

Article

Chemical Recycling of WEEE Plastics—Production of High Purity Monocyclic Aromatic Chemicals

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Abstract: More than 200 kg real waste electrical and electronic equipment (WEEE) shredder residues from a German dismantling plant were treated at 650 °C in a demonstration scale thermochemical conversion plant. The focus within this work was the generation, purification, and analysis of pyrolysis oil. Subsequent filtration and fractional distillation were combined to yield basic chemicals in high purity. By means of fractional distillation, pure monocyclic aromatic fractions containing benzene, toluene, ethylbenzene, and xylene (BTEX aromatics) as well as styrene and α -methyl styrene were isolated for chemical recycling. Mass balances were determined, and gas chromatography–mass spectrometry (GC-MS) as well as energy dispersive X-ray fluorescence (EDXRF) measurements provided data on the purity and halogen content of each fraction. This work shows that thermochemical conversion and the subsequent refining by fractional distillation is capable of recycling WEEE shredder residues, producing pure BTEX and other monocyclic aromatic fractions. A significant decrease of halogen content (up to 99%) was achieved with the applied methods.

Keywords: WEEE; chemical recycling; pyrolysis; recovery of aromatics; oil upgrading; dehalogenation



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1. Introduction

Waste electrical and electronic equipment (WEEE) represents a significant source of almost all precious and critical metals, but their recovery potential is far from being fully exploited as things stand today. At the end of state-of-the-art WEEE treatment processes, one or more output fractions are left behind, which are usually sent to landfills or to energetic utilization in waste incinerators ([1] pp. 131–133), [2,3]. With those fractions, remaining metals get lost, irretrievable for material recovery ([1] pp. 209–212), [4]. At the same time, WEEE and its output fractions contain high-quality plastics like HIPS, ABS, epoxy resins, PS, PE, PP, and PVC [5–7]. However, these plastics show high concentrations of flame retardants (FR) as TBBPA, DDO, HBCD, and DDE [3], resulting in bromine and chlorine concentrations of 0.6–4.0 wt.% [8].

As mechanical recycling recovers plastics in their given polymeric composition, state-of-the-art processes are not able to remove or to eject flame retardants from FR-containing WEEE plastics effectively. The recovery of unpolluted plastics by means of mechanical recycling is thus mostly limited to FR-free fractions ([1] pp. 209–212), [2,3,9]. Against this background, pyrolysis seems to offer a promising solution to complement established mechanical recycling processes, especially regarding highly chlorinated and brominated WEEE-plastics ([1] pp. 131–133), [3,5,8,10].

Due to the importance of effectively recycling and decontaminating WEEE plastics [1–3,9,11–13], numerous researchers have investigated chemical recycling of WEEE or

of the flame retarded plastics present in such [14–24]. Most studies on novel recycling approaches regarding WEEE focus on the recovery of metals [4,25–27], whereas investigations on recycling of nonmetal fractions of real WEEE are limited [12].

Different chemical recycling technologies for WEEE plastics like thermal pyrolysis [4,21,22,28–32], co-pyrolysis [33–36], two step pyrolysis [33,37], catalytic pyrolysis [23,28,38–45], microwave-assisted pyrolysis [28,46,47], and combinations thereof [24,44,47,48] have been studied.

A very recent review by Charitopoulou et al. [12] on recycling of WEEE plastics comes to the conclusion that pyrolysis is considered a favorable technology to recycle FR-containing plastics from WEEE. The formation of PXDD/F is theoretically suppressed due to the absence of oxygen. However, the oxygen already present in the nonmetal fraction of WEEE in practice leads to PXDD/F [11,41,48].

Several pretreatment technologies were studied to remove BFR from WEEE plastics prior to pyrolysis [31,49–56]. Examples of common pretreatment technologies are solvent extraction with isopropanol, toluene, or methanol, as well as supercritical fluid technologies with acetone, methanol, or ethanol as media. Such techniques were found to have good dehalogenation effectiveness. However, their high operational cost and energy consumption limit industrial implementation [12].

Patent research revealed several patent publications in the field of pyrolysis reactors or processes to treat mixed plastic wastes [57–64] as well as WEEE in particular [65–69]. Most reactor and process concepts are designed to either decompose WEEE in order to prevent landfilling of large volumes of hazardous wastes, dehalogenation, and/or to produce valuable chemicals or fuels at temperatures between 200 and 800 °C. Patented reactor concepts include screw reactors [58,70], U-shaped reactors [68], and fluidized bed reactors [61]. Most patents address thermal or catalytic pyrolysis. However, methods including vacuum pyrolysis [67] or the addition of other material, e.g., heavy oil or hydrocracking steams to a pyrolysis process [60,63], were published. Furthermore, methods comprising multistep processes are present. Examples are upstream technologies prior to pyrolysis [63,65,66] or downstream purification technologies to enhance product quality [57,59,60,67]. Flame retarded polymers sum up to on average 30% of WEEE plastics [71,72]. A crucial point in the thermochemical processing of FR-containing plastics is, however, the copper catalyzed formation of hazardous polyhalogenated dibenzo-*p*-dioxins and furans (PXDD/F) as precursors for PXDD/F, namely chlorine and bromine, are present in WEEE [2,73]. In order to prevent or to minimize their formation during thermochemical treatment, the critical temperature for PXDD/F formation between 200 and 600 °C [74,75] should be skipped quickly by rapidly heating up the plastics to >450 °C [4].

Consequently, Fraunhofer UMSICHT developed an innovative thermochemical conversion process for treatment of composite materials, including WEEE [70]. This process is based on an innovative auger reactor equipped with a unique heat exchanger (Section 2.1). The so-called iCycle[®] process (intelligent Composite Recycling) enables the conversion of WEEE fractions at very constant and controlled process conditions (heating up and retention time of feedstock, stability of process temperature). The current contribution deals with the recovery of chemicals from the liquid oil fraction generated during thermochemical treatment of shredder residues from a state-of-the art WEEE dismantling process. By use of iCycle[®] and downstream processing of the oil, the objectives of the current contribution are as follows:

- to investigate suitability and potential of thermochemical conversion for the generation of intermediate products for chemical recycling;
- to isolate monocyclic aromatic fractions for application in the chemical industry and plastics synthesis by a combination of filtration and fractional distillation;
- to analyze the opportunities and limitations of the applied process combination for the removal of chlorine and bromine in order to provide virgin grade basic chemicals.

2. Materials and Methods

2.1. Thermochemical Conversion

The residual WEEE fraction consisted of IT-appliances (collection group 5) and was provided by a manufacturer as shredder residue with a maximum particle size of 20 mm. This shredder residue contained around 40% metals and inorganics and 60% organics. 231 kg of the feedstock was treated in the continuous thermochemical demonstration plant (load capacity ~70 kg/h) illustrated in Figure 1. Prior to treatment, the plant was flushed with nitrogen overnight and heated up to an operating temperature of 650 °C.

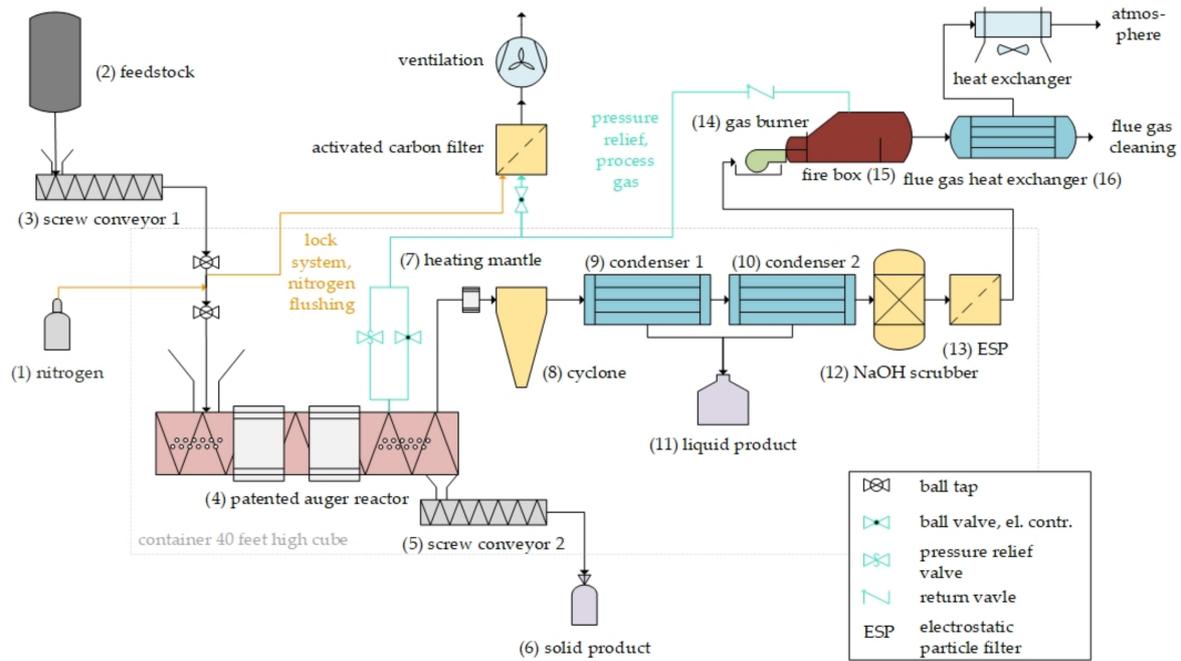


Figure 1. Process flow diagram of the iCycle[®] pilot plant (thermochemical conversion process).

As seen in Figure 1, throughout the treatment, the feedstock material is fed by a screw conveyor (3) batch-wise from a receiver tank (2) into a lock, where it is flushed with N₂ (1) to ensure that no ambient air enters the reactor. Thermochemical treatment and decomposition of the plastic fraction takes place in the reactor (4) at 650 °C. The reactor is a patented system with an innovative heat exchanger design. By use of an Archimedean screw, internal heating by externally preheated cycled spheres can be achieved. Along their way through the auger reactor, the spheres do not get in contact with the feedstock itself as they are moved forward in the inner section of the Archimedean screw. Thus, clogging of feedstock to the hot spheres is prevented. The system in combination with a relatively high temperature of 650 °C ensures a high heating rate of reaction media to avoid the formation of polyhalogenated dioxins and furans due to the presence of flame retardants [4,70]. In addition to the internal heat supply by cycled spheres, external heating is provided by heating sleeves covering the surface of the auger reactor.

Inside the reactor, the auger unit moves the solid material from the feeding point to the discharge point, where remaining solid matter drops out of the reactor and is transferred by a conveyer screw (5) into a collection reservoir (6). The heated auger reactor has a length of 6000 mm and a diameter of 470 mm. Gaseous and vaporous decomposition products (at 650 °C) leave the reactor through a cyclone (7) and subsequently the cooling and condensation train (9, 10), consisting of two tube bundle heat-exchangers, connection pipes, and a pump that transfers the condensate into a collection reservoir (11). All material found in the cooling and condensation train after the experiment is referred to as “condensate”. The remaining gas is cleaned in a NaOH-scrubber unit (12) and an electrostatic particle

filter (ESP) (13) and is subsequently burned on sight (14, 15) in accordance with German Federal Emission Control Act (BImSchG).

2.2. Pyrolysis Oil Pretreatment

Prior to fractional distillation, the pretreatment of condensate was performed to remove solids and aqueous phase present. Two pretreatment methods were conducted in this research. The first method was a vacuum filtration process using a filter paper and a Buchner funnel to separate solids from the crude condensate produced throughout the iCycle[®] process. Filtration was performed within two steps with two different pore sizes of filter paper, i.e., 40 μm and 2 μm . The condensate was then poured through the funnel into a borosilicate flask, and the solids that were larger than the pore size of the filter paper were separated. A vacuum pump (KNF, model: N810FT.18; 100 kPa) was used to initiate the oil suction and enhance the filtration process. The filter paper was frequently replaced, as soon as the filter paper clogs in order to prevent performance decrease. The mass of the total solids that remained in filter papers was measured and prepared for analysis.

Subsequently, a separation of the observable aqueous phase from the filtrate of the second filtration was conducted using a separation funnel. In this way, the lower phase (aqueous) was released by gravitational force via the stopcock (tap) at the bottom of the funnel. The weight of the separated phase was measured and the water phase prepared for analysis.

2.3. Fractional Distillation

For the fractional distillation of 5 kg of the pretreated condensate (oil), a batch distillation system (PILODIST-104) was operated. The plant's column features a stainless-steel wire mesh (20 theoretical stages), arranged with a head temperature sensor and a reflux divider. The column was insulated by a heating mantle, where the temperature was adjusted to maintain at 5 K below the column head temperature to provide an adiabatic condition during the distillation process. The main condenser with a subsequent distillate cooler at the top of the column ensures a sufficient condensation of ascending distillate vapors. The distillation flask at the bottom of the column, surrounded by an insulation mantle, has a volume of 20 L. The heating of the flask was controlled according to the temperature difference (ΔT) between the heating device and the oil temperature inside the heating flask. The reflux ratio was defined by adjusting the off-take time and the reflux time of the distillate fraction. A vacuum pump was connected to the top of the condenser and the fraction collector to maintain the desired pressure. The system was constantly flushed with nitrogen with a flow rate of 0.5 L/min in order to prevent oxidation reactions. A liquid nitrogen cold trap was used to protect the vacuum pump during the distillation with reduced pressure. The following parameters were operated in order to distill the oil generated:

- Operated pressure: 1 atm (RT–85 °C); 100 mbar (>85 °C)
- Temperature difference between heating device and oil in the heating flask: $\Delta T = 100$ K
- Off-take time/reflux time/reflux ratio: 4 s/20 s/5

Based on the boiling points of benzene, toluene, ethylbenzene, and xylene (BTEX aromatics) as well as phenolic compounds present in the operated oil, the temperature intervals and operating pressures depicted in Table 1 were selected to divide the oil into distillate fractions comprising high purities of BTEX-aromatics and monocyclic aromatic substances as styrene, α -methyl styrene, phenol and cresols.

Table 1. Fractional distillation operating parameters.

Fraction	Pressure	Temperature Interval
[-]	[-]	[°C]
1	1 atm	RT–85
2	100 mbar	85–115 (AET ¹)
3	100 mbar	115–140 (AET ¹)
4	100 mbar	140–150 (AET ¹)
5	100 mbar	150–190 (AET ¹)
6	100 mbar	190–205 (AET ¹)
7	100 mbar	205–225 (AET ¹)

¹ Atmospheric equivalent temperature.

2.4. Analysis of Pyrolysis Oil and Fraction Characterization

2.4.1. Gas Chromatography–Mass Spectrometry (GC-MS) Analysis

The composition of oil was analyzed on a gas chromatograph coupled with a mass spectrometer Shimadzu GCMS-QP2020. The chromatograph was equipped with a 30 m nonpolar 0.25 mm inner diameter (i. d.), 0.25 µm film thickness DB-5ms, and 2.5 m middle polar 0.15 mm i. d., 0.15 µm film thickness VF-17ms column set from Agilent Technologies. Helium with 5.0 purity was used as carrier gas for all experiments. The injection volume was set to 1 µL. Dilution was conducted with 1 mg of sample in 1 mL of DCM. The measurements were performed at a constant linear velocity 40 cm/min of carrier gas. The temperature of the GC oven was programmed using the settings starting at 40 °C, 3 min hold to 320 °C, 3 min hold at 10 °C/min. The temperatures of the injector, the MS-interface, and MS were set to 250, 280 and 200 °C, respectively. The quadrupole MS detector was operated at scan speed of 5000 Hz using a mass range of 35–500 m/z. Solvent cut time was 3 min, with the MS start at 3.2 min. Total analysis time was 34 min. BTEX, styrene, α -methyl styrene, phenol, cresols and naphthalene were identified using standards solutions of pure chemicals. NIST-17 Mass Spectral Library was used for all other substance identification. Only the substances detected with the similarity index (SI) of more than 70 were identified. The proportion of each substance in the sample was given in percentage area. Only the proportions of the substances of particular interest in this research were shown in the graph, while other substances were not included and were referred to as “others”.

2.4.2. Energy Dispersive X-ray Fluorescence (EDXRF) Analysis

A quantitative halogen analysis of all the samples was made with an energy dispersive X-ray fluorescence spectrometer (EDXRF) from Shimadzu (EDX 720). The concentrations for chlorine and bromine in oils were calculated based on the calibration curve and the Cl/Br peak intensities measured by EDXRF. Standard solutions were made with 1,3,5-trichlorobenzene, 98% from Alfa AesarTM for chlorine and with 1,3,5-tribromobenzene, and 98% from Alfa AesarTM for bromine. Toluene at 99.8% from Merck was used as a solvent. Each sample was measured three times in order to get statistical data.

2.4.3. Water Content Analysis

Water content in pyrolysis oil and distillate fractions was measured using a Karl-Fischer volumetric titration method. HYDRANALTM—Composite 5 from Honeywell FlukaTM was used as one component reagent titrant and methanol ACS Reagent, while $\geq 99.8\%$ from Honeywell Riedel-de HaënTM was used as a titration medium. All measurements were performed on Metrohm 915 KF Ti-Touch and leaned on DIN 51777. Same as in case of EDXRF, measurements were performed three times.

3. Results

Real WEEE shredder residues were thermally converted by means of pyrolysis at 650 °C with a residence time of 30 min. Solid, liquid, and gaseous products were yielded from this process; these products will be termed solid residue, condensate, and gas here-

inafter, respectively. The obtained condensate underwent two pretreatment steps, namely solids filtration and aqueous phase separation. The obtained product, termed “oil”, has thereafter been divided into eight fractions (including residue) by a fractional batch distillation process. The aim of the processing of the WEEE shredder residues was to produce highly enriched monocyclic aromatic mixtures with reduced content of solids, aqueous phase, and halogen concentrations to make them valuable for industrial reuse. The results of the individual process steps are presented in the following section.

3.1. Thermochemical Conversion

The weights of the treated feedstock material, the collected solid product, and the condensate were determined at 231, 74, and 67 kg. The weight of the gaseous products was determined by a difference at 89 kg. Hence, the products yields were approximately 32, 29, and 39 wt.% for the solid product, the condensate, and the gaseous product, respectively. The results are illustrated in Table 2.

Table 2. Mass balance of the thermochemical conversion process.

Material	Mass	Mass Fraction
[-]	[kg]	[wt.%]
Initial	231	100
Solid (solid residue)	74	32
Liquid (condensate)	67	29
Gas	90	39

The GC-MS analysis of the condensate showed a composition of 6.26 area% benzene, 22.05 area% toluene, 8.39 area% ethylbenzene, 0.73 area% xylenes, 26.63 area% styrene, 6.94 area% phenol, 3.90 area% α -methyl styrene, and 1.91 area% cresols. It follows that the condensate consisted of 72.16 area% of monocyclic aromatic substances to be recovered potentially. The composition is also illustrated in Figure 2 in Section 3.3.

3.2. Pyrolysis Oil Pretreatment

The condensate produced by thermochemical conversion underwent pretreatment processes in order to remove the solids and aqueous phase contained. A filtration process using a Buchner funnel with a filter paper with a pore size of 40 μm was first carried out, followed by a second filtration using a filter paper with a pore size of 2 μm . Subsequently, the observable aqueous phase in the condensate was removed using a separation funnel. Hereinafter, the filtrate <2 μm without aqueous phase will be referred to as oil.

The amount and the mass fraction of the condensate, the filtered condensate, the solids and aqueous phase removed are summarized in Table 3. By means of pretreatment, 0.3846 kg solids (>40 μm), 0.6125 kg solids (2–40 μm), and 0.4739 kg aqueous phase were separated from the condensate, which correspond to mass fractions of 2.59 wt.%, 4.12 wt.%, and 3.19 wt.% of the initial crude condensate, respectively.

After the conducted pretreatment steps, the oil contained chlorine, bromine, and water concentrations of 4833 ± 785 ppm, 2251 ± 135 ppm, and 8267 ± 340 ppm, respectively. Halogen and water concentrations are depicted in Figure 3.

Table 3. Mass balance of condensate pretreatment.

Material	Mass	Mass Fraction
[-]	[kg]	[wt.%]
Crude condensate	14.8477	100.00
Filtrate (<40 µm)	13.5219	91.07
Solids (>40 µm)	0.3846	2.59
Loss (filtration 1)	0.9412	6.34
Filtrate (oil) (<2 µm)	11.7514	79.15
Solids (2–40 µm)	0.6125	4.12
Loss (filtration 2)	1.1580	7.80
Aqueous phase	0.4739	3.19

3.3. Fractional Distillation

The pretreated condensate (referred as oil) was successfully divided into its fractions by means of distillation. The initial boiling point of the oil was 67 °C. The highest column head temperature reached was AET 225 °C at 100 mbar. All substances (and mixtures) with boiling points above 225 °C were considered as residue and were not prepared for analysis. Four pure monocyclic aromatic fractions (referred to as main products) including BTEX aromatics and styrene with a total mass fraction of 46.68 wt.% of the initial oil feed were obtained from distillation. Additionally, three fractions enriched in valuable monocyclic aromatic substances as styrene, phenol, α -methyl styrene, cresols, and polycyclic naphthalene with a total mass fraction of 20.89 wt.% were yielded. Along with these, 27.66 wt.% residue and 2.04 wt.% cold trap fractions were produced. Two cold trap fractions were collected during distillation. A mass balance of the distillation process is presented in Table 4, implying a mass loss of 2.73 wt.%, presumably due to mass hold-up in the column.

Table 4. Distillate fractions with temperature intervals and mass composition.

Fraction	Temperature Interval	Mass	Mass Fraction
[-]	[°C]	[kg]	[wt.%]
Initial	-	5.3830	100
1	RT–85	0.4800	8.92
2	85–115	0.7690	14.29
3	115–140	0.3205	5.95
4	140–150	0.9430	17.52
5	150–190	0.5835	10.84
6	190–205	0.3360	6.24
7	205–225	0.2050	3.81
Residue	>225	1.4890	27.66
Cold trap 1	-	0.0540	1.00
Cold trap 2	-	0.0561	1.04
Loss	-	0.1469	2.73

All fractions yielded by means of distillation are depicted in Figure 4. It can be observed that fractions 1 to 4 were colorless and transparent, indicating high chemical stability. Fractions 5 and 6 showed a light brown color, which is typical for oxidized phenolic compounds contained in the fractions. Fraction 7 and the distillation residue comprise dark brown to black opaque appearance.

Fraction 1 (RT–85 °C), with a mass fraction of 8.92 wt.%, solely consisted of benzene and toluene with a proportion of 88.00 area% benzene and 12.00 area% toluene. The chlorine, bromine, and water concentrations were determined to be 221 ± 25 ppm, 20 ± 1 ppm, and 8833 ± 170 ppm, respectively.

Fraction 2 (85–115 °C) contained mostly toluene with a proportion of 96.23 area% as well as benzene (3.20 area%), 113 ± 33 ppm chlorine, 3 ± 1 ppm bromine, and 1333 ± 125 ppm water. The mass fraction represented 14.29 wt.% of the initial mass.

Fraction 3 (115–140 °C) with a mass fraction of 5.95 wt.% contained a mixture of toluene, ethylbenzene, xylenes, and styrene. The GC-MS result shows that ethylbenzene had the highest proportion with 43.15 area%, followed by 26.83 area% toluene, 25.41 area% styrene, and 4.15 area% xylenes. The fraction had a chlorine concentration of 836 ± 93 ppm, a bromine concentration of 6 ± 1 ppm, and a water concentration of 400 ± 216 ppm.

Fraction 4 (140–150 °C) with a mass fraction of 17.52 wt.% mostly consisted of styrene 79.98 area%. The GC/MS analysis also determined 16.83 area% ethylbenzene, 2.26 area% xylenes, and a trace amount of toluene and 1-methylethyl-benzene. Moreover, this fraction contained 150 ± 23 ppm chlorine, 280 ± 3 ppm bromine, and 333 ± 170 ppm water.

Fraction 5 (150–190 °C) consisted of styrene, phenol, α -methyl styrene, and naphthalene, where phenol 35.13 area% is the most present, followed by 23.52 area% styrene, and 10.48 area% α -methyl styrene. It was noted that this fraction also contained 12.74 area% indene (SI 96%). The bromine concentration of fraction 5 was the highest compared to the other fractions (1100 ± 58 ppm), along with 303 ± 27 ppm chlorine and 1233 ± 125 ppm water. The mass fraction of fraction 5 was 10.84 wt.%

Fraction 6 (190–205 °C), with a mass fraction of 6.24 wt.%, consisted of 37.07 area% phenol, 27.16 area% naphthalene, 19.06 area% benzonitrile (SI 98%), 13.98 area% cresols, trace amounts of aniline, 3-phenyl-2-propenal, and derivatives of benzene, indene, and benzofuran. This fraction exhibited chlorine, bromine, and water concentrations of 99 ± 13 ppm, 249 ± 1 ppm, and 833 ± 170 ppm, respectively.

Fraction 7 (205–225 °C) represented 3.81 wt.% of the initial mass, predominantly containing naphthalene with a proportion of 40.45 area%, followed by 31.81 area% cresols, 6.87 area% 1-methyl-naphthalene (SI 97%), 4.52 area% 2-methyl-benzonitrile (SI 96%), 3.56 area% benzonitrile (SI 98%), 1.24 area% phenol, as well as several derivatives of benzonitrile, naphthalene, benzofuran and traces of other compounds. High chlorine (1914 ± 517 ppm) and bromine (405 ± 10 ppm) concentration compared to lower boiling point fractions were determined. This fraction's water concentration exhibited 900 ± 141 ppm.

In the distillation residue (boiling point >225 °C), derivatives of naphthalene, benzene, fluorene, anthracene, and pyrene were identified, containing high concentrations of chlorine (1538 ± 36 ppm) and bromine (4316 ± 159 ppm).

The results from GC-MS, EDXRF, and water concentration analysis are summarized and presented in Figures 2 and 3.

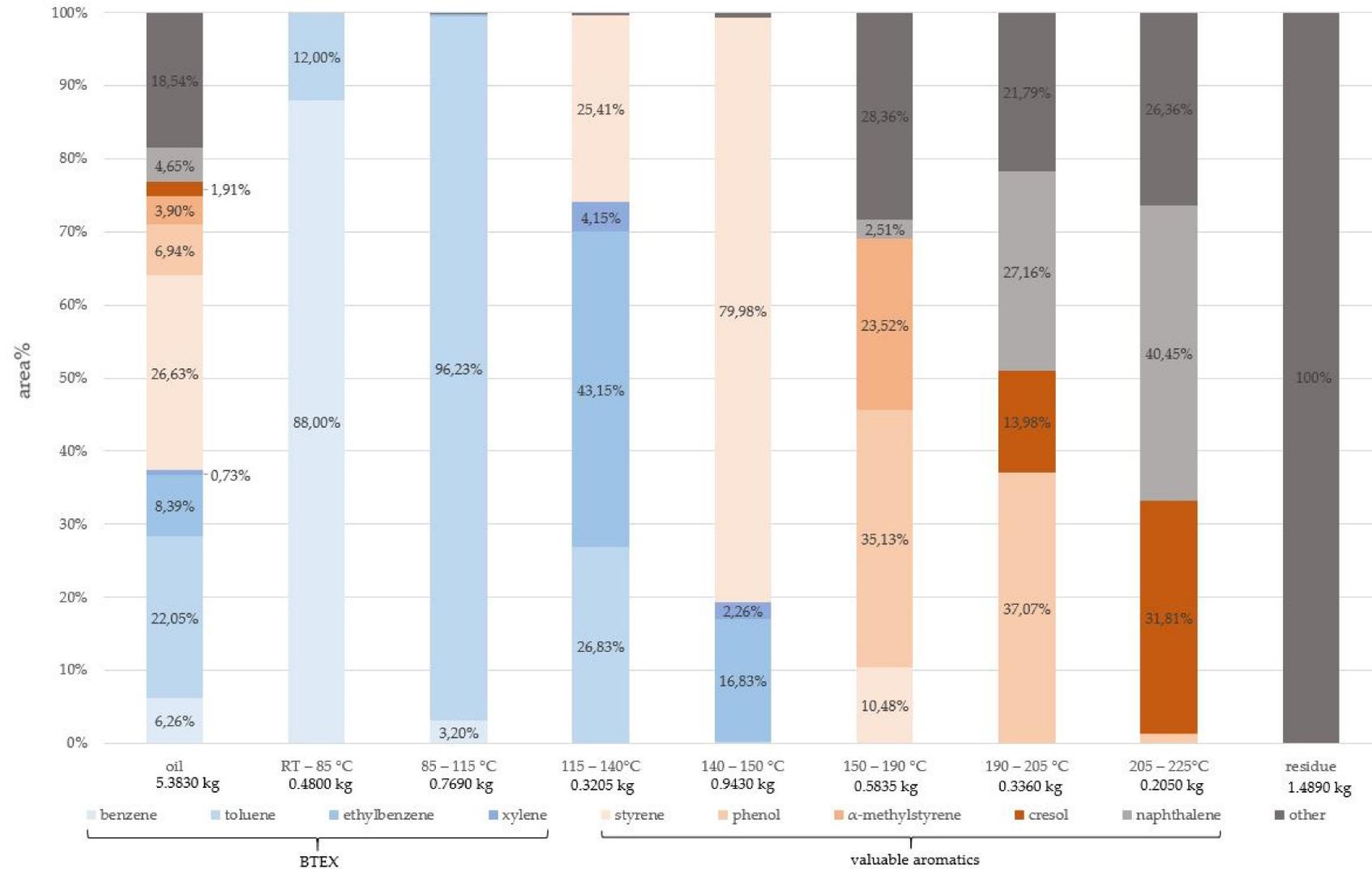


Figure 2. Composition of oil and distillate fractions.

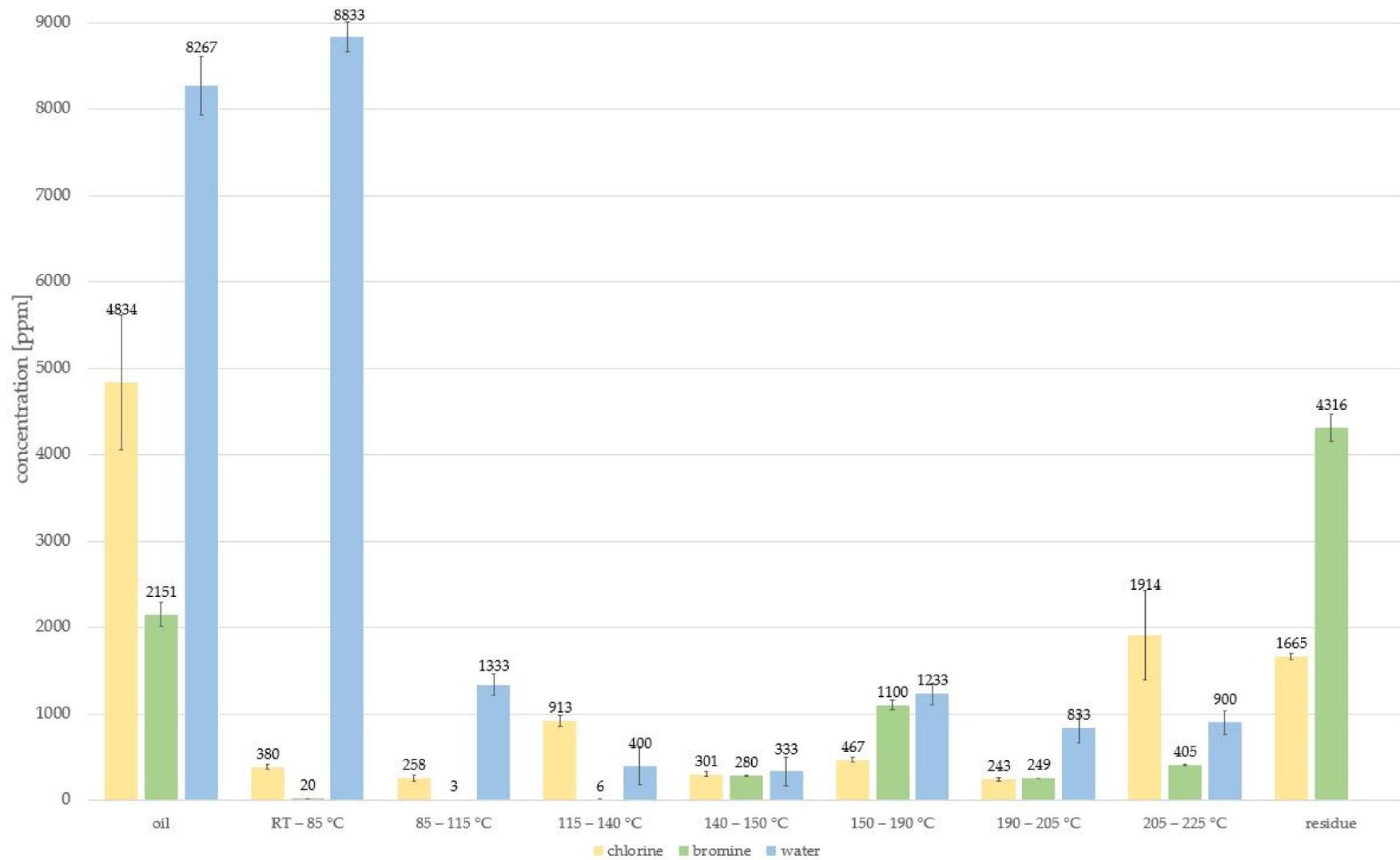


Figure 3. Energy dispersive X-ray fluorescence (EDXRF) results and water concentration analysis of oil and distillate fractions.

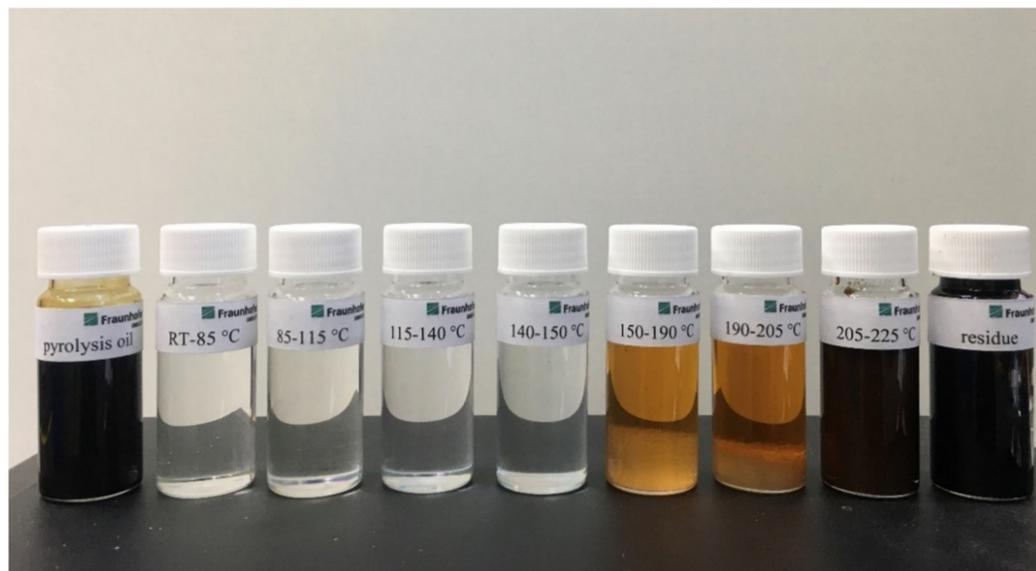


Figure 4. Fractions obtained by fractional distillation.

4. Discussion

The pyrolysis of WEEE or flame-retarded polymers contained in WEEE with and without catalyst has been conducted in a number of recent works [2,6,9,10,15,20–23,30,32,76,77]. Furthermore, mixed WEEE residues can vary widely in terms of composition, strongly depending on their origin [1] (pp. 209–212) [2,3,7,9].

On average, the thermal conversion of WEEE at different temperatures yields 36 wt.% condensate, 39 wt.% gas, and 25 wt.% solid residue [6]. Recent works yielded 71–91 wt.% condensate, 3–21 wt.% solid residue and 2–8 wt.% gas from thermal pyrolysis of real mixed WEEE at 600 °C in a laboratory scale [76,78]. The iCycle[®] process applied for this work yielded 29 wt.% condensate, 32 wt.% solid residue, and 39 wt.% gas on a demonstration scale plant. The converted WEEE contained around 40% metals and inorganics, which explains the comparatively high amount of solids. Due to the operating temperature of 650 °C, the production of 39 wt.% gas is in an expectable range. However, the distribution of the products is, aside from operational parameters and scale, also highly dependent on the composition of the input material. Similar results (40 wt.% condensate, 30 wt.% solid residue, 12.5 wt.% tar, and 13.5 wt.% gas) were found by Vasile et al. [77] throughout the pyrolysis of mixed WEEE in a temperature range of 430–470 °C in a smaller demonstration scale plant. The produced oil (condensate) comprised a comparable content of 62.75 vol% aromatics as BTEX, styrene, and phenol derivatives. The condensate produced throughout the present work was also very rich in monocyclic aromatic compounds (including BTEX aromatics, styrene, phenol, and cresols), representing 76.81 area% in the pretreated pyrolysis oil. Condensates by Santella et al. [76] contained less than 20 wt.% aromatic compounds and mostly styrene. The pyrolysis oil produced from mixed WEEE by Hall et al. [78] consisted mainly of phenol, isopropyl phenol (30.2 wt.%), and styrene (5.9 wt.%), indicating major differences in the composition of the investigated feedstock. However, Hall et al. [78] found a similar chemical composition of the liquid pyrolysis product from waste refrigerators; bromine and chlorine contents of the condensate were 0.3 % and 0.1 %, respectively.

The current investigation showed that the pretreatment of the condensate in terms of filtration and phase separation is capable of removing roughly 10 wt.% of substances as solids and water that are undesired for further upgrading of the oil, as they are likely to disturb the refinement processes to produce other materials, e.g., bulk chemicals or fuels. Hence, the pretreatment technologies are crucial in terms of condensate processing, and they need to be conducted before further upgrading.

The chlorine and bromine concentrations of the investigated pyrolysis oil amount to roughly 5000 ppm chlorine and 2000 ppm bromine. Other related works found less than 600 ppm chlorine and less than 900 ppm bromine in the pyrolysis oil from mixed WEEE [78]. This confirms the enormous differences in WEEE composition [7,72] and manifests the need of the dehalogenation of pyrolysis oil in order to upgrade them to fuels or chemicals.

By means of fractional distillation, pure BTEX fractions and concentrated monocyclic aromatic fractions were produced:

- Benzene fraction (88 area% benzene, 12 area% toluene)
- Toluene fraction (3 area% benzene, 96 area% toluene)
- BTEX/styrene fraction (27 area% toluene, 43 area% ethylbenzene, 4 area% xylenes, 25 area% styrene)
- Styrene fraction (17 area% ethylbenzene, 2 area % xylenes, 80 area% styrene)
- Phenol fraction (35 area% phenol, not considered as main product)

The results evidenced that the pyrolysis of WEEE shredder residues and subsequent distillation of the condensate might be applied to produce high purity chemical fractions which can be used as a feedstock in the chemical industry and in polymer synthesis to produce virgin grade chemical products and polymers and also to substitute crude oil consumption.

The chlorine and bromine concentrations were significantly reduced by up to 99% in the distillate fractions. The EDXRF analysis showed that bromine accumulates in the distillation residue where chlorine concentration is decreased in all fractions, including the residue. The decrease in chlorine concentration in all fractions promote the assumption that chlorine (in the form of HCl) was dissolved in the oil and released throughout distillation [77].

In the first three fractions (RT–140 °C), bromine concentrations do not exceed 20 ppm, which represents a reduction of 99% in relation to the crude condensate and can already be sufficient debromination for the industrial application of the produced chemicals. Fractions 4–7 comprise bromine concentrations roughly between 200 ppm and 400 ppm, representing a significant reduction from the initial oil (2151 ppm).

Fractions 1, 2, 4, and 6 chlorine concentrations were reduced to roughly 250–470 ppm from 4843 ppm in the initial oil. Fraction 3 and 5 still comprise 913 ppm and 1914 ppm chlorine, respectively. Further dehalogenation is needed in order to reuse such fractions for industrial applications [77].

Beside the chemicals, the solid fraction is also suitable for recycling. It can be supplied to copper smelters, where metals are recovered. The gas can be used for energy recovery after treatment as described in Figure 1. The water phase, however, needs to be treated as hazardous waste as it contains metal compounds, organic, and halogen residues.

Several studies in the field of chemical recycling of WEEE have investigated the production of fuels, which is less valuable as a product compared to high-purity monocyclic aromatic fractions. Furthermore, the chemical recycling to valuable basic chemicals and monomers has a positive environmental impact in terms of climate change and fossil resource depletion compared to the productions of fuels. Thus, the conversion of WEEE to valuable chemicals has great potential to close the loop of the nonmetal fraction of WEEE as it will be mainly kept in the material cycle where the production of fuels entails the release of the nonmetal fraction (especially in the form of carbon dioxide) to the atmosphere [79,80].

5. Conclusions

A significant amount of more than 200 kg real WEEE shredder residues from a German recycling company were treated in a demonstration scale pyrolysis plant and the subsequent fraction was distilled, in order to produce basic chemicals with high purity. Such treatment of liquid pyrolysis products from WEEE shredder residues to produce pure chemical fractions have not been reported yet. Thus, a new approach for recovering valuable chemicals like aromatics from pyrolysis oil was investigated and was successfully proven in a demonstration scale plant.

From the conducted experiments, it can be concluded that:

- Pyrolysis is a promising technology for production of an intermediate oil for chemical upgrading.
- Pretreatment such as filtration and phase separation is capable of removing solids and water, which are undesired for the further upgrading of the oil.
- It was proven that a combination of pyrolysis and subsequent fractional distillation is a suitable method for the isolation of high purity BTEX fractions and concentrated monocyclic aromatic fractions.

Current results revealed that a combination of filtration followed by fractional distillation is suitable for the reduction of halogen content. The halogen content was reduced up to more than 99% in the obtained fractions. Therefore, the recovered aromatics have great potential to be used as feedstock in chemical industry.

Estimations made by Fraunhofer UMSICHT suggest that the pyrolysis of WEEE for the recovery of metals is already economically viable in a scale >250 kg/h. The recovery of aromatics from WEEE nonmetal fraction instead of energetic utilization, however, enables significant improvement of both economic and ecologic aspects of WEEE recycling.

Further research works need to be conducted on higher halogen reduction and are part of our current projects. The development and scale-up of the presented technologies are the next steps to implement the recovery of aromatic compounds from different plastic waste streams in industry.

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