Maximizing olefin production via steam cracking of distilled pyrolysis oils from difficult-to-recycle municipal plastic waste and marine litter

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17 List of abbreviations

BSSC	Bench-scale steam cracking unit
BTX	Benzene, toluene, xylenes
CA	Cellulose acetate
CIC	Combustion ion chromatography
CIT	Coil inlet temperature
СОР	Coil outlet pressure
СОТ	Coil outlet temperature
EVA	Ethylene vinyl acetate
EVOH	Ethylene vinyl alcohol
FBP	Final boiling point
FCC	Fluid catalytic cracking
FID	Flame ionization detector
$\mathbf{GC} \times \mathbf{GC}$	Comprehensive two-dimensional gas chromatography
HC	Hydrocarbon
IBP	Initial boiling point
ICP-OES/MS	Inductively coupled plasma coupled to optical emission spectroscopy or mass spectrometry
LOD	Limit of detection
ML	Marine litter
MPW	Mixed plastic waste
NCD	Nitrogen chemiluminscence detector
PA	Polyamide
PE	Polyethylene
PET	Polyethylene terephthalate
PFO	Pyrolysis fuel oil
PP	Polypropylene
ppb(w)	Parts per billion (weight-based)
ppm(w)	Parts per million (weight-based)
PS	Polystyrene
PUR	Polyurethane
PV(D)C	Polyvinyl(idene)chloride
PyGas	Pyrolysis gasoline
qMS	Quadrupole Mass spectrometry
RGA	Refinery gas analyzer
SI	Supporting Information
TCD	Thermal conductivity detector

TLE	Transfer line exchanger
VGO	Vacuum gas oil

18 Abstract

Plastic waste is steadily polluting oceans and environments. Even if collected, most waste is still 19 20 predominantly incinerated for energy recovery at the cost of CO₂. Chemical recycling can contribute to the transition towards a circular economy with pyrolysis combined with steam 21 cracking being the favored recycling option for the time being. However, today, the high variety 22 23 and contamination of real waste remains the biggest challenge. This is especially relevant for waste fractions which are difficult or even impossible to recycle mechanically such as highly mixed 24 25 municipal plastic waste or marine litter. In this work, we studied the detailed composition and the 26 steam cracking performance of distilled pyrolysis oil fractions of two highly relevant waste fractions: mixed municipal plastic waste (MPW) considered unsuitable for mechanical recycling 27 and marine litter (ML) collected from the sea bottom. Advanced analytical techniques including 28 29 comprehensive two-dimensional gas chromatography (GC×GC) coupled with various detectors and inductively coupled plasma – mass spectrometry (ICP-MS) were applied to characterize the 30 feedstocks and understand how their properties affect the steam cracking performance. Both waste-31 32 derived naphtha fractions were rich in olefins and aromatics (~70% in MPW naphtha and ~51% in 33 ML naphtha) next to traces of nitrogen, oxygen, chlorine and metals. ICP-MS analyses showed that sodium, potassium, silicon and iron were the most crucial metals that should be removed in further 34 upgrading steps. Steam cracking of the waste-derived naphtha fractions resulted in lower light 35 olefin yields compared to fossil naphtha used as benchmark, due to secondary reactions of 36 37 aromatics and olefins. Coke formation of ML naphtha was slightly increased compared to fossil naphtha (+~50%), while that of MPW naphtha was more than ~180% higher. It was concluded that 38

- mild upgrading of the waste-derived naphtha fractions or dilution with fossil feedstocks is 39
- sufficient to provide feedstocks suitable for industrial steam cracking. 40
- Keywords: Thermochemical recycling; ocean plastics; pyrolysis; contaminants; ethylene 41 production; coke formation 42

Graphical abstract 43





46 **1. Introduction**

47 Using waste-derived feedstocks in existing industrial sectors is a key aspect in the transition from a linear towards a circular economy. However, several waste streams do not find a proper second 48 life and instead, they are disposed of into the environment or they are incinerated along with CO_2 49 50 emissions at their end-of-life (Geyer et al., 2017). If these secondary resources could be re-used as 51 feedstock to produce chemical building blocks, it would allow the reduction of emissions and the (partial) substitution of fossil resources (Davidson et al., 2021, Jeswani et al., 2021, Lange, 2021). 52 By feeding waste back into the production chain, an important contribution can be made to close 53 the carbon balance and thus to help in preventing the imminent threats of climate change and the 54 further disruption of ecosystems. 55

Both technical and economic reasons prevent a full circularity approach for several waste streams. 56 This is in particular valid for plastic waste which still faces several hurdles when it comes to 57 recycling, leading to more than 42% of collected plastic waste in 2018 being incinerated for energy 58 59 recovery and still almost 25% being disposed of in landfills (Plastics Europe, 2020). Next to the 60 collected plastic waste, whether being recycled or not, depending on the origin of the data between 1.2 and 12.7 Mt of plastic waste end up in seas and oceans every year leading to a long-lasting 61 62 environmental burden (Jambeck et al., 2015, Wayman and Niemann, 2021, Ronkay et al., 2021). This vast pollution leads to severe global hazards such as the disruption of ecosystems due to 63 macro- and microplastics, contamination of food chains and the pollution of beaches (Erni-Cassola 64 et al., 2019, Thushari and Senevirathna, 2020, Wilson et al., 2021, Garcés-Ordóñez et al., 2020, 65 Ford et al., 2022). Furthermore, it may take up to 450 years for a plastic bottle to decompose in 66 marine environments (Whiting, 2018). Considering the amount of litter that already pollutes the 67 marine environments, increased recycling rates are urgently needed. 68

Mechanical recycling is most implemented at this point of time, but in fact, it is known that plastics 69 70 cannot be infinitely mechanically recycled without deterioration of their properties (Hong and 71 Chen, 2017). Furthermore, strict regulations in terms of food-contact applications are in place preventing the substitution of many mechanically recycled packaging products from their original 72 application (Cecon et al., 2021, De Tandt et al., 2021). A promising alternative is chemical 73 recycling with pyrolysis being considered the dominant technology in the coming decades. In 74 75 pyrolysis, polymer waste is decomposed into primarily a liquid product by providing thermal energy. To close the material loop, the pyrolysis oils need to be subsequently steam cracked to 76 obtain base chemicals for the production of second-generation virgin-quality polymeric materials 77 78 (Solis and Silveira, 2020, Dogu et al., 2021, Ragaert et al., 2017, Palos et al., 2021). However, the greatest challenge when using waste-derived feedstocks in steam crackers is the high diversity and 79 the associated high degree of contamination with heteroatoms (i.e., nitrogen, oxygen, halogens) 80 81 and metals (Kusenberg et al., 2022a). There are several sources for heteroatoms and metals in plastic waste, namely heteroatom-containing polymers such as polyethylene terephthalate (PET), 82 polyurethane (PUR), polyamide (PA) and polyvinylchloride (PVC), organic or inorganic residues 83 related to the original use of the plastic material as well as pigments and additives (Roosen et al., 84 2020, Ügdüler et al., 2020, Sundaram and Stancato, 2018). 85

In our previous work, we investigated the feasibility of using blends of untreated polyolefin (i.e., polyethylene (PE) and polypropylene (PP)) waste pyrolysis oils and fossil naphtha as steam cracking feedstocks (Kusenberg et al., 2022b). While the light olefin yields of the pyrolysis oilnaphtha blends were slightly higher than these of pure fossil naphtha, substantial radiant coil coke formation was observed. Next to the high amounts of unsaturated hydrocarbons (i.e., olefins and aromatics), the high coking tendency of plastic waste pyrolysis oils can in most cases be related to 92 the presence of contaminants (i.e., metals), which may have a strong catalytic effect, causing rapid 93 coke formation. Since coke formation is a crucial factor regarding the time on stream of a steam 94 cracking furnace, i.e., the so-called run-length of a steam cracker, special attention is needed 95 towards the effect of waste-derived feedstocks on steam cracking product yields and coke 96 formation, especially in the case of challenging and complex waste inputs.

In this work, we explore the possibility to produce light olefins via steam cracking of distilled 97 pyrolysis oil fractions in the naphtha-range derived from the pyrolysis and distillation of two very 98 99 challenging and environmentally relevant waste streams for which there are, today, no means of recycling. The feedstocks that were used were a municipal plastic waste fraction that was highly 100 contaminated and found unsuitable for mechanical recycling. Hence, the end-of-life of this waste 101 102 fraction will be incineration, if no advanced recycling solution can be found. The other waste 103 fraction was marine plastic litter, directly collected by scuba divers from the ocean floor. The fact that this fraction is not part of any systematic collection and waste management scheme underlines 104 105 that this kind of waste will be a long-lasting burden for the environment, in this case for marine ecosystems, if no recycling method can be found. Hence, both used waste fractions can be 106 considered as "special interest" from an environmental point of view, for which efficient recycling 107 technologies are critically needed. As chemical recycling is often described as an alternative to 108 109 mechanical recycling, in this case, it is clearly a novel recycling technology for fractions that would 110 never be considered for mechanical recycling but would be incinerated for energy recovery, if not discarded into the environment. In order to explore the chemical recycling potential of these "real" 111 waste samples, neither pre-treatment steps such as washing or purification of the waste fractions 112 113 were performed, nor were the pyrolysis products post-treated apart from distillation. Furthermore, to evaluate the effect of contaminants in our study, the waste-derived naphtha fractions were steam 114

115 cracked pure without dilution. On a global scale, it is of crucial importance that recycling 116 technologies are developed that are robust towards waste streams of much lesser quality than these 117 provided from state-of-the-art waste sorting and separation plants. This is especially valid for 118 countries that have less stringent waste collection and management schemes established and for 119 countries that are suffering the most from marine littering. This study is the first available in open 120 literature that investigates the detailed composition and steam cracking performance of naphtha 121 fractions derived from these challenging but crucially important plastic waste streams.

122 **2. Materials and Methods**

123 **2.1. Feedstocks**

124 Two different waste-derived naphtha fractions were used. Both were obtained from distillation of 125 thermal pyrolysis oils that were derived from two different types of highly mixed plastic waste: (i) municipal plastic waste (MPW) provided by a recycling center in Denmark considered unsuitable 126 127 for mechanical recycling, (ii) highly contaminated plastic marine litter (ML) of unknown 128 composition collected from the sea bottom of the Venice Lagoon in Italy (see photo in Fig. S1 in 129 the supporting information (SI). Both waste fractions were pyrolyzed "as is" without detailed 130 characterization or extensive upgrading steps such as washing, purification, melt filtration, etc. 131 Based on the works of (Roosen et al., 2020) and (Kleinhans et al., 2021), the MPW fraction is 132 largely composed of polyolefins (i.e., PE and PP) with considerable amounts of PET, polystyrene (PS) and other polymers such as ethylene vinyl alcohol (EVOH), PA, PVC, PUR and ethylene 133 vinyl acetate (EVA). In the ML fraction, besides plastic containers, also waste from fisheries and 134 135 aquaculture activity was present: mussel farming bags, fishing gears and nylon nets, styrofoam 136 boxes, etc. This is supported in literature where benthic marine litter is reported to comprise fishing gear (32%) and general plastic (68%) (Consoli et al., 2018). Since the ML fraction was not washed,
organic matter was also present as a non-plastic contaminant.

139 The pyrolysis and distillation units used to produce the waste-derived naphtha fractions that were steam cracked in this study have been recently described in full detail by Faussonne et al. (Faussone 140 et al., 2021, Faussone, 2018). Pyrolysis was performed at 400 °C and atmospheric pressure. 141 Furthermore, in both cases (MPW and ML pyrolysis), CaO was added to the pyrolysis reactor to 142 control the formation of corrosive acidic compounds and hence to protect the used process 143 equipment as described elsewhere (Okuwaki et al., 2006). It has to be noted that the pyrolysis 144 process was optimized for the production of diesel-range fuels for transportation purposes, meeting 145 ISO standards (Faussone et al., 2021, Faussone, 2018). The crude pyrolysis oils of both processes 146 147 (MPW and ML pyrolysis) were distilled to obtain a light, naphtha-like product suitable for steam cracking. A photo of the waste-derived naphtha fractions steam cracked in this study can be found 148 149 in Fig. S2 in the SI. The elemental compositions of the steam cracking feedstocks, measured using 150 CHNS/O analysis are given in Table 1.

Feedstock	Fossil naphtha reference	MPW naphtha	ML naphtha	
IBP [°C]	10	14	14	
50% BP [°C]	61	145	148	
FBP [°C]	136	388	352	
Density (20 °C, 1 atm) [g/cm ³]	0.669	0.782	0.772	
Carbon number range	$C_4 - C_9$	$C_{5}-C_{24}$	$C_5 - C_{21}$	
N [wt%]	<lod< th=""><th><lod< th=""><th><lod< th=""></lod<></th></lod<></th></lod<>	<lod< th=""><th><lod< th=""></lod<></th></lod<>	<lod< th=""></lod<>	
C [wt%]	84.33	86.39	85.73	
H [wt%]	15.67	13.09	14.02	
S [wt%]	<lod< th=""><th><lod< th=""><th><lod< th=""></lod<></th></lod<></th></lod<>	<lod< th=""><th><lod< th=""></lod<></th></lod<>	<lod< th=""></lod<>	
O [wt%]	<lod< th=""><th>0.52</th><th>0.25</th></lod<>	0.52	0.25	

Table 1: The elemental compositions, liquid densities as well as initial, 50% and final boiling points (IBP, 50% BP, FPB) of the respective feedstocks. Limit of detection (LOD) for elemental analysis: 1000 ppmw.

The liquid density was obtained using a density meter. Initial, 50% and final boiling points (IBP,
50% BP, FPB) were obtained according to ASTM 2887 (American Society for Testing and

Materials, 2020a). The carbon number range has been obtained via comprehensive two-155 156 dimensional gas chromatography coupled to a flame ionization detector ($GC \times GC$ -FID). Both waste-derived naphtha-range samples had a heavy tail with trace components up to C₂₄ (MPW 157 naphtha) and C_{21} (ML naphtha) which can be related to inaccurate distillative separation and a lack 158 159 of reflux. Next to steam cracking of the light naphtha-range distillation cuts, potential valorization routes of the heavy distillation fractions that were not suitable for steam cracking in terms of the 160 boiling point range have been proposed in literature. These are, for instance, co-feeding of pyrolysis 161 waxes with vacuum gas oil (VGO) from a refinery stream to a fluid catalytic cracking (FCC) unit 162 as elaborated by (Rodríguez et al., 2020). Furthermore, production of lubricating oil from plastic 163 164 waste has been proposed by (Miller et al., 2005) who investigated the hydroisomerization of waxy pyrolysis oil fractions. As a benchmark in terms of the steam cracking performance of a liquid 165 166 hydrocarbon mixture, a typical light fossil naphtha was chosen with the detailed composition given in Table S1 in the SI. 167

168 **2.2. Analytics**

169 **2.2.1.** Comprehensive two-dimensional gas chromatography (GC × GC)

 $GC \times GC$ coupled to a flame ionization detector (FID) was used for the detailed quantitative 170 171 analysis of the samples before steam cracking. The analysis of the feedstocks was performed as 172 described in recent works (Kusenberg et al., 2022c, Dao Thi et al., 2021). Furthermore, the steam 173 cracking products were analyzed on-line using $GC \times GC$ -FID as described recently (Kusenberg et 174 al., 2022b). The quantitative analysis was performed based on the internal standard calibration method and effective carbon number approach as explained previously (Toraman et al., 2014, 175 Djokic et al., 2012, Van Geem et al., 2010). Tentative compound identification was performed 176 using $GC \times GC$ coupled to quadrupole mass spectrometry (qMS). Nitrogen and sulfur compounds 177

were analyzed using $GC \times GC$ coupled to a nitrogen chemiluminescence detector (NCD) and a 178 179 sulfur chemiluminescence (SCD) detector, respectively. GC × GC instruments (Thermo Scientific, 180 Interscience Belgium) have been used, equipped with a two-stage cryogenic liquid CO₂ modulator, as described previously (Toraman et al., 2014, Ristic et al., 2017, Dijkmans et al., 2014). The used 181 182 column combinations and temperature programs are shown in Table S2 in the SI. Analytical gases (helium, nitrogen, hydrogen, carbon dioxide, air, and oxygen) with a minimum purity of 99.999% 183 184 (Air Liquide, Belgium) were used. 3-chlorothiophene (Sigma-Aldrich, Belgium) with a minimum purity of 96% was used as an internal standard for the FID and SCD analyses, 2-chloropyridine 185 (Sigma-Aldrich, Belgium) with a minimum purity of 99% was used for the NCD analyses, as 186 187 explained in previous work (Dijkmans et al., 2015, Kusenberg et al., 2022c, Dao Thi et al., 2021).

188 2.2.2. Elemental analysis

CHNS/O analyses of the waste-derived naphtha fractions were performed on a Flash EA2000 189 elemental analyzer (Interscience, Belgium) equipped with a thermal conductivity detector (TCD) 190 191 (Kusenberg et al., 2022b, Kusenberg et al., 2022c). Samples were injected using a cooled syringe to avoid evaporation prior to analysis. CHNS analyses were performed according to ASTM D 5291 192 (American Society for Testing and Materials, 2015) in combustion mode. Oxygen determination 193 was performed according to ASTM D 5622 (American Society for Testing and Materials, 2017) in 194 195 pyrolysis mode in a separate reactor. The device was calibrated prior to analysis using a 2,5-Bis(5-196 tert-butyl-2-benzo-oxazol-2-yl)thiophene (BBOT) standard (Elemental Microanalysis, United Kingdom). The CHNS/O composition of the samples was derived based on at least four repeat 197 analyses of each sample. 198

199 2.2.3. Combustion Ion Chromatography (CIC)

CIC analyses of the waste-derived naphtha fractions to obtain their halogen content were performed 200 according to ASTM D6470 - 99(2020) (American Society for Testing and Materials, 2020b) as 201 discussed in our previous works (Kusenberg et al., 2022b, Kusenberg et al., 2022c). An ion 202 203 chromatography setup (930 Compact IC Flex, Metrohm, Switzerland), equipped with a Metrosep A Supp 7-250/4.0 column and a conductivity detector was used. Quantification of the halogen 204 concentration was based on linear calibration curves using five standard solutions within the range 205 206 of 0 and 50 ppmw of the analytes of interest. The instrumental parameters and conditions applied during CIC analysis can be found in Table S3 in the SI. 207

208 2.2.4. Quantification of trace metals

Determination of metals in the waste-derived naphtha fractions was performed by the analysis laboratory SGS Belgium N.V (accredited according to ISO/IEC 17025 (International Organization for Standardization (ISO), 2017)) using ICP-OES and ICP-MS after microwave-assisted acid digestion. ICP-MS is capable of detecting ultra-trace concentrations in the low parts per billion range. Based on this advanced analytical depth, it is possible to design upgrading processes that comprehensively address the found feedstock impurities.

215 2.2.5. Liquid density measurement

The liquid density at ambient conditions (20 °C, 1 atm) of all three feedstocks was measured using a Mettler Toledo (USA) DA-100M density meter. The accuracy of the device is 0.001 g/cm³. The liquid density of each sample was derived based on at least three repeat analyses, respectively.

219 2.3. Apparatus and experimental procedure

Steam cracking experiments were performed in a bench-scale steam cracking setup (BSSC) (see
Fig. S3 in the SI). Since the unit was discussed in detail in previous works, only a brief description

of the unit will be given (Harper et al., 2011, De Bruycker et al., 2014, Pyl et al., 2011b, Kusenberg 222 223 et al., 2022b). The unit is designed in a way that the results can be easily scaled-up to a real industrial furnace (Van Geem et al., 2007, Van Geem et al., 2005). The BSSC consists of three 224 sections. First, the feeding section, where the hydrocarbon feedstock and the demineralized water, 225 226 which acts as a diluent after evaporation are fed to the reactor via Coriolis flow-meter (CORI-FLOW) controlled pumps (Bronkhorst, The Netherlands). Second, the furnace/reactor section 227 consisting of a 1.475 m long Incoloy 800HT (Ni: 30-35 wt%, Cr: 19-23 wt%, Fe: > 39.5 wt%) 228 reactor coil with an internal diameter of 6 mm and an electrically heated furnace with eight separate 229 heating zones in which a specific temperature profile can be set. Third, the analysis section, where 230 231 the reactor effluent is sampled online (i.e., during operation) at a temperature of 350 °C in order to prevent condensation of heavy products in the sampling lines. A detailed description of the 232 analytical section was given in our recent work (Kusenberg et al., 2022b). A heated valve-based 233 sampling system is used to inject a gaseous sample of the reactor effluent onto a dedicated 234 GC × GC-FID unit. A so-called Refinery Gas Analyzer (RGA) is used to analyze light products in 235 the C₄₋ range (H₂, CO₂, ethylene, ethane, acetylene, N₂, methane, CO, propane, propylene, 236 propadiene, iso-butane, n-butane, trans-2-butene, 1-butene, cis-2-butene, methylacetylene and 1,3-237 butadiene). The methane concentration is quantified with a well-defined flow of nitrogen which is 238 239 introduced downstream of the reactor, perfectly mixed with the reactor effluent before reaching the RGA and, hence, acting as an internal standard. The entire reactor effluent which was analyzed on 240 the $GC \times GC$ -FID can be quantified using the methane concentration measured on the RGA as a 241 242 secondary internal standard (see Fig. S4 in the SI) (Pyl et al., 2011a, Pyl et al., 2011b, Van Geem et al., 2010, Kusenberg et al., 2022b). Response factors of the light products analyzed via RGA 243 were calibrated using a calibration gas mixture containing well-defined concentrations of the 244 mentioned C₄- compounds (Air Products, Belgium). The response factors of the heavier products 245

in the C₅₊-range were obtained using the effective carbon number approach as described elsewhere (Pyl et al., 2011a, Van Geem et al., 2010, Harper et al., 2011, De Bruycker et al., 2014, Pyl et al., 2011b). The described methods showed good reproducibility and the C and H molar balances closed within $\pm 5\%$.

250 Steam cracking was performed at three different temperature profiles which were set according to the coil outlet temperatures (COT) 820 °C, 850 °C and 880 °C (see Table S4 in the SI for the 251 detailed temperature profiles). The conditions were chosen in line with our previous work 252 253 (Kusenberg et al., 2022b). All three temperature profiles had the same coil inlet temperature (CIT) of 550 °C which was chosen in order to minimize thermal cracking reactions of the feedstocks prior 254 to reaching the reaction zone. The preheating and mixing zones where the feedstocks and the water 255 256 are evaporated and mixed before entering the reactor were set at 400 °C. In all experiments, the coil outlet pressure (COP) was set to 1.7 bara. The liquid hydrocarbon (HC) inlet flow was set to 257 258 150 g/h and a steam dilution of 0.5 wt_{H2O}/wt_{HC} was chosen. Based on the flow rates and reactor 259 geometry, an average coil residence time of 0.48 to 0.57 s was reached, depending on the respective feedstock. The aim for choosing the presented process conditions was to mimic industrial 260 conditions in terms of the cracking severity which can be described as the propylene/ethylene ratio 261 (Van Geem et al., 2005, Van Geem et al., 2007). The mass flows of water and hydrocarbon 262 feedstock were chosen in order to obtain sufficient residence times for the full conversion of 263 264 feedstocks while still minimizing secondary reactions (Kusenberg et al., 2022b).

The radiant coil coke formation of each respective feedstock was assessed in separate experiments analogue to our previous work (Kusenberg et al., 2022b). For the coking experiments, each respective feedstock was steam cracked for a consecutive duration of 6 hours at a constant isothermal reactor temperature of 850 °C. The coke that was deposited in the reactor during the

coking experiments was quantified afterwards by combustion (i.e., decoking) under fixed 269 270 conditions as shown in Table S5 and described in the SI. The volumetric concentration of CO and CO₂ in the reactor effluent that originates from the combustion of the coke is quantified over time 271 using an infrared analyzer (Fuji Electric, Japan) (Pyl et al., 2011a, Kusenberg et al., 2022b). The 272 273 flow rate of the reactor effluent was determined using a volumetric gas flow meter (RITTER, 274 Germany). Combining the volumetric concentrations of CO and CO_2 in the reactor effluent and the 275 flow rate of the reactor effluent, the total coke amount deposited on the inner reactor surface was determined. 276

3. Results and Discussion

278 **3.1. Feedstock characterization**

First, the hydrocarbon composition of the respective naphtha-range feedstocks, analyzed using GC \times GC-FID has been assessed. Subsequently, the detailed analysis of heteroatoms as well as trace concentrations of metals has been determined to gain insight into the most important contaminants.

283 **3.1.1. Hydrocarbon matrix**

 $GC \times GC$ -FID color plots of the three feedstocks are shown in Fig. 1. The differences between the 284 285 fossil naphtha reference and the waste-derived naphtha fractions are clearly visible. In both waste-286 derived feedstocks, a heavy hydrocarbon tail can be seen, which shows that small amounts of heavier compounds were not separated in the distillation steps (see Table 1). According to the 287 288 $GC \times GC$ -FID analysis, the boiling point at which >95% of the mass evaporates is ~171 °C for 289 MPW naphtha and ~240 °C for ML naphtha. This finding indicates that the distillation step in the 290 case of the MPW pyrolysis oil was more efficient. This can be also seen in Fig. 1, where the heavy 291 tail of MPW naphtha (Fig. 1, b) is less pronounced compared to the one of ML naphtha (Fig. 1, c). Fig. 1 further shows that two-dimensional $GC \times GC$ is needed to accurately distinguish the largely overlapping saturated and unsaturated hydrocarbons. Separation of the complex hydrocarbon matrix based on a single mechanism, as in 1D-GC (i.e., boiling point), would be highly difficult if not impossible, especially in the first 15 min of analysis, where the majority of compounds elutes.

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Fig. 1: GC × GC-FID chromatograms of (a) fossil naphtha reference, (b) MPW naphtha and (c) ML naphtha. The hydrocarbon compositions of the naphtha-range feedstocks analyzed using GC × GC-FID are given in Fig. 2. The detailed hydrocarbon compositions ordered according to the compound

families and carbon numbers can be found in section B1 in the SI. It can be seen that the hydrocarbon compositions of the three feedstocks differ substantially. The fossil reference naphtha contains mainly saturated compounds (i.e., paraffins and naphthenes) and smaller amounts of aromatics. On the other hand, the two waste-derived naphtha's contain a wider variety of compound families including high amounts of olefins (linear, branched and diolefins), naphthenes and aromatics.



307

Fig. 2: Hydrocarbon composition of the respective naphtha-range feedstocks steam cracked in this study measured using $GC \times GC$ -FID.

The composition of the MPW naphtha indicates that a diverse mixture of different polymers was pyrolyzed. This can be seen by means of the high concentration of iso-olefins which is an indicator for a high PP concentration in the plastic waste (Tsuge et al., 2011, Sojak et al., 2006, Soják et al., 2007, Al-Salem et al., 2017, Kusenberg et al., 2022a, Kusenberg et al., 2022c). Furthermore, aromatics in pyrolysis oils are likely related to PS or heteroatomic polymers such as PET and PVC

present in the pyrolyzed waste fractions (Zayoud et al., 2022, Cit et al., 2010, Williams and 315 316 Williams, 1999). MPW naphtha also contains low amounts of linear paraffins and α-olefins which indicates that the plastic waste did not contain much PE, which predominantly decomposes into 317 linear products (Tsuge et al., 2011, Sojak et al., 2006, Soják et al., 2007, Al-Salem et al., 2017, 318 319 Kusenberg et al., 2022a, Kusenberg et al., 2022c). The ML naphtha, on the contrary, contains larger 320 amounts of linear paraffins and α -olefins indicating a higher PE concentration in the collected 321 marine litter. In fact, the specific sequence of α,ω -diolefin, α -olefin and n-paraffin, which is characteristic for PE pyrolysis oil, is clearly visible and marked in Fig. 1, c (Kusenberg et al., 322 2022c). However, the still substantial amount of iso-olefins (~16 wt%) indicates that the PP 323 324 concentration in the originally collected marine litter was considerable. It has been reported that the most common plastics found in marine litter are PE, PP, PS, PVC, PET, PA and cellulose 325 acetate (CA) (Andrady, 2015). However, the distribution of the respective polymers in marine 326 environments (i.e., floating in and on top of the water or precipitated to the ocean floor) depends 327 on the respective densities of the polymers. In addition, when exposed to marine water, biofouling 328 can lead to sinking of light polymers such as PE already after a few weeks (Van Melkebeke et al., 329 2020). Since the marine litter was collected by scuba divers in a depth of 20-25 m, it is therefore 330 probable that still large amounts of polyolefins were present (Angiolillo et al., 2015, Erni-Cassola 331 332 et al., 2019).

The high amounts of aromatics, olefins and naphthenes, as found in the two waste-derived feedstocks are likely to cause issues during steam cracking such as increased coke formation and fouling of heat exchangers (Kopinke et al., 1993a, Kopinke et al., 1993b, Müller-Steinhagen et al., 2011, Müller-Steinhagen, 2010). Next to high amounts of olefins, both waste-derived naphtha fractions contain substantial amounts of aromatics compared to the fossil naphtha sample

containing only ~4 wt% of aromatics. Aromatics are prone to formation of polyaromatics which 338 339 are a major cause of coke formation during steam cracking. Next to the total concentration of aromatics in the feedstocks, the type of the aromatic compounds is crucial for the coking tendency 340 which increases with the presence of methyl side groups in the order benzene < toluene < xylene 341 342 < trimethylbenzene (Kopinke et al., 1993b). In both waste-derived naphtha fractions, the relative concentration of benzene (C_6) is quite low, whereas the relative share of C_8 aromatics (i.e., styrene, 343 344 ethylbenzene, xylene) is substantial. Therefore, it can be expected that the two waste-derived naphtha feedstocks are significantly more prone to coke formation. Moreover, styrene was the most 345 prominent aromatic detected in MPW naphtha (~7 wt%), while the ML naphtha contained a wider 346 distribution of aromatic compounds including C₁₀ and C₁₁ aromatics. This finding indicates that 347 the municipal waste feedstock indeed contained higher amounts of PS which predominantly 348 decompose into styrene, while the marine litter likely contained a wider variety of polymers that 349 350 decompose into other aromatic hydrocarbons such as epoxy, PET, PUR, PA and PVC (Tsuge et al., 2011, Pinto et al., 1999, Al-Salem et al., 2017, Eschenbacher et al., 2021, Torres-Herrador et 351 al., 2021, Zayoud et al., 2022). However, it is worth noting that the addition of CaO during 352 pyrolysis may have had a catalytic impact on the decomposition mechanisms of aromatic polymers 353 such as PET, leading to an increased formation of styrene (Kumagai et al., 2015, Wang et al., 2020). 354 355 Hence, the origin of the aromatics in both waste-derived naphtha fractions cannot be allocated to the waste composition with 100% certainty. In any case, due to its double bond and, hence, its 356 higher reactivity, styrene acts as a key compound in the formation of coke during steam cracking 357 358 (Jambor and Hájeková, 2015). Based on the compositions shown in Fig. 2, it can be expected that the ML naphtha shows a better steam cracking performance due to the lower total amount of 359 360 aromatics (and in particular styrene) compared to the MPW naphtha. However, it is also expected

that both waste-derived naphtha fractions lead to more coke formation and fouling issues comparedto the fossil naphtha reference.

363 **3.1.2. Heteroatom analysis**

Fig. 3 shows the measured elemental concentrations of nitrogen, oxygen, sulfur, chlorine and fluorine in the two waste-derived naphtha samples and the comparison with known thresholds for industrial steam crackers as reported by (Baumgartner et al., 2004) and (Sundaram and Stancato, 2018). It has to be noted that the fossil naphtha used in this study is an industrially produced petrochemical feedstock compliant with industrial steam cracker feedstock specifications, thus it is not visualized in Fig. 3.







The waste-derived naphtha fractions contain substantial amounts of heteroatoms exceeding known



especially evident for nitrogen, oxygen and chlorine. The concentration of sulfur is below the
threshold of 500 ppm while the fluorine value only marginally exceeds the threshold of 2 ppm
(Sundaram and Stancato, 2018).

Due to the different origins of the collected waste fractions, there is a high variety of potential 379 380 nitrogen sources. The major nitrogen source in the collected marine litter is most likely PA which is used for the manufacture of fishing gear and nets, and organic residues such as algae which are 381 known to contain considerable amounts of nitrogen (Burczyk et al., 1999). The nitrogen present in 382 the mixed plastic waste is more likely to originate from organic and inorganic residues related to 383 the polymer lifetime. However, nitrogen containing polymers can also be present in the mixed 384 plastic waste (Roosen et al., 2020, Kusenberg et al., 2022c). Therefore, it is difficult to reliably 385 386 relate the findings to certain polymers, due to the fact that the high degree of mixing in the pyrolyzed waste provides a huge variety of potential chemical pathways for nitrogen to be 387 388 integrated into the hydrocarbon matrix of the corresponding pyrolysis oils (Kusenberg et al., 389 2022c). In terms of steam cracking, both naphtha fractions exceed the threshold value for nitrogen substantially. The most established way to remove nitrogen is catalytic hydrotreatment (Prado et 390 al., 2017). However, complete removal of aromatic nitrogen compounds requires harsh conditions 391 in terms of temperature and hydrogen pressure. Furthermore, it is known that nitrogen compounds 392 393 tend to inhibit hydrotreatment catalysts (Kerby et al., 2005, Murena and Gioia, 1998). Alternative 394 removal techniques for nitrogen are adsorption using activated carbon or metal organic frameworks 395 (Kim et al., 2006, Wang et al., 2013). A more simple option would be the blending of the wastederived naphtha feedstock with fossil naphtha in order to dilute the nitrogen concentration down to 396 397 an acceptable level (i.e., with a blending ratio of ~1:10). The detected sulfur concentrations lie below the threshold of 500 ppm indicating that sulfur is a contaminant of lower concern, even whenthe naphtha-based feedstock is derived from very complex waste fractions.

400 Substantial amounts of oxygen were measured in the respective waste-derived naphtha fractions (MPW ~2500 ppm, ML ~5200 ppm). On the one hand, the high oxygen values can be clearly 401 402 related to PET as it is likely present both in the mixed plastic waste fraction as well as in the marine litter which contains high amounts of plastic bottles (Andrady, 2015). On the other hand, organic 403 404 residues attached to the plastics may contribute to the oxygen contamination. Considering the high 405 oxygen concentration in ML naphtha, it is indicated that entrained seaweeds and algae are another important oxygen contributor. Both naphtha fractions require upgrading in terms of the oxygen 406 concentration. Full removal of oxygen is possible using hydrodeoxygenation (Zacher et al., 2014). 407 408 Reduction of the oxygen content to the allowable concentration of 100 ppm via dilution with fossil feedstocks would require large dilution ratios (i.e., ~25-50) for both waste-derived naphtha 409 fractions. 410

411 Both waste-derived naphtha fractions exceed the known thresholds for chlorine by orders or 412 magnitude. This finding shows that addition of CaO to the reaction method is not effective to prevent halogenated products but is mainly important to protect the pyrolysis equipment from 413 corrosion. The chlorine concentration of the ML naphtha (~297 ppm) exceeds the maximum 414 threshold value (3 ppm) by a factor of almost 100. Given the fact that PVC tends to sink down to 415 416 the ocean floor, it can be assumed that indeed considerable amounts of PVC were present in the collected marine litter (Andrady, 2015). The MPW naphtha contains slightly less chlorine 417 (~119 ppm), however, still exceeding the threshold substantially. Halogen compounds can form 418 highly corrosive compounds during steam cracking such as HCl, HBr, or HF (Li et al., 2018, 419 420 Gutzeit, 2000). It is therefore advisable to include a thermal dehalogenation step prior to pyrolysis

(Bockhorn et al., 1999, Ma et al., 2004, Yoshioka et al., 2000). Hydrotreatment to remove Cl from 421 422 the naphtha fractions prior to steam cracking is another possibility (Prado et al., 2017, Khan and 423 Al-Sayed, 2007, Zacher et al., 2014, Lingaiah et al., 2001). Fluorine in steam cracking feedstocks has similar negative effects compared to chlorine and bromine and the threshold (2 ppm) is slightly 424 425 exceeded by both waste-derived naphtha fractions (Elliott et al., 1985). For bromine, no threshold 426 value is known which indicates that additional investigation into the impact of brominated 427 compounds in steam cracker units is needed (Kusenberg et al., 2022a). However, no bromine was detected in either of the waste-derived naphtha fractions. 428

429 **3.1.3.** Metal analysis

Considerable amounts of metals were detected in both waste-derived naphtha fractions. Table 2 430 shows the metal contaminants measured using ICP-MS in the respective samples. The shown 431 concentrations indicate that most of the metals are present in the low ppb range, which would be 432 below the limit of detection of most other frequently applied metal detection methods such as ICP-433 OES. Since naphtha-range distillation cuts were used in the present study, metal contaminants in 434 435 the crude pyrolysis oils originating from entrained particles were removed in the distillation step (Kusenberg et al., 2022c). Metals still present are, therefore, the chemically bound fraction which 436 437 will ultimately reach the steam cracker. The total sum of metals is 17.5 ppm in MPW naphtha and 5.9 ppm in ML naphtha. The total metals of crude non-distilled post-consumer plastic waste 438 pyrolysis oils can be considerably higher as recently reported between 560 and 790 ppm 439 440 (Kusenberg et al., 2022c). Hence it can be stated that the distillation step indeed has a significant reducing effect on the metal concentration and that a large portion of the metals in plastic waste 441 pyrolysis oils are either located in the very heavy fractions of the pyrolysis oils or originate from 442 443 entrained particles during pyrolysis.

	MPW naphtha	ML naphtha		
Element	Parts pe	er billion		
Ag	<lod<sup>a</lod<sup>	<lod<sup>a</lod<sup>		
Al	1081.2	<lod<sup>b</lod<sup>		
As	3.4	3.8		
В	<lod<sup>c</lod<sup>	<LOD ^d		
Ba	0.5	1.7		
Be	<LOD ^a	<lod<sup>a</lod<sup>		
Bi	<lod<sup>a</lod<sup>	<LOD ^a		
Ca	1272.3	3000.0		
Cd	<lod<sup>a</lod<sup>	<LOD ^a		
Со	<lod<sup>a</lod<sup>	<lod<sup>a</lod<sup>		
Cr	4.7	18.0		
Cu	5.3	33.0		
Fe	251.4	180.0		
Κ	1853.0	<lod<sup>b</lod<sup>		
Li	0.4	<LOD ^a		
Mg	22.5	81.0		
Mn	3.6	21.0		
Мо	<LOD ^a	<lod<sup>a</lod<sup>		
Na	125.7	<lod<sup>b</lod<sup>		
Ni	3.6	3.2		
Pb	0.6	3.6		
Sb	0.5	29.0		
Se	74.0	17.0		
Si	12462.8	1900.0		
Sn	36.6	23.0		
Sr	1.1	25.0		
Те	<lod<sup>a</lod<sup>	<lod<sup>a</lod<sup>		
Ti	<lod<sup>a</lod<sup>	3.1		
Tl	<lod<sup>a</lod<sup>	<LOD ^a		
V	<lod<sup>a</lod<sup>	1.4		
W	<lod<sup>a</lod<sup>	8.2		
Zn	285.5	520.0		
Zr	<lod<sup>a</lod<sup>	<LOD ^a		
Total metals [ppb]	17489	5872		

444	Table 2: Metal concentration	s of the distilled	plastic waste	pyrolysis oils	in ppb measured	using ICP-MS.
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445 ^a 1 ppb

446 ^b 50 ppb 447 ^c 5 ppb

448 ^d 10 ppb

Table 2 shows that the metal contamination is different for the two waste-derived feedstocks. The MPW naphtha, on the one hand, contains higher amounts of aluminum (~1.1 ppm) and silicon (~12.4 ppm) which are both important contaminants of municipal waste (aluminum as waste constituent and silicon as additive). Furthermore, since the waste feedstocks were not washed prior

to pyrolysis, clays and inorganic residues are also a source for metals. The ML naphtha, on the 453 other hand, contains a larger set of different metals including traces of vanadium and tungsten. The 454 high variety of (trace) metals in the ML naphtha underlines the diversity of the collected waste and 455 highlights how challenging recycling of marine litter is from a contaminant point-of-view. The 456 detected metal contaminant values are compared with industrial feedstock specifications in Fig. 4. 457 In the figure, only the metals are shown for which maximum allowable concentrations are known. 458 459 No thresholds exist for metals which typically do not occur in fossil feedstocks such as barium, chromium, magnesium, manganese, antimony, and zinc, which is another challenging aspect when 460 using waste-derived feedstocks for industrial steam crackers. 461







The industrial thresholds are exceeded by both waste-derived naphtha fractions in terms of calcium and silicon. Considering the low detection limits of ICP-MS, it is now possible to conclude that the used feedstocks comply with industrial steam cracker feedstock specifications in terms of iron, arsenic, nickel, vanadium and lead which are among the most severe poisons for downstream catalysts of steam crackers. Therefore, the data, for the first time, allows a reliable statement on which metals should be focused in terms of potential upgrading and demetallization steps. In 471 comparison, in prior work in the field it was not possible to detect ultra-low concentrations in the 472 ppb level, thus leaving an uncertainty if certain metal contaminants are indeed absent or simply below the detection limits of used analytical techniques (Kusenberg et al., 2022a). Clearly, silicon 473 (ML naphtha 1900 ppb, MPW naphtha 12463 ppb) exceeds the threshold for industrial steam 474 475 cracker feedstocks substantially. Iron, although compliant with the steam cracker specification of 476 1 ppm, is present in high ppb levels in both fractions. Iron is an active catalytic material and is thus 477 a strong contributor to coke formation in steam cracking (Reid and Nowowiejski, 2003, Baumgartner et al., 2004). Regarding calcium, it needs to be stated that the CaO that was introduced 478 479 during pyrolysis also contributed to the calcium concentration in the pyrolysis products. Since 480 calcium is a prominent metal contaminant in plastic waste pyrolysis oils due to its use as an additive (i.e., as filler in form of CaCO₃), it is one of the most important contaminants as reported previously 481 (Kusenberg et al., 2022a, Kusenberg et al., 2022c). Analyses show that the two waste-derived 482 naphtha fractions contain relatively high amounts of calcium (~1.3 ppm in MPW naphtha and 483 ~3 ppm in ML naphtha) which is lower than values reported in literature for crude pyrolysis oils of 484 mixed plastic waste were no CaO was added during pyrolysis (Kusenberg et al., 2022b, Kusenberg 485 et al., 2022c). In the commercial scale plastic waste liquefaction process described by (Okuwaki et 486 al., 2006), calcium-based additives are added to protect reaction equipment from corrosion. The 487 488 authors reported a calcium concentration of 17 ppm in the light distilled fraction of the pyrolysis 489 oil which could be clearly related to the calcium addition during pyrolysis. Hence, it can be stated 490 that the addition of calcium, while having a protective effect for process equipment, should be 491 avoided from a product quality point-of-view. In any case, the measured calcium concentrations in this study will have an impact on the steam cracking performance, regardless of the original 492 calcium source. Potassium and sodium, next to being strong coking and fouling promotors, might 493 494 cause damage to the reactor coil material (Sundaram and Stancato, 2018, Brayden et al., 2006). For

both, only the MPW naphtha (1853 ppb potassium, 126 ppb sodium) does not comply with the 495 industrial threshold value. This indicates that for the ML, adsorpted salt from sea water is not an 496 issue, while salts attached or embedded in food residues in the (unwashed) municipal waste 497 fractions might cause higher potassium and sodium concentrations in the MPW naphtha. 498 Furthermore, silicon in MPW naphtha (12463 ppb) exceeds the known threshold of 500 ppb by 499 orders of magnitude. Silicon is a strong catalyst poison and fouling promotor (Gazulla et al., 2017, 500 501 Reid and Nowowiejski, 2003). The silicon concentration in ML naphtha (1900 ppb), although still too high, seems to be less problematic compared to MPW naphtha and can be reduced by mild 502 blending with fossil feedstocks. 503

In general, it can be stated that the required upgrading in terms of the metal contaminants is 504 505 moderate for both feedstocks. Special emphasis is required for siliconand calcium which are largely present in both waste-derived feedstocks. Furthermore, sodium, potassium and iron need careful 506 507 monitoring. It can, however, be stated that without upgrading, metals present in the waste-derived naphtha fractions will lead to an increase in coke formation due to catalytic activity as well as to 508 fouling in heat exchangers (Kusenberg et al., 2022a) and downstream catalyst poisoning in 509 commercial steam crackers. Further metal removal techniques are therefore needed such as 510 hydrodemetallization, solvent extraction (Ali and Abbas, 2006) or filtration (Ates and Uzal, 2018). 511 It can further be concluded that distillation is not sufficient as a method to completely remove metal 512 contaminants below industrial feedstock contaminant thresholds (Kusenberg et al., 2022a). 513

514 **3.2**.

3.2. Steam cracking performance

515 Three different steam cracking severities were chosen according to the coil outlet temperatures 516 820 °C, 850 °C and 880 °C (see Table S4 in the SI). The respective on-line $GC \times GC$ -FID chromatograms of the reactor effluents when steam cracking the three feedstocks at a COT of
850 °C (i.e., temperature profile 2), are shown as an example in Fig. S5 in the SI.

519 **3.2.1.** Steam cracking product yields

Table 3 shows the concentrations of the most important products obtained from steam cracking 520 521 analyzed using on-line $GC \times GC$ -FID. The complete overview of individual product yields can be found in section B2 in the SI. Substantial amounts of heavy aromatic products (i.e., diaromatics, 522 naphthenodiaromatics and triaromatics) were detected in the steam cracking effluent of the waste-523 derived naphtha fractions compared to the fossil naphtha reference feedstock. The products, on the 524 525 one hand, stem from secondary reactions of aromatics (i.e., styrene) or diolefins present in the feedstock (see Fig. 2). On the other hand, at the lower severity condition (i.e., COT 820 °C) it is 526 possible that heavy (aromatic) compounds present in the feedstocks are only partly converted. 527 528 Heavy products in the pyrolysis fuel oil (PFO) range (C_{10+}) are problematic in steam cracking due to condensation in the transfer line exchanger (TLE) section downstream of the reactor, which 529 leads to fouling of the inner tube walls, ultimately causing blockages. 530

Comparing the two waste-derived feedstocks in terms of their overall steam cracking product 531 distribution, it can be stated that the ML naphtha performs reasonably well, in a comparable range 532 533 with fossil naphtha, in terms of light products (C_4) . The MPW naphtha, on the contrary, has a much lower share of light products along with a substantial amount of products in the pyrolysis gasoline 534 535 (PyGas) range (C_5 - C_9)) and the PFO range (C_{10+})). This can be directly related to the very high share of aromatic compounds in the feedstock which cause the formation of heavier (primarily 536 537 aromatic) products. It can be concluded that the MPW naphtha is not suitable for steam cracking 'as is' and that the aromatics should rather be recovered before cracking, which is especially valid 538 for styrene due to its large coking tendency and high value as a base chemical. Furthermore, with 539

540 more severe cracking conditions (i.e., higher COT), the total yield of light products (C₄) of the 541 waste-derived feedstocks does not strongly increase as observed with the fossil naphtha reference 542 feedstock, but remains rather stable and even decreases at the highest COT along with a substantial 543 increase of heavy products.

544 Table 3: Result summary of the most important steam cracking product yields according to the coil outlet545 temperature.

	Fossil naphtha reference			MPW naphtha			ML naphtha		
COT [°C]	820	850	880	820	850	880	820	850	880
Total C ₄ . [wt%]	67.9	75.8	76.6	52.3	51.7	49.3	61.5	66.0	63.7
Total C ₅ -C ₉ [wt%]	31.4	23.3	21.1	39.8	40.0	40.0	31.9	27.5	28.1
Total C ₁₀₊ [wt%]	0.7	1.0	2.2	8.0	8.3	10.7	6.5	6.5	8.2
Propylene/Ethylene	0.77	0.62	0.47	0.77	0.61	0.45	0.60	0.49	0.37
СО	0.0	0.0	0.0	0.9	1.0	1.2	0.6	0.7	0.9
CO ₂	0.0	0.0	0.0	0.1	0.1	0.2	0.1	0.1	0.1
Methane	10.3	13.7	16.0	8.8	10.7	12.0	9.6	12.3	14.0
Ethylene	21.8	27.0	30.4	15.5	17.1	17.9	22.4	26.0	27.2
Ethane	2.9	3.1	2.9	2.8	2.6	2.2	3.4	3.4	3.0
Propylene	16.9	16.8	14.2	12.0	10.4	8.1	13.4	12.7	10.2
1-butene	3.2	2.1	1.2	1.5	0.8	0.3	2.3	1.1	0.4
Iso-butene	3.9	3.3	2.3	4.8	3.5	2.2	2.3	1.8	1.2
1,3-butadiene	4.6	5.1	5.0	3.7	3.4	2.8	5.1	5.0	4.1
Benzene	4.3	6.9	9.2	8.0	12.5	12.1	7.6	11.1	11.6
Toluene	2.2	3.3	3.6	6.7	8.2	10.4	6.3	5.3	5.0
Xylenes	0.1	0.2	0.3	2.3	1.9	2.3	1.8	1.0	1.3
Indene	0.1	0.2	0.5	0.7	0.9	1.4	0.7	0.6	1.0
Naphthalene	0.1	0.1	0.9	1.2	1.7	3.0	1.1	1.3	2.3
Anthracene & Phenanthrene	0.0	0.1	0.0	0.1	0.2	0.2	0.0	0.1	0.1
BTX	6.5	10.4	13.0	17.1	22.6	24.8	15.7	17.4	17.9
Others	29.7	17.9	13.5	30.9	25.3	23.8	23.4	17.4	17.6

The most important products in steam cracking are the light olefins ethylene, propylene, and 1,3butadiene which are the most prominent building blocks for the subsequent production of polymers.
At the lowest severity (i.e., COT 820 °C), the ML naphtha outperforms the fossil naphtha reference
in terms of the ethylene yields (see Fig. 5). Higher ethylene yields at lower cracking severity were

also observed in a previous study, where crude pyrolysis oils of polyolefin-rich waste were steam 550 cracked in the same experimental unit: using the identical temperature profile corresponding to a 551 COT of 820 °C, steam cracking of a PE-rich pyrolysis oil/fossil naphtha blend yielded 23.6 wt% 552 ethylene which is in good agreement with the yields detected for the ML naphtha (Kusenberg et 553 al., 2022b). The slightly lower ethylene yield of the ML naphtha obtained in this study (22.4 wt.%) 554 can be explained by the considerable aromatic concentration in the feedstock leading to more heavy 555 products. At higher cracking severities, especially at a COT of 880 °C, the ethylene yield of the 556 ML naphtha does not increase as strongly as that of the naphtha reference which also relates to 557 increased formation of heavy products (see Table 3). 558



559

Fig. 5: Steam cracking yields of methane, ethylene, propylene and 1,3-butadiene as function of the COT.
Regarding the light olefin yields it can be stated that MPW naphtha performs quite poorly. The
results demonstrate that non-polyolefins in the original plastic waste (i.e., PS, PET, PVC, PA) have

a direct negative impact on the performance in steam cracking due to high amounts of (heavy) aromatics in the pyrolysis products. Next to the hydrocarbon products, considerable amounts of CO and CO_2 were formed when cracking the waste-derived feedstocks which is clearly related to the oxygen contamination in the waste-derived naphtha fractions (see Fig. 3).

567 **3.2.2.** Coke formation

568 The amount of coke formed in the reactor was assessed after a consecutive steam cracking duration of 6 hours at a COT of 850 °C which is equivalent to 900 grams of feedstock per steam cracking 569 experiment. Steam cracking of the fossil naphtha benchmark lead to a radiant coke formation of 570 571 \sim 13 mg/h. The observed coke formation of the ML naphtha was moderately higher (\sim 21 mg/h) and that of MPW naphtha was substantially higher (~41 mg/h). The higher coking tendency of the 572 waste-derived feedstocks was expected based on the high amounts of olefins and aromatics, and 573 574 the detected metal concentrations. However, considering that the feedstocks were cracked pure without dilution, the coke formation can be considered moderate, especially in the case of ML 575 naphtha (+~50%), which is highly promising considering the presence of catalytically active 576 metals, such as iron, as well as olefins and aromatics. Given a likely industrial scenario in which 577 waste-derived feedstocks are blended with fossil naphtha, it can be expected that the ML naphtha 578 does not cause a substantial increase in coke formation when used in industrial scale. The coke 579 formation of the MPW naphtha was substantial which can be related especially to styrene (Kopinke 580 et al., 1993b, Jambor and Hájeková, 2015). However, considering the hydrocarbon composition 581 582 and the contaminant concentrations, blending of MPW naphtha with fossil naphtha feedstocks at moderate mixing ratios will still be feasible from a coke formation and product yields point-of-583 view. Of course, further research is needed to elaborate on the individual effects of different metal 584 585 compounds on fouling and coke formation. However, comparing the obtained results with a previous study, where the coke formation of crude plastic waste pyrolysis oils blended (1:3) with naphtha was assessed in the same experimental unit and substantially higher coking rates were observed, it can be stated that distillation is indeed an effective first treatment step in terms of coke formation reduction (Kusenberg et al., 2022b). In order to close the gap towards industrially acceptable feedstocks, next to blending, hydrotreatment (Prado et al., 2017, Zacher et al., 2014) is an effective method to remove unwanted heteroatomic contaminants as well as to reduce unsaturated hydrocarbons.

593 4. Conclusions and Outlook

Two naphtha-range feedstocks obtained via pyrolysis and distillation of municipal plastic waste 594 and marine litter have been thoroughly characterized and subsequently steam cracked in a 595 continuous unit in order to assess the product yields and coke formation compared with a fossil 596 naphtha reference feedstock. It was found that, although the waste-derived feedstocks were highly 597 598 contaminated with nitrogen, oxygen, chlorine and metals, along with high amounts of olefins and aromatics, no practical operating issues were encountered. MPW naphtha contained high amounts 599 of aromatics which explained the lower light olefin yields in steam cracking as well as the higher 600 601 (+~180%) coke formation compared to the fossil naphtha reference feedstock. ML naphtha, on the other hand, performed well in terms of light olefin yields and more moderate increase $(+\sim 50\%)$ in 602 coke formation. 603

The observed differences in product yields and coke formation of MPW naphtha and ML naphtha are mainly related to the high concentration of aromatics in MPW naphtha, which should best be removed prior to steam cracking. Both feedstocks exceeded the known feedstock specifications substantially in terms of the nitrogen, oxygen and chlorine concentrations. Furthermore, both waste-derived naphtha fractions had similar metal contaminations, partly exceeding known

feedstock specifications. By using the highly accurate ICP-MS for metal analysis, it was found that 609 610 the most important metal contaminants in the naphtha fractions were silicon, calcium, iron, potassium and sodium. In light of severe issues such as corrosion and potential catalyst poisoning 611 in commercial steam crackers, waste-derived feedstocks have to be screened carefully and potential 612 613 sources of heteroatoms in the pyrolyzed waste fractions such as PVC, PA, PET, or PUR, and organic residues must be reduced prior to chemical recycling. It can be concluded that pyrolysis, 614 615 distillation and subsequent steam cracking of highly mixed and difficult-to-recycle waste is a feasible and robust option if certain steps such as dilution or minimal additional feedstock 616 purification are performed. This way, chemical recycling could significantly aid in the transition 617 618 from a linear to a circular economy by extending the potential feedstocks towards environmentally highly relevant waste fractions such as marine litter, ultimately reducing the environmental burden 619 that is plastic waste. Furthermore, the fact that the feedstocks can be produced in a rather simple 620 621 process via pyrolysis and distillation is very promising and enables the valorization of waste fractions in a decentralized way without the need for high-tech solutions. This is especially 622 interesting for areas of the world that are most affected by marine pollution but have less access to 623 624 sophisticated engineering solutions.

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632 **Declaration of competing interest**

633 The authors declare no conflict of interest.

634 CRediT authorship contribution statement

- 635 Marvin Kusenberg: conceptualization, methodology, investigation, writing original draft,
- 636 writing review & editing. Gian Claudio Faussone: conceptualization, resources, funding
- 637 acquisition, writing review & editing. Hang Dao Thi: investigation, writing review & editing.
- 638 Martijn Roosen: investigation, writing review & editing. Miha Grilc: conceptualization,
- 639 resources, writing review & editing. Andreas Eschenbacher: writing review & editing. Steven
- 640 De Meester: writing review & editing. Kevin M. Van Geem: conceptualization, project
- 641 administration, funding acquisition, supervision, writing review & editing.

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