Contaminant removal from plastic waste pyrolysis oil via depth filtration and the impact on chemical recycling: a simple solution with significant impact

Marvin Kusenberg[1], Martijn Roosen[2], Astrid Doktor[3], Leonor Casado[4], Anas Jamil Abdulrahman[1], Behzad Parvizi[1], Andreas Eschenbacher[1], Emmanuelle Biadi[5], Nicolas Laudou[5], Daniel Jänsch[3], Steven De Meester[2], Kevin M. Van Geem[1,*]

[1] Laboratory for Chemical Technology (LCT), Department of Materials, Textiles and Chemical Engineering, Faculty of Engineering & Architecture, Ghent University, B-9052 Zwijnaarde, Belgium;

[2] Laboratory for Circular Process Engineering (LCPE), Department of Green Chemistry and Technology, Faculty of Bioscience Engineering, Ghent University, B-8500 Kortrijk, Belgium;

[3] PALL Corporation, D-55543 Bad Kreuznach, Germany;

[4] PALL Corporation, ES-28108 Madrid, Spain

[5] PALL Corporation France

*Corresponding author: Kevin.VanGeem@UGent.be

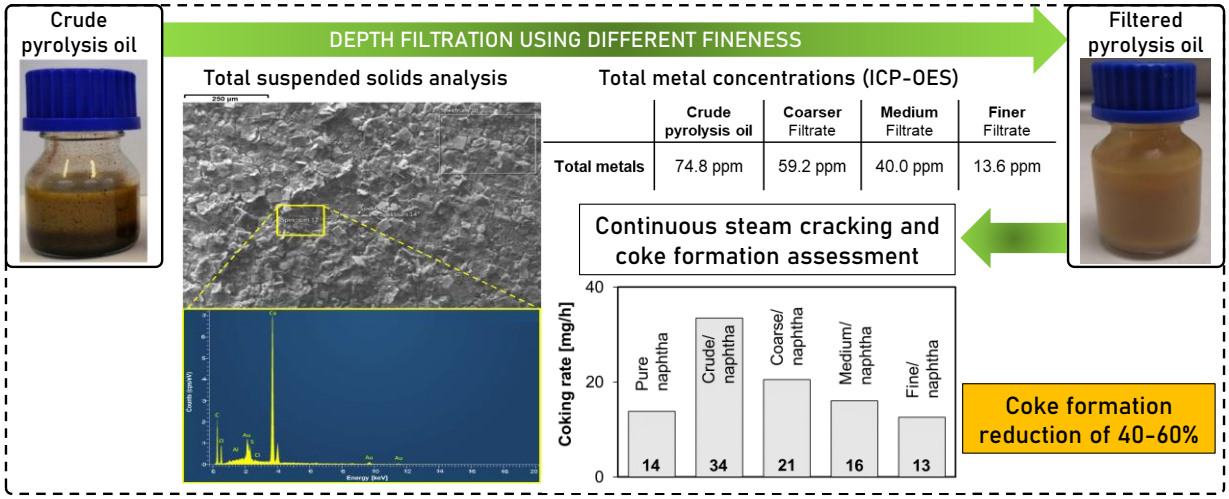
List of abbreviations

BSSC	Bench-scale steam cracking setup
CIT	Coil inlet temperature
COT	Coil outlet temperature
EDX	Energy dispersive X-ray
FID	Flame ionization detector
FT-ICR-MS	Fourier-transform ion cyclotron resonance mass spectrometry
GC × GC	Comprehensive two-dimensional gas chromatography
HC	Hydrocarbons
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
PP	Polypropylene
ppb	Parts per billion (weight-based)
ppm	Parts per million (weight-based)
PS	Polystyrene
PVC	Polyvinylchloride
RGA	Refinery gas analyzer
SEM	Scanning electron microscopy
SI	Supporting Information
TCD	Thermal conductivity detector
TLE	Transfer line exchanger
TSS	Total suspended solids

Abstract

Recycling of mixed plastic waste via pyrolysis and subsequent steam cracking towards light olefins is a promising solution for the ever-growing plastic waste crisis. However, the pyrolytic recycling pathway is still not established on industrial scale due to the large variety of pyrolysis oil contaminants that hamper the application in (petro-)chemical processes. In short, plastic waste pyrolysis oils are unfeasible for steam crackers without upgrading. In this work, depth filtration for the removal of particulate contamination from a post-consumer mixed polyolefin (MPO) pyrolysis oil was performed using three different filter media with different porosity. Comprehensive analyses using SEM-EDX of the retained particles as well as ICP-OES and GC×GC-FID of the filtered oils allowed to understand the efficacy of filtration. Most of the particulate contamination was removed by filtration leading to a reduction from 69 mg/L in the unfiltered sample to <2 mg/L in the filtered samples. Particle characterization confirmed that the main contamination is composed of iron, calcium and silicon-based contaminants in combination with carbon-based species. It was confirmed by ICP-OES that after filtration, important contaminants such as nickel, vanadium and lead were reduced below contamination thresholds for steam crackers indicating that filtration is an efficient, and potentially cost-effective upgrading technique for pyrolysis oils. When steam cracking the filtered oils, results show that radiant coil coke formation was reduced by 40-60% compared to the unfiltered oil without changes in product selectivity, confirming the strong impact of particulate contamination on coke formation during steam cracking.

Graphical abstract



Keywords: Steam cracking; coke formation; particle contamination; polyolefins; metals

1. Introduction

Chemical recycling of plastic waste has the potential to overcome current hurdles of end-of-life management of plastics. Mechanical recycling, which is the current main recycling pathway, has limitations in terms of processing mixed and contaminated waste streams such as end-of-life plastic packaging which makes up approximately 40% of the entire collected plastic waste. Consequently, recycled products are often of lower quality than their virgin counterparts and hence cannot be used in their original application due to strict regulations in terms of, for instance, food-contact applications (i.e., downcycling) [1-4]. Chemical recycling of plastic packaging waste that mostly consists of polyolefins (i.e., polyethylene (PE), polypropylene (PP)) with smaller amounts of polystyrene (PS), polyethylene terephthalate (PET) and others, is believed to be more robust towards certain contaminants and mixed feedstocks [5]. Furthermore, converting waste polymers into their chemical building blocks via (thermo)chemical processes such as pyrolysis followed by steam cracking enables the production of virgin-grade polymer products suitable for any application [5-8]. The associated reduction of greenhouse gas emissions by avoiding waste incineration and the (partial) substitution of fossil feedstocks for steam crackers can be an important contribution to prevent imminent global threats such as depletion of fossil fuels and climate change [9-12]. Furthermore, the increasing trend in electrification of petrochemical processes can be another driving factor towards drastically reduced emissions when pursuing chemical plastic waste recycling [13, 14]. Recently, processing plastic packaging waste towards petrochemical feedstocks via pyrolysis has been gaining momentum in the chemical industry [15-21].

Pyrolytic plastic waste recycling still faces several hurdles which are related to the high variety of different polymers present in plastic waste and the extensive use by the manufacturers of a wide range of performance-enhancing additives in the formulation [22-24]. Pyrolysis of mixed plastic

waste leads to a highly complex liquid product that covers a wide boiling point range and contains a complex hydrocarbon matrix which is dependent on the process conditions and pyrolyzed polymer material. In a nutshell, there are two degrees of complexity when dealing with plastic waste pyrolysis oils. (i) The hydrocarbon composition including a substantial amount of unsaturated hydrocarbons (i.e. olefins, diolefins and aromatics). In two recent studies by Abbas-Abadi et al. [25, 26], the first degree of complexity was highlighted by studying the pyrolysis of virgin-grade polyolefins showing that the complexity of pyrolysis oils is already substantial, even if no real waste is used. (ii) The amount of contaminants derived from additives, organic and inorganic residues present in real post-consumer waste fractions. Functional additives make up the largest share of metal contaminants while residues from catalysts or abrasion from plastics manufacture are further relevant sources. Mainly, metal-containing additives are introduced as inert fillers, which are often silicon- (SiO_x), calcium- ($CaCO_3$) or magnesium-based (talc), color pigments (e.g., TiO_2 or organometallic compounds such as copper phthalocyanine) and stabilizers [24, 27-29]. The resulting contamination with metals and also heteroatoms originating from polymers such as PET, polyvinylchloride (PVC), polyamide (PA), and others, as well as organic residues is the key reason why it remains challenging to establish pyrolysis on an industrial scale [30]. In fact, high levels of contaminants are not acceptable for large-scale industrial steam crackers in terms of operational risks, i.e., corrosion of process equipment (i.e., reactor surfaces, heat exchangers), increased coke formation or downstream catalyst poisoning [22, 31, 32]. This has been shown in our recent work, where we steam cracked untreated, highly olefinic plastic waste pyrolysis oils blended with fossil naphtha [33]. While the ethylene product yields of the pyrolysis oil/naphtha blends were slightly higher compared to pure fossil naphtha, substantial coke formation was observed which could be related on the one hand to the higher olefin and aromatic concentrations of the pyrolysis oil and on the other hand to high amounts of metal contaminants

such as iron or sodium present in the pyrolysis oils. The associated uncertainty of pyrolysis oils in terms of operational issues are the main reason why, to this day, no large-scale industrial application of pyrolysis oils for the production of new circular polymers is being performed. Based on this conclusion, it is clear that the missing link between pyrolysis of plastics and industrial-scale application of pyrolysis oils is the decontamination or upgrading of oils, leading to an acceptable feedstock for further rather sensitive processes such as steam cracking. Hence, to fully employ the potential of advanced recycling for the most heterogeneous waste fractions, developing or optimizing pre-treatment processes that have a purifying effect on the feedstock, e.g., by removing certain metals, will be an important step forward.

Therefore, in this work, we investigated the potential of depth filtration as an effective upgrading step to remove particles and metal contaminants from crude plastic waste pyrolysis oils. The objective of this study was to assess the filtration effectiveness of three depth filter media with different fineness by thoroughly characterizing the pyrolysis oils before and after filtration. Analytic techniques used were inductively coupled plasma - optical emission spectrometry (ICP-OES) and comprehensive two-dimensional gas chromatography (GC × GC) coupled to flame ionization detection (FID). Furthermore, the filtration efficacy was assessed via a total suspended solids (TSS) analysis showing the particle size distribution before and after filtration. Retained particles were further analyzed using scanning electron microscopy (SEM) combined with energy dispersive X-ray (EDX) analysis.

In order to assess the effect of the filtration step on the steam cracking performance, continuous experiments have been performed in a bench-scale steam cracking unit including the detailed on-line analysis of the entire product range and the quantitative assessment of the radiant coil coke formation. With this study, we shed light on the potential of depth filtration for the removal of

metals and metalloids (from hereafter referred to as metals) and its effect on the steam cracking performance pushing chemical recycling of mixed packaging waste one step closer to technical application.

2. Materials and Methods

2.1. Feedstocks

The pyrolysis oil filtered in this study was produced using a continuous pilot-scale pyrolysis unit consisting of a single-screw extruder (LabTech, Thailand) connected to a 5.7 L stirred-tank reactor as described in our previous works [25, 34, 35]. Pyrolysis was carried out at 450 °C and atmospheric pressure leading to a very heavy (i.e., waxy) pyrolysis oil which was solid at room temperature with a melting point of ~80 °C (see our previous study [33]). The starting material was a contaminated post-consumer mixed polyolefin (MPO) fraction collected from curb-side and was afterwards treated by shredding, float-sink separation, wind-sifting, cold-water washing, and extrusion. The material consisted mostly of PE (~76 wt.%) and PP (~16 wt.%) and ~8 wt.% of other polymers such as PET, PA, PS, PVC and others (see Fig. 1).

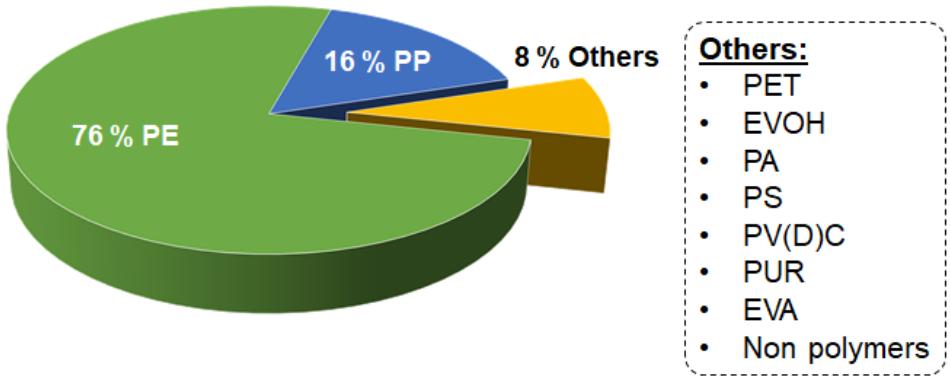


Fig. 1. Composition of the post-consumer MPO waste feedstock [33].

The pyrolysis oil was part of our previous study where we investigated the steam cracking performance of crude untreated plastic waste pyrolysis oils blended with naphtha [33]. As a

reference feedstock to benchmark the steam cracking performance including product yields and coke formation, a typical fossil naphtha feedstock was used with the detailed composition given in Table S1 in the supporting information (SI).

2.2. Apparatus and experimental procedure

2.2.1. Filtration experiments

Constant flowrate filtration tests were conducted using three different depth filter media with retention rates between 2.5 µm and 20 µm, labeled coarse filter medium (F1), medium filter medium (F2) and fine filter medium (F1). The main filter material components are cellulose, diatomaceous earth and/or perlite, and polymer resins. Typical industrial applications for the filters used in the present study are clarifying filtration of viscous and highly viscous oils (F1), catalyst retention from various solutions (F2) and the retention of fine particles such as activated carbon (F3). The filter media were installed in stainless steel discs or segment holders equipped with pressure gauges. Filtration tests were performed at 80 °C using a peristaltic pump (Watson-Marlow 520S, UK) with a constant flow rate set at 50 mL/min. A respective total volume of 3000 mL of pyrolysis oil was processed per filter type. In order to minimize leaching of the filter materials, the filtrate obtained in the first 20 minutes of the filtration experiments (i.e., the first 1000 mL) was discarded. Furthermore, filter media have been pre-conditioned using hexane to minimize leaching during filtration. The remaining filtrate was collected and blended for a thorough product analysis. This work focused on the detailed analysis of the filtrates in dependence of the filtration grade, rather than on the potential deviation of the filter media characteristic over time. For upscaling of filter systems, it is, of course, essential to assess the time dependent filter performance, which will be subject of a follow-up work.

For the selected filtration media F1 to F3, increased Δp values at constant flow for the given volume of 3000 mL of pyrolysis oil were observed. The resulting differential pressure at a constant flow rate during filtration of 3000 mL sample was increased from 0 to 100 mbar for the coarsest medium (F1), from 0 to 200 mbar for medium F2 and from 100 mbar to 500 mbar for the finest medium F3. These deviations are attributed to the physical parameters of the filter media, such as porosity, thickness, pore size, etc. Retention behavior, attributed to the media characteristics, is an influencing factor for the filter lifetime and filter sizing and thus needs to be considered as one important measure when engineering a continuous process.

2.2.2. Bench-scale steam cracking (BSSC) unit

Steam cracking experiments were performed using a continuous bench-scale steam cracking unit (BSSC) which has been described in recent articles [33, 36, 37] (see Fig. S1 in the SI). The BSSC is specifically designed to facilitate scale-up to real industrial furnaces as described by Van Geem et al. [38, 39]. The experimental unit comprises a dedicated on-line analysis section as described in detail elsewhere [33, 36, 37]. The analysis section consists of two dedicated analytical setups. The light products (i.e., C_{4-}) are analyzed on the so-called Refinery Gas Analyzer (RGA) where the concentrations of H_2, CO_2, CO, N_2, methane, ethane, ethylene and acetylene are detected by a thermal conductivity detector (TCD) and 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 using FID. Quantification of the compounds is possible using a well-controlled continuous flow of nitrogen acting as internal standard [33, 36, 37]. The response factors of each component were determined using a calibration gas mixture provided by Air Liquide (Belgium). The methane concentration determined on the RGA is subsequently used as a secondary internal standard to quantify the entire reactor effluent composition which has been injected on-

line (i.e., during operation) via heated transfer lines onto the GC × GC-FID unit (see Fig. S2 in the SI) [40]. The response factors of the C_{5+} compounds were determined with the effective carbon number approach as described elsewhere [36, 37, 40-42]. With the described procedure, C and H molar balances were closed within ± 5 % (not including formed coke).

The steam cracking conditions were chosen analogue to our previous work where we steam cracked the untreated pyrolysis oil blended with naphtha (see Table S2 in the SI) [33]. In order to facilitate comparability and to isolate the impact of the removed contaminants using filtration, the same fossil naphtha reference feedstock and the same mixing ratio (i.e., weight-based 1:3 with fossil naphtha) have been used. Two temperature profiles were chosen according to the coil outlet temperature (i.e., the last heating zone in the reactor furnace, COT): 820 °C and 850 °C. The coil inlet temperature (CIT) was kept at 550 °C for every experiment and the evaporation and mixing section was operated at 500 °C. The coil outlet pressure was kept at 1.7 bar for all experiments. The hydrocarbon flow rate was set at 150 g/h with a steam dilution rate of 0.5 wt_{H2O}/wt_{HC}, which corresponds to an average coil residence time of around 0.5 s. In light of the high viscosity and melting point of the pyrolysis oil feedstocks used in the present study, a heating mantle was used in the feeding section, keeping the feedstock bottle at ~60 °C which was sufficient to keep the pyrolysis oil/naphtha blends in a liquid homogeneous state.

The amount of coke that was deposited in the reactor during a 6-hour experiment was burned off via a well-controlled procedure that allows quantification of the deposited coke. Using an infrared (IR) analyzer (Fuji Electric, Japan), the CO and CO_2 concentrations in the reactor effluent during the decoking experiment were measured [41]. For the decoking experiment, the reactor was heated to 850 °C in all heating zones (see detailed decoking conditions in Table S3 in the SI). After flushing with nitrogen to zero-calibrate the IR-meter and to remove residual hydrocarbons from

198 the reactor, air was fed to the reactor together with steam to start the decoking process. Once most
199 of the coke was burned off (i.e., the CO_2 value decreased below 1 vol.%), the steam flow was
200 stopped and the reactor temperature was increased to 900 °C in all zones to thoroughly decoke the
201 reactor. Using a volumetric gas flow meter (Ritter, Germany), the volumetric concentration of the
202 reactor effluent was measured. Combining the volumetric flow rate with the volumetric
203 concentrations of CO and CO_2 measured using the IR-meter, the coke that was formed and
204 deposited in the reactor during the steam cracking experiments was quantified. Based on multiple
205 decoking experiments using fossil naphtha, an estimated uncertainty of ~10% can be assumed. This
206 is due to the possibility that residual hydrocarbons that remained after the experiments either in the
207 convection section or the downstream section of the unit are combusted as well during the decoking
208 process. The formed CO/CO_2 will then falsely be included into the coke formation assessment.
209 However, this error source was minimized to the possible extent by thoroughly cleaning the
210 downstream section of the reactor before decoking, as well as, by keeping the evaporation section
211 temperature during decoking sufficiently low to avoid combustion of any residual hydrocarbons
212 (i.e. <200 °C).

213 ## 2.3. Analytics

214 ### 2.3.1. Total suspended solids (TSS) analysis

215 The amount of total suspended solids (TSS) present in the samples (i.e., the three filtrates and the
216 unfiltered sample) was separately determined by a gravimetric technique: 100 mL of heated sample
217 was filtered through a 47 mm diameter pre-weighted 0.8 μm analysis membrane (nylon). The
218 membrane was then rinsed with 0.45 μm filtered solvent (hexane, acetone, xylene). Once rinsed,
219 the membrane was dried in an oven for 30 min at 80 °C and desiccated. The amount of solids
220 collected on the test membrane was determined by subtracting the clean membrane weight from

the final weight of the membrane. The TSS present in the sample were calculated in mg/L. Next to the total particle count, the particles found per 1 mL of sample in the following particle size ranges were counted individually: >5 μm, >10 μm, >20 μm, >50 μm and >100 μm. The solids collected on the test membrane were further observed under an Olympus BH12 (Japan) microscope and a microphotograph of a representative area of the membrane was taken at a magnification of ×100. To assess the stability of the filtrates over time, the TSS analysis of the filtered products has been repeated including re-heating/melting of the samples after 2 days of storage at room temperature.

2.3.2. Scanning electron microscopy (SEM) and Energy dispersive X-ray (EDX) analysis

TSS filter membranes were analyzed after filtration and rinsing using scanning electron microscopy (Zeiss EVO 10, Germany) at 20 kV acceleration voltage in secondary- and back scattered electron imaging mode. In this mode sample areas comprising elements of higher atomic number appear brighter compared with those comprising elements of lower atomic number. Determination of the chemical composition of the particles retained on the TSS membranes was performed using energy dispersive X-ray (EDX) analyses for elements with an atomic number ≥ 6 (carbon). Before analysis, the membranes were sputtered with gold. A total of 7 membranes used for the TSS assessment was analyzed: a single membrane for the unfiltered pyrolysis oil and two membranes for each of the filtered products, respectively (tested immediately after filtration and after a storage period of 2 days).

For the automated SEM analysis using an Aspex PSEM eXpress benchtop scanning electron microscope (USA), parts of the membranes (between 1/8 and 1/4) were suspended in 30 mL of n-heptane. The resulting suspensions were filtered through a 0.4 μm Nucleopore membrane and investigated as follows: The investigations were performed with an automated SEM by imaging and measuring of particles in back scattered electron imaging mode at 20 kV acceleration voltage.

The maximum length of the particles was defined as the particle size and particles with a length/width ratio of ≥ 6 were defined as fibers. The particle concentrations were measured for the respective membrane areas which ranged from ~300 mm^2 to ~1200 mm^2. Analyses were carried out in duplicates. The chemical composition of the counted particles was determined through the integrated EDX analyzer and reported in a table of particle classes by size and composition. Particles were categorized according to their EDX signals and the respective typical database EDX signals of specific elements and materials according to Table S4 in the SI. The chemical compositions of the non-carbon particle constituents were approximated based on the percentage of normalized K-ratio values (ratio between peak intensity and the peak intensity of a material standard). It is important to note that the present samples contain both light and heavy elements and hence it is possible that disturbances such as, among others, attenuation or secondary excitation take place. Furthermore, agglomeration phenomena as well as secondary contamination from solvent residues must be considered. Moreover, analyses were not performed under clean-room conditions, hence, minor contamination with dust cannot be excluded. Therefore, quantification results may contain a considerable uncertainty. Nevertheless, SEM-EDX was a valuable tool for identification of elements and quantitative comparisons of the elemental composition of the retained particles.

2.3.3. Comprehensive two-dimensional gas chromatography (GC × GC)

Comprehensive two-dimensional gas chromatography (GC × GC) coupled to a flame ionization detector (FID) was used to quantitatively determine the detailed hydrocarbon composition of the pyrolysis oil samples 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 [40, 42]. 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 [35]. The detailed GC × GC settings for on- and off-line analysis can be found in Table S5 in the SI. The exact quantification procedure of on- and off-line analyses using the internal standard concentration and the response factors of the individual compound groups have been explained in detail elsewhere [42-45].

2.3.4. Inductively coupled plasma – optical emission spectrometry (ICP-OES)

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, 0.50 ± 0.05 g of each sample was digested via an Anton Paar (Graz, Austria) Multiwave 5000 microwave oven equipped with a 20SVT-rotor and PTFE-TFM digestion vessels. 8.0 mL of concentrated HNO_3 (7%, Sigma Aldrich) was added to the weighted 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 45 min heating time. After digestion, the remaining liquid was transferred to a 5 mL volumetric flask. This was three times repeated to obtain sufficient volume for ICP-analysis. 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 determined 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. Filtration test

3.1.1. Total suspended solids (TSS) analysis

Microphotographs of the TSS test membranes of the analyzed samples (i.e., unfiltered pyrolysis oil and the three filtrates) are shown in Fig. 2. Optical microscope assessment indicated that contamination in the original pyrolysis oil was composed of brown fines with a size of 5 to 10 μm that cover the analysis membrane and coarser white crystal-like particles with a size of 20 to 50 μm. It can be seen qualitatively that with all three filter media it was possible to remove the majority of suspended solids from the pyrolysis oil. The crude (unfiltered) pyrolysis oil sample contained a total particular contamination of 69 mg/L. Particles in the sample are mostly present as fine particles in the ranges >5 μm (2595 particles per mL of sample), >10 μm (1420) and >20 μm (599) with smaller amounts of larger particles in the ranges >50 μm (91) and >100 μm (14). The global average particle size is hence lower than 10 μm (which is also confirmed by SEM-EDX as indicated in section 3.1.2.). Particles in pyrolysis oils can originate both from contamination during plastic usage and inorganic additives such as pigments.

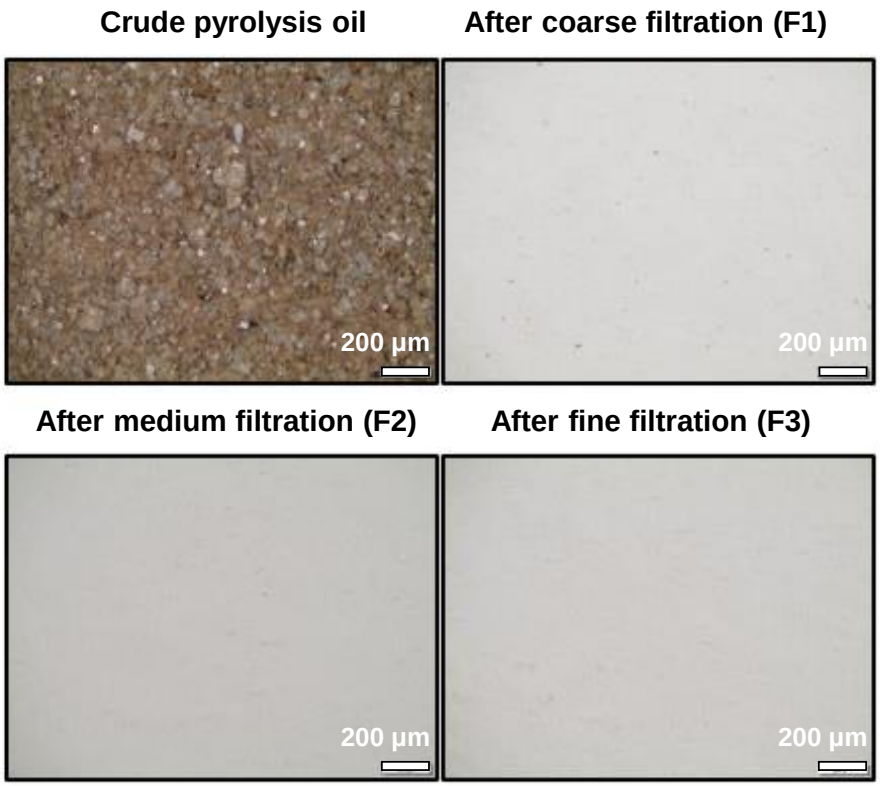


Fig. 2. Photographs (magnification ×100) of the TSS test filter membranes (0.8 µm, nylon) immediately after filtration.

The detailed TSS and particle counts per mL of sample are listed in Table 1.

Table 1. Particle count per 1 mL of sample and TSS of the crude oil and filtrates.

	Particle count per 1 mL of sample					
Tested medium	**<5 µm**	**<10 µm**	**<20 µm**	**<50 µm**	**<100 µm**	**TSS [mg/L]**
Unfiltered pyrolysis oil	2595	1420	599	91	14	69
Filtrate of coarse filter medium (F1)	7	4	1	0.8	0	2
Filtrate of F1 after 2 days storage	18	7	2	2	0.9	7
Filtrate of medium filter medium (F2)	5	3	1	0.4	0	<1
Filtrate of F2 after 2 days storage	17	6	1	15	3	4
Filtrate of fine filter medium (F3)	1	0.9	0.5	0.1	0	<1
Filtrate of F3 after 2 days storage	3	1	0.5	0	0	2

All filter media were effective in removing particles with a removal efficacy of at least 97% of the coarse media and with TSS values of <1 mg/L (limit of detection) for the fine medium (F3) and middle medium (F2). Moreover, even if the best result was obtained with the finest filtration grade, >99% of small particles in the range of >5 µm were removed with all filter grades. It is important

to note that some inorganic particles which are used as plastic additives are even smaller than 5 μm. For instance, titanium dioxide which is used as a white pigment in plastic products is typically below 1 μm [46].

Next to the particle removal efficiencies immediately after filtration, the TSS analysis was repeated after a pyrolysis oil storage period of 2 days. It was found that after 2 days, the TSS of the filtrates increased again from 2 mg/L to 7 mg/L for F1 (coarse), from <1 mg/L to 4 mg/L for F2 (medium) and from <1 mg/L to 2 mg/L for F3 (fine). This observation indicates that re-agglomeration of finer particles occurred to a certain extent [47, 48]. Based on this finding, it is advisable to directly apply the filtration step in a continuous process to avoid process-related issues due to larger particles. In such a scenario, filtration steps could be applied in a more continuous way prior to (petro-)chemical processes such as steam cracking of pyrolysis oils. Furthermore, observation of the stability of the filtrates over time is crucial in determining the long-term efficacy and to draw sound conclusions regarding the particle size distribution.

3.1.2. Analysis of retained particles

It is clear that for the design of continuous filtration processes including the upscaling of processes towards industrial scale, it is important to understand the distribution of particles according to their size and shape as well as their elemental composition. The chemical composition of the particles was simultaneously analyzed and approximated using SEM-EDX analysis (see Fig. 3). The SEM analysis showed that the unfiltered pyrolysis oil contained particles in a range between 5 and 50 μm with an average size of 7 μm. 99.9% of the particles were <50 μm, 81.6% <10 μm and 44.4% <5 μm, confirming the optical microscope analysis of the TSS membranes. It is important to note that multiple EDX spectra were collected of chosen areas of the TSS membranes. Therefore, there is a considerable uncertainty when approximating the global particle composition of the entire

sample. However, by analyzing multiple areas of the tested membranes, a sound conclusion of the contamination can be drawn. The EDX spectrum shows that the particles in the marked area are mainly composed of calcium, aluminum, chlorides and other carbon-based species. Furthermore, small amounts of sulfur were detected in this particular area. It is important to note that carbon and oxygen signals can be partially dedicated to the composition of the membrane media.

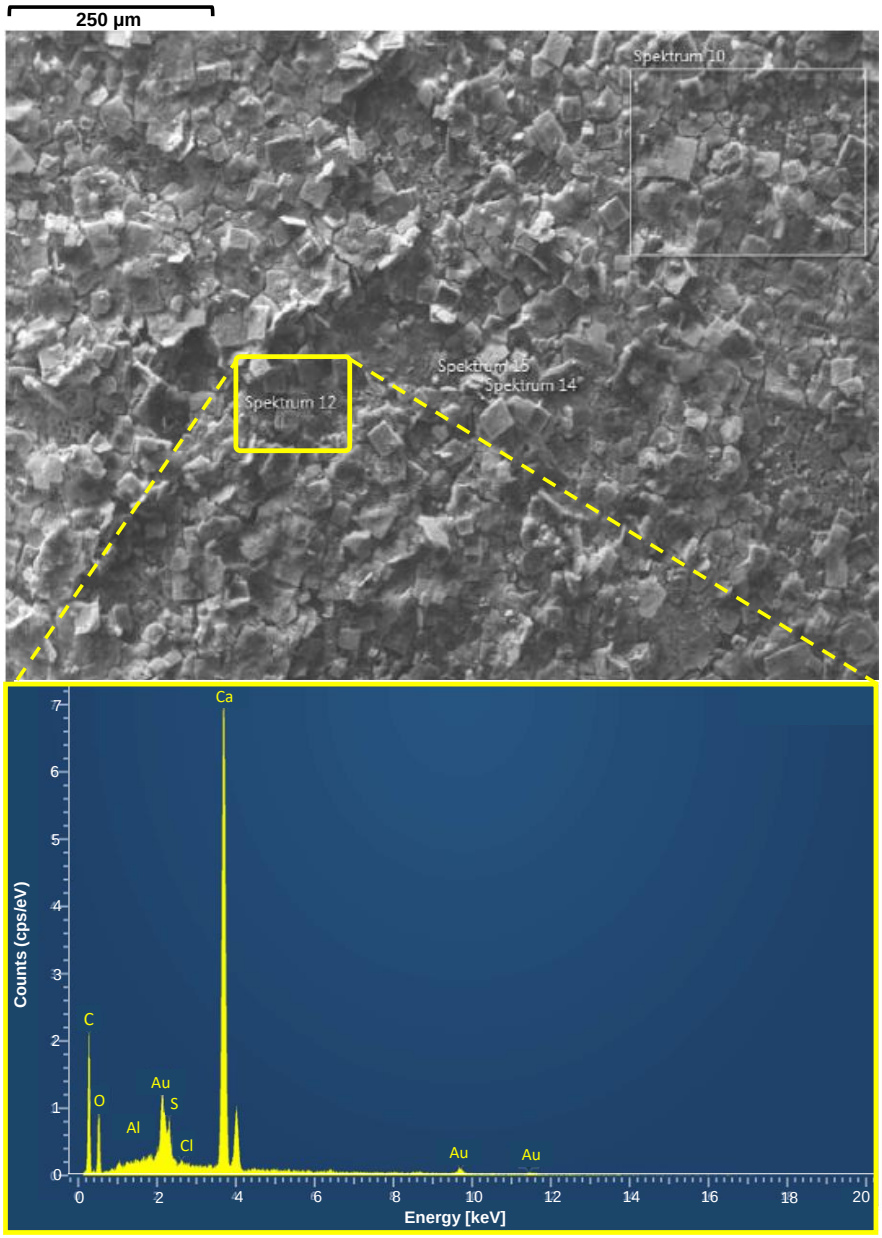


Fig. 3. SEM-EDX overview of the TSS membrane of unfiltered pyrolysis oil. Signals of carbon derive from the membrane material and possible solvent residues, signals of gold derive from coating of the membranes.

Recorded EDX signals of the analyzed particles from automated particle analysis were correlated with known material signals (see Fig. S4 in SI) and sorted according to the particle size. The results for the TSS membrane of the unfiltered pyrolysis oil are shown in Table 2. The SEM-EDX results show that of the total 6291 counted particles, more than half could be allocated to known material signals, while 2839 particles were classified as "others", underlining the complexity of the particulate contamination in plastic waste pyrolysis oils. EDX characterization of particles in the unfiltered pyrolysis oil confirmed that the main contamination is composed of iron/metals, calcium and silicon-based particles. This finding indicates that additives are indeed a major source of contaminants in plastic waste pyrolysis oils with calcium and silicon (especially SiO_x) being the dominant constituents. The fact that silicon was detected in various other chemical forms such as in combination with aluminum, calcium, potassium and oxygen underlines the large variety of potential sources of this particular element. The detected non-iron metals can be related to pigments, as for instance TiO_2. Moreover, considerable amounts of salts were detected which rather originate from the plastics' use phase, stemming from food residues and other packaged products. Iron oxide is the second most used pigment in plastics after titanium oxide [49], however, iron can also possibly originate from abrasion of process equipment during plastics manufacture, shredding of the collected waste and pyrolysis [50]. The detection of 222 particles categorized as high-alloy steel supports this hypothesis.

365 **Table 2.** SEM/EDX analysis of Nucleopore membrane with filtrated suspension from the TSS membrane of unfiltered MPO pyrolysis oil. EDX
366 signals of the particles were correlated with known material signals (Table S4 in SI) and sorted according to the particle size.

	SUM particles	**<1 µm**	**<2 µm**	**<3 µm**	**<4 µm**	**<5 µm**	**<7.5 µm**	**<10 µm**	**<12.5 µm**	**<15 µm**	**<20 µm**	**<50 µm**	**<100 µm**
Al (dominant)	97	0	2	7	13	15	37	9	5	1	4	4	0
Ca (dominant)	989	1	18	127	184	162	273	120	60	26	12	6	0
Chlorinated polymers	3	0	0	1	0	0	0	2	0	0	0	0	0
Cr (dominant)	12	0	0	1	2	4	1	0	3	0	1	0	0
Zn (dominant)	32	0	0	7	5	4	7	5	1	2	1	0	0
Coatings	11	0	0	0	0	2	6	0	2	0	1	0	0
Cu-Zn brass	270	0	1	30	34	47	82	28	22	9	11	6	0
Fluorinated polymers	13	0	0	0	1	1	3	3	0	1	2	2	0
Fe (dominant)	234	0	1	17	26	29	80	31	22	16	8	4	0
High-alloy steel	65	0	1	0	4	4	19	10	6	9	6	6	0
Inorganic fibers	192	0	1	16	17	16	44	36	16	12	14	19	1
Non-iron metals	2839	0	42	331	422	357	669	376	238	150	152	100	2
Others	339	0	3	30	34	57	100	45	33	15	12	10	0
Salts	53	0	1	1	2	1	9	17	8	7	3	3	1
Si (dominant)	35	0	2	6	5	7	5	3	1	2	3	1	0
Si-Al-Ca	103	0	1	6	7	15	40	13	12	5	2	2	0
Si-Al-K-O	961	0	3	41	112	137	366	124	69	33	27	45	4
Si-O	43	0	0	1	5	7	9	6	5	5	3	2	0
SUM particles	6291	1	76	622	873	865	1750	828	503	293	262	210	8

367

The respective particle categories show a rather similar distribution according to the particle size with calcium-based particles being the most prominent in the smaller particle ranges. This hypothesis can be further investigated comparing the main relative chemical compositions of the particles according to the respective size (see Fig. 4). It is important to note that carbon was not included in the composition as carbon signals can be derived from membrane materials and solvent residues rather than the actual sample, hence, only non-carbon elements were considered. Furthermore, gold was used to coat the sample membranes prior to analysis. The results show that the smaller particles mostly consist of inorganic oxygen, calcium and silicon which all range above a relative share of 15%. Oxygen is a major element throughout all particle sizes which confirms that indeed most of the metals are present in oxygenated forms. Next to oxygen, calcium is the major element in all particle sizes below <12.5 μm, after which silicon becomes the dominating element. Iron, which is an important contaminant in steam cracking due to strong coke formation tendencies makes up roughly 7% of non-carbon elements for most particle size ranges. This finding indicates that filtration is a viable step to remove most parts of silicon while it is likely that calcium- and iron-based contaminants next to aluminum and smaller amounts of silicon will reach the filtered products, considering that the lowest retention of the finest filter medium was 2.5 μm. The most challenging contaminants for further application are mainly silicon and calcium and to a smaller extent iron, sodium, aluminum, nickel, copper, and lead due to the fact that they are present in the very small particle ranges that will partly pass through typical filtration systems. The results further show that calcium-containing particles are typically so small that they will likely pass through any commercially available filter material and hence require special attention in terms of upgrading. This is especially important as calcium is one of the main metal contaminants in pyrolysis oils [22] and further is a highly active fouling-inducing contaminant in steam cracking [31]. The data further shows that the largest particles (50-100 μm) are mostly comprised of oxygen

and silicon. The relative elemental compositions sorted according to the particles sizes can be found in Table S7 in the SI.

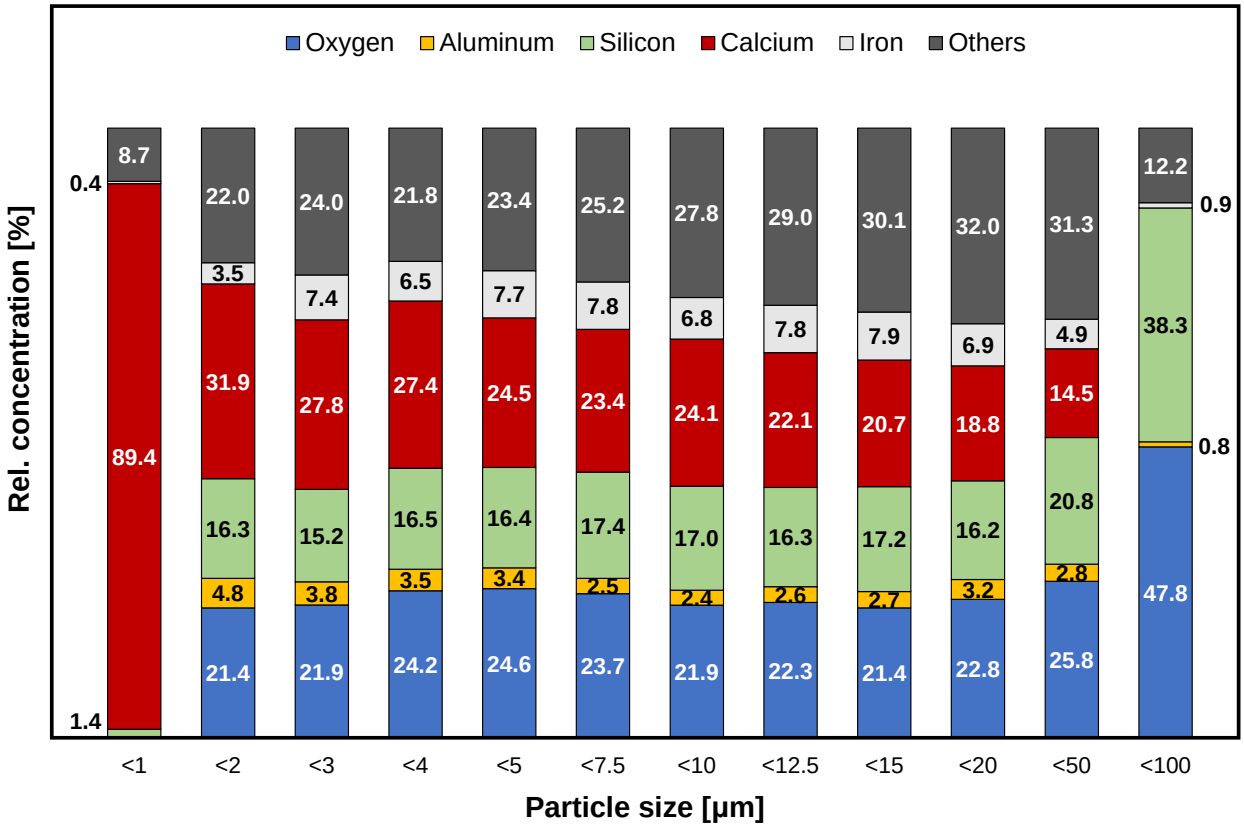


Fig. 4. Relative contribution of main elements according to the particle sizes.

With regard to the relative elemental composition of the filtered products, it can indeed be stated that the relative share of iron, copper and nickel, among others increased in the filtered samples while the relative share of calcium was reduced substantially. This can be seen in the relative elemental compositions of the filtered products sorted according to the particles sizes in Tables S8, S9 and S10 in the SI. As silicon dioxide (SiO_2) is the main component of diatomaceous earth [51] and perlite [52] which are part of the used filter material, an increase of particles in the filtered samples that can be allocated to silicon oxide based on their EDX signals would indicate leaching of the test media during filtration. In the unfiltered pyrolysis oil a total of 961 particles were allocated to SiO_x. On the contrary, in the respective filtrates the amount of SiO_x particles was

substantially lower: 37 in the coarse grade filtrate (F1), 31 in medium grade filtrate (F2) and 34 in the fine grade filtrate (F3). Furthermore, the majority of particles in diatomaceous earth ranges between a size of 10 to 50 µm, depending on the granularity [53]. In this particular range, no increase in number of particles was detected, hence, leaching of filter material during filtration was negligible.

Furthermore, SEM-EDX analysis confirmed that after 2 days of storage at room temperature, re-agglomeration occurred. This is exemplary shown in Fig. 5, depicting an SEM image of the membranes used for TSS analysis immediately after filtration and after two days for the fine filter medium (F3), which showed the best performance of the three filter media in terms of particle removal.

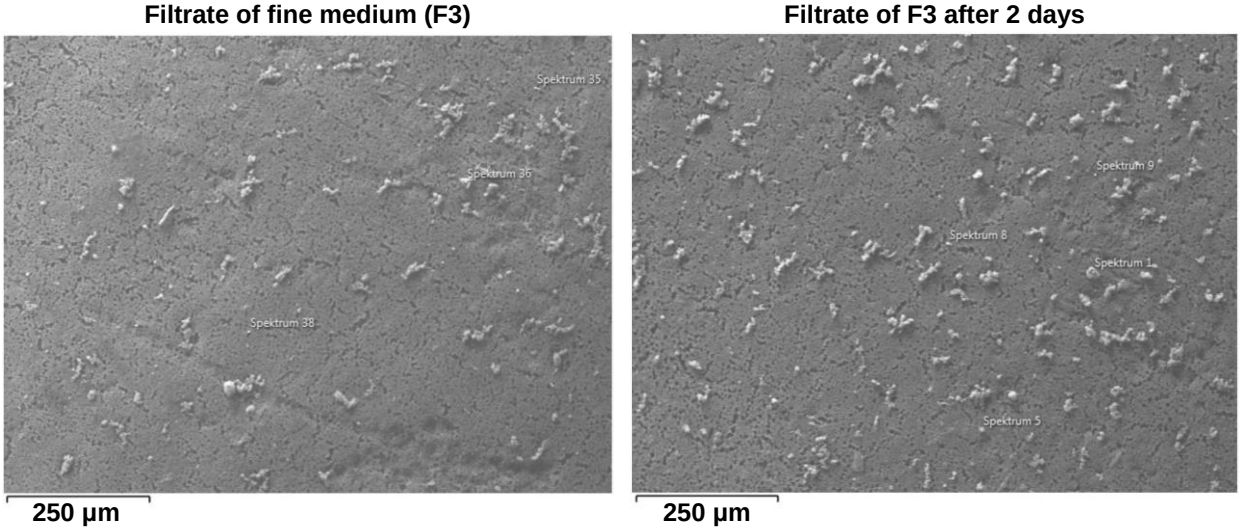


Fig. 5. SEM images of the membranes used for total suspended solid analysis of filtrate F3 immediately after filtration and after 2 days of storage at room temperature.

It can be clearly seen that more and bigger particles were retained in the TSS analysis membrane two days after filtration using medium F3. With respect to the relative elemental composition of the retained particles directly after filtration and after 2 days it is evident that the relative oxygen

and silicon concentrations of the particles are considerably higher after 2 days, which indicates that aging of the samples takes place to a certain extent (see Fig. 6).

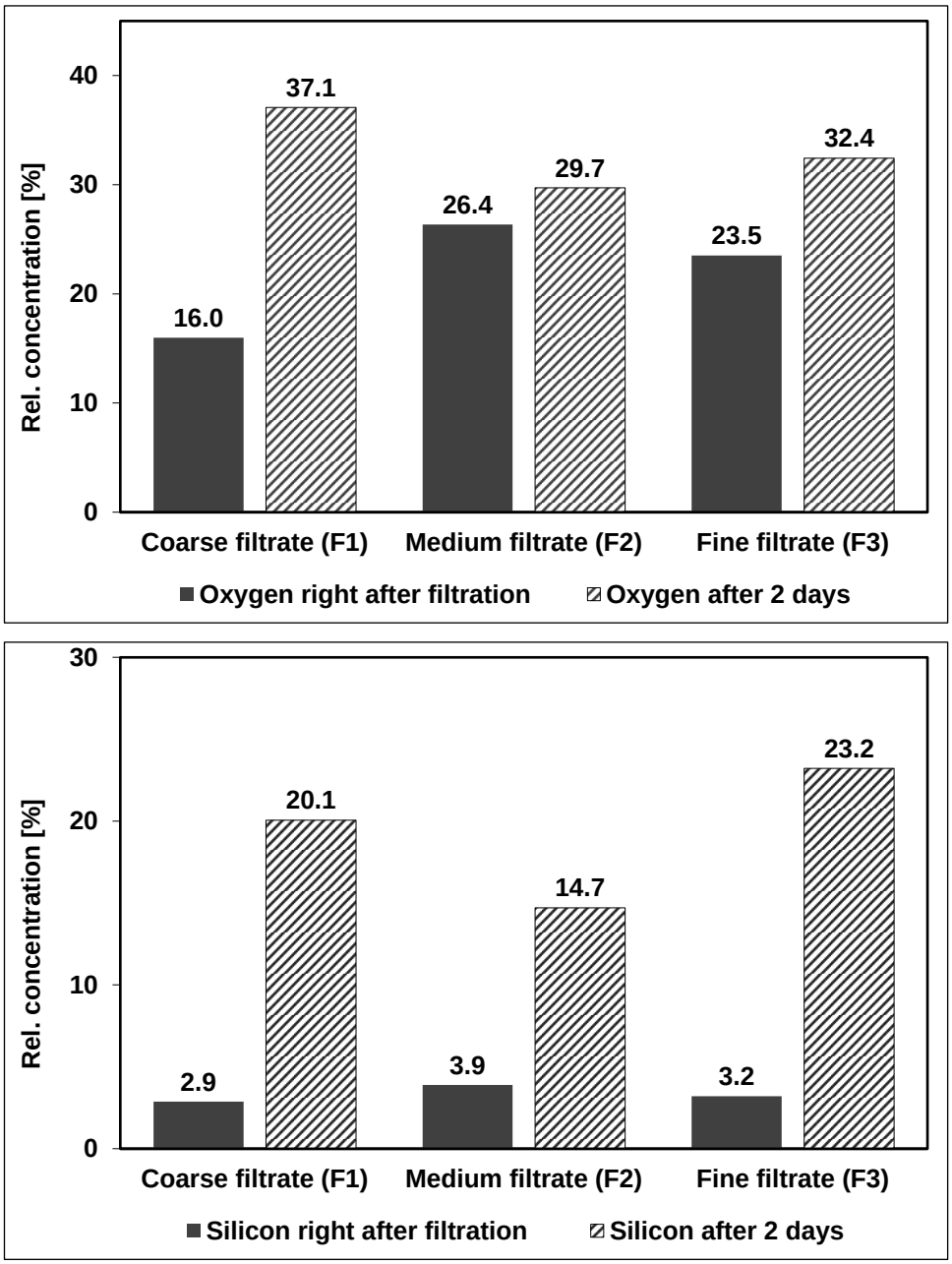


Fig. 6. Relative oxygen and silicon concentrations of the particles right after filtration and after a waiting period of 2 days.

Simultaneously, the relative concentrations of calcium, iron and several other low-concentration elements decreased. This finding is highly important for the storage stability of the filtrates as it

shows that samples should be stored under inert atmosphere if not processed further directly after filtration in a continuous manner. Furthermore, the finding shows that silicon-rich particles are prone to re-agglomeration. The relative elemental compositions of the filtered products after a storage period of 2 days, sorted according to the particles sizes can be found in Tables S11, S12 and S13 in the SI. This work highlighted the importance of understanding the particle characterization of the unfiltered oil with respect to the selection of the filtration material and design. Limitations of the applied filtration media in retention characteristics of critical particle contamination were identified. Specifically, the constrained retention efficiency of calcium, or titanium-containing particles accentuate that further work on filtration and separation technologies is essential. To address the retention of finest particles by filtration requires detailed knowledge about elements present in the solid contamination. The presented results can therefore be an important foundation in terms of filter material design.

3.2. Chemical analysis of the filtered products

To shed further light on the filtration efficacy, the filtered pyrolysis oils were analyzed using ICP-OES as well as comprehensive two-dimensional GC × GC-FID. This way the filtrates could be comprehensively assessed in terms of their applicability for light olefin production via steam cracking both from a contaminant and a hydrocarbon point-of-view. It is important to note that via the ICP-OES detection limits down to ppb levels were achieved. As the previous discussion of the SEM-EDX analysis was rather qualitative, in the following section quantitative results will be presented.

3.2.1. Contaminants

The characterization results of the filter membranes have shown that substantial parts of the original particulate contamination were removed in the filtration steps. To further assess the individual filter

performances, ICP-OES analyses were performed to detect the absolute contaminant concentrations in the respective filtrates (see Table 3). By means of the total metals, F3 (fine) is performing best with a total metal removal of 81.5% compared to a removal of 47.3% (medium – F2) and 25.0% (coarse – F1). It is likely that in the filtration step most of the particles that were entrained during pyrolysis were removed, while organometallic species and very small particles partially passed the filters and remained in the filtered products as discussed in the previous section. In terms of individual elements, it was indicated by the particle analysis that the removal is not proportional for every contaminant but that some elements are removed more efficiently than others, confirming that the elements can be present in different forms. First of all, it can be seen that the concentrations of elements that predominantly occur in the filter material (i.e., diatomaceous earth), silicon, aluminum and iron did not increase in the respective filtrates which confirms that leaching of the filter material did not occur to a considerable extent.

Table 3. Absolute contaminant concentrations (in ppm) in the unfiltered pyrolysis oil and the respective filtrates measured via ICP-OES. The limits of detection and quantification are listed in the SI.

Element	Unfiltered oil	Coarse filtrate (F1)	Medium filtrate (F2)	Fine filtrate (F3)
Al	12.37	12.37	8.41	2.56
As[a]	0.31	0.24	0.22	0.12
Ca	16.75	13.25	5.07	2.08
Cd	0.17	0.15	0.15	<0.01
Co	0.11	0.35	0.78	0.09
Cr	1.81	1.89	2.06	1.65
Cu	3.73	4.87	1.57	0.87
Fe	6.57	5.81	3.54	1.42
Mg	0.56	0.63	0.84	0.24
Mn	0.06	0.03	0.03	<0.01
Na	18.83	10.29	6.98	1.72
Ni	0.15	<0.01	<0.01	<0.01
Pb	0.11	<0.01	<0.01	<0.01
Sb[a]	2.10	0.50	1.62	0.83
Se[b]	0.05	<0.01	<0.01	<0.01
Si[a]	2.00	1.38	<0.04	0.59
Sr	0.11	0.13	0.04	<0.02

Ti	0.24	0.16	0.18	0.14
Tl	0.17	<0.01	<0.01	<0.01
V	0.10	<0.01	<0.01	<0.01
Zn	8.54	7.19	8.54	1.31
SUM [ppm]	**74.82**	**59.22**	**40.03**	**13.61**

a: metalloid
b: non-metal

Metal contaminants in steam crackers are unwanted for several reasons, however, the two most important reasons are coke formation/fouling and downstream catalyst poisoning. In terms of coke formation in steam cracking, iron is a very important contaminant due to its catalytic activity facilitating coke formation [31, 54]. Therefore, according to industrial plant operators, iron contamination of steam cracker feedstocks must not exceed 1 ppm [55]. A substantial iron reduction close 1 ppm was reached with the fine filter medium F3 (reduction of ~78%), which complies with the feedstock specifications in terms of iron if it is blended in a mild ratio with fossil steam cracker feedstocks. For the other filter media, dilution with iron-free feedstocks at a slightly higher mixing ratio would also suffice to comply with industrial specifications. Another prominent coke precursor is sodium which is also present in all filtrates, still exceeding the industrial threshold of 1 ppm [31, 55]. However, an observed sodium reduction of 91% with the fine medium down to 1.72 ppm is particularly promising. Calcium in steam cracker feedstocks is known to contribute to fouling of heat exchanger surfaces [31]. While all filtrates still exceed the industrial threshold concentration for calcium (0.5 ppm), a substantial reduction could be achieved, again with the best performance by the finer filter medium (2.08 ppm, reduction of ~88%). The remaining concentration of silicon in the respective filtrates is close to the industrial threshold value of 0.5-1 ppm in the cases of F3 (0.59 ppm) and F2 (<0.04 ppm), while the filtrate of F1 slightly exceeds the specification (1.38 ppm). Given the abovementioned observation that silicon is an element prone for re-agglomeration it can be concluded that silicon is a more challenging element when it

comes to filtration purification. In a technical application, it can be considered to first pass the pyrolysis oils through a filter of medium or coarse grade (such as F2 or F3), before passing the filtrate through a finer filter medium (e.g., 0.8 μm) to remove the finest particles. Ideally, different combinations of filters with varying fineness should be tested in following research, taking into account technical aspects, such as removal efficiencies and pressure drops, as well as techno-economic aspects.

Furthermore, most elements which occurred in lower concentrations in the unfiltered pyrolysis oil could be reduced below the limit of detection such as cadmium, manganese, nickel, lead, selenium, strontium, thallium and vanadium. Strong catalyst poisons which are relevant in downstream processes of the steam cracker are arsenic, lead, and vanadium [55-59]. Especially, the concentration of arsenic still exceed the maximum allowable concentration in steam cracking feedstocks of 0.005 ppm, even after filtration with the finest filter medium F3 (0.12 ppm) [55]. Interestingly, concentrations of chromium and titanium are both almost unchanged in the filtrates compared to the unfiltered oil. This observation indicates that both elements are present either as ultra-fine particles with sizes below the lowest retention of the finest filter medium (<2.5 μm) or in metalloorganic form dissolved into the oils. The presence of both metals in pigments and dyes in plastic products makes thus further monitoring imperative. Furthermore, detailed analysis using sophisticated techniques such as Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) would be needed to further investigate the exact molecular form of metalloorganics. Moreover, Table 3 shows that increased values for some trace contaminants were measured in the filtered samples compared to the unfiltered one. This is valid for cobalt and magnesium in the respective filtrates of F1 and F2. This finding is likely related to analytical uncertainty during ICP-OES analysis which allows to use only quite low amounts of samples. Dealing with heavy waxy

liquids is thus more challenging in achieving very low limits of detection as compared to lighter liquids. Hence, the limits of detection achieved in this work required thorough method development pushing the boundaries of ICP-OES for waxy samples. Indeed, uncertainties remain which are the explanation for the found increase. However, the overall metal analysis is meaningful as a paired t-test exhibits a significant difference (P-value is 0.016) between the unfiltered oil and the fine filtrate, but also between the coarse filtrate and the fine filtrate (P-value is 0.013). To further lower the contaminant concentrations, it could be interesting to explore approaches such as dissolving the pyrolysis oils to extract or precipitate out the extra fine contaminants.

Summarizing, it can be stated that the metal reduction shown in Table 3, while substantial, is still not sufficient to comply with the maximum feedstock specifications for all metals. However, considering the likely scenario of co-feeding of plastic waste pyrolysis oils with fossil feedstocks on an industrial scale, the most severe metal-related impact can be leveled out by appropriate mixing ratios. For instance, a hypothetical 1:10 mixture using the finer filtrate F3 and a contaminant-free fossil naphtha would comply with the threshold values in terms of calcium, copper, lead, iron and vanadium. Furthermore, it would almost comply with the sodium threshold of 0.125 ppm. Hence, filtration proves to be an efficient technique for reducing the content of metal contaminants in plastic waste derived pyrolysis oils. As has been reported that metal contaminants are mostly present in the heavy fractions of pyrolysis oils, distillation of pyrolysis oils would yield a fairly clean light fraction that can be used for steam cracking while the majority of contaminants would accumulate in the heavier fractions. [22]. The heavier fractions could then be purified by filtration and used for other applications such as the production of lubricating oil [60]. However, from a mass-balance point-of-view, the fraction used for steam cracking and hence for the

production of circular plastics would be rather small if only the light cut would be used, considering the heaviness of pyrolysis oils.

Importantly, filtration proved effective as an upgrading step to removal metals and particles, however, heteroatoms that are chemically bound in hydrocarbon structures, i.e., oxygenates, nitrogenates, sulfur- and chlorine-containing components can also lead to unwanted effects during steam cracking such as corrosion or off-spec products. The most important techniques to remove heteroatoms are hydrogen-based, i.e., hydrodeoxygenation [61-63], hydrodesulfurization [64, 65], hydroenitrogenation [66, 67] and hydrodechlorination [68]. In an integrated industrial system, respective processes can be performed after filtration to reduce the risk of catalyst deactivation caused by metal contaminants in pyrolysis oils.

3.2.2. Hydrocarbon composition

Next to the particle and contaminant composition of the filtrates, the hydrocarbon composition is highly important for the further application in processes such as steam cracking. Table 4 shows the hydrocarbon composition of the respective filtrates in comparison with the crude pyrolysis oil as published in previous work [33]. The results were obtained using comprehensive two-dimensional GC × GC coupled to FID.

Table 4. Hydrocarbon composition of the respective filtrates and the crude pyrolysis oil (taken from [33]).

	Unfiltered pyrolysis oil [33]	**Coarse filtrate (F1)**	**Medium filtrate (F2)**	**Fine filtrate (F3)**
n-paraffins	31.97	31.71	32.20	32.38
Iso-paraffins	6.25	6.08	5.71	6.36
α-olefins	24.00	24.26	23.88	23.85
Iso-olefins	18.51	18.82	18.79	18.30
Linear dienes	3.53	3.27	3.20	3.28
Branched dienes	1.32	1.07	1.25	1.19
Naphthenes	12.36	12.35	12.68	12.46
Aromatics	2.06	2.44	2.29	2.18

548 It can be seen that the hydrocarbon compositions of the respective filtrates are very similar
549 compared to each other and to the crude pyrolysis oil. As it could be expected, the results indicate
550 that the filtration step did not have a significant effect on the hydrocarbon composition of the
551 respective samples. In terms of steam cracking product yields, it can thus be expected that all
552 samples perform in a similar way, while technical issues such as coke formation and fouling can
553 be severely affected by the different contaminant concentrations.

554 ## 3.3. Steam cracking performance

555 ### 3.3.1. Product yields

556 A 25 wt.% pyrolysis oil/ 75 wt.% fossil naphtha mixture was used for steam cracking with the
557 composition shown in Table 5. The hydrocarbon compositions of the used blends show that the
558 high olefin concentrations of the pure pyrolysis oil samples (as shown in Table 4) were reduced
559 substantially to a combined amount of ~11 wt.%. Compared to the fossil naphtha reference, the
560 blends further contain slightly lower amounts of n-paraffins and considerably lower amounts of
561 iso-paraffins. Furthermore, the concentrations of naphthenes and aromatics are slightly lower in
562 the blends compared to the fossil naphtha reference.

563 **Table 5**. Hydrocarbon composition of the used blends for steam cracking experiments according to the
564 blending ratio with fossil naphtha.

	Fossil naphtha	Unfiltered pyrolysis oil/naphtha blend	Coarse filtrate (F1)/naphtha blend	Medium filtrate (F2)/naphtha blend	Fine filtrate (F3)/naphtha blend
n-paraffins	36.5	35.4	35.3	35.4	35.5
Iso-paraffins	42.2	33.2	33.2	33.1	33.2
α-olefins	0.0	6.0	6.1	6.0	6.0
Iso-olefins	0.0	4.6	4.7	4.7	4.6
Linear dienes	0.0	0.9	0.8	0.8	0.8
Branched dienes	0.0	0.3	0.3	0.3	0.3
Naphthenes	17.3	16.1	16.1	16.2	16.1
Aromatics	4.0	3.5	3.6	3.6	3.6

Fig. 7 depicts the most important steam cracking product yields methane, ethylene, propylene and 1,3-butadiene obtained from steam cracking of the pure fossil naphtha reference and all pyrolysis oil/naphtha blends.. As can be seen in the figure, the different filtrates perform very similar to each other as well as to the crude pyrolysis oil cracked in a previous study [33]. Hence, it can be concluded that the filtration step had no significant effect on the steam cracking product yields which indicates that the remaining metal contaminants in the filtrates have no measurable effect on the steam cracking chemistry in terms of catalytic effects. However, from the figure it can also be seen that the addition of 25 wt% of pyrolysis oil to fossil naphtha leads to an enhancement in ethylene yields compared to the pure fossil naphtha feedstock. This observation confirms the lower thermal stability of the heavier hydrocarbon chains present in the pyrolysis oils, thus demonstrating the potential of pyrolysis oils as drop-in steam cracker feedstocks in terms of the ethylene yields [33]. The detailed product yields including the full range of measured products can be found in section B2 in the SI.

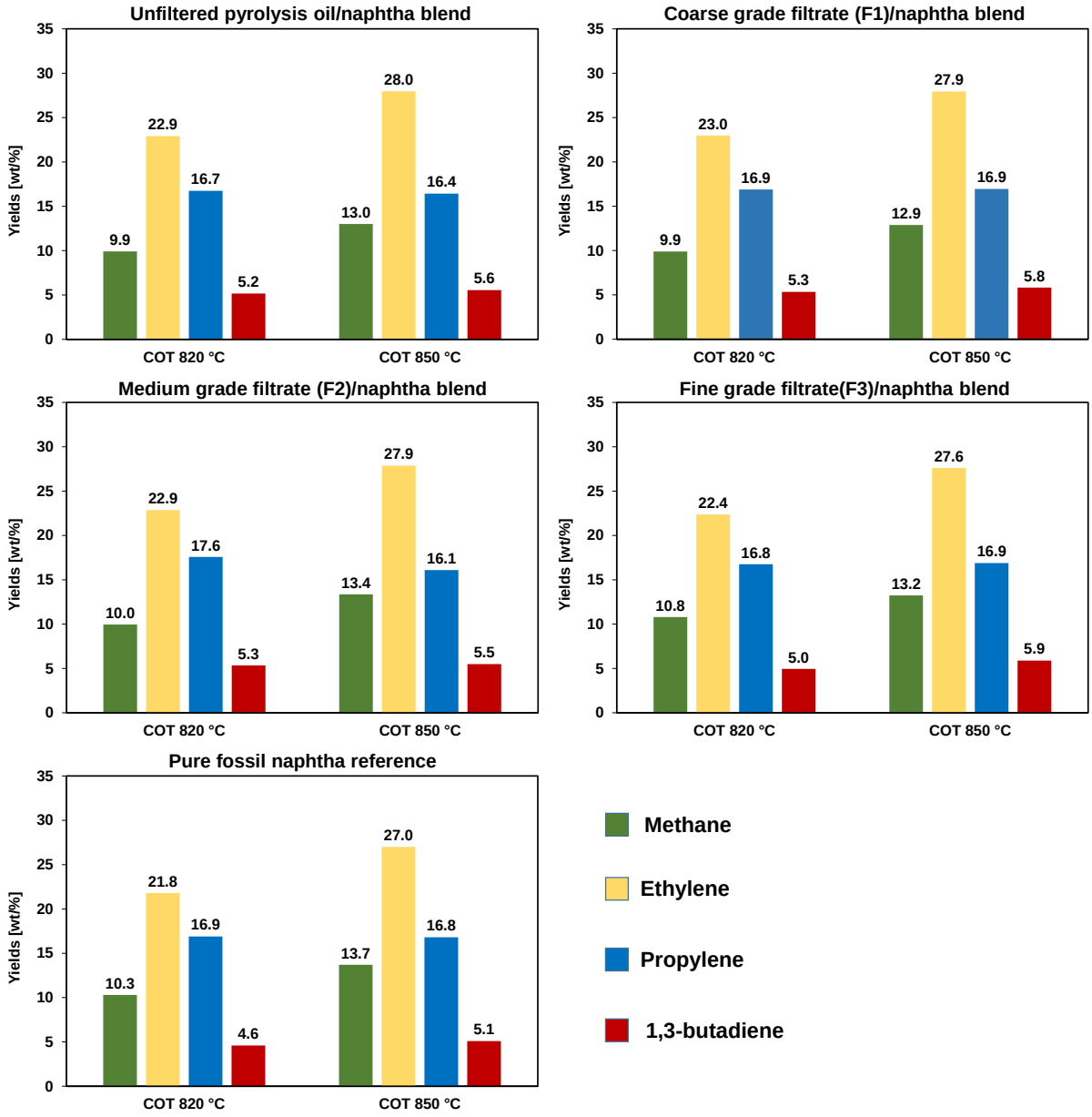


Fig. 7. Steam cracking yields of the most important products methane, ethylene, propylene and 1,3-butadiene measured using on-line GC × GC-FID. Unfiltered pyrolysis oil/naphtha blend and pure naphtha reference was cracked in a previous study [33].

3.3.2. Radiant coil coke formation

Coke formation is highly relevant for the run-length of an industrial steam cracking furnace. Shorter run-lengths due to more frequent decoking cycles lead to economic penalties, ultimately making the use of plastic waste pyrolysis oils unfeasible as steam cracking feedstocks. Some metals can have a severe catalytic effect on coke formation (i.e., iron, nickel, sodium) [22, 69, 70]. This

is important for the initial coking phase, the so-called catalytic coke formation. In this phase, carbon atoms diffuse through a metal particle in the reactor wall (mostly chromium) creating a porous layer of carbon filaments. Over time, the metal particles are encapsuled by carbon which leads to an initial layer of coke on the metal surface [70, 71]. When steam cracking contaminated pyroysis oils, it is likely that next to the coking induction by active metal sites located at the inner surface of the reactor coil (material used in this study: Incoloy 800HT Ni: 30-35 wt%, Cr: 19-23 wt%, Fe: > 39.5 wt%), the initial coking phase is accelerated by catalytically active metal contaminants introduced with the pyrolysis oils.

Given that the used pyrolysis oil/naphtha blends have essentially the same hydrocarbon composition (Table 5), it can be expected that the observed coke formation is related to metal contaminants. Based on the metal concentrations in the filtered products (Table 3), a decreased coke formation during steam cracking of the filtrates could be expected in the order crude pyrolysis oil > F1 > F2 > F3. It is important to note that due to the chosen blending rate, the metal concentrations in the cracked blends were reduced accordingly to a total of 18.7 ppm in the unfiltered oil/naphtha blend, 14.8 ppm in the coarse filtrate/naphtha blend, 10.0 ppm in the medium filtrate/naphtha blend and to 3.4 ppm in the fine filtrate naphtha blend.

Fig. 8 shows the radiant coil coking rates of all filtrate/naphtha blends, the unfiltered pyrolysis oil/naphtha blend as well as pure fossil naphtha, measured after the respective steam cracking experiment including an uncertainty of 10%, according to the methods described in the methodology section. As Fig. 8 shows, there is a significant reduction in the radiant coil coking rate after filtration of the pyrolysis oil corresponding well to the step-wise reduction of metals depending on the respective filter grade. The reduction of coke formation ranges from 39% (F1), over 52% (F2) to 62% (F3) compared to the unfiltered pyrolysis oil naphtha blend. In fact, the fine

grade filtrate/naphtha blend had a coking rate in the same range as fossil naphtha, specifically, even lower than pure naphtha. A possible explanation for the low coking rate of the fine filtrate/naphtha grade is, next to the absence of the most important metal contaminants, the fact that important coke precursors such as naphthenes and aromatics were slightly reduced compared to the pure naphtha reference. However, given the experimental uncertainty of ~10% it can be stated that both pure fossil naphtha and the fine filtrate/naphtha blend showed a very similar coke formation. Hence, the initial coking phase, as measured in these experiments, of pure naphtha was not measurably lower compared to the fine filtrate/naphtha blend, and not substantially lower compared to the medium and coarse grade filtrate/naphtha blends.

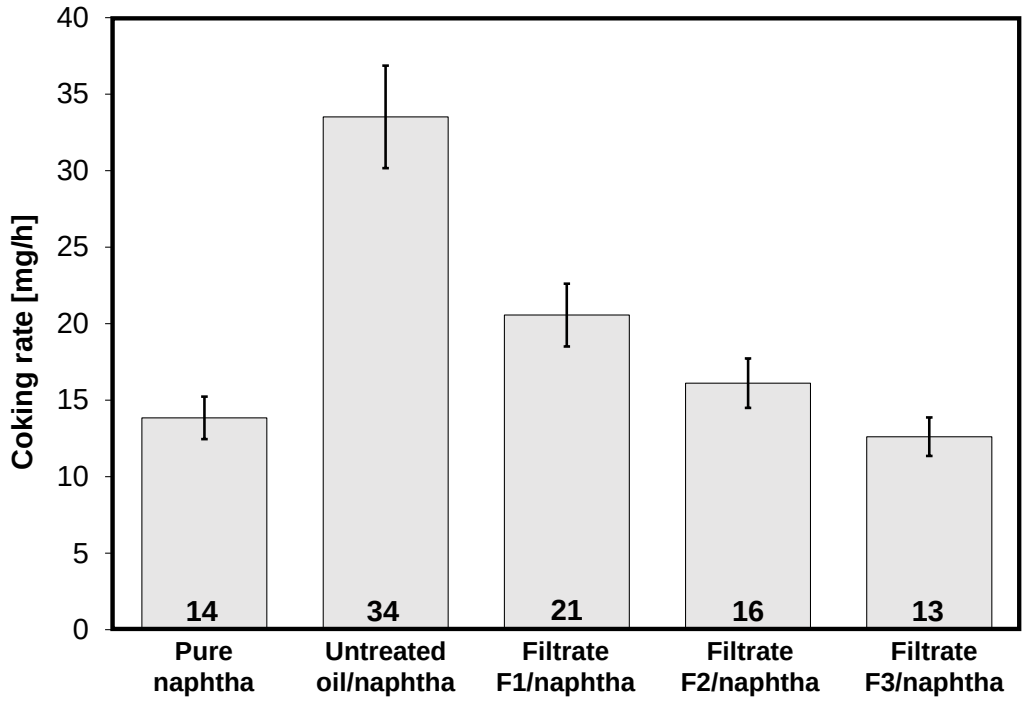


Fig. 8. Radiant coil coke formation results in mg/h of cracking of the filtered samples/naphtha blends. Data of pure naphtha and the untreated oil/naphtha blend is taken from [33].

However, next to coking in the reactor, important process-related issues are fouling in the convection section and transfer line exchanger (TLE) section of the cracker. Both phenomena can be amplified substantially by contaminants in the feedstocks such as silicon and calcium. Indeed,

during the steam cracking experiments, increased fouling in the downstream and TLE sections were observed making a substantially increased cleaning effort necessary after the experiments compared to pure fossil naphtha. Hence, it is important to note that the impact of contaminants during steam cracking cannot be limited to coke formation but also to fouling in other sections of the cracker which can lead to important technical issues. However, this effect can be amended by removing fouling inducing contaminants from the feedstocks, for which depth filtration proved to be a viable method. It is further important to note that the coke formation was observed only in the initial phase of the cracking and that no long-term studies were performed. Thus, additional research at a larger scale is required to conclusively evaluate the steam cracking feasibility of the filtered products. Furthermore, fouling effects were observed in the present study, but not investigated in detail, let alone quantified. However, the results show that filtration of pyrolysis oils for the removal of particles leads to a considerable reduction in radiant coil coke formation and, hence, to an improved applicability of pyrolysis oils in the context of chemical recycling.

4. Conclusions and Outlook

A detailed depth filtration study of a representative contaminated post-consumer plastic waste pyrolysis oil was performed, including the thorough analysis of the filtered products to assess the impact of filtration on the steam cracking performance. It was confirmed with ICP-OES analyses that the used filter media were effective in reducing the particulate contamination of the pyrolysis oil depending on the fineness of the used filter media. While the coarse filter medium led to a reduction of ~20 % of the metal contaminants, with the finest medium, a metal reduction of ~81 % could be reached. At the same time, the hydrocarbon composition of the pyrolysis oils was not affected by the filtration step which was confirmed using comprehensive GC × GC.

Furthermore, the nature of the particles in the unfiltered pyrolysis oil and the respective filtrates was investigated via SEM-EDX analyses. It was found that the particle composition is highly dependent on the particle size with calcium being the dominant element in the smallest particles (<5 μm) while oxygen and silicon become the main elements at higher particle sizes (50-100 μm). Furthermore, the particularly relevant steam cracking contaminant iron has been found as one of the main elements in the investigated particles. Moreover, re-agglomeration phenomena were observed in the filtrates after 2 days of storage which showed a substantial increase of the relative oxygen and silicon concentrations indicating that aging occurred to a certain extent. This observation also shows that silicon and oxygen are particularly prone to re-agglomeration after filtration.

Next to the analytical investigation of the filtered products, the steam cracking performance of the filtrates was assessed and compared to the unfiltered pyrolysis oil. Very similar steam cracking product yields (i.e., ~23 wt.% ethylene at a coil outlet temperature (COT) of 820 °C and ~28 wt.% at a COT of 850 °C) were obtained with the filtered product regardless of the filtration step or the fineness of the filter which was confirmed with on-line GC × GC-FID. This finding was expected based on the very similar hydrocarbon compositions of the samples before and after filtration. On the contrary, a significant reduction of 40-60% of the radiant coil coke formation was observed with the filtered products compared to the unfiltered pyrolysis oil.

This study shows that depth filtration can be an efficient purification technique to remove particles and metals from contaminated plastic waste pyrolysis oils to substantially increase the steam cracking performance towards closed-loop recycling. Based on this lab-scale investigation, technical filtration systems at a larger scale can be designed utilizing multi-stage filtration and continuous processing of the filtered products. Particularly, a continuous multi-stage process is

advisable to combine filtration steps of different fineness in order to remove particles from the pyrolysis oils in a subsequent way without risking high differential pressures over the respective filter modules. Furthermore, given the observed re-agglomeration phenomena it is advisable to directly utilize the filtered products in a continuous process instead of storing them for a longer period of time.

Moreover, the most important constituents of the particulate contamination in the samples were calcium, silicon, iron and oxygen indicating that the use of plastic additives by the manufacturers is indeed the main source of metal contaminants. This is an important insight that can be used by plastics manufacturers with regard to design-for-chemical-recycling guidelines.

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Declaration of competing interest

The authors declare no conflict of interest.

CRediT authorship contribution statement

Marvin Kusenberg: conceptualization, methodology, investigation, writing – original draft, writing – review & editing. **Martijn Roosen**: methodology, investigation, writing – review & editing. **Astrid Doktor**: investigation. **Leonor Casado**: investigation. **Anas Jamil Abdulrahman**: investigation. **Behzad Parvizi**: investigation. **Andreas Eschenbacher**: conceptualization, writing – review & editing. **Emmanuelle Biadi**: conceptualization, project administration, writing –

review & editing. **Nicolas Laudou**: conceptualization, project administration. **Daniel Jänsch**: methodology, investigation, writing – review & editing. **Steven De Meester**: conceptualization, writing – review & editing. **Kevin M. Van Geem**: conceptualization, project administration, funding acquisition, supervision, writing – review & editing.

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