Assessing the feasibility of chemical recycling via steam cracking of untreated plastic waste pyrolysis oils: feedstock impurities, product yields and coke formation

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16 List of abbreviations

50 % BP	50 % boiling point
BSSC	Bench-scale steam cracking unit
BTX	Benzene, toluene, xylenes
CIC	Combustion ion chromatography
CIP	Coil inlet pressure
CIT	Coil inlet temperature
COP	Coil outlet pressure
COT	Coil outlet temperature
CSTR	Continuous stirred tank reactor
EVOH	Ethylene vinyl alcohol
FBP	Final boiling point
FCC	Fluid catalytic cracking
FID	Flame ionization detector
GC × GC	Comprehensive two-dimensional gas chromatography
HC	Hydrocarbons
IBP	Initial boiling point
ICP	Inductively coupled plasma
IR	Infrared
LOD	Limit of detection
LOQ	Limit of quantification
MPO	Mixed polyolefins
OES	Optical emission spectrometry
PA	Polyamide
PE	Polyethylene
PET	Polyethylene terephthalate
PFO	Pyrolysis fuel oil
PP	Polypropylene
ppb	Parts per billion
ppm	Parts per million
PS	Polystyrene
PTV	Programmable temperature vaporizer
PUR	Polyurethane
PV(D)C	Polyvinyl(idene)chloride
PyGas	Pyrolysis gasoline
RGA	Refinery gas analyzer

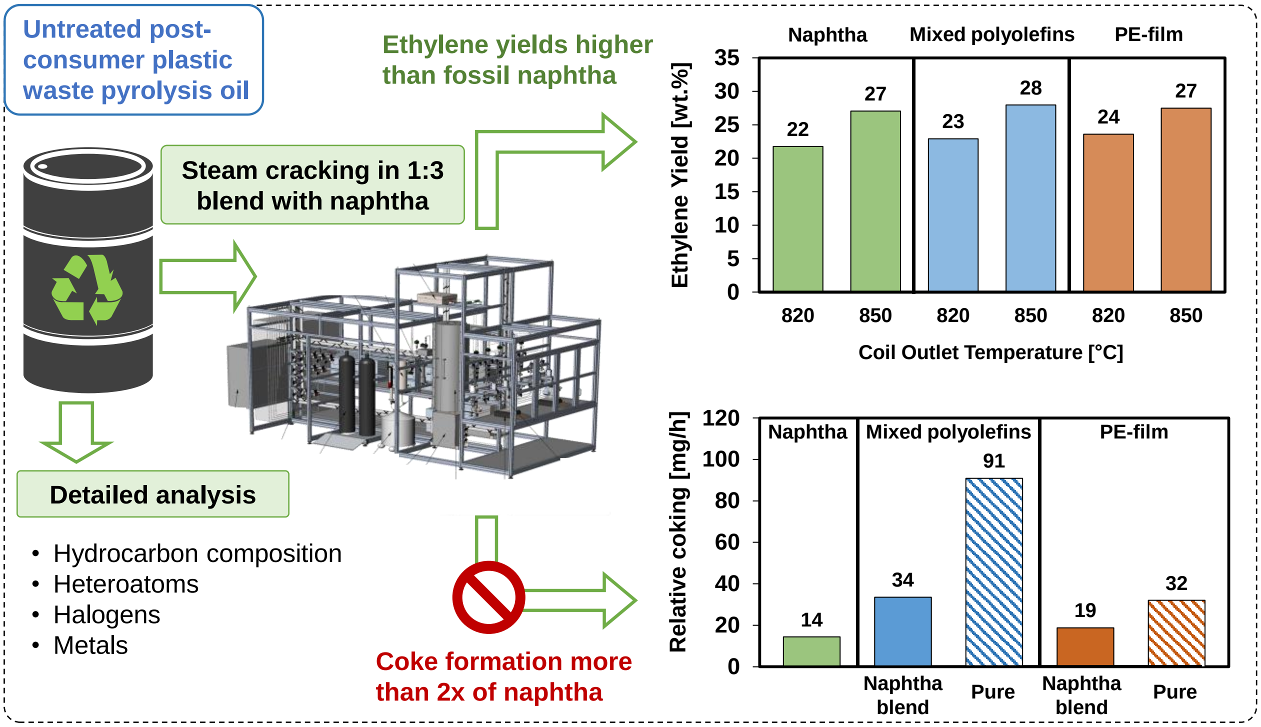
SI	Supporting Information
TCD	Thermal conductivity detector

Abstract

Chemical recycling of plastic waste to base chemicals via pyrolysis and subsequent steam cracking of pyrolysis oils shows great potential to overcome the limitations in present means of plastic waste recycling. In this scenario, the largest concern is the feasibility. Are plastic waste pyrolysis products acceptable steam cracking feedstocks in terms of composition, product yields and coke formation? In this work, steam cracking of two post-consumer plastic waste pyrolysis oils blended with fossil naphtha was performed in a continuous bench-scale unit without prior treatment. Product yields and radiant coil coke formation were benchmarked to fossil naphtha as an industrial feedstock. Additionally, the plastic waste pyrolysis oils were thoroughly analyzed including the detailed hydrocarbon composition using two dimensional gas chromatography coupled to a flame ionization detector as well as specific analysis for heteroatoms, halogens and metals. It was found that both pyrolysis oils are rich in olefins (~48 wt.%) and that the main impurities are nitrogen, oxygen, chlorine, bromine, aluminum, calcium and sodium.

Steam cracking of the plastic waste derived feedstocks led to ethylene yields of ~23 wt% at a coil outlet temperature of 820 °C and ~28 wt.% at 850 °C, exceeding the ethylene yield of pure naphtha at both conditions (~22 wt.% and ~27 wt.%, respectively). High amounts of heavy products were formed when steam cracking both pyrolysis oils. Furthermore, a substantial coking tendency was observed for the more contaminated pyrolysis oil, indicating that next to unsaturated hydrocarbons, contaminants are a strong driver for coke formation.

Graphical abstract



Keywords: Thermochemical recycling; post-consumer plastic waste; pyrolysis; steam cracking; contaminants; radiant coil coke formation

1. Introduction

Global plastics production exceeded 350 million tons in 2018 and will likely double within the next twenty years. About 40 % of the produced plastic is used as packaging material, predominantly consisting of polyolefins (polyethylene (PE), polypropylene (PP)) and polystyrene (PS) (Plastics Europe, 2020). According to the newest data, only 29 % of the collected plastic packaging waste in Europe is recycled today. The rest is either landfilled or incinerated for energy recovery giving CO_2 emissions (Plastics Europe, 2019).

Due to impurities in plastic waste streams, mechanically recycled plastics are often either of lower quality or more expensive compared to virgin polymers (Vollmer et al., 2020, Gabriel et al., 2015). Therefore, thermochemical conversion into base chemicals represents a promising recycling option (Solis and Silveira, 2020, Dogu et al., 2021). This route contains two thermal decomposition steps, namely pyrolysis of solid plastic waste and subsequent cracking of the pyrolysis oils to produce base chemicals such as ethylene, propylene, 1,3-butadiene and benzene among others (Ragaert et al., 2017). The use of waste plastics and its pyrolysis derivatives in a petrochemical context using refinery units has been recently reviewed by (Palos et al., 2021). According to the authors, possible unit operations suitable for the direct valorization of solid plastic waste are fluid catalytic cracking (FCC) or hydroprocessing units, while the pyrolysis products can be ideally used in steam crackers and coker units without the need to modify or replace units within the refinery complex. Further pathways to directly valorize polyolefinic plastic waste were proposed by different authors (Vela et al., 2021, Vela et al., 2020, Palos et al., 2018), including co-feeding of plastic waste to a hydrocracking unit for the direct production of fuels. Furthermore, (Thunman et al., 2019) investigated ways to transform a petrochemical steam cracker infrastructure into a thermochemical plastic waste recycling plant and concluded that a full replacement of fossil steam cracking feedstocks with plastic waste derived feedstocks is economically attractive. Furthermore, using plastic waste streams in combination with electrification could drastically reduce the emissions of the steam cracking process (Van Geem et al., 2019, Van Geem and Weckhuysen, 2022). However, there are still many unknowns in terms of the feasibility of plastic waste pyrolysis oils as steam cracking feedstocks. These are mostly related to the high degree of mixing in plastic waste and the corresponding uncertainty in terms of high contaminant concentrations and their impact (Kusenberg et al., 2022a). In an industrial context, several demonstration projects are currently either being launched or are already in operation (Fitzsimons, 2020, Bailey, 2020, Pilkington, 2020, Young, 2021, Recycling Today, 2019).

Pyrolysis of polyolefins follows a random scission mechanism which yields liquid products with a wide boiling point range, containing a complex hydrocarbon mixture rich in unsaturated compounds which can be used as steam cracking feedstock (Ragaert et al., 2017, Al-Salem et al., 2010, Angyal et al., 2010). For steam cracking, strict feedstock specifications exist in terms of maximum concentrations of olefins, aromatics but also contaminants (i.e., heteroatoms and metals) (Sundaram and Stancato, 2018). Compliance with these industrial specifications is a prerequisite for pyrolysis oils from plastic waste to be feasible steam cracker feedstocks. In case the quality is insufficient, upgrading requirements or necessary blending ratios with (contaminant-free) fossil feedstocks such as naphtha need to be determined. This has been extensively described in the recent review article of (Kusenberg et al., 2022a).

Plastic waste inherently contains more and different contaminants than fossil feedstocks due to plastic’s use as consumer material with a wide variety of applications. Furthermore, cross-contamination during sorting might occur (Roosen et al., 2020, Eriksen et al., 2018, Carneado et al., 2015, Ügdüler et al., 2020). The most prominent contaminants in plastic waste are believed to be nitrogen, sulfur, oxygen, chlorine and metals (Kusenberg et al., 2022a). In steam cracking, these contaminants are known to cause severe issues such as corrosion, fouling and increased coke formation as well as downstream catalyst poisoning (Sundaram and Stancato, 2018, Baumgartner et al., 2004, Patil et al., 2019, Kusenberg et al., 2022a). Furthermore, it is generally accepted that aromatics and olefins in steam cracker feedstocks have a substantial impact on coke formation and fouling of heat exchanger surfaces (Kopinke et al., 1993a, Kopinke et al., 1993b, Ibrahim, 2012, Müller-Steinhagen et al., 2011, Müller-Steinhagen, 2010).

Only a very limited number of studies are available that investigated the potential of plastic waste pyrolysis oils as liquid steam cracker feedstocks. In the pioneering work of Angyal et al., it was reported that the high olefin content in distilled fractions of plastic waste pyrolysis oils did not significantly reduce the ethylene and propylene yields compared to a fossil equivalent (Angyal et al., 2010). Hajekova et al. investigated steam cracking of crude pyrolysis oils from different virgin polyolefins blended with naphtha. All the studied pyrolysis oils resulted in enhanced light olefin yields compared to naphtha (Hájeková et al., 2007). In an earlier study, the same authors reported that coke formation of the virgin, contaminant-free pyrolysis oil/naphtha blends during steam cracking was equal to the one observed for pure fossil naphtha (Hájeková and Bajus, 2005). It must be pointed out that in the mentioned studies by Hajekova et al., virgin plastics were used and that it was shown in several demonstration projects during the 1990s that thermal degradation of real post-consumer plastic waste lead to severe operational issues ultimately making processes unfeasible (Hájeková et al., 2007, Hájeková and Bajus, 2005, Tukker et al., 1999). So far, there is no systematic study investigating the effect of untreated, contaminated post-consumer plastic waste pyrolysis oils on steam cracking yields and radiant coil coke formation.

In this work, two different representative post-consumer plastic waste fractions have been pyrolyzed in a continuous pyrolysis unit and the obtained pyrolysis oils have been blended with fossil naphtha and steam cracked without pre-treatment in a continuous bench-scale steam cracking unit. Steam cracking product yields and radiant coil coke formation results have been benchmarked to pure fossil naphtha. Prior to steam cracking, the detailed chemical composition was thoroughly analyzed using comprehensive two-dimensional gas chromatography coupled with a flame ionization detector (GC × GC-FID). Contaminants in the plastic waste pyrolysis oils were tracked using inductively coupled plasma – optical emission spectroscopy (ICP-OES) and combustion ion chromatography (CIC).

2. Materials and Methods

2.1. Apparatus and experimental procedure

Plastic waste samples have been pyrolyzed in a pilot-scale pyrolysis unit as depicted in Fig. 1. The unit consists of an extruder connected to an externally heated continuous stirred-tank reactor (CSTR) as described in the recent works of (Zayoud et al., 2022) and (Kusenberg et al., 2022b). The extruder is used to melt the plastic waste pellets and to feed the polymer melt to the heated pyrolysis reactor. The pyrolysis products leave the reactor in vapor form. In the downstream section of the reactor, liquid products are condensed and collected. The flow of non-condensable gaseous products is measured using a volumetric gas flow meter (RITTER, Germany). The solid residue remains in the reactor and is removed and weighed separately after completion of each experiment. Both plastic waste fractions were pyrolyzed at 450 °C and atmospheric pressure.

Steam cracking experiments were carried out using a bench-scale steam cracking setup (BSSC) as described in previous works (Harper et al., 2011, De Bruycker et al., 2014) (see Fig. S1 in the supporting information (SI)). The design of the BSSC unit is as such that the results can be easily scaled-up to a real industrial furnace (Van Geem et al., 2007). The unit consists of three sections, namely the feeding section, the furnace/reactor section and the analysis section. The feeding section controls the supply of the feedstock and the demineralized water (serving as a diluent after evaporation) to the reactor coil via Coriolis flow-meter (CORI-FLOW) controlled pumps (Bronkhorst, The Netherlands). The reactor has a length of 1.475 m, an internal diameter of 6 mm and is made of Incoloy 800HT (Ni: 30-35 wt.%, Cr: 19-23 wt.%, Fe: > 39.5 wt.%). The furnace is electrically heated and has eight separate heating zones to set a specific temperature profile. Two pressure transducers, placed at the inlet and outlet of the reactor, indicate the coil inlet (CIP) and the coil outlet pressure (COP), respectively. At the reactor outlet, the injection of nitrogen provides an internal standard for analytical measurements. The reactor effluent is sampled online, i.e., during operation, at high temperature (350 °C) in order to avoid condensation of heavy steam cracking products. Via a valve-based sampling system and uniformly heated transfer lines, a gaseous sample of the reactor effluent is injected onto the GC × GC-FID unit. Further downstream, the reactor effluent is cooled, water and condensed heavier products are removed, while a fraction of the gaseous effluent is analyzed on the so-called Refinery Gas Analyzer (RGA). On the RGA, H_2, CO_2, CO, N_2, methane, ethane, ethylene and acetylene are detected by a thermal conductivity detector (TCD), while methane, ethane, ethylene, propane, propylene, acetylene, propadiene, iso-butane, n-butane, trans-2-butene, 1-butene, cis-2-butene, methylacetylene and 1,3-butadiene are analyzed via FID. The concentration of methane is quantified using the well-defined nitrogen flow introduced downstream of the reactor. The compounds methane, ethane, ethylene and acetylene are measured twice on the RGA (with TCD and FID, respectively), thus providing an internal validation. On the GC × GC-FID, the entire reactor effluent is analyzed. The methane concentration measured using the RGA is used as a secondary internal standard to quantify the products in the range above C_5 (see Fig. S2 in the SI) (Pyl et al., 2011a, Pyl et al., 2011b, Van Geem et al., 2010). Response factors of N_2, H_2 and C_{4-} compounds were determined using a well-defined calibration gas mixture (Air Liquide, Belgium). The response factors of the remaining C_{5+} compounds were determined using the effective carbon number method (Pyl et al., 2011a, Van Geem et al., 2010, Harper et al., 2011, De Bruycker et al., 2014, Pyl et al., 2011b). The procedure showed good repeatability with C and H molar balances closing within ± 5 %.

Two coil outlet temperatures (COT) have been tested in the steam cracking experiments, namely 820 °C and 850 °C. For both COTs, temperature profiles were set (see table S1 in the SI for the detailed conditions). The coil inlet temperature (CIT) was set to 550 °C for all experiments in order to limit cracking reactions before the reaction zone. The temperature in the preheating and mixing zones were set to 500 °C to ensure evaporation of the entire feedstock. The coil outlet pressure (COP) was set to 1.7 bar for all experiments. The liquid hydrocarbon flow was set to 150 g/h with a steam dilution of 0.5 $\text{wt.}_{H2O}/\text{wt.}_{HC}$ leading to an average coil residence time of 0.48 to 0.55 s depending on the feedstock. The process conditions were chosen in a way to best mimic industrial conditions in terms of cracking severity (i.e., propylene/ethylene ratio) as described in detail by Van Geem et al. (Van Geem et al., 2005, Van Geem et al., 2007). It has to be noted that the effect of the steam cracking conditions is different for different feedstocks depending on the chemical composition. For instance, cracking of shorter hydrocarbon chains (as found in fossil naphtha) requires a higher temperature than cracking of longer chains due to the higher thermal stability. Furthermore, the mass flows and steam dilution ratio were chosen in a way to obtain sufficient residence times to, on the one hand, achieve full conversion of feedstocks and, on the other hand, to minimize secondary reactions. Both plastic waste pyrolysis oils were blended with fossil naphtha in a 1:3 (weight-based) mixing ratio due to their waxy state and high melting point (~85 °C) which made it impractical to feed it pure to the steam cracking unit. To reduce the viscosity of the feedstock and to prevent solidification in the feeding lines, the feeding bottle was heated during the experiment using an electrical heating mantle at ~60 °C.

The amount of coke which was deposited during each respective steam cracking experiment was quantified by combusting the deposited coke after 6 hours of operation. An infrared (IR) analyzer (Fuji Electric, Japan) was used to measure the volumetric concentration of CO and CO_2 in the reactor effluent during this controlled decoking experiment (Pyl et al., 2011a). Initially, the reactor was heated to 850 °C in all zones. Before decoking, the reactor was flushed with N_2 in order to zero-calibrate the IR-meter and to clean the reactor from residual hydrocarbons. At the start of the decoking experiment, steam and air were introduced. Once most of the coke was burned off (CO_2 < 1 vol.%), the flow of steam was stopped and the decoking was continued with air only at 900 °C in all zones until CO and CO_2 were no longer detected in the reactor effluent. The detailed conditions of the decoking experiment are shown in Table S2 in the SI. The volumetric flow rate of the reactor effluent was measured using a volumetric gas flow meter (RITTER, Germany). The volumetric concentrations and the flow rate were used to determine the total coke amount deposited on the inner reactor surface.

2.2. Materials and standards

Two separate post-consumer plastic waste fractions in pellet-form have been pyrolyzed. The first was a PE-film sample. The second was a mixed polyolefin (MPO) sample. The PE-film fraction largely consisted of monolayer films while the MPO fraction contained a higher contamination with other polymers. Next to the main constituents PE and PP, small amounts of heteroatomic polymers such as such as polyethylene terephthalate (PET), ethylene vinyl alcohol (EVOH), polyamide (PA), polyvinyl(idene)chloride PV(D)C, polyurethane (PUR) and ethylene vinyl acetate (EVA) were present. Both waste materials were curbside collected and went through a typical waste sorting and separation line including shredding, washing, float-sinking separation, drying, wind shifting as well as extrusion (Kleinhans et al., 2021). The compositions of the plastic waste streams are given in Fig. S3 in the SI. A typical industrial light naphtha was used as a reference feedstock for steam cracking with the composition given in Table S3 in the SI.

For dilution of the (viscous) pyrolysis oils prior to GC × GC-FID analysis, carbon disulfide (≥99 %, Sigma-Aldrich, Belgium) was used. 3-chlorothiophene (Sigma-Aldrich, Belgium) with a minimum purity of 96 % was used as internal standard for feedstock analyses. Analytical gases (helium, nitrogen, hydrogen, carbon dioxide, air, oxygen) were used with a minimum purity of 99.999 % (Air Liquide, Belgium). For the on-line quantification of the steam cracking effluent, a dedicated calibration gas mixture (Air Liquide, Belgium) was used, containing well-defined concentrations of C_1 to C_4 compounds. For the quantification of formed coke, a calibration gas (Air Liquide, Belgium) containing well-defined concentrations of CO and CO_2 was used.

2.3. Analytics

Comprehensive two-dimensional gas chromatography (GC × GC) coupled to a flame ionization detector (FID) was used to quantitatively determine the detailed composition of the plastic waste pyrolysis oils and the reference naphtha prior to steam cracking as well as to on-line analyze the steam cracking effluent. Thermo Scientific TRACE GC × GC setups (Interscience, Belgium) equipped with a two-stage cryogenic liquid CO_2 modulator have been used (Van Geem et al., 2010, Pyl et al., 2011b). Prior to off-line analyses, samples have been prepared using carbon disulfide as diluent as well as 3-chlorothiophene as internal standard at a concentration of 3-4 wt.%. Due to potential instability, the samples were kept in a refrigerator at temperatures between 3-5 °C. In the GC × GC oven, a typical non-polar/polar column set was used (Kusenberg et al., 2022b). The detailed GC × GC settings for on- and off-line analysis can be found in Table S4 in the SI. The exact quantification procedure of on- and off-line analyses using the internal standard concentration and the response factors have been explained in detail by (Toraman et al., 2014, Djokic et al., 2012, Van Geem et al., 2010, Dao Thi et al., 2021). Using the described methods, the composition of the respective pyrolysis oils could be characterized.

The carbon, nitrogen, hydrogen, sulfur and oxygen (CHNS/O) composition of the feedstocks was determined using a Flash EA2000 elemental analyzer (Interscience, Belgium) equipped with a TCD. CHNS analysis was performed in combustion mode according to the ASTM D 5291 standard method (American Society for Testing and Materials, 2015). Oxygen determination was performed in pyrolysis mode according to the ASTM D 5622 standard method in a separate reactor (American Society for Testing and Materials, 2017). The CHNS/O composition of the two samples was derived based on at least four repeat analyses of each sample.

Halogen analysis of the plastic waste pyrolysis oils was performed according to the ASTM standard method D6470 - 99(2020) (American Society for Testing and Materials, 2020b). The halogen concentrations (i.e., fluorine, chlorine, and bromine) were determined with ion chromatography (930 Compact IC Flex, Metrohm, Switzerland), equipped with a Metrosep A Supp 7-250/4.0 column and conductivity detector. Quantification was based on linear calibration curves using five standard solutions within the range of 0 and 50 ppm of the analytes of interest. The instrumental parameters and conditions applied during IC analyses can be found in Table S5 in the SI.

Inductively coupled plasma – optical emission spectrometry (ICP-OES) was performed on a Thermo Scientific iCAP 7200 model, equipped with Qtegra Software (Thermo Scientific iCAP 7000 Plus Series ICP-OES, Thermo Fisher Scientific Brand, USA) and a CETAC AXP 560 autosampler (Teledyne Technology, USA). Standards for calibration (ranging from 0.001 ppm up to 20 ppm) were prepared using XVI Certipur multi-element standard solution (100 mg L^{-1} in 10 %

HNO_3), containing Cd, Cu, Co, Zn, Fe, Mn, Pb, Li, Mg, Sr, Tl, Sb, Ti, Ca, Mo, V, As, Ni, Al, Be, Si, Na, Se, and Cr. Prior to ICP-OES analyses, the samples were digested via an Anton Paar (Austria) Multiwave 5000 microwave oven equipped with a 20SVT-rotor and PTFE-TFM digestion vessels. 0.5000 ± 0.0500 g of each sample was weighed in a digestion vessel. Subsequently, 10.0 mL of concentrated HNO_3 (70 %, Sigma Aldrich) and 3.0 mL of double-distilled water was added to the weighed sample. The vessels were transferred to the microwave oven and subjected to the following heating program: 20 min ramping time up to a temperature of 200 °C and 15 min heating time. After digestion, the samples were diluted to a volume of 50 mL with double-distilled water. Blanks were prepared using the same procedure without addition of sample. Afterwards, the samples were filtered using a syringe filter (0.45 μm syringe filter, PP filter media, CHROMAFIL). The limit of detection (LOD) of the ICP-OES analysis was quantified by multiplying the standard deviation of the blank by 3. The limit of quantification (LOQ) was quantified by multiplying the standard deviation of the blank by 10. The values for the LOD and LOQ are given in table S6 in the SI.

3. Results and Discussion

3.1. Feedstock characterization

Fig. 2 shows the GC × GC-FID color plots of the crude MPO and PE-film pyrolysis oils. The hydrocarbon compositions of the plastic waste pyrolysis oils as well as the fossil reference naphtha feedstock measured using GC × GC-FID are given in Table 1. Initial, 50 % and final boiling points (IBP, 50 % BP, FPB) were obtained according to ASTM 2887 (American Society for Testing and Materials, 2020a). Elemental compositions were measured using CHNS/O elemental analysis. The detailed hydrocarbon compositions of the plastic waste pyrolysis oils and the reference naphtha ordered according to the compound families and carbon numbers can be found in section B1 in the

SI. From Table 1 it can be seen that both plastic waste pyrolysis oils have a wide carbon number range of $C_5 - C_{52}$ and $C_5 - C_{50}$, respectively, compared to the narrow range of the light fossil naphtha ($C_4 - C_9$). This can also be seen by means of the IBP and FBP values. Furthermore, both pyrolysis oils contain high amounts of olefins with the higher concentration of branched olefins (~20 wt.%) in the MPO pyrolysis oil. This can be explained by the larger PP concentration in the original waste material (Kusenberg et al., 2022b) (see Fig. S3 in the SI). Furthermore, MPO and PE-film pyrolysis oil contain similar amounts of diolefins which are known to be prominent coke precursors in steam cracking (Guisnet and Magnoux, 2001). MPO pyrolysis oil further contains substantial amounts of naphthenes (~12 wt.%) and higher amounts of aromatics (~3 wt.%) compared to the PE-film pyrolysis oil (~6 wt.% and ~1 wt.%, respectively). The higher aromatic content of MPO pyrolysis oil may be attributed to minor amounts of PS in the original plastic waste which yields almost exclusively aromatic compounds when thermally decomposed (Pinto et al., 1999, Zayoud et al., 2022). The use of GC × GC allows an accurate detection of aromatics and naphthenes, as it is able to distinguish overlaps with the dominant saturated hydrocarbons and olefins that would occur in one-dimensional GC (see Fig. 2). The presented hydrocarbon composition is in agreement with the recently published results by (Kusenberg et al., 2022b) who investigated the pyrolysis and product composition of similar post-consumer packaging waste fractions.

Olefins, naphthenes and aromatics are less favored in steam cracking due to a substantial impact on coke formation and fouling in heat exchangers (Kopinke et al., 1993b, Kopinke et al., 1993a, Ibrahim, 2012, Müller-Steinhagen et al., 2011, Müller-Steinhagen, 2010, Kusenberg et al., 2022a). Therefore, upgrading is needed with hydrotreatment being the most promising technology (Prado et al., 2017, Zacher et al., 2014). In this study, both pyrolysis oils were blended down with fossil naphtha in a weight-based 1:3 blending ratio. According to the blending ratio, the PE-film/naphtha blend contained ~71 wt.% paraffins, ~12 wt.% olefins, ~14 wt.% naphthenes and ~3 wt.% aromatics. The MPO/naphtha blend contained ~68 wt.% paraffins, ~12 wt.% olefins, ~16 wt.% naphthenes and ~4 wt.% aromatics. Based on the similar hydrocarbon compositions of the pyrolysis oil/naphtha blends, similar product yields can be expected in the steam cracking experiments with higher amounts of heavy products expected for the MPO pyrolysis oil due to the slightly higher amounts of aromatics, naphthenes and branched olefins.

According to the CHNS/O analysis, both pyrolysis oils contain substantial amounts of nitrogen (0.67 wt.% in MPO pyrolysis oil vs. 0.18 wt.% in PE-film pyrolysis oil) and oxygen (0.32 wt.% vs. 0.43 wt.%) with no detectable sulfur. This indicates that sulfur in plastic waste pyrolysis oil is a contaminant of lesser concern which is in agreement with the findings of (Kusenberg et al., 2022b). The oxygen concentration in the pyrolysis oil, amongst others, originating from PET impurities, may lead to the formation of organic acids such as benzoic acid or terephthalic acid which cause corrosion and fouling issues in steam cracker units (Li et al., 2007, Ristic et al., 2017). The nitrogen concentrations detected in both pyrolysis oils may lead to explosive gum formation in the cold-box sections of industrial crackers (Adam et al., 2009, Letzsch and Ashton, 1993, Charlesworth, 1986, Dinneen and Bickel, 1951, Sundaram and Stancato, 2018, Dijkmans et al., 2015). Therefore, diluting the pyrolysis oils with fossil feedstocks in order to reduce the contaminant concentrations is the most likely industrial scenario (Kusenberg et al., 2022a). A potential technique to reduce the nitrogen and oxygen values would be catalytic hydrotreatment (Prado et al., 2017, Zacher et al., 2014). In this study, the nitrogen and oxygen concentrations of the MPO pyrolysis oil were reduced according to the mixing ratio to approximately 0.17 wt.% and 0.08 wt.%, respectively. The nitrogen and oxygen concentrations in PE-film pyrolysis after blending were approximately 0.05 wt.% and 0.1 wt.%.

Next to the unsaturated hydrocarbons and heteroatoms, metal and halogen contaminants are crucial to determine the feasibility of plastic waste pyrolysis oils as steam cracking feedstocks (see Table 2). Table 2 shows that both plastic waste pyrolysis oils contain substantial amounts of halogens and metals with the MPO pyrolysis oil being more contaminated. The chlorine concentrations found in both oils can be explained with chlorinated polymer impurities such as PV(D)C in the original plastic waste fractions. Bromine is an element that is typically used in additives such as brominated flame retardants (Ügdüler et al., 2020). Steam cracking of these feedstocks may lead to the formation of HCl and HBr which cause corrosion of materials and formation of halogenated compounds such as chlorobenzene or bromobenzene (Yoshioka et al., 2008, Miranda et al., 1999, Sakata et al., 2003, Zadgaonkar, 2006). The maximum allowable concentration of chlorine in industrial steam cracker feedstocks has been reported as 3 ppm and is exceeded substantially by both plastic waste pyrolysis oils (Baumgartner et al., 2004, Alanazi et al., 2017). The chlorine values of the MPO/naphtha and PE-film/naphtha blends used in this study were reduced to ~87 ppm and ~56 ppm, respectively by blending them down with naphtha. Given the fact that these values are still exceeding the industrial threshold substantially, it becomes obvious that blending alone will not be sufficient to comply with industrial feedstock specifications from a chlorine point-of-view. Therefore, dechlorination steps need to be performed either prior to, during, or after pyrolysis in order to reach the required feedstock quality for industrial steam crackers. Dehalogenation of the waste fractions can be performed prior to the pyrolysis. Techniques include thermal dehalogenation which can be performed as a stand-alone process (Bockhorn et al., 1999, Yoshioka et al., 2000, Ma et al., 2004, Sakata et al., 1998), or in combination with extrusive feeding (Saito and Narita, 2001, Fukushima et al., 2010, Okuwaki et al., 2006, Kobayashi et al., 2019). Furthermore, corrosive products such as HCl, which form during pyrolysis of PVC-containing plastic waste, can be bound by so-called acid scavengers which often involve calcium-based sorbents (Sakata et al., 2003, Karayıldırım et al., 2005, Bhaskar et al., 2003, Uddin et al., 1999, Uddin et al., 2002). Finally, Cl can be removed from the pyrolysis oils via hydrotreatment using Ni-Mo or HZSM-5 catalysts (Furimsky and Massoth, 2005, Miller et al., 2006, Sundaram and Stancato, 2018, Baumgartner et al., 2004, Alanazi et al., 2017).

Several metals were detected in the pyrolysis oils. Metals typically stem from additives which are added to the plastics in order to enhance their properties (Ügdüler et al., 2020). Aluminum contamination in both fractions can be explained by aluminum foils and other aluminum constituents which were not separated from the waste fractions (Roosen et al., 2020). Calcium is another important metal due to its use as additive in form of $CaCO_3$ (Ügdüler et al., 2020). Calcium in steam cracker feedstocks may lead to increased fouling and corrosion according to (Sundaram and Stancato, 2018), leading to a maximum reported concentration of 0.5 ppm for industrial steam crackers. It can be seen that the threshold is exceeded substantially by both pyrolysis oils. Furthermore, copper is known to have a catalytic activity ultimately leading to increased coke formation during steam cracking (Kusenberg et al., 2022a). Iron was detected in both pyrolysis oils with MPO pyrolysis oil having the higher concentration. Iron contamination in steam cracker feedstocks may induce rapid coke formation (Orriss, 1996). Furthermore, iron is a strong poison for downstream catalysts leading to a maximum allowable concentration of <1 ppb, underlining the importance of highly accurate measurements such as ICP-MS (Sundaram and Stancato, 2018). Sodium was found in both pyrolysis oils which has been reported as a highly problematic contaminant due to severe corrosion issues, leading to a depletion of the reactor coil material over time (Orriss, 1996). Furthermore, sodium has been reported as a strong coke formation promoter (Brayden et al., 2006). Due to the issues associated with sodium, a maximum tolerable concentration of around 125 ppb has been reported which is exceeded substantially by both pyrolysis oils, even in the blended form used in this study (Sundaram and Stancato, 2018). Silicon has only been detected in PE-film pyrolysis oil and has been reported to cause process fouling leading to a maximum allowable concentration between 0.5 and 1 ppm in liquid steam cracker feedstocks (Sundaram and Stancato, 2018, Baumgartner et al., 2004, Reid and Nowowiejski, 2003). The concentrations of other metals were either below the limit of detection or below the limit of quantification (see table S6 in SI) which does not exclude the possibility that trace amounts of harmful metals are still present in the pyrolysis oils. It can be concluded that the contaminant levels of both pyrolysis oils exceed known maximum threshold values for industrial liquid steam cracker feedstocks even in the diluted form used in this study.

Based on the entire composition of the pyrolysis oils it can be expected that issues such as coke formation and heat exchanger fouling will occur during steam cracking due to both the high amounts of unsaturated hydrocarbons as well as the presence of contaminants. In fact, MPO pyrolysis oil contains ~1.8x more total metals compared to the PE-film pyrolysis oil, including the strong coke promotors copper (~6x more), iron (~5x more) and sodium (~8x more). In can therefore be expected that MPO pyrolysis oil has a higher coking tendency compared to PE-film pyrolysis oil.

3.2. Steam cracking product yields

Fig. 3 shows the respective on-line GC × GC-FID chromatograms of the reactor effluents when steam cracking the feedstocks at a COT of 850 °C, respectively. Steam cracking of the plastic waste pyrolysis oil/naphtha blends yields a vast number of compounds, as can be found in the list containing all detected products in section B2 in the SI. Formation of higher aromatics such as triaromatics and naphthenodiaromatics (see Fig. 3(b)) is caused in particular by large amounts of unsaturated hydrocarbons in the feedstocks (Towfighi et al., 2002, Ristic et al., 2018). Fig. 4 shows the yields of methane and the most important light olefins ethylene, propylene and 1,3-butadiene in the reactor effluent for the two plastic waste pyrolysis oil/naphtha blends and the reference naphtha at both COTs.

The differences in the product yields between the feedstocks are substantial but lower than expected based on the different feedstock compositions. The COT has a substantial effect on the ethylene yields for all feedstocks but is most pronounced for the reference naphtha with a sharp increase from 21.8 wt.% at a COT of 820 °C to 27.0 wt.% at a COT of 850 °C. At both COTs, but especially at 820 °C, the ethylene yields of the pyrolysis oil/naphtha blends exceed these of fossil naphtha which can be explained by the heavier nature of these feedstocks. Long chain molecules crack easier than short chain equivalents and, hence, a higher conversion is reached at lower temperatures for the pyrolysis oil/naphtha blends. This observation is in line with the work of (Hájeková et al., 2007). In fact, a COT of 820 °C is too low for steam cracking of fossil naphtha as can be seen by means of the large difference between the ethylene yields at a COT of 820 °C and 850 °C. Furthermore, it can be seen that the ethylene yields of the PE-film/naphtha blend are higher at a COT of 820 °C compared to the MPO/naphtha blend which can be explained by the presence of larger amounts of straight chain compounds, i.e., n-paraffins and α-olefins as shown in Table 1. However, due to the blending with naphtha, the overall effect of the different hydrocarbon compositions of the pyrolysis oils is less pronounced.

When studying the steam cracking product yields, it becomes clear that the chosen temperature profiles are quite optimal for the pyrolysis oil/naphtha blends but are slightly too low for the pure fossil naphtha. An additional more severe condition at, for instance, a COT of 880 °C, would lead to substantially higher ethylene yields with fossil naphtha but certainly to even higher heavy aromatic yields in the C_{10+} range with the pyrolysis oil/naphtha blends. Exceeding the mentioned

COTs would lead to so-called over-cracking which means that the ethylene and propylene yields would start decreasing at the expense of increasing methane and heavy aromatic product yields and coke formation (Pyl et al., 2012). More detailed product yields are listed in Table 3. Both pyrolysis oil/naphtha blends have higher CO and CO_2 yields compared to pure naphtha which can be explained by the presence of oxygen in both plastic waste pyrolysis oils (see Table 1). Regarding the BTX (benzene, toluene, xylenes) yields, large similarities are found for the respective feedstocks which can be explained by the similar aromatic contents of the respective samples. However, it can be seen in Table 3 that the BTX yield of the MPO/naphtha blend is lower compared to the other feedstocks and that higher amounts of polyaromatics (i.e., naphthalene, anthracene, phenanthrene) were formed with the MPO/naphtha blend. Both pyrolysis oil/naphtha blends yield high amounts of heavy aromatic products in the pyrolysis fuel oil (PFO) (C_{10+}) range with the MPO/naphtha blend exceeding the PE-film/naphtha blend by a factor of almost 2. A likely explanation for this is the high tendency of olefins and diolefins to form heavy (aromatic) products such as indene (C_9 naphthenoaromatic), naphthalene (C_{10} diaromatic) or phenanthrene and anthracene (C_{14} triaromatics). The higher degree of branching and the higher concentration of naphthenes in the MPO pyrolysis oil is a potential explanation for the higher PFO yield compared to the PE-film pyrolysis oil. In contrast to the plastic waste pyrolysis oils, the PFO yields of the pure reference naphtha are only minor which underlines the strong effect of the unsaturated hydrocarbons present in the pyrolysis oils even in the diluted form used in this study.

It has been shown that blends of highly unsaturated plastic waste pyrolysis oils with fossil naphtha lead to slightly higher light product yields compared to pure fossil naphtha. This observation is promising, considering the likely industrial scenario of using plastic waste pyrolysis oils as drop-in feedstocks for industrial crackers rather than as a replacement. However, the PFO yields of the pyrolysis oil/naphtha blends compared with the pure reference naphtha were still substantial showing the large impact of unsaturated hydrocarbons even in the diluted form. Consequently, in order to improve the steam cracking feasibility of highly olefinic plastic waste pyrolysis oils, hydrotreatment is a viable technology to lower the concentration of unsaturated compounds (Scherzer and Gruia, 1996, Eberline et al., 1957). Furthermore, using a distilled cut without the heavy tail of the pyrolysis oils can be a first solution.

3.3. Coke formation

The amount of coke formed in the reactor is shown in Fig. 5. The total mass of radiant coil coke was put in relation to the total duration of the respective steam cracking experiments (i.e., 6 hours). For the sake of comparison, the approximate radiant coil coke formation of the respective pure plastic waste pyrolysis oils was estimated via extrapolation, considering the mixing ratio of the naphtha blends (1:3). Steam cracking of the pyrolysis oil/naphtha blends resulted in substantial additional coke formation in the reactor compared to the pure reference naphtha feedstock. Especially the coke formation of the MPO/naphtha blend exceeded the one of pure naphtha by a factor of ~2.5. Considering the radiant coil coke formation of pure fossil naphtha and the fact that only 25 wt.% of the blend was pyrolysis oil, the pure pyrolysis oils would have resulted in a radiant coke formation of approximately 91 mg/h for MPO pyrolysis oil and 32 mg/h for PE-film pyrolysis oil. By means of the moderate concentrations of olefins and aromatics (~12 wt.% and ~3-4 wt.%, respectively) in the pyrolysis oil/naphtha blends, it becomes obvious that the coking tendencies of the feedstocks cannot be exclusively attributed to the molecular composition but must also be related to contaminants which lead to a substantial amount of additional coke formation. This is supported by the results of (Hájeková and Bajus, 2005), who reported that the coke formation during steam cracking of contaminant-free virgin plastic pyrolysis oils lies in the same range as of pure fossil naphtha. Due to the fact that several metal contaminants act as strong coke promotors (Sundaram and Stancato, 2018), the detected metal contamination is an explanation for the high radiant coil coke formation (see Table 2). This is especially valid for MPO pyrolysis oil which contains substantial amounts of copper, iron and sodium. Although the coking tendency of the PE-film/naphtha blend is higher than of pure fossil naphtha, the results are still in a reasonable range considering the metal concentrations which still exceed maximum allowable concentrations for industrial liquid steam cracker feedstocks by orders of magnitude. The results suggest that certain treatment steps prior to steam cracking such as hydrotreatment to reduce unsaturated hydrocarbons and to remove heteroatoms and metals would suffice to reduce the coke formation to a more acceptable value. Furthermore, filtration is a potential technique to remove metals from the crude pyrolysis oils prior to steam cracking that will be investigated in future work.

Next to coke formation in the reactor coil, issues such as convection section or transfer line exchanger fouling can occur when using plastic waste derived feedstocks (Van Geem et al., 2009). PE-film pyrolysis oil contains high amounts of silicon which is known to cause heat exchanger fouling and which can explain minor fluctuations in the feeding rate observed during the experiment. Furthermore, insufficient evaporation due to trace amounts of very heavy compounds in the pyrolysis oils can also lead to fouling of the heat exchanger surfaces in the convection section. In case of co-feeding plastic waste pyrolysis products with light fossil feedstocks such as naphtha, it is therefore important that the boiling point ranges of the pyrolysis oils and the fossil feedstock used for blending are similar to guarantee homogeneous mixing and evaporation. This can be achieved by using selected distillation cuts instead of the crude plastic waste pyrolysis oils which will be subject of future work. Distillation can also be applied to remove organometallic compounds such as metalloporphyrins reducing the metal contamination of the pyrolysis oils. It was reported that most metal contaminants appear in the respective heavy distilled fractions (C_{30+}) of plastic waste pyrolysis oils (Okuwaki et al., 2006, Kusenberg et al., 2022a). Thus, cutting off of the heaviest fractions of the crude plastic waste pyrolysis oils might already solve contaminant related problems to a certain extent. Detailed analysis of the contaminants across the respective fractions will shine light on this important issue. Another possible means to directly produce pyrolysis oils with narrower boiling point ranges lies in the pyrolysis step itself. By increasing the temperature and/or residence time in the pyrolysis reactor, a lighter liquid product could be obtained which would contain less C_{30+} compounds (Williams and Williams, 1997, Predel and Kaminsky, 2000, Al-Salem et al., 2017). Hence, less coke formation and fouling issues in steam cracking would be caused. However, higher temperatures in the pyrolysis step also lead to higher amounts of gaseous products and coke residue and thus to lower liquid product yields.

The presented results suggest that thermochemical recycling of mixed post-consumer packaging waste could be integrated in a plastic waste recycling scheme as proposed by (Kusenberg et al., 2022a) and (Thunman et al., 2019), where sorted polyolefinic fractions are directly sent to a petrochemical cluster (i.e., “chemical recycling plant”). Depending on the purity of sorted plastics, pre-treatment steps such as dechlorination can be directly integrated in a continuous process. The produced pyrolysis oils can then be integrated into the petrochemical infrastructure including typical upgrading steps such as fractionation, desulfurization, or hydrotreatment, before being sent to a steam cracker as a blended feedstock. The results of this study clearly indicate that the proposed chemical recycling pathway would be feasible if certain treatment steps are performed prior to steam cracking. However, additional research is needed to shed more light on the effect of individual contaminants on crucial aspects such as coke formation and fouling.

4. Conclusions and Outlook

Steam cracking of two plastic waste pyrolysis oil/naphtha blends resulted in higher ethylene yields compared to a pure fossil naphtha reference feedstock. MPO pyrolysis oil blended with naphtha led to an ethylene yield of ~22.9 wt.% at a coil outlet temperature of 820 °C and ~28.0 wt.% at 850 °C. A slightly higher ethylene yield (~23.6 wt.%) was obtained with PE-film pyrolysis oil blended with naphtha at a COT of 820 °C and a slightly lower ethylene yield (~27.5 wt.%) at a COT of 850 °C. Lower ethylene yields were obtained with the fossil naphtha reference feedstock at both temperature profiles, respectively (~21.8 wt.% and ~27.0 wt.%). However, substantial amounts of heavy products as well as high coke formation and fouling issues were observed with both pyrolysis oil/naphtha blends.

Both coke formation and fouling have been put in relation with heteroatoms and metal contaminants present in the post-consumer plastic waste pyrolysis oils. Consequently, using plastic waste derived feedstocks for industrial steam crackers poses opportunities and risks. On the one hand, these feedstocks are attractive as they help to close the material loop. On the other hand, use of these feedstocks may lead to operational issues because of increased coke formation and fouling. Therefore, the “unknowns” in plastic waste pyrolysis oils and their individual influence on industrial steam crackers must be further investigated.

This study shows that purification of the pyrolysis oils before steam cracking will be a prerequisite to allow viable steam cracking towards closed-loop plastic waste recycling. Therefore, the results of this study provide a benchmark case which serves as a starting point for further research work including the assessment of different mixing ratios with conventional feedstocks and different pre-treatment steps such as distillation, filtration and hydrotreatment.

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Figures and Tables

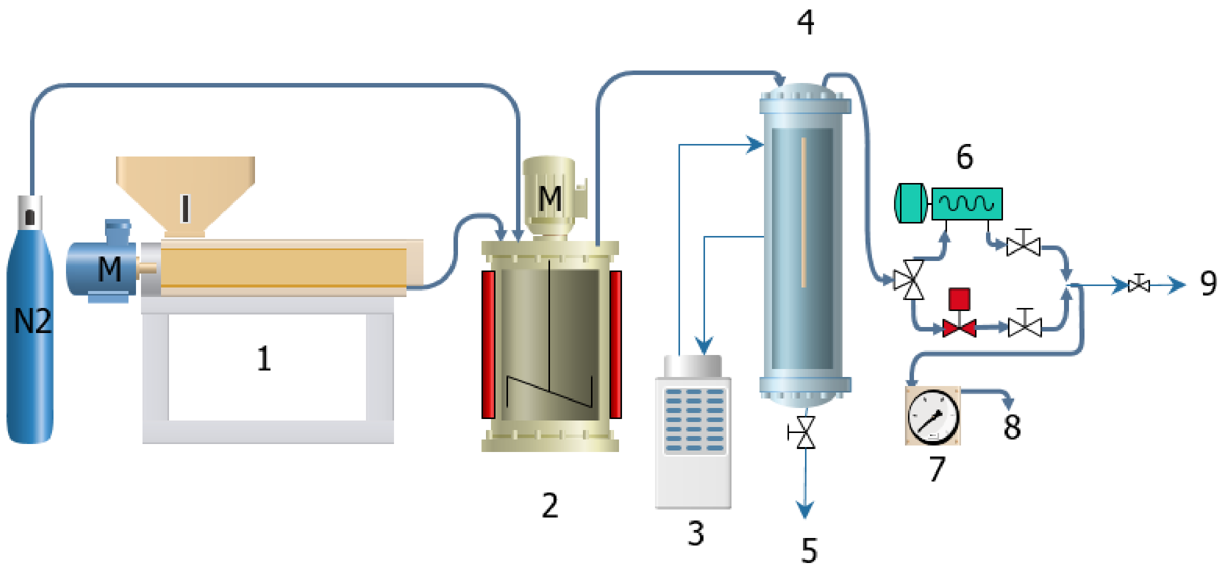

Fig. 1: Pilot-scale pyrolysis unit: (1) extruder, (2) stirred-tank reactor, (3) cooler, (4) condensation section, (5) liquid product sampling, (6) vacuum pump, (7) volumetric gas flow-meter, (8) vent, (9) gaseous product sampling, (M) motor.

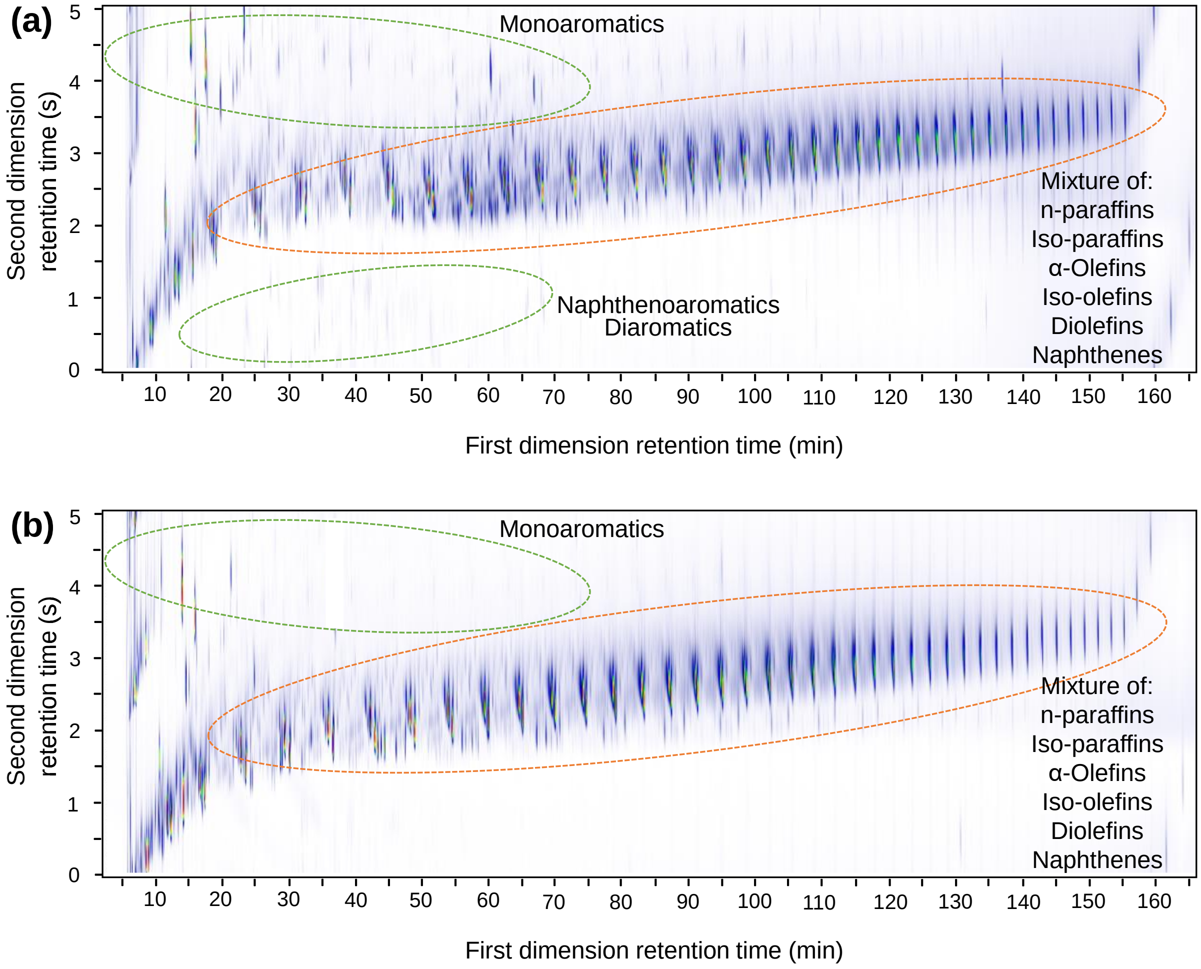

Fig. 2: GC × GC-FID chromatograms of the crude MPO pyrolysis oil (a) and the crude PE-film pyrolysis oil (b) steam cracked in this study.

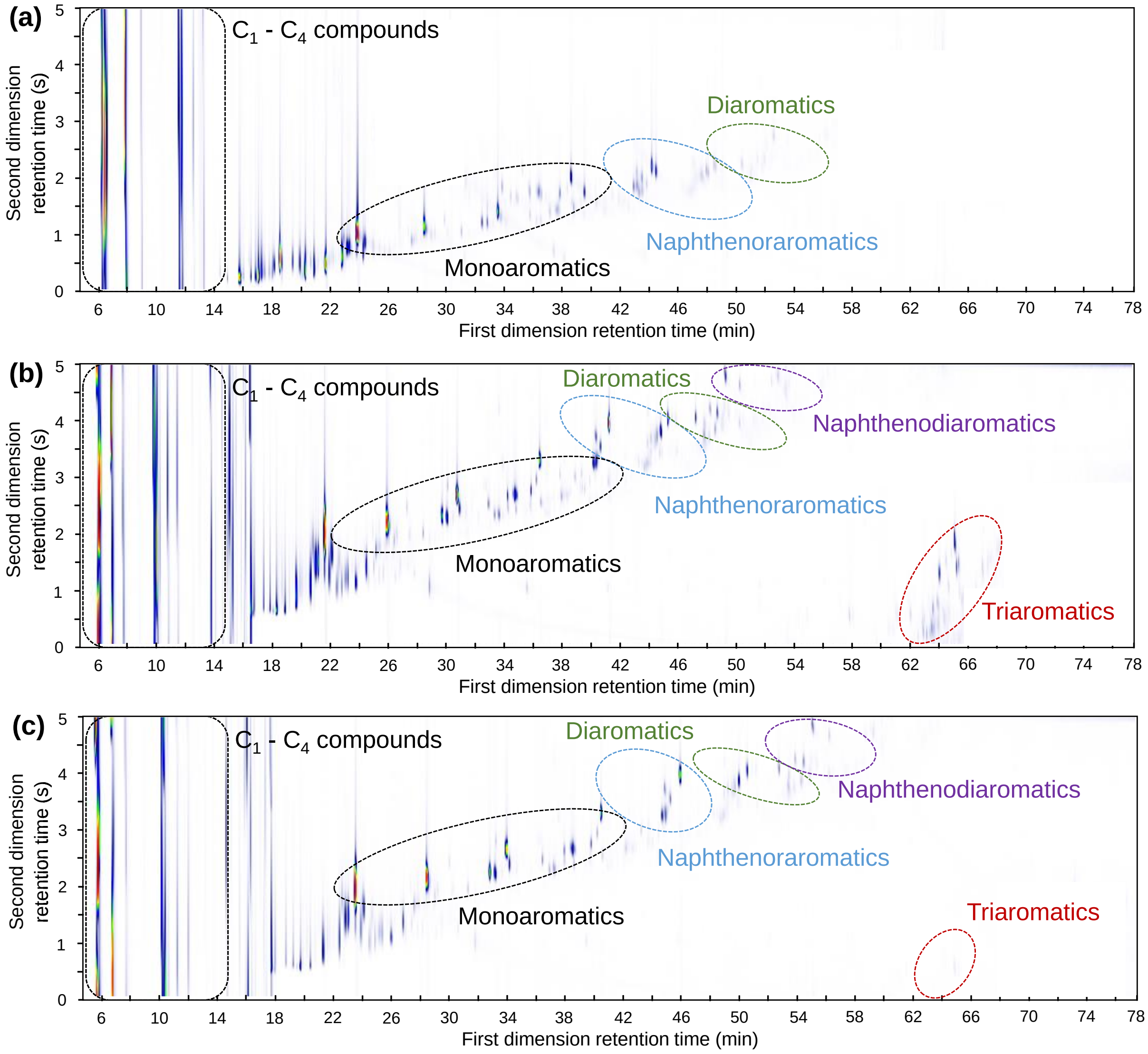

Fig. 3: On-line GC × GC-FID chromatograms of the steam cracker effluent at a COT of 850 °C, steam dilution of 0.5 and residence time of ~0.5 s: (a) pure fossil naphtha, (b) MPO/naphtha blend and (c) PE-film/naphtha blend. Compound families are marked individually.

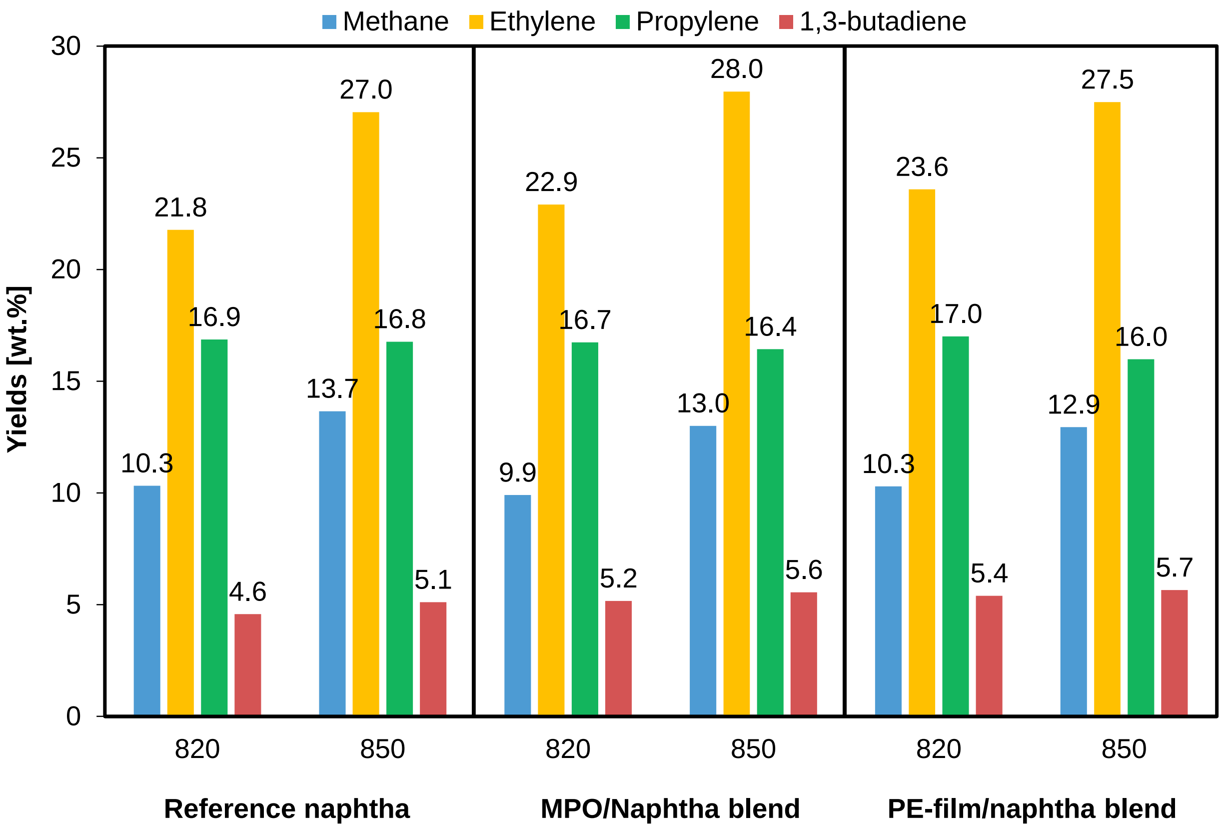

Fig. 4: Steam cracking yields of methane, ethylene, propylene and 1,3-butadiene of the two plastic waste pyrolysis oil/naphtha blends and the fossil reference naphtha as function of the COT.

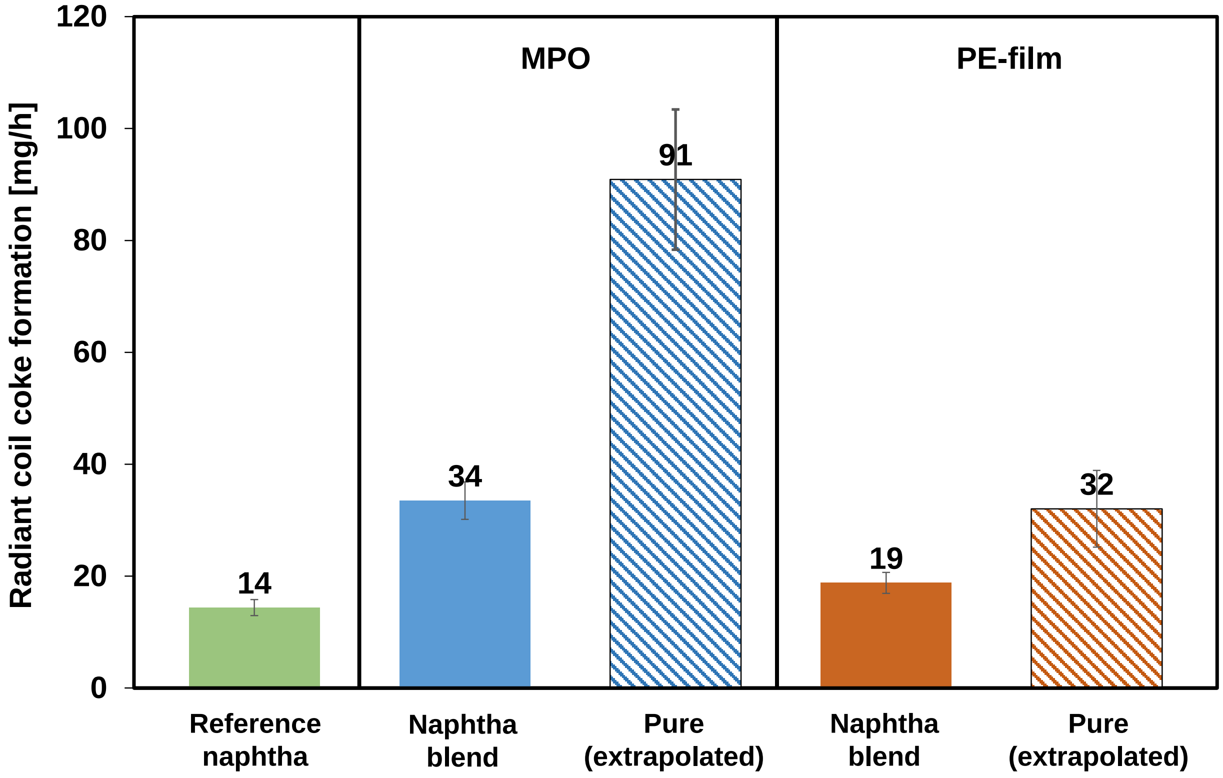

Fig. 5: Radiant coil coke formation in mg/h for all feedstocks including extrapolated values for the pure pyrolysis oils (hatched) and the corresponding uncertainty.

Table 1: Detailed composition of the feedstocks used in this study.

Feedstock	Reference naphtha	MPO pyrolysis oil	PE-film pyrolysis oil
IBP [°C]	10	14	14
50 % BP [°C]	61	334	340
FBP [°C]	136	603	592
Carbon number range	$C_4 – C_9$	$C_5 – C_{52}$	$C_5 – C_{50}$
Paraffins [wt.%]	34.9	32.2	41.9
Iso-paraffins [wt.%]	44.1	3.7	3.5
α-Olefins [wt.%]	0.0	23.5	33.0
Iso-olefins [wt.%]	0.0	20.0	10.6
Diolefins [wt.%]	0.0	5.3	4.5
Naphthenes [wt.%]	17.0	12.4	5.5
Monoaromatics [wt.%]	4.0	2.7	1.0
Naphthenoaromatics [wt.%]	0.0	0.2	0.1
Diaromatics [wt.%]	0.0	0.1	0.0
N [wt.%]	<LOD	0.67	0.18
C [wt.%]	84.33	84.75	84.90
H [wt.%]	15.67	14.26	14.49
S [wt.%]	<LOD	<LOD	<LOD
O [wt.%]	<LOD	0.32	0.43

Table 2: Halogen and metal concentrations of the plastic waste pyrolysis oils. Ppm values are mass based.

	MPO pyrolysis oil	PE-film pyrolysis oil
Element	**PPM**	
Cl	349.2	222.8
F	<LOD	<LOD
Br	31.6	4.3
Al	13.6	6.7
As	<LOD	<LOD
Be	<LOD	<LOD
Ca	17.4	12.2
Cd	<LOQ	0.1
Co	<LOQ	<LOD
Cr	2.0	<LOQ
Cu	3.1	0.5
Fe	4.9	1.1
Li	<LOQ	0.5
Mg	<LOD	<LOQ
Mn	<LOQ	<LOD
Mo	<LOD	<LOD
Na	19.3	2.5
Ni	<LOQ	0.2
Pb	<LOD	<LOD
Sb	2.3	0.4
Se	<LOD	<LOD
Si	<LOQ	17.2
Sr	<LOD	0.1
Ti	<LOD	<LOQ
Tl	<LOQ	<LOD
V	<LOD	<LOD
Zn	8.3	0.4
Total metals	70.9	41.9

Table 3: Result summary of the most important product yields.

Feedstock	**Reference naphtha**		**MPO/naphtha blend**		**PE-film/naphtha blend**	
			Overview			
COT [°C]	820	850	820	850	820	850
Total C_1-C_4 [wt.%]	67.88	75.78	68.51	75.90	70.09	74.91
PyGas (C_5-C_9) [wt.%]	31.41	23.26	28.19	18.08	27.95	21.67
PFO (C_{10+}) [wt.%]	0.71	0.97	3.30	6.02	1.96	3.42
Propylene/Ethylene	0.77	0.62	0.73	0.59	0.72	0.58
	Concentration of important products in the reactor effluent [wt.%]					
CO	0.01	0.04	0.08	0.12	0.08	0.16
CO_2	0.00	0.01	0.03	0.03	0.03	0.02
Methane	10.32	13.66	9.91	13.00	10.29	12.95
Ethylene	21.77	27.04	22.91	27.97	23.59	27.49
Ethane	2.90	3.14	3.06	3.25	3.20	3.20
Propylene	16.87	16.77	16.74	16.43	17.01	15.98
1-butene	3.20	2.14	3.24	2.06	3.19	1.91
Iso-butene	3.87	3.30	3.40	3.21	3.31	2.71
1,3-butadiene	4.58	5.11	5.17	5.55	5.40	5.66
1.3-cyclopentadiene	0.13	0.18	0.34	0.16	0.29	0.17
Benzene	4.25	6.95	4.36	5.24	4.81	6.51
Toluene	2.19	3.25	2.05	2.10	2.91	3.07
Xylenes	0.11	0.21	0.14	0.21	0.35	0.41
Indene	0.10	0.20	0.11	0.28	0.17	0.39
Naphthalene	0.13	0.14	0.31	1.12	0.23	0.63
Anthracene & Phenanthrene	0.02	0.15	0.38	0.62	0.40	0.28
Others	29.56	17.70	27.79	18.63	24.75	18.44