene production

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ABSTRACT

The mounting crisis of plastic waste, coupled with the shortcomings of mechanical recycling, underscores the urgent need for scalable chemical recycling solutions. Among these, pyrolysis followed by steam cracking emerges as a promising pathway to transform polyolefin-rich waste into virgin-grade olefins. Yet, the complex nature of pyrolysis oils has hindered their industrial use. In this study, hydrotreatment was investigated as an upgrading strategy for distilled pyrolysis oils derived from real mixed plastic waste. Two diesel-range fractions of pyrolysis oil, raw and hydrotreated, were characterized using two-dimensional gas chromatography (GC × GC) and evaluated in a bench-scale steam cracker. Hydrotreatment provided significant compositional refinement, lowering nitrogen from 1546 mg·kg^{-1} to <10 mg·kg^{-1}, reducing olefins from 51 wt% to 8 wt%, and eliminating detectable oxygen (1776 mg·kg^{-1} initially). These changes brought the product within industrial feedstock specifications. These improvements translated into enhanced cracking performance. The hydrotreated pyrolysis diesel blend achieved ethylene yields of up to 32 wt% at 880 °C, surpassing fossil naphtha while suppressing CO and aromatic by-products such as benzene, toluene, and xylenes (BTX). The results establish hydrotreatment as a critical enabler for converting waste-derived pyrolysis oils into cracker-ready feedstocks, supporting their integration into petrochemical infrastructure and advancing a circular economy for plastics.

1. Introduction

The growing accumulation of plastic waste poses serious environmental and human health challenges. In 2023, global plastic production was estimated to range between 400 and 436 million tons, mainly fossil-based (PlasticsEurope, 2024; UNCTAD, 2025). However, only about 9 % of plastic waste was effectively recycled. (Jehanno et al., 2025; Li et al., 2022; PlasticsEurope, 2024). Projections show production may exceed one billion tons by 2050, with recycling reaching only 17 % by 2060 (OECD, 2022). Most unrecycled plastic waste is either incinerated, releasing greenhouse gases, or leaks into the environment, underscoring the urgency for scalable circular solutions.

While mechanical recycling remains the most established route, it is limited to clean, well-sorted waste streams and results in downcycling (Li et al., 2022). Chemical recycling offers broader feedstock flexibility by converting plastics into monomers, thereby enabling the production of high-quality recycled plastics. Among chemical recycling technologies, pyrolysis is a promising route for polyolefin-rich waste, producing mainly pyrolysis oil (Py-oil) alongside gases and char. The produced Py-oil, which can be integrated into existing steam crackers to produce valuable base chemicals, such as ethylene and propylene, aligns with circular economy goals (Karaba et al., 2020; Kusenberg et al., 2024; Kusenberg et al., 2022a; Kusenberg et al., 2022b; Li et al., 2022; Palos et al., 2021; Ragaert et al., 2017; Thunman et al., 2019; Zou et al., 2023). However, direct use of Py-oils in steam crackers presents technical and economic barriers. These Py-oils typically exhibit broad boiling ranges, high olefin and aromatic content, and elevated levels of nitrogen, oxygen, halogens, and metals.

Pyrolysis of pure polyolefin waste produces hydrocarbon liquids with very low heteroatom levels (Aboulkas et al., 2010). However, in reality, MPW feedstocks are often contaminated with polar plastics and biomass-related residues, such as paper fibers, food waste, and other lignocellulosic materials (Aboulkas et al., 2012; Dahman et al., 2025).

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Nomenclature

Term/Abbreviation	Definition
AED	Atomic Emission Detector
BSSC	Bench-scale Steam Cracking unit
COT	Coil Outlet Temperature
CIT	Coil Inlet Temperature
COP	Coil Outlet Pressure
CSTR	Continuous stirred-tank reactor
PFR	Plug flow reactor
FBP	Final Boiling Point
FID	Flame Ionization Detector
GC × GC	Comprehensive Two-Dimensional Gas Chromatography
H_2/HC	Hydrogen-to-Hydrocarbon feed ratio
HDT	Hydrotreatment or Hydrotreated
HDT Py-Diesel	Hydrotreated diesel-range fraction of pyrolysis oil from mixed plastic waste
IBP	Initial Boiling Point
WHSV	Weight Hourly Space Velocity ($kg_{feed} \cdot h^{-1} \cdot kg_{cat}^{-1}$)
MPW	Mixed Plastic Waste
NCD	Nitrogen Chemiluminescence Detector
NiMo/γ-Al_2O_3	Nickel-Molybdenum on gamma-alumina catalyst
PE	Polyethylene
PET	Polyethylene Terephthalate
PP	Polypropylene
PS	Polystyrene
PUR	Polyurethane
PVC	Polyvinylchloride
PIONA	Paraffins, *iso*-paraffins, olefins, naphthenes, and aromatics
BTX	Benzene, toluene, and xylenes
Py-Diesel	Diesel-range fraction of raw pyrolysis oil from mixed plastic waste
Py-oil	Crude plastic waste pyrolysis oil
RGA	Refinery Gas Analyzer
TOF-MS	Time-of-Flight Mass Spectrometry
wt.%	Weight percent

These impurities enrich the resulting pyrolysis oils with chlorine, nitrogen, oxygenated species, and metals, thereby promoting coke formation, fouling, corrosion, and shortened run lengths in steam crackers. Although olefins are not strictly considered contaminants, their high concentrations in pyrolysis oils also compromise feed stability and steam cracker operability by accelerating the formation of coke and deposits. Proof-of-concept studies have shown that co-feeding raw or partially upgraded Py-oils with fossil naphtha can produce comparable light olefin yields (Hájeková & Bajus, 2005; Hájeková et al., 2007; Karaba et al., 2025; Kusenberg et al., 2022c; Kusenberg et al., 2023; Kusenberg et al., 2022d; Mandviwala et al., 2024; Ren et al., 2006). However, drawbacks such as elevated coke and CO formation, heavy by-products, and process instability persist. Pretreatment methods, such as filtration (Kusenberg et al., 2023) and fractionation (Faussone, 2018; Tomar et al., 2025; Zeb et al., 2025; Zeb et al., 2023), help reduce particulates and narrow the boiling range. However, these pretreatment methods cannot remove chemically bound contaminants and unsaturated hydrocarbons, which continue to impact product quality and operational reliability. Therefore, further upgrading, such as hydrotreatment, is required to eliminate these contaminants and enhance feedstock quality. Hydrotreatment is a catalytic process performed in the presence of hydrogen to saturate unsaturated hydrocarbons and remove contaminants, yielding more stable and cracker-compatible feedstocks. Hydrotreatment is a well-established process in petroleum refining and petrochemical processing, and it is readily applicable for upgrading pyrolysis oils (Cañete et al., 2025; Dabros et al., 2025; Kim et al., 2025; Yoon et al., 2024; Zacher et al., 2014; Zou et al., 2023). It removes heteroatoms (e.g., N, O, Cl), saturates olefins and aromatics, and lowers metal contaminants, yielding more stable, cracker-compatible feedstocks. This process could directly address the limitations that prevent large-scale adoption of plastic-derived oils in the petrochemical sector.

Previous studies have explored the hydrotreatment to improve the quality of plastic-derived pyrolysis oils (Cañete et al., 2025; Dabros et al., 2025; Kim et al., 2025; Lim et al., 2025; Neuner et al., 2022; Yoon et al., 2024). However, the impact of hydrotreatment on the steam-cracking performance of these plastic-derived pyrolysis oils, particularly those derived from real post-consumer packaging waste, remains largely unexplored. This study addresses this gap by systematically evaluating the impact of hydrotreatment on the composition of distilled pyrolysis oils and their compatibility with steam crackers, with a particular emphasis on product yields, contaminant removal, and operational performance. The findings provide new insights into the upgrading requirements and feedstock compatibility of plastic-derived oils for integration into existing olefin production routes. Diesel-range fractions of pyrolysis oils, both raw and hydrotreated, were characterized in detail using comprehensive two-dimensional gas chromatography (GC × GC) to determine their hydrocarbon profiles and concentrations of contaminants. Their steam-cracking performance was then evaluated in a bench-scale unit, using fossil naphtha as a benchmark. The results offer a clear pathway for incorporating upgraded plastic-derived oils into existing petrochemical operations, supporting circular economy solutions for hard-to-recycle municipal waste streams.

2. Apparatus and experimental procedure

2.1. Feedstocks preparation and hydrotreatment

Two diesel-range pyrolysis oils were investigated in this study: a raw sample (Py-Diesel) and a hydrotreated sample (HDT Py-Diesel), both obtained from the same real, highly mixed municipal plastic waste (MPW) that is unsuitable for mechanical recycling. The MPW feedstock primarily consisted of polyolefins (polyethylene (PE), polypropylene (PP)), with contamination from polystyrene (PS), and various polar polymers, including polyethylene terephthalate (PET), ethylene–vinyl alcohol (EVOH), ethylene–vinyl acetate (EVA), polyvinyl chloride (PVC), polyurethane (PUR), and polyamide (PA). A comprehensive description and characterization of the mixed plastic waste (MPW) feedstock and the pyrolysis process can be found in our previous work, where crude pyrolysis oil was produced using a continuous pilot-scale pyrolysis unit (Kusenberg et al., 2022e). The first sample, denoted as Py-Diesel in this work, is the sample obtained from the fractionation of a full-range pyrolysis oil. The fractionation of the full-range Py-oil was performed to narrow the boiling range and reduce metal contaminants. For this purpose, a vacuum distillation unit was used to fractionate the Py-oil, as described earlier by Zeb et al. [12]. The second sample, referred to in this work as HDT Py-Diesel, is the hydrotreated Py-Diesel fraction. The hydrotreatment upgrading was carried out in a multiphase continuous stirred-tank reactor (CSTR) with a Robinson–Mahoney design as shown in Fig. 1. The CSTR setup is a 250 mL stainless steel (SS316) unit from Autoclave Engineers, designed to operate under hydrotreatment conditions with pressures up to 120 bar and temperatures up to 400 °C, reaching the demanding ranges typically applied in industrial hydrotreating processes (Lauwaert et al., 2017). CSTRs provide more uniform mixing and better catalyst wetting than plug flow reactors (PFRs), which makes them well-suited for studying intrinsic kinetics and evaluating catalyst performance (Lauwaert et al., 2017). Therefore, our group has employed the CSTR setup to investigate the hydrotreatment kinetics of pyrolysis oil (Ureel et al., 2025). However,

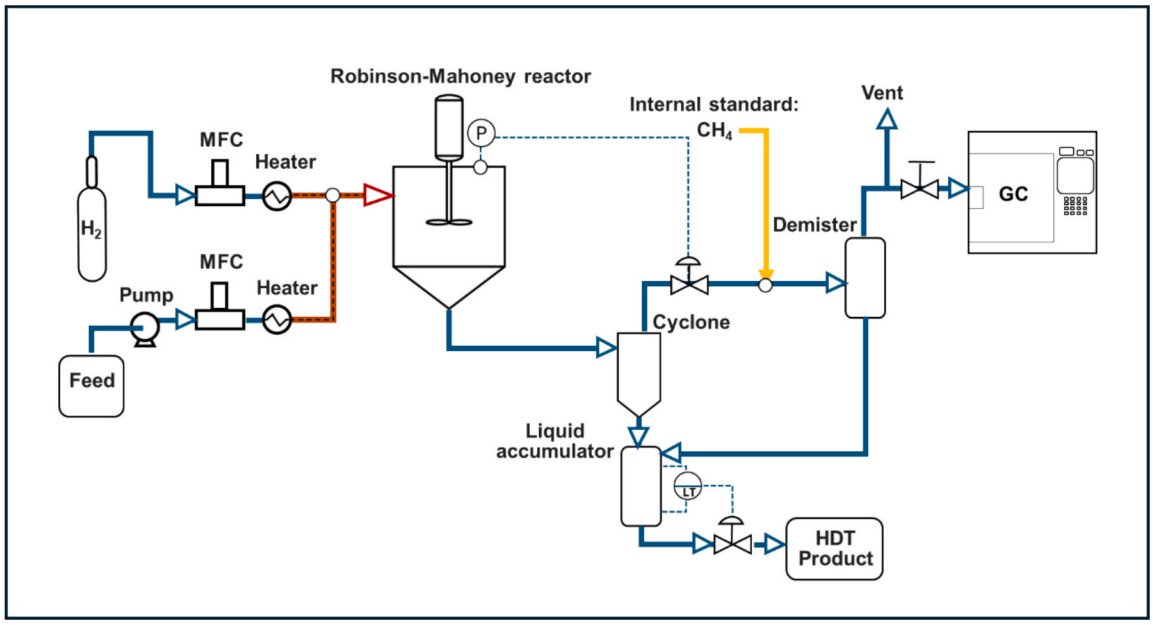


Fig. 1. The schematic of the hydrotreatment setup, highlighting the key components.

only the diesel fraction of the pyrolysis oil could be investigated. The lighter fraction, namely naphtha, would completely vaporize under the applied hydrotreatment conditions, and operation in the gas phase would no longer correspond to the intended CSTR mode of operation. The hydrotreatment was conducted using a commercial NiMo/γ-Al_2O_3 hydrotreatment catalyst under optimized conditions to maximize olefin saturation. The temperature was maintained at 330 °C and the pressure at 70 bar. The weight hourly space velocity (WHSV) was 5.76 $kg_{feed}{\cdot}h^{-1}{\cdot}kg_{cat}^{-1}$, and the hydrogen-to-hydrocarbon feed ratio (H_2/HC ratio) was 866.7 $Nm^3{\cdot}m^{-3}$. Further details about the experimental setup are provided in (Lauwaert et al., 2017). Further details about the hydrotreatment procedure are provided in previous reports (Piña, 2025; Ureel et al., 2025).

The diesel-range pyrolysis oils (raw and hydrotreated) were steam cracked in blends with a fossil naphtha reference. This approach was employed to safeguard the experimental equipment from potential issues such as corrosion and fouling in the convection and transfer line exchanger sections, and more critically, from blockages and damage in the sampling systems of the steam cracking unit. These risks are primarily attributed to corrosive or deposit-forming contaminants commonly found in waste-derived feedstocks. Furthermore, given the significant disparity in production scale between fossil steam cracker feedstocks and plastic-waste pyrolysis oils, blending with fossil naphtha is expected to remain the prevailing strategy at the industrial level rather than using pure pyrolysis oils. In this context, blends containing 25 wt% diesel-range pyrolysis oil (raw or hydrotreated) and 75 wt% reference fossil naphtha (1:3 wt ratio) was prepared for the steam cracking trials. The same fossil naphtha used for blending was also cracked pure as a benchmark for the steam cracking performance of diesel-range pyrolysis oils.

2.2. Feedstocks characterization

The hydrocarbons and heteroatoms in the diesel-range pyrolysis oils were analyzed using two-dimensional gas chromatography (GC × GC) coupled with various detectors. The hydrocarbon composition was determined using a flame ionization detector (FID), as detailed in the supporting information (SI). The GC × GC-FID results were used to estimate the carbon number range and boiling points (IBP, 50 %, and FBP) according to the ASTM D2887 method (Moon, 1975). Further GC × GC-FID analysis was conducted on samples treated with Ag–SiO_2 sorbent. This method was employed to selectively isolate olefinic compounds from complex pyrolysis oil matrices, enabling a more accurate assessment of olefin content, as outlined in the analytical section of the supporting information (SI) and described in greater detail in the previous work by Auersvald et al. (Auersvald et al., 2025). Nitrogen compounds were analyzed using a nitrogen-chemiluminescence detector (NCD) connected to flow-modulated GC × GC instruments (Agilent, 8890 GC system), as detailed in the Supporting Information (SI). The oxygen and chlorine content in the investigated diesel-range pyrolysis oils was assessed using GC × GC coupled with Atomic Emission Detection (AED), as summarized in the supporting information (SI). The liquid density (25 °C) was measured using a Mettler Toledo (USA) DA-100 M density meter with an accuracy of 0.001 $g{\cdot}cm^{-3}$.

2.3. Steam cracking bench-scale setup

The steam cracking evaluation was conducted using the bench-scale steam cracking (BSSC) setup at the Laboratory for Chemical Technology (LCT) at Ghent University. Detailed descriptions of the setup and procedures can be found in previous works (Harper et al., 2011; Kusenberg et al., 2022d; Pyl et al., 2011). The BSSC unit is designed for easy scale-up to industrial furnaces. It comprises three sections: the feeding section, the reactor (furnace) section, and the analysis section, as illustrated in the schematic representation of the BSSC unit provided in the supporting information (SI). The reactor is electrically heated and constructed from Incoloy 800HT, measuring 1.475 m in length and having an internal diameter of 6 mm. The feedstock and demineralized water are supplied via Coriolis flow meter-controlled pumps to the evaporation section, where the feedstock is vaporized and mixed with steam before entering the reactor. The steam cracking conditions examined in this study are detailed in the supporting information (SI). Throughout the experiments, the liquid hydrocarbon flow rate was kept at 150 g/h, with a steam dilution weight ratio (H_2O/HC) of 0.5. The coil outlet pressure (COP) was consistently maintained at 1.7 bar. The preheating and mixing zones were held at 350 °C to ensure complete vaporization of the feedstock. The coil inlet temperature (CIT) was set at 550 °C for all experiments, while three coil outlet temperatures (COTs) were tested: 820 °C, 850 °C, and 880 °C. The reactor effluent was analyzed online using a custom-developed heated valve-based sampling system

connected to three separate gas chromatographs, allowing for real-time analysis without delay. Nitrogen was injected as an internal standard before the effluent was sampled at 350 °C via the valve-based online sampling system. Samples were transferred through heated lines for online analysis using GC × GC-FID. A portion of the gaseous effluent was analyzed using a refinery gas analyzer (RGA). The RGA was used to analyze C_4- compounds. H_2, CO_2, CO, N_2, methane, ethane, ethylene, and acetylene were detected by a thermal conductivity detector (TCD), while C_1-C_4 hydrocarbons were detected using the FID detector. The GC × GC-FID was employed for the quantification of higher hydrocarbons (C_{5+}). The quantification in the GC × GC-FID analysis was performed using the effective carbon number method (Beens et al., 1998; De Bruycker et al., 2014), with methane from the RGA analysis serving as a secondary internal standard. The specifications used in the RGA and GC × GC-FID are summarized in Tables S5 and S6 in the Supporting Information (SI). These qualitative and quantitative analyses provide a comprehensive assessment of the entire steam cracking product range, achieving a mass balance closure within ±5 wt% relative to the feedstock.

3. Results and discussion

3.1. Feedstock analysis

First, the hydrocarbon composition of the diesel-range pyrolysis oils (raw and hydrotreated) was assessed using GC × GC-FID. Subsequently, a detailed analysis of heteroatomic compounds was conducted using GC × GC-NCD and GC × GC-AED. This allowed us to identify key contaminants and to trace their conversion during steam cracking.

3.1.1. Hydrocarbon matrix

Fig. 2 provides a contour plot representation of the GC × GC-FID chromatograms for the diesel-range pyrolysis oils, the raw feedstock (Py-Diesel, (a)), and the hydrotreated feedstock (HDT Py-Diesel, (b)). Both samples contain highly branched hydrocarbon fractions. These fractions pose significant analytical challenges, particularly in distinguishing branched *iso*-olefins from branched *iso*-paraffins. Therefore, to address this challenge, we applied the $AgNO_3/SiO_2$-based olefin removal method followed by GC × GC-FID analysis, following the approach reported by Auersvald et al. (Auersvald et al., 2025). This approach enabled more group-type separation and visualization of branched *iso*-olefins and diolefins, which is challenging in the GC × GC chromatogram of untreated samples. The method selectively retains compounds containing aliphatic olefinic functionalities (e.g., olefins and styrenes), while allowing the elution of *iso*-alkanes, n-alkanes, cycloalkanes, and alkylbenzenes that lack such groups, as demonstrated by the differences between the chromatograms of untreated and $AgNO_3/SiO_2$-treated samples shown in the supporting information (SI).

The key characteristics of the diesel-range pyrolysis oils and fossil naphtha are summarized in Fig. 3 and detailed in Table 1 below. Based on their boiling ranges (136–425 °C) and carbon number distributions (C_9 to C_{25}), both Py-Diesel and HDT-Py-Diesel are classified as middle distillate-range fractions. The Py-diesel has a low hydrogen-to-carbon (H/C) ratio of 1.98. This lower ratio is mainly due to a higher content of olefins and aromatics, which decreases the overall hydrogen content of the feedstock. On the other hand, fossil naphtha has a higher H/C ratio of 2.28. A higher H/C ratio is preferable because it indicates a paraffin-rich feedstock, which results in higher olefin yields and reduced coke formation. After hydrotreatment, the H/C ratio of Py-Diesel increased to 2.03, bringing it closer to that of fossil naphtha and improving its suitability for steam cracking. This increase in H/C ratio

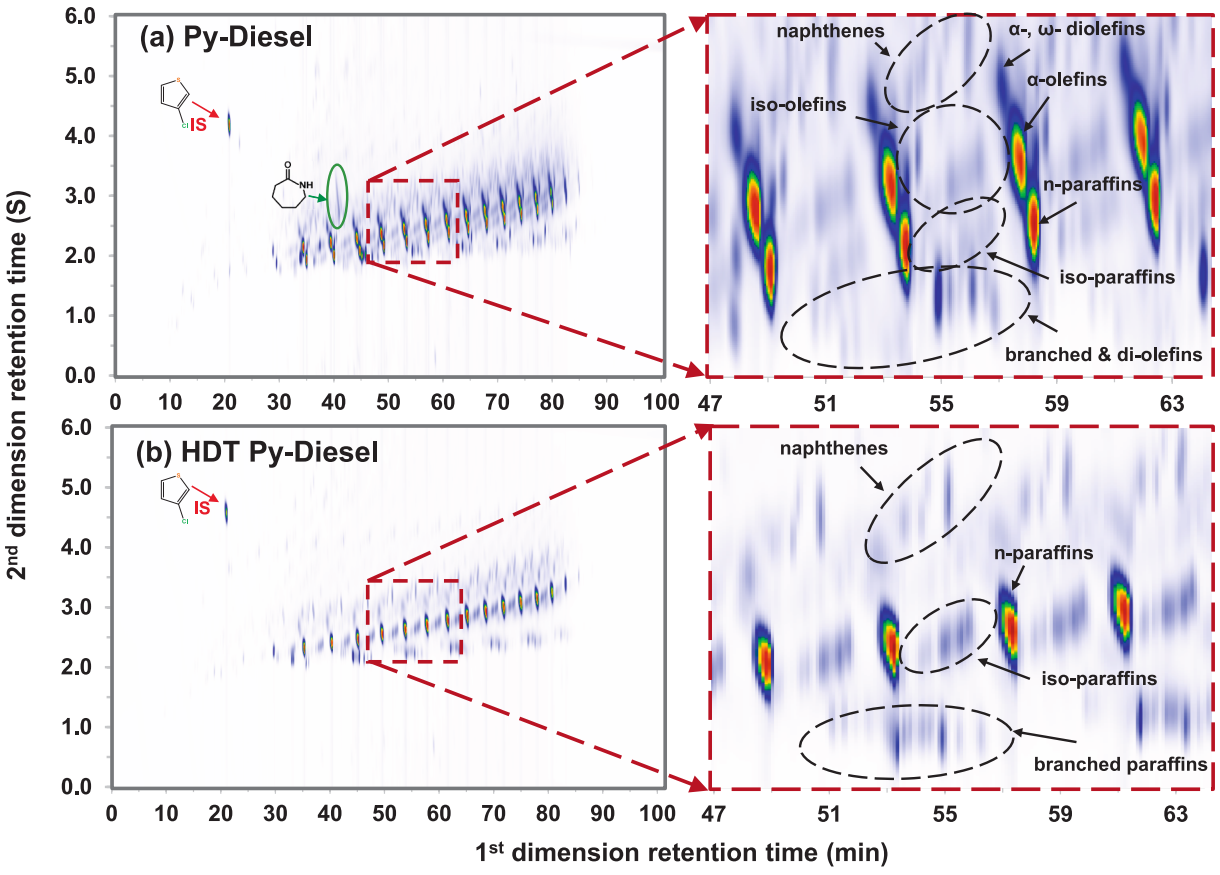


Fig. 2. GC × GC-FID chromatograms of the two diesel-range pyrolysis oils investigated in this study: (a) a raw sample (Py-Diesel) and (b) a hydrotreated sample (HDT Py-Diesel).

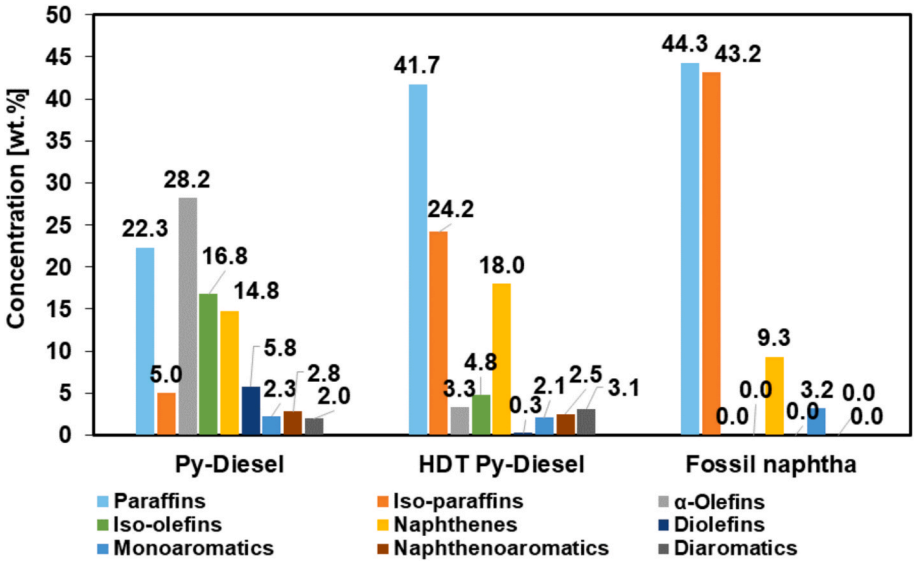


Fig. 3. Hydrocarbons distribution for the investigated feedstocks: (a) Py-Diesel, (b) HDT Py-Diesel, and (c) benchmark fossil naphtha.

Table 1
Summary for the hydrocarbon group composition of the Py-Diesel and HDT Py-Diesel feedstocks used in the steam cracking experiments, as analyzed using GC × GC-FID.

Feedstock	Py-Diesel	HDT Py-Diesel	Fossil naphtha
IBP [°C]	136	136	14
50 % BP [°C]	291	291	50
FBP [°C]	425	425	161
H/C molar ratio	1.98	2.03	2.28
Carbon number range	$C_9 - C_{25}$	$C_9 - C_{25}$	$C_5 - C_{10}$
Density (20 ∘C) [g/cm^3]	0.807	0.795	0.675
	PIONA [wt.%]		
Paraffins [wt.%]	22.3	41.7	44.3
Iso-paraffins [wt.%]	5.0	24.2	43.2
α-Olefins [wt.%]	28.2	3.3	–
Iso-olefins [wt.%]	16.8	4.8	–
Diolefins [wt.%]	5.8	0.3	–
Naphthenes [wt.%]	14.8	18.0	9.3
Monoaromatics [wt.%]	2.3	2.1	3.2
Naphthenoaromatics [wt.%]	2.8	2.5	–
Diaromatics [wt.%]	2.0	3.1	–

reflects substantial changes in the hydrocarbon composition of Py-Diesel following hydrotreatment. The untreated Py-Diesel is predominantly composed of unsaturated hydrocarbons, with α-olefins, *iso*-olefins, and diolefins accounting for 28.2 wt%, 16.8 wt%, and 5.8 wt%, respectively, resulting in a combined olefins and dienes content of 50.8 wt%. After hydrotreatment, these unsaturated contents were largely saturated, reducing their concentrations to 3.3 wt%, 4.8 wt%, and 0.3 wt%, respectively, with a combined total of approximately 8.4 wt%. Correspondingly, the contents of paraffins and *iso*-paraffins increase substantially from 22.3 wt% to 41.7 wt% and from 5.0 wt% to 24.2 wt%, respectively. Additionally, naphthenes increased from 11.9 wt% to 18.0 wt%. On the other hand, the aromatic content decreased, driven by the hydrogenation of monoaromatics and naphthenoaromatics, which explains the higher naphthene content in the hydrotreated sample. Diaromatics, however, slightly increased, possibly due to condensation reactions or partial saturation of polyaromatic species.

While both n-paraffins and *iso*-paraffins increased as expected after hydrotreatment, the rise in *iso*-paraffins was slightly more pronounced, despite the sample being richer in α-olefins and α,ω-diolefins. This is attributed to the hydroisomerization of olefins and dienes into *iso*-paraffins (Ureel et al., 2025). The observed increase in naphthenes can be attributed to the hydrogenation of aromatics and cyclic olefins, which convert them into naphthenes (Neuner et al., 2022; Ureel et al., 2025).

3.1.2. Contaminant analysis

The composition of mixed plastic waste strongly influences both the quality of the resulting pyrolysis oil and its behavior during upgrading and steam cracking. Non-polyolefin polymers such as PVC, PET, PA, and PUR introduce chlorine-, oxygen-, and nitrogen-containing species that elevate heteroatom levels and promote the formation of acids, CO/CO_2, and coke precursors during downstream processing. Previous studies (Kusenberg et al., 2022b; Roosen et al., 2020) demonstrated that these heteroatoms originate primarily from non-polyolefin and multilayer components (e.g., PVC, PET, EVOH, and PA) present in post-consumer waste. Even small fractions of such materials can significantly increase the concentrations of Cl, O, and N in pyrolysis oils, thereby reducing feed stability and steam-cracking performance (Kusenberg et al., 2022b). During hydrotreatment, no significant catalyst deactivation was observed under the relatively short time-on-stream (TOS) conditions applied in this (Piña, 2025; Ureel et al., 2025). This finding is supported by the consistent product composition and contaminant removal observed at repeated evaluation points. The absence of notable deactivation can be partly attributed to the prior distillation step, which effectively removes metals and high-boiling contaminants, thereby reducing catalyst contamination and the formation of coke precursors. Consequently, more pronounced coke deposition and faster catalyst aging are expected during the hydrotreatment of full-range MPW-derived or more contaminated pyrolysis oils, where such impurities are present at higher concentrations.

Fig. 4 summarizes the key components of concern for industrial steam crackers, namely the olefins, oxygen, nitrogen, and chlorine concentrations in the Py-Diesel, as well as the effect of hydrotreatment and blending within contaminant-free fossil naphtha. Nitrogen, oxygen, and chlorine contaminants were analyzed using GC × GC-NCD, GC × GC-AED-O, and GC × GC-AED-Cl. Their corresponding chromatograms are shown in the contaminants analysis section of the supporting information (SI). Chlorine (5 $mg \cdot kg^{-1}$) in the Py-Diesel is of lesser concern, whereas nitrogen (1159 $mg \cdot kg^{-1}$), oxygen (1776 $mg \cdot kg^{-1}$), and olefins (51 wt%) exceed industrial thresholds for light feedstocks by more than an order of magnitude and represent the primary barriers to direct use in steam crackers (Kusenberg et al., 2022e). Blending with fossil naphtha at a 1:3 ratio helps reduce nitrogen to 387 $mg \cdot kg^{-1}$, oxygen to 442 $mg \cdot kg^{-1}$, and olefins content to 13 wt%, but still exceeds industrial thresholds of 100 $mg \cdot kg^{-1}$ for the nitrogen and oxygen and 2 wt% for the olefins (Kusenberg et al., 2022e).

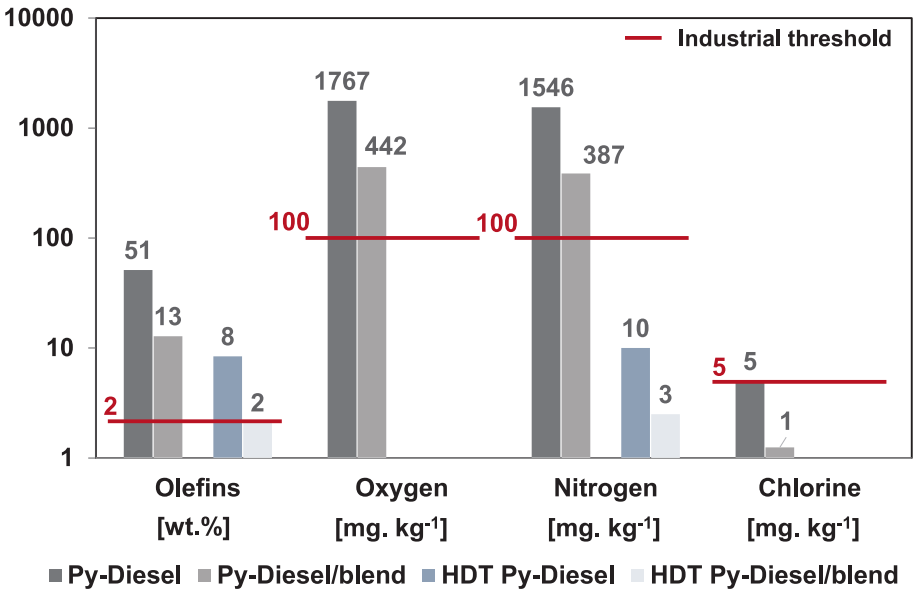


Fig. 4. Summary of primary contaminants (olefins, oxygen, nitrogen, and chlorine) in Py-Diesel, HDT Py-Diesel, and their estimated levels after blending with fossil naphtha.

Metals and sulfur are additional parameters relevant for assessing the suitability of Py-Diesel for steam cracking. Previous investigations on full-range MPW pyrolysis oils established that fractional distillation effectively removes metal contaminants, reducing their concentrations below detection limits and yielding fractions suitable for steam cracking (Kusenberg et al., 2022c; Zeb et al., 2025; Zeb et al., 2023). The present study builds upon this foundation by examining the diesel-range fraction of pyrolysis oil, assessing the impact of hydrotreatment on heteroatom removal, and quantifying its influence on steam cracking performance. In contrast to nitrogen- and halogen-containing species, sulfur contaminants are usually found in MPW pyrolysis oils at much lower concentrations. They are therefore not expected to affect furnace integrity or product yields significantly. At these trace levels, sulfur compounds are generally tolerated under conventional steam-cracking conditions. They can even exert a protective effect by passivating metal surfaces through the formation of a sulfide layer, thereby reducing catalytic coke formation and extending the furnace run length (Reyniers & Froment, 1995; Wang et al., 2008).

Hydrotreatment significantly improves the quality of the feedstock. Following hydrotreatment, no oxygen was detected. The olefin content in the hydrotreated Py-Diesel was reduced to 8 wt% and further decreased to 2 wt% through blending, thereby meeting the threshold required for steam cracking. Nitrogen levels were lowered to below 10 $mg{\cdot}kg^{-1}$ in the hydrotreated Py-Diesel and to less than 3 $mg{\cdot}kg^{-1}$ after blending. These results demonstrate that while blending alone is sufficient for meeting chlorine content specifications, hydrotreatment is still necessary for reducing oxygen, nitrogen, and olefin levels to meet industrial steam cracking specifications.

To comply with steam cracker specifications through blending alone, the required weight-based ratio with fossil naphtha would be 1:25 for olefins and 1:11 for nitrogen. With hydrotreatment, however, nitrogen and oxygen are sufficiently reduced to allow the hydrotreated Py-Diesel to be fed directly to a steam cracker, without the need for blending to meet their respective limits. Olefins, however, remain the limiting factor, allowing a maximum blending ratio of 1:3 (hydrotreated Py-Diesel to fossil naphtha) to stay below the 2 wt% threshold. Hydrotreatment improves the quality of plastic-derived pyrolysis oils by addressing key contaminant concerns. However, distillation is still required to narrow the boiling range of the Py-oil and make it compatible with steam cracker feed specifications. While the distillation step effectively reduces the boiling range, it also lowers the overall Py-oil yield and increases process complexity. Furthermore, aromatics and naphthenes persist even after hydrotreatment, which negatively impacts steam cracker operability and product selectivity. In comparison with current petrochemical product standards, the impurity levels achieved after upgrading are consistent with those observed in existing naphtha crackers that feed directly into polymerization units (Kusenberg et al., 2022d). The low contaminant concentrations attained indicate that the upgraded MPW-derived pyrolysis oils could be seamlessly integrated into existing olefin purification and polymerization systems without requiring additional upgrading steps.

Several strategies could enhance overall carbon recovery by mitigating these losses and enabling the utilization of the heavy fraction. Catalytic pyrolysis can increase the yield of lighter hydrocarbons suitable for blending or steam cracking (Elordi et al., 2012; Kusenberg et al., 2022a). The heavy fraction can also be recycled back to the pyrolysis reactor for further conversion, thereby increasing the yield of lighter and more crackable hydrocarbons. Alternatively, the heavy fraction can be fed to refinery upgrading units (e.g., fluid catalytic cracking (FCC) (Tomar et al., 2025), delayed coking (Kusumi et al., 2024), hydrocracking) (Kim et al., 2025). Additionally, the heavy fraction can be utilized for the production of high-value hydrocarbons, such as lubricating oils (Neuner et al., 2022), thereby enhancing overall carbon efficiency and circularity. The integration of hydrotreatment with hydrocracking enables the conversion of heavier, aromatic-rich fractions into lighter, paraffinic hydrocarbons while processing the entire boiling range of MPW pyrolysis oils directly, thereby minimizing the need for fractionation and improving overall liquid yields. However, controlling metal contaminants in the hydroprocessing of the full-range pyrolysis oils is crucial to avoid catalyst poisoning and premature deactivation. More sustainable techniques that can be applied to reduce trace metals further before hydroprocessing include depth filtration (Kusenberg et al., 2023; Velghe et al., 2011) and low-cost guard beds (Ali & Abbas, 2006; Kusenberg et al., 2022b). This hydrotreatment–hydrocracking integration is the focus of ongoing work aimed at developing a robust scheme for producing cracker-ready feedstocks from MPW pyrolysis oils.

3.2. *Performance in steam cracking*

In this section, the raw Py-Diesel and HDT Py-Diesel are evaluated as a co-feed, blended at 25 wt% with a fossil naphtha in a bench-scale

steam cracker. Table 2 below summarizes the main characteristics of the feedstock blends and the reference fossil naphtha used in the steam cracking experiments. The fossil naphtha used in this work, both as a blending feedstock and as a benchmark, is a high-paraffin naphtha, comprising 87.5 wt% paraffins with a nearly equal distribution between n-paraffins (44.3 wt%) and *iso*-paraffins (43.2 wt%), along with smaller fractions of naphthenes (9.3 wt%) and monoaromatics (3.2 wt%). No olefins or diolefins were detected in the fossil naphtha. Its C_5–C_{10} carbon number distribution, combined with its composition, makes it categorized as a light naphtha, a typical feedstock for steam cracking.

Three different cracking severities were selected, corresponding to coil outlet temperatures (COTs) of 820 °C, 850 °C, and 880 °C (see the supporting information). These severities are within the typical cracking severity range for naphtha steam cracking and also enable comparison with the performance of MPW Py-oil feedstocks tested earlier on the same setup (Kusenberg et al., 2024; Kusenberg et al., 2022c; Kusenberg et al., 2023; Kusenberg et al., 2022d). The GC × GC-FID chromatograms for the online sampling of the reactor effluent during cracking are presented in the supporting information (SI). The analysis of the GC × GC chromatograms was grouped based on carbon number range and process relevance of components into simplified fractions: C_{4-}, C_5–C_9, and fractions. The C_{4-} fraction includes light olefins, alkanes, and non-condensable gases such as CO, CO_2, and H_2. The C_5–C_9 range, referred to as pyrolysis gasoline (Pygas), comprises mid-boiling products rich in aromatics and unsaturated hydrocarbons. Finally, the C_{10+} fraction, referred to as pyrolysis fuel oil (PFO), is primarily composed of heavier aromatic hydrocarbons.

Fig. 5 shows the yields of the most essential products, including methane, light olefins (ethylene, propylene, 1,3-butadiene), Pygas, and PFO, in the reactor effluent as a function of the coil outlet temperature (COT). Across all feedstocks, increasing the COT resulted in higher total C_{4-} and ethylene yields. Meanwhile, Pygas yields declined with increasing temperature, indicating a greater degree of cracking of the C_{5+} fractions of the feedstocks. On the other hand, the PFO yields increased with temperature, indicating the formation of heavier aromatics at higher severities. This trend suggests that cracking at higher temperatures (more severe conditions) boosts ethylene yields on the one hand, but also promotes secondary reactions that generate heavier aromatic by-products on the other hand, leading to coke formation and fouling issues. Depending on the feedstock properties, a favorable trade-off point in cracking severity exists that balances the maximization of ethylene yield with the minimization of coke formation (De Bruycker et al., 2014; Van Geem et al., 2005; Zimmermann & Walzl, 2009). This operating point is commonly characterized by the propylene-to-ethylene (P/E) ratio [$kg \cdot kg^{-1}$]. Lower severity (higher P/E ratios) corresponds to milder cracking conditions, which reduce coke production but result in lower feed conversion and an increased formation of lower-value products. In contrast, higher severity (lower P/E ratios) enhances olefin yields but increases the risk of excessive coke formation and shorter furnace operation. While there is no strict operating range, a P/E ratio of 0.4——0.5 is a typical range for industrial naphtha crackers (De Bruycker et al., 2014; Van Geem et al., 2005).

As shown in Fig. 5 and detailed in Table 3 below, the Py-Diesel blend produced higher ethylene yields than the reference fossil naphtha at all investigated COTs (i.e., 820, 850, and 880 °C). Similar enhancements in ethylene yields were also reported by Kusenberg et al. for full-range pyrolysis oils, from which the diesel fraction investigated in this study was derived (Kusenberg et al., 2022d). As evidenced by the chromatogram in Fig. 2, the Py-Diesel contains a large PE-derived fraction. PE-derived pyrolysis oils are reported to produce higher ethylene yields during steam cracking than fossil naphthas, which is attributed to their high content of linear and paraffinic compounds (Hájeková et al., 2007; Kusenberg et al., 2024). The total paraffins content (n- and *iso*-paraffins) in the Py-Diesel blend was ~ 72.5 wt%, which increased to ~ 82.1 wt% after hydrotreatment, bringing it closer to, yet still below, the total paraffins content of fossil naphtha (87.5 wt%). Despite this, the Py-Diesel blends produced higher ethylene yields than fossil naphtha. This can be attributed to the longer carbon chain length of the pyrolysis-derived feed (C_5–C_{25}), compared to the shorter C_5–C_{10} range of fossil naphtha. The heavier hydrocarbons in Py-Diesel are more susceptible to thermal decomposition via successive β-scission reactions, which in turn leads to higher ethylene yields (Herbinet et al., 2007; Kusenberg et al., 2024; Pyl et al., 2012a). Additionally, the Py-Diesel blend also showed enhanced performance in producing lower yields of the PyGas fractions. The PFO fraction is higher for the diesel-range blends than for fossil naphtha, yet remains substantially lower, nearly halved, compared to that of the full-range pyrolysis oil previously reported by Kusenberg et al. (Kusenberg et al., 2022d). This highlights the benefit of fractional distillation in reducing the formation of undesired heavy by-products. Higher amounts of CO were formed during steam cracking of the waste-derived feedstocks, which can be attributed to the presence of oxygen-containing contaminants in the diesel fractions (see Fig. 4 in the contaminant analysis section). Previous studies have shown that the presence of oxygenates in feedstocks promotes the formation of CO and CO_2 in steam cracking (De Bruycker et al., 2014; Pyl et al., 2012a; Pyl et al., 2011; Pyl et al., 2012b).

Regarding the impact of hydrotreatment, ethylene yields increased across all investigated COTs, reaching a maximum of 31.7 wt% for the 25 wt% HDT Py-Diesel blend at 880 °C (see Table 3). This yield is approximately 2 wt% higher than that of pure fossil naphtha (29.6 wt%) under identical cracking conditions. Although the difference may appear modest, it is industrially significant given the large-scale throughput of steam crackers, where even a 2 wt% yield improvement translates into considerable gains in ethylene production and economic value (Zimmermann & Walzl, 2009). Extrapolating these results to a pure HDT Py-Diesel feed suggests an ethylene yield of approximately 38.2 wt%, compared with 36.6 wt% for the untreated Py-Diesel, confirming the beneficial effect of hydrotreatment on feed quality and cracking performance. These improvements reflect not only enhanced ethylene yields but also indicate cleaner cracking behavior, as evidenced by reduced CO formation, which is a concern in the cracker downstream, as it affects product yields and contaminates downstream catalysts (Pyl et al., 2012a). Hydrotreatment also enhanced the compatibility of pyrolysis oils with steam crackers by significantly reducing the olefin content. Olefins are known to promote coke formation and fouling (Kusenberg et al., 2022c), resulting in both short- and long-term operational issues. Industrial steam crackers are designed for paraffinic

Table 2
Summary for the hydrocarbon group composition of the feedstock blends and reference fossil naphtha used in the steam cracking experiments, as determined by GC × GC-FID.

Feedstock	25 wt% Py-Diesel blend	25 wt% HDT Py-Diesel blend	Fossil naphtha [a]
IBP [°C]	14	14	14
50 % BP [°C]	110	110	50
FBP [°C]	425	425	161
H/C molar ratio	2.21	2.22	2.28
Carbon number range	C_5 – C_{25}	C_5 – C_{25}	C_5 – C_{10}
Density (20 ∘C, 1 atm) [g/cm^3]	0.708	0.705	0.675
	PIONA [wt.%]		
Paraffins [wt.%]	38.8	43.6	44.3
Iso-paraffins [wt.%]	33.7	38.5	43.2
α-Olefins [wt.%]	7.1	0.8	–
Iso-olefins [wt.%]	4.2	1.2	–
Diolefins [wt.%]	1.5	0.1	–
Naphthenes [wt.%]	10.7	11.5	9.3
Monoaromatics [wt.%]	3.0	2.9	3.2
Naphthenoaromatics [wt.%]	0.7	0.6	–
Diaromatics [wt.%]	0.5	0.8	–

[a] Same reference fossil naphtha used as blending feed for Py-Diesel and HDT Py-Diesel;

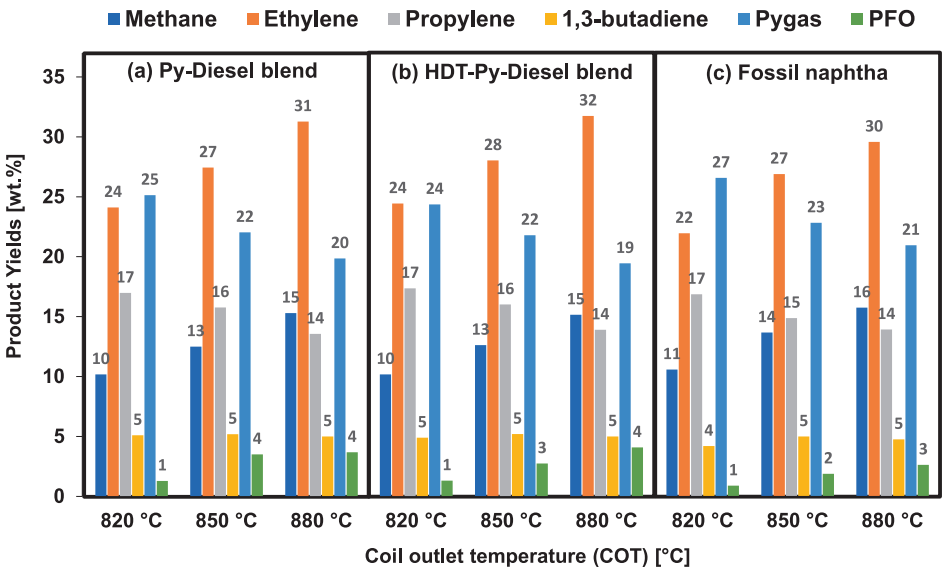


Fig. 5. Comparison of the most important product yields as a function of the coil outlet temperature (COT) for: (a) 25 wt% Py-Diesel blend, (b) 25 wt% HDT-Py-Diesel blend, and (c) Pure fossil naphtha.

Table 3
Result summary of the most important steam cracking product yields according to the coil outlet temperature (COT).

	Py-Diesel blend			HDT Py-Diesel blend			Fossil naphtha		
COT [°C]	820	850	880	820	850	880	820	850	880
Total C_1-C_4 [wt.%]	73.51	74.39	74.39	74.31	75.45	76.45	72.5	75.3	76.4
PyGas (C_5-C_9) [wt.%]	25.17	22.07	19.88	24.35	21.79	19.44	26.55	22.82	20.94
PFO (C_{10+}) [wt.%]	1.32	3.54	3.71	1.33	2.76	4.10	0.91	1.89	2.65
Propylene/Ethylene [-]	0.70	0.58	0.43	0.71	0.57	0.44	0.77	0.55	0.47
Propylene + Ethylene [wt.%]	41.15	43.26	44.90	41.78	44.02	45.63	38.80	41.75	43.47
Concentration of important products in the reactor effluent [wt.%]									
H_2	0.94	1.08	1.28	0.98	1.20	1.43	1.02	1.28	1.41
CO	0.27	0.25	0.37	0.19	0.26	0.26	0.10	0.20	0.19
Methane	10.21	12.53	15.33	10.19	12.63	15.16	10.58	13.67	15.74
Ethylene	24.14	27.47	31.31	24.42	28.01	31.72	21.94	26.88	29.55
Ethane	3.29	3.26	3.09	3.38	3.29	3.20	3.05	3.22	2.94
Propylene	17.01	15.80	13.59	17.36	16.01	13.90	16.86	14.87	13.92
1-butene	3.21	1.95	0.92	3.41	2.02	0.96	3.17	1.99	1.17
Iso-butene	3.11	2.48	1.73	3.05	2.44	1.69	3.88	3.24	2.25
1,3-butadiene	5.13	5.22	5.02	4.91	5.21	5.01	4.21	5.00	4.77
1-pentene	2.93	0.87	0.45	3.07	0.91	0.60	3.79	2.12	0.78
1,3-cyclopentadiene	1.32	1.73	2.20	1.25	1.86	2.09	0.98	1.60	2.19
Benzene	3.79	6.02	8.96	3.29	5.84	7.97	2.70	5.01	7.94
Toluene	2.10	2.72	2.92	1.67	2.30	2.80	1.62	2.24	2.80
Xylenes	0.49	0.73	0.52	0.42	0.53	0.61	0.62	0.47	0.56
Indene	0.09	0.33	0.45	0.09	0.29	0.51	0.10	0.25	0.43
Naphthalene	0.13	0.55	0.79	0.11	0.42	0.84	0.12	0.33	0.65
BTX	6.37	9.47	12.40	5.38	8.67	11.38	4.93	7.72	11.30
Others	21.85	16.99	11.06	22.21	16.77	11.24	25.26	17.64	12.69

feedstocks, which vaporize smoothly in the convection section without inducing pre-cracking, fouling, or coke formation, thereby enabling efficient thermal cracking in the radiant zone to produce light olefins. Olefins, on the other hand, are thermally less stable and prone to premature polymerization and secondary reactions. These reactions not only reduce selectivity toward the desired light olefins but also form high-molecular-weight, chemically stable hydrocarbons that deposit on reactor surfaces, accelerating fouling and coke formation. By reducing the olefin content, hydrotreatment minimizes these risks and helps align the feedstock behavior with the operational design of conventional steam crackers, improving process stability and product yields.

Hydrotreatment reduced the formation of the Pygas fraction and BTX aromatics. For example, the BTX yield decreased from 12.4 wt% at a coil outlet temperature (COT) of 880 °C for the Py-Diesel blend to 11.4 wt% after hydrotreatment, which is consistent with the reduction of olefins and dienes, key precursors for aromatic formation in steam cracking. On the other hand, the effect of hydrotreatment on the PFO fraction was not apparent, as both the Py-Diesel blend and the HDT Py-Diesel blend exhibited similar yield trends, which were higher than those of fossil naphtha. This behavior can be attributed to the comparable quantities of naphthenes and aromatics in both pyrolysis oil blends (see Table 2). The naphthene content in the Py-Diesel and HDT Py-Diesel blends is 10.7 wt % and 11.5 wt%, respectively, compared with 9.3 wt% for the fossil naphtha. The Py-Diesel blend, HDT Py-Diesel blend, and fossil naphtha all have similar monoaromatic contents, approximately 3 wt%. The total content of naphthenoaromatics and diaromatics in the Py-Diesel blend and the HDT Py-Diesel blend is 1.2 wt% and 1.4 wt%, respectively. The fossil naphtha, however, contains no naphthenoaromatics or diaromatics. It is also worth mentioning that the difference between the Py-Diesel blend and the HDT Py-Diesel blend, on the one hand, and fossil

naphtha, on the other hand, extends not only to the quantities of naphthenes and aromatics but also to their carbon range. Most of the naphthenes and aromatics present in the Py-Diesel blend, and the HDT Py-Diesel blend are heavy hydrocarbons (C_{10+}), compared with lighter naphthenes and aromatics (C_6-C_{10}) present in the fossil naphtha. More details are provided in the detailed PIONA analysis in the supporting information (SI).

Heavy aromatic and naphthenic residues exert interconnected effects on steam-cracking performance. The higher PFO yields observed from cracking both HDT and Py-Diesel primarily result from the presence of heavier C_{10+} species found in the Py-oils, mainly aromatics and naphthenes. Heavy aromatics tend to condense and dehydrogenate under cracking conditions, generating coke precursors that accelerate deposit formation and lower olefin selectivity (De Bruycker et al., 2014; Herbinet et al., 2007; Kopinke et al., 1993a; Li et al., 2013). Naphthenes are readily transformed into aromatics through dehydrogenation reactions, further contributing to aromatic accumulation and coke growth (Kopinke et al., 1993b; Melius et al., 1996; Pyl et al., 2012a). Together, these mechanisms account for the elevated PFO yields and reduced ethylene selectivity typically observed in MPW pyrolysis oils, which are enriched in aromatics and naphthenes, compared to virgin feedstocks such as fossil naphtha. Additionally, these heavy aromatic residues and naphthenes exhibit low volatility and high thermal stability, which hinder complete vaporization and promote condensation and fouling during steam cracking. Although this behavior could not be directly investigated in the current setup, follow-up experiments are planned using our dedicated Fouling Assessment SeTup (FAST) unit (Vargette et al., 2024; Shirazi et al., 2025). From an industrial perspective, however, such fouling and deposit formation pose significant operational challenges that must be mitigated to ensure long-term process stability. Furthermore, large-scale implementation will require addressing additional factors such as corrosion, catalyst deactivation, feedstock variability, and hydrogen consumption, underscoring the need for optimized process integration and economic evaluation. Regarding catalyst evaluation, to ensure realistic assessment and industrial practicality, future investigations on hydrotreatment and other hydroprocessing catalysts will be conducted under industrially relevant fixed-bed (PFR-type) conditions, including the use of full-range pyrolysis oil.

The overall greenhouse gas (GHG) balance of the studied pathway was not assessed in this work, as the focus was primarily on feedstock upgrading and steam-cracking performance. However, the key parameters influencing the overall carbon footprint can be clearly identified. The primary emission savings result from the avoidance of incinerating an equivalent amount of mixed plastic waste, which typically generates an environmental burden of approximately 3 kg CO_2-eq per kg of plastic. In comparison, chemical recycling routes, such as pyrolysis, have been reported to generate approximately 0.3 kg CO_2-eq per kg of plastic, about one order of magnitude lower than incineration (Eschenbacher et al., 2022). However, the inclusion of a hydrotreatment step introduces additional energy and hydrogen demand, which can increase GHG emissions (Gracida-Alvarez et al., 2023). This thereby reduces the overall benefit compared with direct co-feeding of purified pyrolysis oil. Nevertheless, using renewable or low-carbon hydrogen can mitigate this effect and lower cradle-to-gate emissions. Additionally, CO and CO_2 are formed during the steam cracking of oxygenated compounds present in the feed and are substantially reduced after hydrotreatment, as shown in this work. These experimental results provide a foundation for an ongoing process-level GHG assessment that integrates hydrogen use, product yields, and process energy requirements to evaluate the overall carbon impact of MPW pyrolysis-oil upgrading.

Although blending was necessary to protect the experimental setup and ensure stable operation, it partially masks the observable differences between the fossil reference and the pyrolysis oils, as well as the effects of hydrotreatment. Nevertheless, these differences remain distinguishable beyond the range of experimental variability, as demonstrated by the standard deviations reported in the supporting information (SI). This conclusion is further reinforced by the high reproducibility of the steam cracking experiments, each of which was conducted in more than five replicates, allowing for a meaningful comparison within a 95 % confidence interval. For future studies, pure pyrolysis oil cracking or higher blending ratios are recommended to fully capture the mechanistic effects of upgrading on steam cracking performance.

4. Conclusions and Outlook

Two diesel-range feedstocks were produced from post-consumer plastic packaging waste via pyrolysis and distillation, with one further upgraded through hydrotreatment. Both were thoroughly characterized and evaluated in steam cracking, using fossil naphtha as both a benchmark and blending base to gauge integration potential. Hydrotreatment significantly improved feed quality by shifting the hydrocarbon composition toward a higher paraffin content and enhancing overall compatibility with steam crackers. In cracking trials, the polyethylene-derived Py-Diesel blend outperformed fossil naphtha in ethylene yield. Hydrotreatment further improved performance, increasing light olefin production while suppressing the formation of CO and BTX aromatics. Nonetheless, high PFO output persisted, driven by heavier C_{10+} species such as diaromatics and naphthenes. These results demonstrate that upgraded pyrolysis oils derived from mixed plastic waste can serve as viable feedstocks for steam crackers. The combination of blending, distillation, and hydrotreatment addresses key compositional barriers, enabling the valorization of low-quality plastic waste streams that would otherwise be incinerated or landfilled. Looking ahead, integrating hydrotreatment with hydrocracking presents a promising pathway to minimize the need for fractionation, simplify processing, and maximize yield. Future work will focus on implementing this integrated hydroprocessing approach to reduce aromatic content, improve feed quality, and optimize pyrolysis oil conversion for a truly circular plastic economy. Kinetic and process modeling of steam cracking will support the industrial-scale translation of these findings.

CRediT authorship contribution statement

Anas Jamil Abdulrahman: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Marvin Kusenberg:** Writing – review & editing, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Miloš Auersvald:** Writing – review & editing, Visualization, Methodology, Investigation, Conceptualization. **César Pernalete Piña:** Writing – review & editing, Investigation. **Behzad Parvizi:** Methodology, Investigation, Conceptualization. **Mohammadhossein Havaei:** Visualization, Validation, Methodology, Conceptualization. **Joris W. Thybaut:** Methodology, Investigation, Conceptualization. **Kevin M. Van Geem:** Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition, Conceptualization.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2025.115287.

Data availability

Data will be made available on request.

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