



Reduction of brominated flame retardants (BFRs) in plastics from waste electrical and electronic equipment (WEEE) by solvent extraction and the influence on their thermal decomposition

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ABSTRACT

Consumption of electronics increases due to modern society's growing needs, which leads to increasing generation of waste electrical and electronic equipment (WEEE). Recycling of WEEE has been a global concern during the last few decades because of the toxic compounds that are produced during recycling. Different recycling techniques have been adapted on a commercial scale in order to overcome this issue, but the recycling of WEEE still lacks the technology to treat different kinds of feedstocks and to maximise the recycling rates. Pyrolysis is an alternative that has not been commercialised yet. One of the challenges for the implementation of this technology is the toxic brominated organic compounds that can be found in the pyrolysis oils.

In this study, tetrabromobisphenol A (TBBPA), one of the major flame retardants, is reduced in three different WEEE fractions through solvent extraction as a treatment prior to pyrolysis. Two solvents have been experimentally investigated: isopropanol and toluene, the latter of which can be derived from pyrolysis oil. The results indicate that TBBPA was extracted during pre-treatment. Moreover, the total bromine content of WEEE material was reduced after the treatment with a maximum reduction of 36.5%. The pyrolysis experiments indicate that reduction of several brominated organic compounds was achieved in almost all the tested cases, and two brominated compounds (2,4,6-tribromophenol and 2,5-Dibromobenzo(b)thiophene) reached complete removal. Also, the thermal decomposition behaviour of the raw samples and the treated was investigated, showing that the reduction of TBBPA influences the decomposition by shifting the starting decomposition temperature.

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1. Introduction

Waste electrical and electronic equipment (WEEE), also known as e-waste, has become a global concern in the last years. Its increasing amounts in conjunction with its high concentration of inherent toxic substances has made it a high priority risk for environmental and human health concerns (Perkins et al., 2014). Policymakers globally are struggling to find new strategies for minimizing its generation, while researchers focus on improving the waste treatment techniques for minimizing the environmental impact of recycling (Bhutta et al., 2011).

One of the main concerns regarding the recycling of WEEE is its high concentration of brominated flame retardants (BFRs) (Jonkers et al., 2016), which limits the recycling feasibility in existing technologies (Birnbbaum and Staskal, 2004). BFRs have been proven to be very persistent and toxic. Numerous environmental reports show that traces of these compounds have been found in both wetlands and soil close to waste treatment facilities (Segev et al., 2009). Moreover,

other studies relate human exposure to such compounds with negative endocrine, reproductive and behavioural effects (Birnbbaum and Staskal, 2004; Lyche et al., 2015). Human exposure risks to BFRs are high both during the manufacturing and the recycling processes of electronic products, which enhance the need to find alternative routes for closed systems of production and recycling (European Communities, 2006).

The use of flame retardants in electrical and electronic applications is vital for safety reasons, since their components are usually subject to thermal stress. Even though electronic manufacturers are trying to find new alternatives for substituting the BFRs, they have been used in the manufacturing process of electronic components for decades, which is also reflected on the waste streams (Hull et al., 2014). BFRs are present in most of the WEEE fractions worldwide and will continue to be present for the coming years. Therefore, the end-of-life solutions for WEEE should be improved in order to reduce their environmental impacts.

Various recycling technologies are applied to WEEE today, mostly focusing on mechanical separation of its different components. After several steps of sorting, size reduction and mechanical recycling, an inhomogeneous mixture of flame retarded plastics, met-

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als and ceramic materials constitute the most challenging fraction of WEEE. For this complex mixture, two recycling techniques with drawbacks have been proposed, such as: (1) landfilling, which is not sustainable because of the risk of diffusion of toxic compounds into the aquifer (Osako et al., 2006), (2) incineration, which only satisfies the energy recovery while the risk of environmental pollution due to dioxin formation is high because of the high temperature of the process and the oxidative atmosphere (Birnbbaum and Staskal, 2004). A promising recycling technique which has not yet been fully studied is (3) chemical recycling, which satisfies both the energy recovery (by producing liquid/gas energy carriers) and the material recycling of WEEE (by producing chemicals that could be used for manufacturing other materials) and is therefore the most environmentally friendly option (Ma et al., 2016).

Previous studies have highlighted pyrolysis as a promising and valuable alternative for recycling of the organic content of complex fractions from today's recovery of WEEE. One of the main benefits of pyrolysis is the production of valuable condensable liquids for feedstock recycling or for liquid fuel production (Chen et al., 2014; Williams, 2013). On the other hand, waste fractions that include BFRs produce pyrolysis liquids mixed with brominated compounds, limiting their direct recovery.

Various ways of removing brominated compounds from the pyrolysis oil mixture have been studied previously. Several studies have focused on single step solutions during the pyrolysis process whereby adjusting the process conditions, they have managed to reduce the transfer of brominated compounds to the liquid fraction (Evangelopoulos et al., 2015a). Other studies have focused on end of pipe solutions such as catalytic treatment for oil upgrading (Yechezkel et al., 2013) or bromine removal through bromophenols reduction and bromomethane evolution (Blazso et al., 2002). On the other hand, BFRs can also be removed before the pyrolysis process. Zhang et al. have investigated the removal of BFRs in plastics through a solvothermal technique and have concluded that alcohols can efficiently remove TBBPA, which is one of the main flame retardants used in the manufacturing process of electrical and electronic plastic components (Zhang and Zhang, 2012). Vilaplana et al. have investigated the solvent extraction of specific additives such as the TBBPA and decabromodiphenyl ether from plastics being subject to microwave extraction (Vilaplana et al., 2009). This work concluded that the most important factors that influence the extraction are the time and the temperature of the process. Most of previous studies are using pure plastic fractions where BFRs are added to the fractions for experimental purposes, indicating a gap in the literature on experiments performed on real WEEE fractions.

This study investigates the removal of TBBPA from real WEEE fractions through soxhlet solvent extraction as a pre-treatment to the pyrolysis process. The degree of removal is evaluated both by analysis of the liquid effluent and by analysing the bromine content of treated and untreated materials. Furthermore, this work aims to correlate the products of pyrolysis with and without pre-treatment for removal of TBBPA, which has not been investigated in previous studies. Finally, the materials' thermal decomposition characteristics are investigated by thermogravimetric analysis in order to further evaluate the influence of the TBBPA reduction.

2. Materials and methods

2.1. Material composition

Fractions of brominated WEEE were collected from the recycling plant of Stena Technoworld AB located in Halmstad, Sweden. On the

recycling site, after WEEE has been sorted and detoxified from mercury, the WEEE fractions are shredded and the plastics are separated based on their physical properties. The three tested WEEE fractions selected for this investigation was those whose elemental analysis revealed substantial amounts of bromine. The name chosen for each tested fraction has been adopted by the company's internal identification system. The first tested fraction of WEEE is (1) "brominated plastics" which is separated from recyclable plastics by density separation methods. The second fraction of WEEE investigated is (2) "modern wifi plastics", derived from the recycling process of such devices. The last examined fraction is (3) "printed circuit boards (PCBs)". The collection of the material was performed on site and the amount collected was enough in order to verify that the samples were representative. All the different examined fractions were homogenized before the experiments through intensive mixing. Also, their particle sizes were reduced to a size of <0.9 mm.

2.2. Methods

Two solvents were chosen for the liquid extraction based on their chemical properties: isopropanol and toluene. Isopropanol was selected because of its high relative polarity (E_T^N isopropanol=0.546) while toluene was chosen because of its low relative polarity (E_T^N toluene=0.099) (Reichardt, 1994; Reichardt and Welton, 2010). Moreover, the toxicity of a solvent is also another parameter for consideration when designing a process. Isopropanol is considered to be a low toxicity solvent, while toluene is more toxic (Macfarland, 1986).

Toluene was chosen because it is one of the main condensable products that are derived from pyrolysis of the three examined WEEE fractions (Evangelopoulos et al., 2015a). In terms of liquid extraction being an industrial application for WEEE treatment, this solvent can be separated from the pyrolysis products and recirculated for the solvent extraction pre-treatment. The solvent could then be purified with typical solvent recovery methods and reused again in the process. This process can improve the recycling efficiency by closing the loop of materials. Both solvents used were of 99.9% HPLC purity grade purchased by Sigma Aldrich and the thimbles used for the soxhlet apparatus were high purity glass microfiber thimbles (300 mm × 100 mm) in order to be totally inert during the extraction process.

Liquid extraction of the three investigated fractions was performed with a soxhlet extractor. One gram of the WEEE sample was placed in the thimble in the soxhlet apparatus, while a spherical flask was filled with 100 ml of solvent according to the examined case. The flask was then submerged in a heated oil bath. The temperature of the extraction was based on the boiling point of the solvent used: 132 °C for the isopropanol extraction while for the toluene extraction the temperature was 153 °C for all the investigated fractions. The total time of the extraction was 6 h for all the tested cases.

2.2.1. Bromine content analysis of the WEEE fractions

The samples, raw and treated, were studied by a scanning electron microscope (SEM) coupled with an Energy-dispersive X-ray spectroscopy (EDS) detector, both for observing the surface changes of the original plastic sample and for identifying differences in the elemental composition to evaluate the degree of debromination. Three spots per picture of zoom x50 were analysed by SEM-EDS and the statistical analysis was performed. The equipment used was a Hitachi Analytical Table Top Microscope/Benchtop SEM TM3030.

2.2.2. Liquid analysis of the effluent

The liquids obtained by the extraction were firstly filtered in order to remove any solid remainings of the sample, followed by analysis using an Agilent 7890A gas chromatograph with an Agilent 5975C MSD mass spectrometer (GC/MS). The column used for the chromatographic separation was an HP5ms fused with phenyl methyl silox (30 m long, 250 μ m film thickness, 0.25 mm inner diameter). The temperature profile used was started at 125 °C and was held for 1 min, followed by a heating rate of 10 °C/min to a final temperature of 325 °C, which was held for 5 min. Selected ion monitoring (SIM) analysis was performed targeting the specific ions for the determination of TBBPA (63, 76, 89, 151, 152, 181, 196, 212, 277, 291, 293, 295, 525, 527, 529, 530, 531, 533, 542, 544, 546) to indicate its presence according to the NIST11 library.

2.2.3. Decomposition behaviour of WEEE fractions

A simultaneous Thermogravimetric analysis from Mettler Toledo (TGA/DSC1 Star System) was used in order to evaluate and compare the decomposition of both the raw and treated samples. All the samples were heated in the TGA furnace from 50 to 850 °C with a heating rate of 10 °C/min under a nitrogen atmosphere.

2.2.4. Analytical pyrolysis experiments of WEEE fractions

The initial and the treated samples were pyrolysed using a PyroLa® 2000 pyrolyzer coupled to the GC/MS previously mentioned. The pyrolyzer consists of a Pt filament, which makes it possible to control pyrolysis temperature and time with a heating rate similar to flash pyrolysis. The pyrograms obtained were analysed to evaluate the degree of extraction of brominated flame retardants and their influence on the composition of derived pyrolytic vapours. The temperature of pyrolysis was set to 700 °C, and details about the analysis can be found elsewhere (Evangelopoulos et al., 2015a).

3. Results and discussion

3.1. Material characterisation

The elemental compositions of the three examined fractions are presented in Table 1. Chosen WEEE fractions are representative since they have been collected from an industrial recycling site. As mentioned earlier, the fraction of “brominated plastics” passed through various separation processes at the recycling site, resulting in high plastic content. The high amount of oxygen indicates that the plastics in this fraction are mainly oxygenated polymers. The examined fraction “modem wifi” plastics also has high volatile content,

Table 1

Proximate and ultimate analysis of the tested fractions.

	Brominated plastics	Modem wifi plastics	Printed circuit boards (PCBs)
<i>Proximate analysis (wt %)</i>			
Ash @550 °C	9.70	21.00	79.70
Volatile	86.50	74.50	17.00
Fixed carbon	3.80	4.50	3.30
<i>Ultimate analysis (wt %)</i>			
Carbon (C)	74.64	83.54	63.55
Hydrogen (H)	7.20	7.72	6.40
Nitrogen (N)	2.27	4.65	2.32
Chlorine (Cl)	1.06	0.39	0.20
Sulphur (S)	0.07	0.06	0.79
Bromine (Br)	0.86	2.22	8.03
Oxygen* (O)	13.90	1.42	18.77

* Oxygen is calculated by difference.

but relatively low oxygen content. The “printed circuit boards (PCBs)” fraction contains high quantity of metal and ceramic materials, which can be seen from the high ash content.

The bromine content has also been analysed across all tested fractions, since bromine is a main constituent of the polymer chain in flame retardants. The highest amount of bromine was therefore found in “printed circuit boards (PCBs),” since it had the highest percentage in ash free basis.

3.2. SEM-EDS analysis

The examined waste fractions have also been analysed by SEM-EDS for elemental composition analysis. The results are illustrated in Fig. 1 together with the standard deviation for each measurement, which shows the degree of bromine reduction of the treated samples compared with the bromine content of the raw materials.

Firstly, the results indicate that the bromine content was reduced in all the treated samples. On the other hand, complete removal of the bromine was not achieved under the tested conditions. There are still traceable amounts of bromine in the plastic fractions, even though the maximum reduction reached 36.45% for the isopropanol-treated “brominated plastics.” Moreover, for the “brominated plastics” and “modem wifi plastics” fractions, isopropanol seems to more efficiently remove bromine, in contrast with the “printed circuit boards” fraction.

The results also indicate that isopropanol is better compared to toluene in terms of bromine removal for “brominated plastics” and “modem wifi plastics”, while toluene extraction also works well, especially for the “printed circuit boards (PCBs)” fraction. This indicates that isopropanol, with high relative polarity has proven to be more efficient in the removal bromine. It should be pointed out that the SEM-EDS analysis focused only on the surface of the analysed sample.

3.3. Liquid analysis on the effluent solvents

The liquid analysis of the effluent solvents after the extraction is summarized in Fig. 2. Since the method of analysis focused on only one compound (TBBPA), only results for this specific compound are presented and compared for the different samples and treatments. For the sake of comparison, non linear scale is used. Moreover, the results are also normalised according to the volatile matter percentage of each WEEE sample since TBBPA only exists in the organic part of the tested materials (Area/wt% of volatiles).

The results indicate that TBBPA was successfully extracted from all the examined WEEE samples and for both solvents used. For all examined WEEE fractions there is a clear trend indicating that

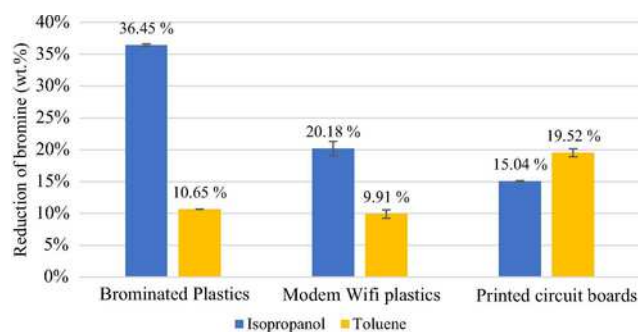


Fig. 1. Reduction of the bromine content based on SEM-EDS analysis of the raw samples and samples treated with isopropanol and toluene.

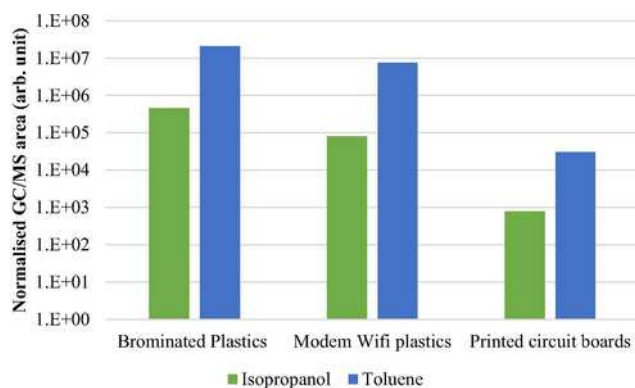


Fig. 2. Liquid analysis of the solvents after the extraction.

toluene is a more efficient solvent for extracting TBBPA compared to isopropanol. This result is also in accordance with Zhong et al. (2012), that also observed interesting results of toluene as solvent for extraction of TBBPA from WEEE. This indicates that even though the chemical characteristics of the solvent play a significant role in the extraction (Vilaplana et al., 2009), the extraction temperature might have further enhanced the extraction of TBBPA from these WEEE fractions.

3.4. Thermogravimetric analysis

The raw and treated WEEE samples were evaluated in a thermogravimetric analyzer. Fig. 3 shows the thermal decomposition behaviour as well as the first derivative curve (DTG) in order to identify the inflection points. Moreover, these curves also indicate the different steps of thermal decomposition.

Based on Fig. 3a, which illustrates the “brominated plastics” fraction, the thermal decomposition of the material was significantly influenced by the solvent extraction treatment. It is clear that the treated samples follow a steeper decomposition, starting at a lower temperature compared with the raw sample. More specifically, toluene’s treated sample seems to shift the decomposition temperature by almost 25 °C lower based on the DTG curve peaks. Therefore, the decomposition delay due to the flame retardant was reduced and the decomposition is initiated at lower temperature. Furthermore, in the same figure (Fig. 3a), the final mass of the samples varies, which is probably because of the organic content that was removed through the solvent extraction process. TBBPA can reach up to 0.26 wt% of acrylonitrile butadiene styrene (ABS) plastic based on the Pivnenko et al. (2017), which can be the case for these samples, since it is a concentrated “brominated plastic” fraction.

Similar effects can be also observed on the “modem wifi plastics” fraction in Fig. 3b. The thermal decomposition indicates that the toluene treated material was highly affected, since the final mass is lower than for the raw sample. This shows, as mentioned for the previous tested fraction, that the organic content was reduced due to the solvent extraction. On the other hand, the influence on the initiation of the decomposition is not so high in terms of temperature, but more in terms of rate, since the decomposition follows also a steeper, more direct trend. This is in accordance with the data acquired by the SEM-EDS. By correlating the results acquired from SEM-EDS and from the effluent liquid, even though the brominated compounds detected were high, reduction of bromine in the soxhlet treatment was poor, as presented in Fig. 1. This shows that the brominated flame retardants might have been in excess on this fraction. Therefore, the

fraction after the solvent treatment may have contained enough bromine in order to disturb the decomposition process.

The fraction of “printed circuit boards (PCBs)” also shows a similar effect on the mass loss, which verifies the hypothesis that several organics were removed through the solvent extraction process. On the other hand, the influence on the thermal decomposition by the solvent extraction was difficult to observe, since the organic content of this fraction is rather low. Moreover, the reduction of the brominated species was not severe based on the results acquired by the pyrolysis experiments.

3.5. Pyrolysis experiments

Numerous organic compounds have been identified from the pyrolysis of WEEE fractions. The pyrolysis of plastic materials produces fragments from their polymeric structure. Therefore, hydrocarbons and aldehydes are usually expected. In terms of waste management, all these compounds can be utilised for production of other chemicals and polymeric materials after a proper separation technology is applied.

During the decomposition of “brominated plastics”, the brominated compound with the lowest molecular weight is hydrogen bromine (HBr), one of the main products found based on similar studies (Wu et al., 2014). Unfortunately, the setup of the GC/MS and this arrangement in general are not suitable for the detection of compounds with such low molecular weights due to the scan range selected based on the method. Therefore, the first peak that is seen in the pyrogram is bromomethane (CH₃Br), which is one of the lightest detectable organic compounds that is derived from the thermal decomposition pathway of the brominated flame retardants. More specifically, it has been detected at the 4.79-min mark according to the method used for the analysis (Evangelopoulos et al., 2015a).

Several brominated species that originate from the TBBPA have been detected in the GC/MS analysis. In all the investigated cases, a clear trend shows that less brominated compounds were produced from the pre-treated samples in comparison to the compounds produced from the raw materials. Table 2 presents the brominated compounds that were found in the pyrolysis products from GC/MS analysis as well as their degree of reduction, compared to the product intensity of the organic compounds produced from the pyrolysis of the raw samples. This result is based on the detected total peak area, and has been normalised based on the mass used for each test. In specific cases, several brominated compounds were not detected at all, referred to as below detection limit (BDL) in the results, which means that the degree of reduction reached 100%. On the other hand, the reduction of TBBPA can influence the kinetics and the pyrolysis products differently. For example, in the cases of the “modem & wifi” fraction treated with toluene, even though all the detectable brominated species were reduced, the bromomethane content increased. This indicates that the decomposition mechanism has changed, producing more bromomethane instead of other brominated compounds.

Based on the reaction mechanisms of pyrolysis of TBBPA, which has been proposed in other studies (Hornung et al., 2003), the removal of the tetrabromobisphenol can minimize the production of brominated species in two different ways. Firstly, since less bromine is present compared to the initial sample, the production of brominated organic compounds is obviously less. Secondly, the ratio of available H radicals and the bromine is higher, which enhance the production of HBr instead of brominated organic compounds of high molecular weight. This explains the fact that the reduction of Br based on the SEM-EDS data is lower compared with the reduction calculated based on the brominated species produced in pyrolysis.

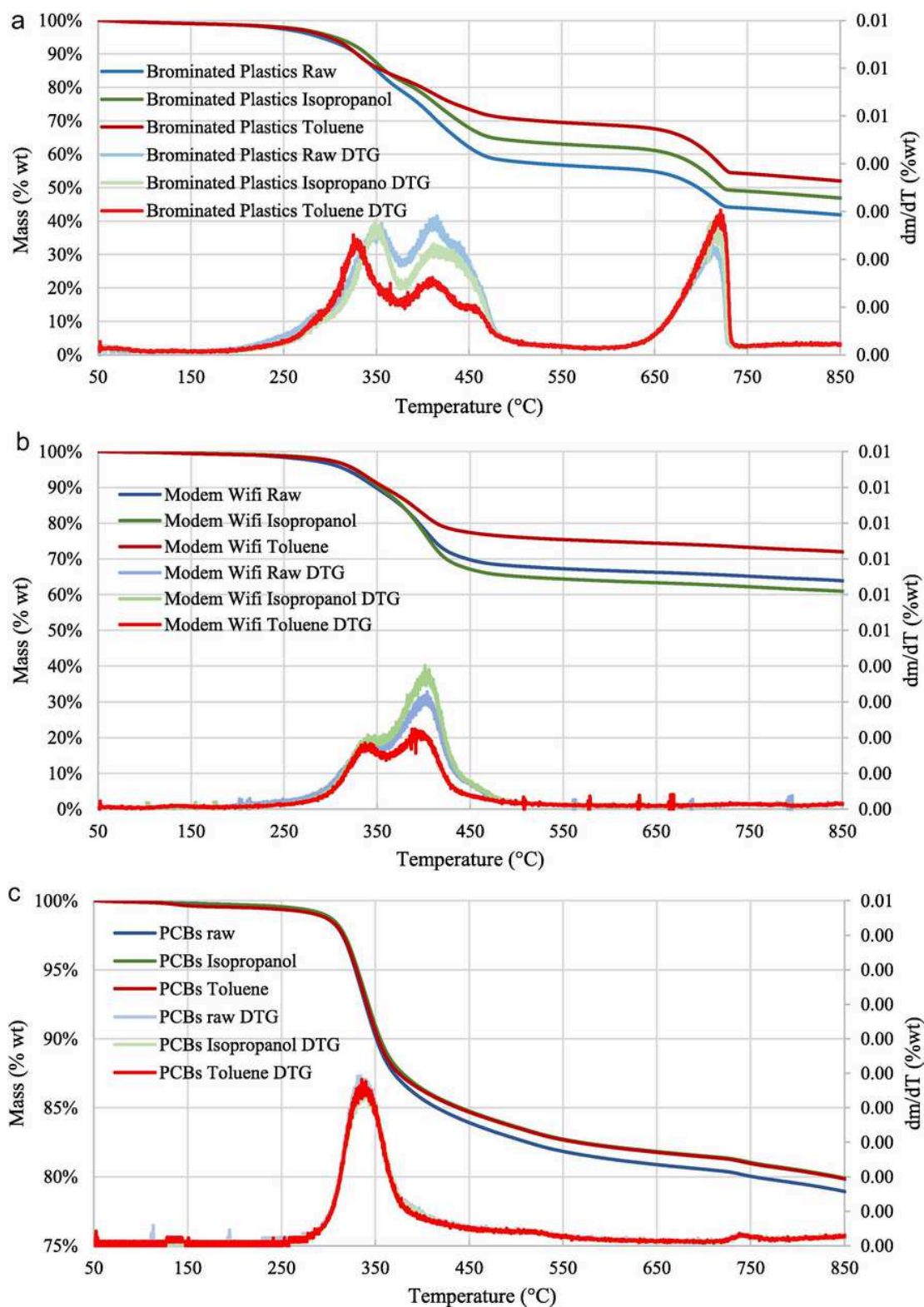


Fig. 3. Thermal decomposition of WEEE plastics for the raw samples, treated with isopropanol and with toluene.

Table 2

Detected brominated compounds on the pyrograms and their reduction based on their area detected.

Brominated compounds	Isopropanol treated (%)
<i>Brominated plastics</i>	
Bromomethane	55.57
TBBPA	24.06
2,4,6 tribromophenol	89.58
2,5-Dibromobenzo(b)thiophene	BDL*
<i>Modem & wifi plastics</i>	
Bromomethane	49.09
TBBPA	77.05
2,4,6 tribromophenol	90.44
Phenol 2,4-dibromo-	95.30
3,5-Dibromobenzo(b)thiophene	83.65
<i>Printed circuit boards</i>	
Bromomethane	54.95
TBBPA	63.17
Phenol 2,4-dibromo-	55.81
Bicyclo[4.2.0]octa-1,3,5-triene,7,8-dibromo-	44.98

* Below detection limit.

4. Conclusions

The removal of bromine from three different fractions of WEEE has been carried out by means of soxhlet extraction. The raw fractions were analysed by elemental compositions in order to verify their bromine content and thereby indicate the presence of brominated flame retardants.

The reduction of the bromine content was evaluated from the SEM-EDS elemental analysis both on the initial material and the treated. Isopropanol seems to be more efficient in terms of removing bromine from the solid material. On the other hand, an insignificant difference on the surface of the material was observed based on SEM microscope images taken. This result is also verified by the analysis on the brominated organic compounds reduction detected on the pyrolysis liquids.

Based on the analysis of the effluent liquid used during extraction that indicates the removal of TBBPA specifically, the toluene seems to be more efficient. Even though toluene is considered to be a toxic solvent, the benefit of recirculating it from the pyrolysis products can improve the economics of such a process and make the materials re-

covery more feasible. Although the degree of removal is relatively low for the chosen experimental conditions, the trend clearly shows that by adjusting other operation parameters, such as time or temperature, the extraction can be improved. Those findings are supported by the liquid effluent solvent analysis, the pyrolysis products analysis and the SEM-EDS analysis.

Finally, the decomposition behaviour of the treated and the raw samples was evaluated by thermogravimetric analysis. Only the fraction "brominated plastics" had substantial removal, which influenced its decomposition path. For the other tested fractions, the removal was not enough to initiate decomposition at a lower temperature, even though there was visible bromine removal on each fractions' mass loss curve.

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