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PYROLYSIS OF WASTE ELECTRICAL AND ELECTRONIC EQUIPMENT (WEEE) FOR RECOVERING METALS AND ENERGY: PREVIOUS ACHIEVEMENTS AND CURRENT APPROACHES

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Abstract

The amount of collected Waste Electrical and Electronic Equipment (WEEE) in Europe is growing about 7 wt.-% per year (2007-2012). It contains a number of economically relevant base, precious and high-tech metals. However, only a limited number of these metals can be recovered by currently applied recycling processes. Especially high-tech metals like gallium, germanium and tantalum get lost during the treatment of WEEE. The pyrolysis technology allows an accumulation of these metals from WEEE-fractions without oxidation as well as the generation of high calorific gases and liquids for energetic utilization. This paper provides a literature based review of lab and medium-scale investigations on pyrolysis processes of different WEEE-fractions like printed wiring boards (PWB) or plastics to outline opportunities and challenges for recovering critical metals from WEEE via pyrolysis. The key procedural challenges are dehalogenation, avoidance of highly-toxic emissions (mainly PBDD/F) as well as preparation and accumulation of metals for recycling processes.

Key words: critical metals, metal recycling, pyrolysis, WEEE

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1. Introduction

The raw material supply of many industrial nations e.g. in the European Union is vulnerable due to fading geogenic reserves or export restrictions and political conflicts in countries of exploration. To enable a continuous and sustainable supply, the recovery of raw materials from secondary resources offers promising potential. Waste Electrical and Electronic Equipment (WEEE) is a source of various metals and polymers but also hazardous substances. WEEE became one of the fastest growing waste streams in the world, especially in industrial nations (Ciocoiu et al., 2013). The amount of collected

WEEE in the EU-27 increased about 7 wt.-% per year (2007-2012) (Eurostat, 2015). Relating to this, the WEEE-directive (2012/19/EU) defines recycling targets referring to a minimum weight of recovered materials, regardless the type of recovered material (EC Directive, 2012). However, WEEE contains a number of different critical elements, whereof many are not recovered yet (Bakas et al., 2014; Buchert et al., 2012; European Commission, 2013).

Against this background, pyrolysis offers the opportunity to enable both, a recovery of these critical elements and an energetic utilization of organic materials. The purpose of this work is to outline the state-of-the-art and challenges of this

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thermo-chemical technology as part of a process chain, to recover metals and energy. The findings of the review will be used to design a pyrolysis process, which is focused on the recovery of critical metals, whose end-of-life recycling rates from WEEE are less than one percent.

2. Waste Electrical and Electronic Equipment – WEEE

2.1. Amount and composition of WEEE

In the year 2012 the total amount of WEEE collected in the EU 27 was about more than 3.5 Mio. tons (Eurostat, 2015). An average composition of WEEE is shown in Fig. 1 (Eurostat, 2015; Haig et al., 2012; Reuter et al., 2013). Beside base metals like Fe, Al and Cu, WEEE mainly consists of different plastics like acrylonitrile-butadiene-styrene (ABS), polystyrene (PS), polycarbonate-ABS (PCABS),

polyethylene (PE), polyvinyl chloride (PVC), styrene acrylonitrile (SAN) or ethylene-propylene-diene monomer (EPDM). In addition to these main components, WEEE contains a number of precious and critical metals. Bakas et al. (2014) reported the amount of critical metals contained in waste mobile phones, laptops (both including batteries), computers and flat-screens in the EU for 2010.

Fig. 2 shows that the amount of some critical metals contained in these WEEE holds the potential for covering a considerable part of the demand of these metals in the EU: The percentages indicate that between 0.5 wt.-% (W) and up to 17.5 wt.-% (Co) of the total metal-demand in the EU could be supplied by WEEE. This quantity amounts to about 2,000 tons per year. According to current market data, the amount of Pd and Co in WEEE equals a value of 215 Mio. € (Bakas et al., 2014; European Commission, 2013; Johnson Matthey, 2012; Mineralprices.com, 2014).
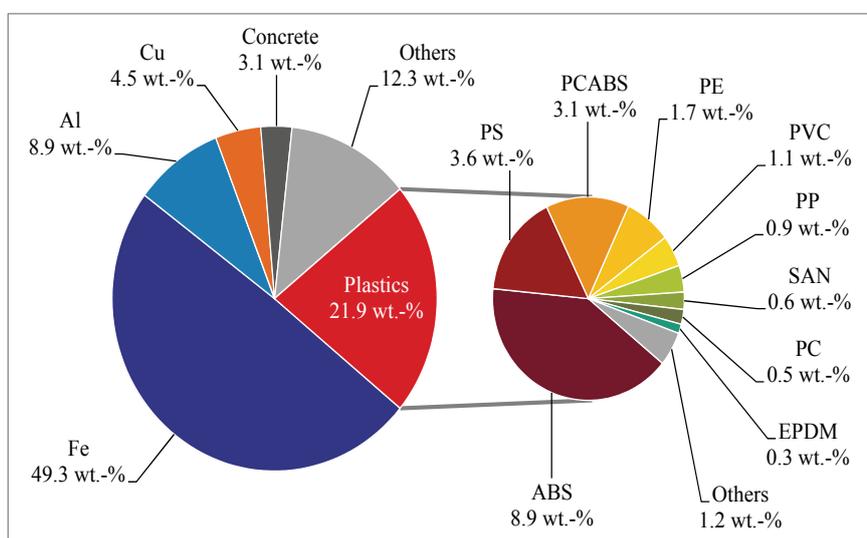

Fig. 1. Average composition of collected WEEE in the European Union for 2012 (without categories 5, 8, 9, 10; composition stands for 98.6 wt.-% of all WEEE collected) (Eurostat, 2015; Haig et al., 2012; Reuter et al., 2013)
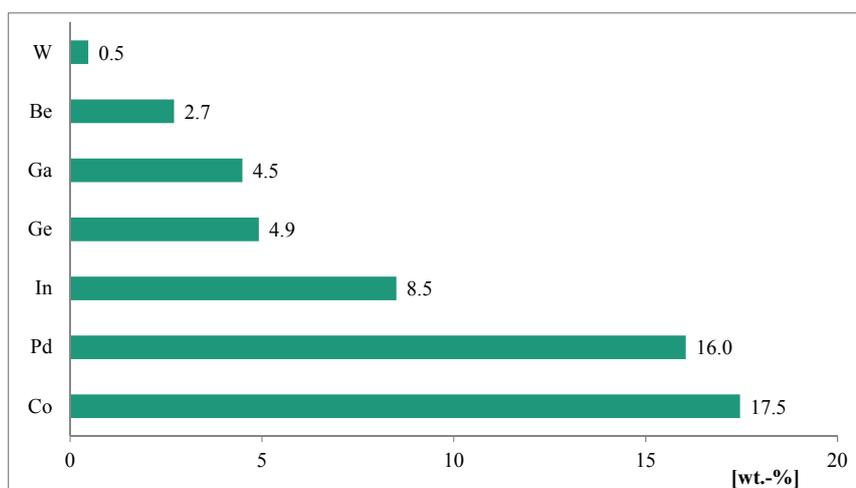

Fig. 2. Ratio of critical metals contained in waste mobile phones, laptops (both including batteries), desktop computers, and flat screens and the total demand for these metals in the EU (2010) (Bakas et al., 2014; European Commission, 2013; Johnson Matthey, 2012)

Next to plastics and metals, there are also components that cause problems in recycling processes. Generally, about one quarter of plastics from WEEE contain flame retardants (Eionet, 2013), of which one third are based on halogens (EFRA, 2007). However, the amount of halogens in plastic fractions from WEEE could reach up to 10.9 wt.-% Br (Hall et al., 2008) and 57.8 wt.-% Cl (Ma et al., 2002). Since the use of selected brominated substances as flame retardants, namely poly-brominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE), is limited in EU countries by Directive 2011/65/EU on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS) (EC Directive, 2011), alternative materials, mainly phosphorous- or nitrogen-based, were developed. However, the production of halogenated flame retardants still increases. Most are combined with inorganic compounds like aluminum or magnesium hydroxide ($Al(OH)_3$, $Mg(OH)_2$) and antimony trioxide (Sb_2O_3). For example, the amount of Sb in brominated ABS and high-impact polystyrene (HIPS) is in between 3.2 wt.-% and 4.6 wt.-%, respectively. Sb_2O_3 acts as synergist in the condensed as well as the gaseous phase of a flame (EFRA, 2007). In addition, decomposition products of Sb_2O_3 are catalysts for recombination of hydrogen, hydroxyl and oxygen radicals (Lewin, 2001; Dettmer, 2001).

Thermal decomposition on halogenated flame retardants can cause the formation of highly toxic and persistent polycyclic aromatic hydrocarbons (PAH), polyhalogenated aromatic hydrocarbons (PHAH) as well as dioxins and furans like polybrominated dibenzo-p-dioxins and furans (PBDD/F) (Reuter et al., 2013). The formation starts under presence of oxygen and is catalytically increased by presence of heavy metals, mainly copper and its oxides (Dettmer, 2001; Sakai et al., 2001). Dibenzo-p-dioxins and furans (PCDD/F) and PBDD/F are mainly formed in a temperature range between 260 °C and 430 °C (heating phase) and between 250 °C and 450 °C (cooling phase) (Dettwiler et al., 1997). Therefore, these temperature ranges should be skipped as fast as possible to prevent the formation of these toxic substances. Applying a pyrolysis temperature above 850 °C leads to decreased total yield of PCDD/F and PBDD/F (Lai et al., 2007). In general, most of these substances are absorbed by solid residues like char and just a small amount can be found in flue gas (Lai et al., 2007). This may be related to the high molecular weights and low vapor pressure of PCDD/F and PBDD/F (Birnbaum et al., 2003).

2.2. Status Quo of WEEE-treatment

In most industrialized countries, state-of-the-art initial treatment of WEEE is a combination of different mechanical processes and physical and / or optoelectronic separation systems. Usually, this treatment starts with a manual dismantling, followed by shredding and separation, for example with magnetic, eddy-current or infrared systems. Heterogeneous fractions like mixed plastics can be further split into halogenated and non-halogenated plastics with optoelectronic systems (Husemann et al., 2010). Recovered fractions like non-halogenated plastics or metals are handed over to recycling processes to recover secondary raw materials, while hazardous materials like halogenated plastics are usually landfilled or incinerated. Metal-rich WEEE like mobile phones or components like printed wiring boards (PWB) are given to pyrometallurgical plants to recover metals and to use the plastics as energy source and reduction agent. Modern processes in the copper industry are able to recycle up to 17 metals (Hagelüken and Corti, 2010), however limited to base and precious metals. The recycling usually starts with a smelter process, in which critical metals like Be, Ga, Ge, Nb, W and a number of Rare Earth Elements (REE) contained in WEEE oxidize and become slagged due to their ignoble character (Bakas et al., 2014; Kumar et al., 2014). Due to this, the end-of-life recycling rates of most critical metals from WEEE are less than one percent (Bakas et al., 2014; Buchert et al., 2012; Graedel et al., 2011).

3. Pyrolysis of WEEE: Review of previous achievements and current approaches

In pyrolysis processes, organic compounds are degraded in an inert atmosphere. Due to this, contained metals are not oxidized during the thermo-chemical process. Pyrolysis can be operated under different conditions mainly based on temperature, heating rate or dwell time, depending on the input material and desired product quantities and qualities.

Some of the previous achievements in the pyrolysis of WEEE are successfully handled already by mechanical or pyrometallurgical treatment of WEEE; that is why they are not further pursued in this paper. For example, an issue of achievements was pyrolysis of PWB (Williams, 2010). However, as mentioned above, PWB could efficiently be recycled in copper smelting processes, as far as the recycling of base and precious metals is concerned (Hagelüken and Corti, 2010).

Due to the described increasing demand for critical elements (chapter 1) a promising future application of pyrolysis can be the separation and recovery of critical metals, which are not recycled, yet. A pyrolysis process could become part of a process chain to separate critical metals and to generate fuels with low yields of halogens for an energetic utilization. Products of this thermo-chemical process would be (1) a mixture of certain metals, (2) a char-metal mixture, which could be treated in copper processes, as well as (3) calorific gas and oil for an energetic utilization, e.g. in a combined heat and power (CHP) plant. This energetic utilization of pyrolysis oil and gas is an

appropriate option, because these products can present fuels with heating values, which are often comparable to conventional fuels like diesel fuel (41.8 MJ·kg^{-1}) or natural gas (CH_4: 35.9 MJ·m^{-3}) (Bauforumstahl, 2015).

Results from a review of different papers, which present heating values of pyrolysis oils and gases from WEEE plastics, PWB or other materials from WEEE, are shown in Table 1. From the results it can be seen that the ranges of this values are between 26.5 and 44.8 MJ·kg^{-1} for liquid products and between 12.3 and 48.6 MJ·m^{-3} for gaseous products. However, there is currently no paper presenting a closed energy balance for all pyrolysis products (solids, liquids and gases) from WEEE or WEEE plastics.

The following sections of this chapter give an overview on how pyrolysis processes are influenced by the main parameters temperature, heating rate, residence time, operation mode (one- vs. two-stage), and additives as well as the influence of these parameters on quality and quantity of pyrolysis products and emissions. The first section (3.1) describes current achievements in thermal decomposition of halogenated plastics from WEEE with and without additives. Section 3.2 shows different approaches to dehalogenate pyrolysis products. The last part (3.3) focuses on those reactions between bromines and metals, which are relevant for a recycling of mainly ignoble critical metals, to achieve optimal results regarding the enrichment of these high-tech-metals.

Table 1. Pyrolysis product yields and corresponding heating values for different input materials at given pyrolysis temperatures

Input material	Pyrolysis temperature	Pyrolysis product yields[1]		Heating values (*LHV; **HHV)		Reference
	[°C]	[wt.-%]		[MJ·kg^{-1}]	[MJ·m^{-3}][2]	
Plastics						
from WEEE containing Cathode Ray Tubes	600	S:	14.5	---	---	Hall and Williams (2007a)
		L:	83.9	---	---	
		G:	1.4	37.4*	48.6*	
from refrigeration equipment	600	S:	20.4	---	---	Hall and Williams (2007a)
		L:	76.5	---	---	
		G:	3.0	29.5*	28.2*	
from mixed WEEE	600	S:	21.1	---	---	Hall and Williams (2007a)
		L:	70.6	---	---	
		G:	7.8	11.9*	18.2*	
PWB						
from Computers	500	S:	78.0	---	---	Jie et al. (2008)
		L:	9.1	---	---	
		G:	12.9	58.8*	21.2*	
from Computers	800	S:	68.9	---	---	Hall and Williams (2007b)
		L:	22.7	---	---	
		G:	4.7	16.6*	13.4*	
from Televisions	800	S:	60.0	---	---	Hall and Williams (2007b)
		L:	28.5	---	---	
		G:	6.5	17.5*	16.6*	
from Mobile Phones	800	S:	82.2	---	---	Hall and Williams (2007b)
		L:	15.2	---	---	
		G:	2.3	16.2*	12.3*	
Mixture	500	S:	76.5	---	---	de Marco et al. (2008)
		L:	16.2	26.5**	---	
		G:	7.3	---	---	
Mixture	500	S:	37.0	---	---	Chiang et al. (2010)
		L:	39.0	35.6 - 39.8*	---	
		G:	24.0	---	---	
Others						
PE-Wires[3]	500	S:	32.9	---	---	de Marco et al. (2008)
		L:	44.1	44.8**	---	
		G:	23.0	---	---	
Table Phones[4]	500	S:	34.4	---	---	de Marco et al. (2008)
		L:	53.5	37.9**	---	
		G:	12.2	---	---	
Mobile Phones[4]	500	S:	30.3	---	---	de Marco et al. (2008)
		L:	57.4	34.2**	---	
		G:	12.3	---	---	

[1]*S: Solid products, L: Liquid products, G: Gaseous products; [2]Heating values in MJ·m^{-3} were calculated under standard conditions (0 °C and 1,01325 bar); [3]PE-rich fraction after conventional removing of Al und Cu by Flotation; [4]Waste streams after grinding and separation of magnetic parts from table and mobiles phones, respectively*

3.1. Behavior of halogenated compounds in pyrolysis processes

In order to reach the aims of metal accumulation and fuel generation from WEEE, a fundamental understanding of chemical reactions in pyrolysis processes is necessary. The following part of this chapter describes these reactions for plastics and polymers with additives like halogenated compounds, mainly tetrabromobisphenol A (TBBPA), and Sb_2O_3. The reaction behavior of halogens and Sb_2O_3 is important for both metal accumulation and fuel generation, because due to the reactions, metals can be lost and fuels can contain Sb or halogens, which could cause problems in an energetic utilization.

To understand different decomposition ways of BFR, Marongiu et al. (2007) developed a detailed kinetic model for the decomposition of TBBPA in a pyrolysis process. They showed four representative reaction classes: initiation, propagation, molecular and termination reactions. An increase of process temperature or duration time let debromination start with a release of Bisphenol A as well as HBr and later phenol. By a further increase of temperature or time, larger organic compounds and later char are produced, while CH_4 and CO are emitted.

Similar, but quantitative results were published by Grause et al. (2008). They investigated the pyrolysis behavior of TBBPA containing paper-phenol resin laminated PWB. Thermal gravimetric analyzes (TGA) in a temperature range between 40 and 1000 °C and degradation experiments in a temperature range between 50 and 800 °C were performed. It was possible to characterize the Br-products generated during different temperature levels. Three levels in which the samples degraded where found. In a first step, with a maximum at 272 - 280 °C, H_2O and CO_2 evaporated from decomposition of cellulose. During the second step (270 - 370 °C) the contained fire retardants degraded by forming Br-products. The production of HBr, as main product from decomposition of BFRs, proceeded in a temperature range between 270 and 500 °C and was characterized by two single peaks, located at 305 °C and 398 °C. During the third step, beginning with a temperature of 370 °C, phenol resins were decomposed and char was formed. The generation of brominated aromatic compounds took place just in a temperature range between 270 and 400 °C. Above 400 °C, Br-products were formed primarily as HBr, so that phenol products generated at 450 °C showed a low concentration of Br. Therefore it was concluded, that a pyrolysis at 450 °C produces mainly HBr, which is easily separable in a water trap, and just a small yield of brominated aromatic compounds, which could act as precursors for the generation of PBDD/F (Marongiu et al., 2007).

As mentioned above, BFR are often applied in combination with metal oxides like Sb_2O_3, which act as synergist. Depending on the temperature during thermal treatment of fractions of WEEE, various Me_x-X_y-Br_z-compounds are formed. These reactions are an interesting aspect concerning pyrolysis processes as part of a recycling chain for recovering metals from WEEE. On the one hand, due to Br-fixation reactions, metals could vaporize as Me_x-X_y-Br_z-compounds and become enriched in the liquid or gaseous phase. On the other hand, the presence of metals and metal oxides could influence the production of brominated compounds which could act as precursors for the generation of PBDD/F (Marongiu et al., 2007). As an example Bhaskar et al. (2002) revealed that HIPS containing both Sb_2O_3 and decabromodiphenylene ethers (deca-BDE) produces dioxins at a temperature of 275 °C. To figure out the reaction behavior of Sb-oxides, mainly Sb_2O_3, Jakab et al. (2003) investigated the thermal decomposition of HIPS with BFR, whereat selected samples contained Sb_2O_3. They presented, that the thermal decomposition of PS was not affected by presence of BFR. PS decomposed mainly in one single peak at about 440 °C. In contrast, the thermal decomposition of PS with addition of 5 wt.-% Sb_2O_3 took place in two single peaks at approximately 370 °C and 440 °C. As suggested by Luijk et al. (1991), pyrolysis tests at 420 °C confirmed that Br vaporized during the first stage of decomposition in form of $SbBr_3$ and different brominated organic compounds. Rzyman et al. (2010) pyrolysed TBBPA and Sb_2O_3 up to a temperature of 650 °C and quantified the yield of $SbBr_3$. Between 440 and 650 °C the maximum yield of $SbBr_3$ (above 60 wt.-%) vaporized. Due to a further increase of temperature above 650 °C, the reduction of Sb_2O_3 started with the result that Sb remained in the solid residue as elementary Sb. Bhaskar et al. (2007) and Mitan et al. (2008) treated samples of mixed brominated plastics, with and without adding Sb_2O_3 in a two-stage pyrolysis at 330 °C, for two hours, and 430 °C, till the end of the experiment. Sb_2O_3 mainly reacted with Br by forming $SbBr_3$, which was identified just in oils from the first pyrolysis stage but not in those from stage two. A small yield of Sb was found in the residue. By adding Sb_2O_3, the yield of oil from stage one was highly increased, whereas the yield of step two oils decreased slightly. Also, there was a slight increase of gas yield and a high increase of solid residues. The results revealed that in a pyrolysis of brominated plastics degradation takes place in three steps while at 450 °C mainly HBr and just a small amount of brominated aromatic compounds are formed. However, due to the presence of metal oxides both levels of degradation and Br containing products as well as the yield of solid, liquid and gaseous products can vary.

3.2. Dehalogenation

Dehalogenation of pyrolysis products is one of the main topics concerning thermo-chemical

treatment of WEEE. The subject summarizes methods and techniques to gain pyrolysis products with low yields of halogens and to reduce toxic emissions as much as possible. Only if the pyrolysis products have low yields of halogens, they can be utilized appropriate. For example, in order to apply produced liquid fuels in a CHP for the production of power and heat, a considerably low content of halogens has to be ensured.

There are several ways for dehalogenation, which could be classified as (1) separation of pyrolysis and dehalogenation, (2) the use of additives in a co-pyrolysis, and (3) procedural approaches as well as combinations of these three ways. In a co-pyrolysis not only WEEE is thermally treated but also other waste materials or additives. An example for the first mentioned approach is the "Pyromaat" process, which was developed to recover Br from WEEE in a process combination of pyrolysis and gasification. The pyrolysis runs at 550 °C for a minimum of 15 minutes. The produced char-metal mix was used as feedstock for pyrometallurgical processes. The uncondensed gas fraction was lead through a high temperature gasifier at 1230 °C to crack tars and to produce a syngas. The syngas is cleaned by a NaOH-scrubber to remove and recover halogens as NaBr / NaCl. The remaining syngas is used in a combustion chamber, where NH_3 is injected as neutralization agent for remaining halogenated compounds. Halogens from the input material volatilized as HBr / HCl, Br_2 / Cl_2 and, in connection with Sb_2O_3, as different halogenated Sb-compounds, which hydrolyze to Sb_2O_3 in the scrubber. The described process was able to recover up to 96 wt.-% of Br and 97 wt.-% of Cl (Boerrigter et al., 2002).

The use of biomass as an additive is another approach for dehalogenation and prevention of PBDD/F. Liu et al. (2013) performed a co-pyrolysis of plastics from WEEE and biomass. Adding biomass to the pyrolysis of WEEE seems to prevent the formation of PBDD/F due to a high amount of hydrogen, which leads to a formation of HBr / HCl. However, to increase the amount of hydrogen in the feedstock, hydrogen-rich waste plastics like PP could be added to receive the same results (Hornung et al., 2005).

A two-stage pyrolysis, with or without additives, is the third option to reduce the amount of halogens, mainly in the pyrolysis oil. It is based on the different temperature dependencies of thermal degradation of polymers and flame retardants. Bockhorn et al. (1998) and Ma et al. (2002) described this degradation behavior for chlorinated, Hornung et al. (2003) and Jakab et al. (2003) for brominated polymers. However, due to the composition of the feedstock and the use of additives, there could be different levels of thermal degradation. The following sections will give a brief overview at which temperatures thermal degradation of BFR containing plastics takes place and how thermal decomposition is affected by additives like calcium compounds or BFR synergists like Sb_2O_3.

Bockhorn et al. (1999) investigated the thermal degradation behavior of halogenated plastics, mainly PVC, and showed that dehydrohalogenation takes place at lower temperatures than the degradation of thermoplastics. Due to this, they estimated that a separation of pyrolysis products in fractions containing halogens and halogen free fractions could be possible, corresponding to the two degradation stages. They developed a two-stage process, called Haloclean®, that was operated at 350 (first stage) and 450 °C (second stage) under nitrogen atmosphere. However, it could not be shown that the process is able to produce halogen-free oil, but in comparison to other process parameters, with the two-stage pyrolysis at 350 and 450 °C for two hours each, the lowest yields of PBDD/F in the solid residues could be achieved (Koch, 2007). Later the process chain was successfully upgraded with a downstream polypropylene-reactor, to clean the oil from halogens and to produce HBr (Hornung et al., 2007).

Zhu et al. (2008) examined the decomposition of PVC samples with different Ca-based additives ($CaCO_3$, CaO, $Ca(OH)_2$) by TGA. Ca is an effective additive to capture hydrogen-halogen compounds, mainly HCl and HBr, in the solid residue as $CaCl_2$ / $CaBr_2$. The degradation of PVC took place between 280 and 400 °C with a maximum at 320 °C as well as between 400 and 560 °C with a maximum at 482 °C. HCl was released in the first stage, hydrocarbons in the second one. Without additives, Cl was completely found as HCl after degradation. By adding Ca-based additives, the yield of HCl decreased while the yield of $CaCl_2$ increased. To use the tested Ca-based additives as agents to achieve less HCl in the pyrolysis products, Ca/Cl molar ratios of 1.5 for $Ca(OH)_2$, 1.5-2.5 for CaO and 2.6 for $CaCO_3$ were recommended. To enhance the efficiency of dehalogenation by a Ca-based additive, Bhaskar et al. (2002, 2004) formed a Ca-C catalyst by kneading, molding and calcination of a mixture of $CaCO_3$ and phenol resin. Pyrolysis tests of a plastic-mixture containing Cl and Br were performed at 430 °C and revealed that the tested catalyst seemed to be very effective: without catalyst, pyrolysis oils contained a minimum of 0.49 wt.-% of Br and 0.12 wt.-% of Cl. In contrast, oils from a pyrolysis test with 20 - 80 wt.-% of Ca-C catalyst contained a maximum of 0.07 wt.-% of Br and 0.01 wt.-% of Cl. Due to the addition of the catalyst, the yield of liquids and solid residues decreased while those of gaseous products increased. In addition, the composition of the liquid products changed: the yield of C_6-C_{10} hydrocarbons increased highly by 50 wt.-% and the yield of C_{11}-C_{15} hydrocarbons slightly, but higher hydrocarbons (C_{16}-C_{20}) decreased significantly. Similar results were published by Mitan et al. (2007), who tested different catalysts during thermal degradation of HIPS-Br and ABS-Br at 450 °C. It was concluded that a combined catalytic system based on folded sheet mesoporous silica (FSM) and a "calcium to carbon composite" offers low concentrations of Br, N and O in the oil

and the highest quantities of oil and gas with mainly short-chained hydrocarbons. These results, obtained by Bhaskar et al. (2002, 2004) and Mitan et al. (2007), reveal that a process with an effective dehalogenation by additives is able to produce fuels with good quality concerning energetic utilization (low amounts of metals, halogens, N, O and higher hydrocarbons ($>C_{16}$)). Using other additives like red mud or calcined limestone can present another option to decrease the parameters of Br- and Sb-yields. Wu et al. (2014) conducted pyrolysis tests at 500 °C with HIPS containing BFR and Sb_2O_3 in addition with red mud, calcined limestone or natural zeolite at a ratio of 5 to 1. Mainly by adding red mud or limestone, the content of Sb and Br in pyrolysis oils decreased significantly between 72 and 81 wt.-% for Sb and between 88 and 90 wt.-% for Br, respectively.

The effectiveness of two-stage pyrolysis processes for dehalogenation is strongly affected by the composition of the input material. Tests by Blaszo et al. (2002) revealed that the effectiveness decreases e.g. for PWB. Experiments with PWB-samples consisting of brominated phthalic polyester and ceramic fibers were conducted at 450 and 600 °C for 20 seconds each. The authors recommended that the decomposition of the contained flame retardant bisphenol A was not successful by two-stage pyrolysis. Furthermore, pyrolysis tests with different additives (CaO, ZnO, Na_2CO_3, Na_2SiO_3, NaOH and two kinds of molecular sieves (5A and 13X)) were performed to identify relative amounts of CH_3Br as well as Br- and Br_2-phenols. Concerning matters of health, safety and product utilization, the quantity of these products is crucial. For instance, CH_3Br is hardly inflammable, potentially explosive and toxic (Sigma Aldrich, 2014). An increased yield of CH_3Br occurred after the addition of molecular sieve 5A, ZnO and NaOH. The addition of CaO or ZnO resulted in an increased yield of Br- and Br_2-phenols, whereas all other kinds of additives, mainly NaOH and Na_2SiO_3, caused a decreased yield.

The most significant reduction of CH_3Br, Br- and Br_2-phenols was observed after the addition of molecular sieve 13X as well as after the addition of Na_2SiO_3 (Fig. 3). These results revealed that the use of molecular sieve 5A, ZnO or NaOH is disadvantageous while that of molecular sieve 13X or Na_2SiO_3 seems to be advantageous. Further analyses on the formation of other brominated compounds, mainly HBr, molecular bromine (Br_2) and brominated metals, are necessary to figure out which additives have the most promising effects.

3.3. Halogen fixation with metals and metal oxides

As shown in the previous part 3.2, a number of scientific papers deal with the co-pyrolysis of plastics from WEEE with metal oxides or silicates. One of the main reasons for the application of additives is to bind halogens as Me_xX_z or $Me_xO_yX_z$. Concerning the recycling of mainly ignoble critical metals, the reactions are relevant to understand vaporization of these metals from the solid residue into the condensable phase. The following section focuses on the halogen fixation with metals and metal oxides in pyrolysis processes.

Alston and Arnold (2011) operated pyrolysis tests at 800 °C with two different mixtures of plastics, both typically used in EEE. One of these samples contained an amount of 11.4 wt.-% Cl, mainly from PVC and 6.7 wt.-% Ca, mainly in form of $CaCO_3$, which serves as a filler material in PVC-plastics. The yield of potential fuels was about 72.0 wt.-% (45.5 wt.-% permanent gases and 27.8 wt.-% oils including tars). The authors presented an interesting aspect on bromine fixation: the amount of Cl and Ca in the solid residue was much lower than in the input material. In addition, only a small amount of Cl and no Br was detected in the liquid phase. The authors suggested that Cl reacted with $CaCO_3$ by forming water-soluble $CaCl_2$, which could be removed in a water-trap.
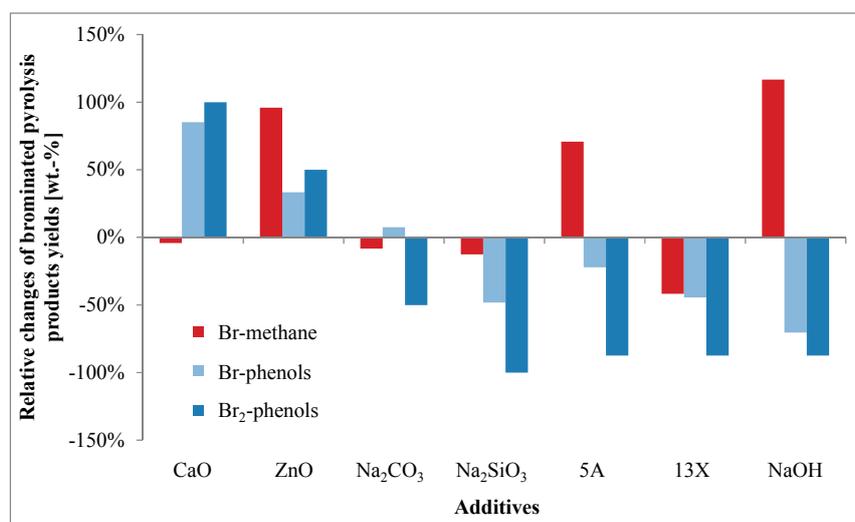
Fig. 3. Relative changes of brominated pyrolysis products yields (Br-methane, Br-phenols and Br_2-phenols) in relation to the yields without additives (Blazsó et al., 2002)

Grabda et al. (2009, 2011) investigated a stoichiometric mixture of ZnO and TBBPA (3.34:1). The impact of temperature and process duration on the formation and vaporization of $ZnBr_2$ has been examined. The tests clearly revealed that the diffusion of $ZnBr_2$ significantly depends on dwell time. At even higher temperatures of 850 °C and above, a deoxidation process of $ZnBr_2$ into elementary Zn took place with char reacting as reductive while CO and CO_2 were formed.

Further studies on Br-fixation reactions by metal oxides are published by Terakado et al. (2011, 2013). In the first examination they compared the Br-fixation ability of ZnO, Fe_2O_3, La_2O_3, CaO und CuO during the thermal degradation of TBBPA. Both TGA and pyrolysis experiments were carried out at 400 °C and 800 °C under He-atmosphere with mixtures of 1:1 for Fe_2O_3 and 1:2 (TBBPA : metal oxide) for all other oxides. Similar to those results of Grause et al. (2008) (chapter 3.1), the amount of HBr strongly increased at higher temperatures, regardless the presence of metal oxides. In case of pure TBBPA, about 90 wt.-% of Br was formed as HBr at a process temperature of 800 °C. The addition of metal oxides decreased the amount of HBr by minimum 30 wt.-% (CuO) and maximum 99 wt.-% (La_2O_3). To take a look at other WEEE fractions, Terakado et al. (2013) examined the Br-fixation ability of metal oxides using PWB as feedstock material. Fe_2O_3 showed similar suppressive effects on HBr formation like with the TBBPA as a feedstock. However, the impact of CaO and La_2O_3 decreased while the impact of CuO and ZnO increased. The authors explained the

reduced effect of CaO by deactivation reactions with glass fibers contained in PWB, e.g. due to the formation of Ca-silicates. With respect to the yield of precursor compounds of PBDD/F, due to the addition of ZnO no bromophenols were formed. Furthermore, the addition of metal oxides led to an enhanced yield of CO_2 in the pyrolysis gas and of heavy metals in the solid residue. Heavy metals, especially Cu, act as catalyst during the formation of PBDD/F (Dettmer, 2001; Sakai et al., 2001).

Oleszek et al. (2013a) investigated the distribution of Cu, Ag and Au in a mixture with TBBPA and TTBPA-TBBPA-diglycidyl ether copolymer (TTDE) at different temperatures between 320 and 1000 °C. Pyrolysis of mixtures with TTDE delivered the following results: at 370 °C, about one quarter of Cu was brominated. At 600 °C, more or less half of the present Cu and Ag was brominated and, in case of Cu, a very small amount of CuBr / $CuBr_2$ was vaporized (0.4 wt.-%). Due to a further increase of temperature up to 1000 °C, more than one third of Cu and Ag was vaporized as MeBr, whereas Au did not react with Br. The study points towards fixation of Br in form of metal bromides, which explains the translocations of metals in WEEE pyrolysis. Two further studies by Oleszek et al. (2013b, 2013c), dealing with pyrolysis of TBBPA-Fe_2O_3 and TBBA-PbO mixtures, delivered similar results concerning metal bromination. The results from the different tests concerning reactions of metals and metal oxides with brominated compounds TTDE (Cu, Ag) and TBBPA (PbO, Sb_2O_3, ZnO) are shown in Fig. 4.
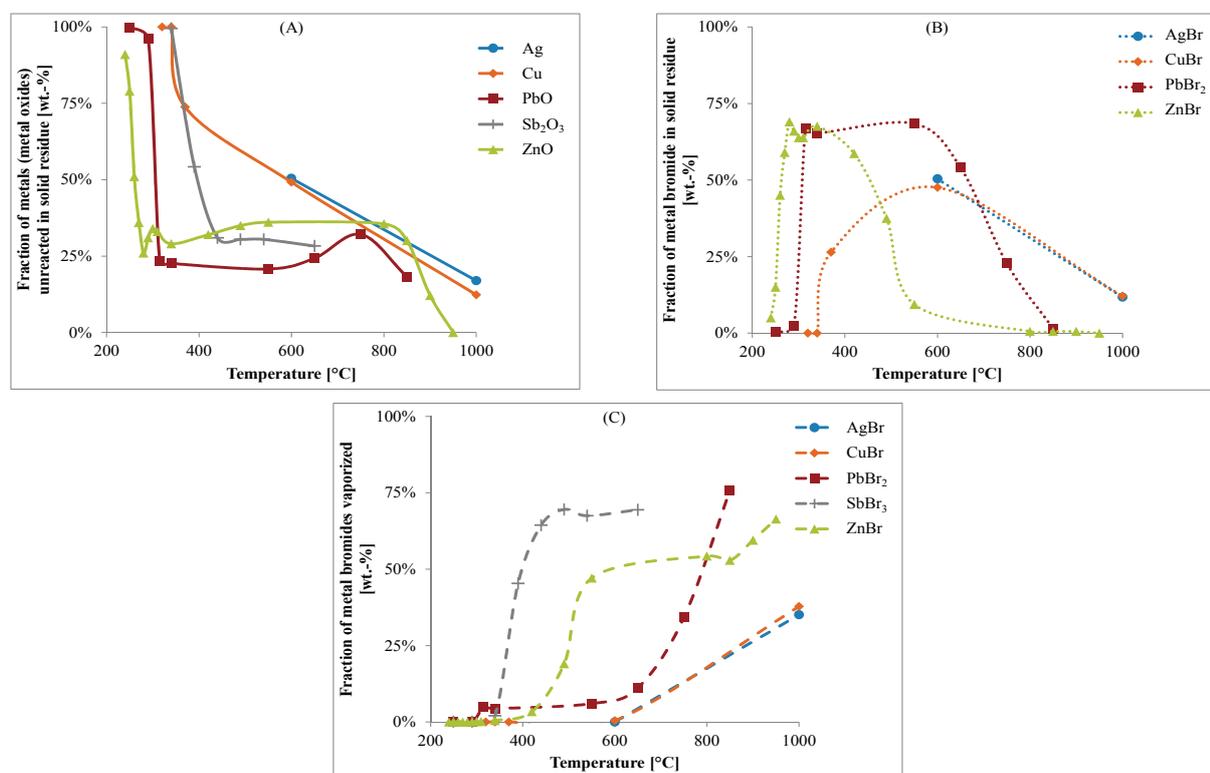

Fig. 4. Fractions of metals (metal oxides) unreacted in solid residues (A), metal bromides in solid residues (B) and metal bromides vaporized (C) (Grabda et al., 2009, 2011; Oleszek et al., 2013a, 2013c; Rzyman et al., 2010)

The available results from literature so far suggest that pyrolysis temperatures below 600 °C do not affect vaporization of (brominated) copper and precious metals. However, less noble metals like Sb, Pb or Zn become brominated, and increasingly vaporize with a rise of temperature and dwell time. After being separated, either from the liquid and gaseous phase or from the fly ash, these metals can be subjected to special electrochemical recycling processes for further treatment. However, the investigations also revealed that the better part of metals does not vaporize in pyrolysis processes. Due to char in the solid residual fraction, metal oxides usually become deoxidized, so that remaining metals may easily be separated by density slicing. Further analyses on different metals to identify their reaction behavior with halogens in a pyrolysis process are necessary.

4. Conclusions and outlook

WEEE contains a number of economically relevant metals like Cu and precious metals, and also critical metals such as Ga, Ge and a number of REE. However, the end-of-life recycling rates from WEEE are low and sometimes even less than one percent. Pyrolysis of WEEE-fractions offers the opportunity to separate valuable metals from plastic matrixes and to produce liquid and gaseous fuels at the same time. The process could represent a main part in a more comprehensive process chain to separate organic matter on the one hand and different fractions enriched with metals on the other hand. These metal fractions can be further sorted and subjected to specialized electro- and pyrometallurgical post treatment. The key procedural challenges for such a process chain are dehalogenation, avoidance of highly-toxic emissions (mainly PBDD/F) as well as preparation and accumulation of metals for the specialized recycling processes.

To design this process chain, temperatures between 250 °C and 450 °C should be avoided to prevent the formation of PBDD/F. Br has to be captured either as evaporating compound, mainly in the form of HBr or $SbBr_3$, or in the solid phase in the form of metals as metal bromines. To achieve a translocation of Br as HBr with only low amounts of brominated aromatic compounds, pyrolysis should be operated in a temperature range between 450 and 500 °C. The water-soluble brominated products HBr and $SbBr_3$ could easily be captured by downstream H_2O- or NaOH-filters. At lower temperatures, predominantly brominated organic compounds, with mainly brominated phenols, are formed. They could act as precursor substances for the formation of PBDD/F. Other options for dehalogenation were presented, which could be advantageous for dehalogenation of remained Br and Cl. Two-stage pyrolysis shows a good way in case of selected Cl or Br containing plastics. However, in a mixture consisting of plastics and other compounds like

PWB, metals and ceramics, dehalogenation by two-stage pyrolysis did not show the desired success. In this case, thermal decomposition of plastics took place in two or more peaks with the negative effect that not only oil from the first pyrolysis stage contained halogens but also that oil from the second stage. Another option for dehalogenation is to capture halogens as part of the solid residue, e.g. by Na- or Ca-based additives. Mainly Na_2SiO_3, $CaCO_3$ and Ca-C composites seem to be very effective to fixate Br as NaBr or $CaBr_2$, respectively.

Furthermore, investigation of the quality of pyrolysis oils is necessary in respect to energetic utilization. Due to the addition of a Ca-C catalyst, for example parameters characterizing the quality of produced oil were optimized, mainly because the amount of higher hydrocarbons strongly decreased while the amount of smaller ones ($<C_{10}$) increased. In addition, more analyses has to be conducted concerning the quantity of all remaining Br-compounds HBr, Br_2, Br-phenols, brominated metals and toxic compounds like CH_3Br, since the process configuration loses its merit, if on the one hand most Br is captured as $CaBr_2$, but on the other hand the yields of hazards like CH_3-Br increases.

From a practical point of view, the obtained findings suggest that the pyrolysis technology offers an opportunity for recovering metals and energy from WEEE. Actually an accumulation of base and precious metals is still possible without using additives. However, concerning the recovery of critical metals a co-pyrolysis with different additives should be tested, in order to capture halogens before they could react with this kind of metals. In this context especially further analyses on different metals are necessary to identify their reaction behavior with halogens in a pyrolysis process. Additionally, there are several additives which modify the quality and quantity of produced oil and gas. These are potential fuels for a decentralized, energetically self-sufficient process chain for treating different fractions from the WEEE treatment.

References

Alston S.M., Arnold J.C., (2011), Environmental impact of pyrolysis of mixed WEEE plastics Part 2: Life Cycle Assessment, *Environmental Science & Technology*, **45**, 9386-9392.

Bakas I., Fischer C., Haselsteiner S., McKinnon D., Milios L.., Harding A., Kosmol J., Plepys A., Tojo N., Wilts H., Wittmer D., (2014), *Present and potential future recycling of critical metals in WEEE*, Copenhagen Resource Institute (Ed.), Copenhagen, Denmark.

Bauforumstahl, (2015), *Fire loads and heat values*, (in German), Bauforumstahl E.V. (Ed.), Düsseldorf, Germany, On line at: https://www.bauforumstahl.de/brandbelastungen-und-heizwerte.

Bhaskar T., Matsui T., Kaneko J., Uddin M.A., Muto A., Sakata Y., (2002), Novel calcium based sorbent (Ca-C) for the dehalogenation (Br, Cl) process during

halogenated mixed plastic (PP/PE/PS/PVC and HIPS-Br) pyrolysis, *Green Chemistry*, **4**, 372-375.

Bhaskar T., Kaneko J., Muto A., Sakata Y., Jakab E., Matsui T., Uddin M.A., (2004), Pyrolysis studies of PP/PE/PS/PVC/HIPS-Br plastics mixed with PET and dehalogenation (Br, Cl) of the liquid products, *Journal of Analytical and Applied Pyrolysis*, **72**, 27-33.

Bhaskar T., Hall W.J., Mitan N.M.M., Muto A., Williams P.T., Sakata Y., (2007), Controlled pyrolysis of polyethylene/polypropylene/polystyrene mixed plastics with high impact polystyrene containing flame retardant: Effect of decabromo diphenylethane (DDE), *Polymer Degradation and Stability*, **92**, 211-221.

Blaszo M., Czégény Z., Csoma C., (2002), Pyrolysis and debromination of flame retarded polymers of electronic scrap studied by analytical pyrolysis, *Journal of Analytical and Applied Pyrolysis*, **64**, 249-261.

Birnbaum L., Staskal D.F., Diliberto J.J., (2003), Health effects of polybrominated dibenzo-p-dioxins (PBDDs) and dibenzofurans (PBDFs), *Environment International*, **29**, 855-860.

Bockhorn H., Hornung A., Hornung U., (1998), Stepwise pyrolysis for raw material recovery from plastic waste, *Journal of Analytical and Applied Pyrolysis*, **46**, 1-13.

Bockhorn H., Hornung A., Hornung U., Jakobströer P., Kraus M., (1999), Dehydrochlorination of plastic mixtures, *Journal of Analytical and Applied Pyrolysis*, **49**, 97-106.

Boerrigter H., Oudhuis A.B.J., Tange L., (2002), *Bromine Recovery from the Plastics Fraction of Waste of Electrical and Electronic Equipment (WEEE) with stages Gasification*, European Brominated Flame Retardant Industry Panel (EBFRIP) (Ed.), Brussels, Belgium.

Buchert M., Manhart A., Bleher D., Pingel D., (2012), *Recycling of Critical Materials from waste electronic equipment*, (in German), Landesamt für Natur, Umwelt und Verbraucherschutz (LANUV) Nordrhein-Westfalen, Recklinghausen, Germany.

Chiang H.-L., Lo C.-C., Ma S.-Y., (2010), Characteristics of exhaust gas, liquid products, and residues of printed circuit boards using the pyrolysis process, *Environmental Science and Pollution Research*, **17**, 624–633.

Ciocoiu N., Hîncu D., Dobrea C., Târţiu V., Burcea S., (2013), Driving forces of WEEE Management: A PEST Analysis of Romania, *Environmental Engineering and Management Journal*, **12**, 535-548.

de Marco I., Caballero B.M., Chomón M.J., Laresgoiti M.F., Torres A., Fernández G., Arnaiz S., (2008), Pyrolysis of electrical and electronic wastes, *Journal of Analytical and Applied Pyrolysis*, **82**, 179–183.

Dettmer F.T., (2001), *Bromine organic flame retardants, Analytical requirements and thermal formation of polybrominated dibenzo-p-dioxins and dibenzofurans*, (in German), PhD Thesis, Technical University Carolo-Wilhelmina, Braunschweig, Germany.

Dettwiler J., Karlaganis G., Studer C., Joss S., Chambaz D., (1997), *Dioxins and Furans, location determination, assessment basis, actions*, (in German), Federal Office for the Environment FOEN (Ed.), Ittigen, Switzerland.

EC Directive, (2011), Directive 2011/65/EU of the European Parliament and of the Council of 8 June 2011, on the restriction of the use of certain hazardous substances in electrical and electronic equipment (recast), *Official Journal of the European Communities*, L 174/88, 01.07.2011, Brussels.

EC Directive, (2012), Directive 2012/19/EU of the European Parliament and of the Council of 4 July 2012, on waste electrical and electronic equipment (WEEE) (recast), Official Journal of the European Communities, L 197/38, 24.07.2012, Brussels.

EFRA, (2007), *Flame retardants, frequently asked questions*, The European Flame Retardants Association (EFRA) (Ed.), Brussels, Belgium.

Eionet, (2013), *What is waste?*, European Topic Centre on Sustainable Consumption and Production, Kopenhagen, Danemark, On line at: http://scp.eionet.europa.eu/themes/waste/#6.

European Commission, (2013), *Report on critical raw materials for the EU, Critical raw materials profiles*, European Commission, Brussels, On line at: http://ec.europa.eu/enterprise/policies/raw-materials/files/docs/crm-critical-material-profiles_en.pdf.

Eurostat, (2015), Waste Electrical and Electronic Equipment (WEEE) [env_waselee], European Commission, Brussels, On line at: http://appsso.eurostat.ec.europa.eu/nui/show.do?dataset=env_waselee&lang=en.

Grabda M., Oleszek-Kudlak S., Shibata E., Nakamura T., (2009), Influence of temperature and heating time on bromination of zinc oxide during thermal treatment with tetrabromobisphenol A, *Environmental Science & Technology*, **43**, 8936–8941.

Grabda M., Oleszek-Kudlak S., Shibata E., Nakamura T., (2011), Vaporization of zinc during thermal treatment of ZnO with tetrabromobisphenol A (TBBPA), *Journal of Hazardous Materials*, **187**, 1-3.

Graedel T.E., Allwood J., Birat J.-P., Buchert M., Hagelüken C., Reck B.K., Sibley S.F., Sonnemann G., (2011), *Recycling rates of metals, A status report*, United Nations Environment Programme (UNEP) (Ed.), Nairobi, Kenya.

Grause G., Furusawa M., Okuwaki A., Yoshioka T., (2008), Pyrolysis of tetrabromobisphenol-A containing paper laminated printed circuit boards, *Chemosphere*, **71**, 872-878.

Hagelüken C., Corti C.W., (2010), Recycling of gold from electronics: Cost-effective use through 'Design for Recycling', *Gold Bulletin*, **43**, 209-220.

Haig S., Morrish L., Morton R., Wilkinson S., (2012), Electrical product material composition, Overview of updated data within the Market Flows Model of Electronic Products, Waste & Resources Action Programme (WRAP), Oxon, United Kingdom.

Hall W.J., Williams P.T., (2007a), Analysis of products from the pyrolysis of plastics recovered from the commercial scale recycling of waste electrical and electronic equipment, *Journal of Analytical and Applied Pyrolysis*, **79**, 375–386.

Hall W.J., Williams P.T., (2007b), Separation and recovery of materials from scrap printed circuit boards, *Resources, Conservation and Recycling*, **51**, 691–709.

Hall W.J., Miskolczi N., Onwudili J., Williams P.T., (2008), Thermal processing of toxic flame-retarded polymers using a waste fluidized catalytic cracker (FCC) catalyst, *Energy & Fuels*, **22**, 1691-1697.

Hornung A., Balabanovic, A.I., Donner S., Seifert H., (2003), Detoxification of brominated pyrolysis oils, *Journal of Analytical and Applied Pyrolysis*, **70**, 723-733.

Hornung, A., Donner S., Balabanovich A., Seifert H., (2005), Polypropylene as a reductive agent for dehalogenation of brominated organic compounds, *Journal of Cleaner Production*, **13**, 525-530.

Hornung A., Schöner J., Seifert H., Tumiatti V., (2007), *Pyrolysis of WEEE*, In: *Stewardship Commitment, Packaging Waste, Waste Electrical and Electronic Equipment, End-of-Life Vehicles* (in German), Thomé-Kozmiensky K., Versteyl A., Beckmann M. (Eds.), TK Verlag Thomé-Kozmiensky, Neuruppin, Germany, 367-372.

Husemann K., Peuker U.A., Simon F., Reinsch E., Albrecht V., (2010), *Development and optimization of processes to sort relevant plastic waste mixtures by electro-sorting* (in German), Institut für Mechanische Verfahrenstechnik und Aufbereitungstechnik der Technischen Universität Bergakademie Freiberg (IMVA), Leibniz-Institut für Polymerforschung Dresden e.V. (IPF), Freiberg Dresden, Germany.

Jakab E., Uddin Md.A., Bhaskar T., Sakata Y., (2003), Thermal decomposition of flame-retarded high-impact polystyrene, *Journal of Analytical and Applied Pyrolysis*, **67-69**, 83-99.

Jie G., Ying-Shun L., Mai-Xi L., (2008), Product characterization of waste printed circuit board by pyrolysis, *Journal of Analytical and Applied Pyrolysis*, **83**, 185–189.

Johnson Matthey, (2012), *Platinum 2012, Interim Review*, Johnson Matthey Public Limited Company, Royston, England, On line at: http://www.platinum.matthey.com/documents/market-review/2012-interim/full-review/english.pdf.

Koch W., (2007), *Development of a thermo-chemical process for the treatment of WEEE – the "Haloclean"-Pyrolysis* (in German), PhD Thesis, Institute for Technical Chemistry, Karlsruhe, Germany.

Kumar M., Lee J.-C., Kim M.-S., Jeong J., Yoo K., (2014), Leaching of metals from waste printed circuit boards (WPCBs) using sulfuric and nitric acids, *Environmental Engineering and Management Journal*, **13**, 2601-2607.

Lai Y.-C., Lee W.-J., Li H.-W., Wang L.-C., Chang-Chien G.-P., (2007), Inhibition of polybrominated dibenzo-p-dioxin and dibenzofuran formation from the pyrolysis of printed circuit boards, *Environmental Science & Technology*, **41**, 957-962.

Luijk R., Wever H., Olie K., Govers H.A.J., Boon J.J., (1991), The influence of the polymer matrix on the formation of polybrominated dibenzo-p-dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs), *Chemosphere*, **23**, 1173-1183.

Lewin M., (2001), Synergism and catalysis in flame retardancy of polymers, *Polymers for Advanced Technologies*, **12**, 215-222.

Liu W.-J., Tian K., Jiang H., Zhang X.-S., Yang G.-X., (2013), Preparation of liquid chemical feedstocks by co-pyrolysis of electronic waste and biomass without formation of polybrominated dibenzo-p-dioxins, *Bioresource Technology*, **128**, 1-7.

Ma S., Lu J., Gao J., (2002), Study of the low temperature pyrolysis of PVC, *Energy & Fuels*, **16**, 338-342.

Marongiu A., Bozzano G., Dente M., Ranzi E., Faravelli T., (2007), Detailed kinetic modeling of pyrolysis of tetrabromobisphenol A, *Journal of Analytical and Applied Pyrolysis*, **80**, 325-345.

Mineralprices.com, (2014), Platinum Group Metals, Mineralprices.com, Toronto, Canada, On line at: http://mineralprices.com/.

Mitan N.M.M., Brebu M., Bhaskar T., Muto A., Sakata Y., (2007), Individual and simultaneous degradation of brominated high impact polystyrene and brominated acrylonitrile-butadiene-styrene and removal of heteroelements (Br, N, and O) from degradation oil by multiphase catalytic systems, *Journal of Material Cycles and Waste Management*, **9**, 56-61.

Mitan N.M.M., Bhaskar T., Hall W.J., Muto A., Williams P.T., Sakata Y., (2008), Effect of decabromodiphenyl ether and antimony trioxide on controlled pyrolysis of high-impact polystyrene mixed with polyolefins, *Chemosphere*, **72**, 1073-1079.

Oleszek S., Grabda M., Shibata E., Nakamura T., (2013a), Distribution of copper, silver and gold during thermal treatment with brominated flame retardants, *Waste Management*, **33**, 1835-1842.

Oleszek S., Grabda M., Shibata E., Nakamura T., (2013b), Fate of lead oxide during thermal treatment with tetrabromobisphenol A, *Journal of Hazardous Materials*, **261**, 163-171.

Oleszek S., Grabda M., Shibata E., Nakamura T., (2013c), Study of the reactions between tetrabromobisphenol A and PbO and Fe_2O_3 in inert and oxidizing atmospheres by various thermal methods, *Thermochimica Acta*, **566**, 218-225.

Reuter M., Hudson C., van Schaik A., Heiskanen K., Meskers C., Hagelüken C., (2013), *Metal recycling, Opportunities, limits, infrastructure, A Report of the Working Group on the Global Metal Flows to the International Resource Panel*, United Nations Environment Programme (UNEP), Nairobi, Kenya.

Rzyman M., Grabda M., Oleszek-Kudlak S., Shibata E., Nakamura T., (2010), Studies on bromination and evaporation of antimony oxide during thermal treatment of tetrabromobisphenol A (TBBPA), *Journal of Analytical and Applied Pyrolysis*, **88**, 14-21.

Sakai S., Watanabe J., Honda Y., Takatsuki H., Aoki I., Futamatsu M., Shiozaki K., (2001), Combustion of brominated flame retardants and behavior of its byproducts, *Chemosphere*, **42**, 519-531.

Sigma Aldrich, (2014), Bromomethane ≥99%, Sigma-Aldrich Co. LLC. (Ed.), St. Louis, USA, On line at: http://www.sigmaaldrich.com/catalog/product/aldrich/295485?lang=de&region=DE.

Terakado O., Ohhashi R., Hirasawa M., (2011), Thermal degradation study of tetrabromobisphenol A under the presence metal oxide: Comparison of bromine fixation ability, *Journal of Analytical and Applied Pyrolysis*, **91**, 303-309.

Terakado O., Ohhashi R., Hirasawa, M., (2013), Bromine fixation by metal oxide in pyrolysis of printed circuit board containing brominated flame retardant, *Journal of Analytical and Applied Pyrolysis*, **103**, 216-221.

Williams P.T., (2010), Valorization of Printed Circuit Boards from Waste Electrical and Electronic Equipment by Pyrolysis, *Waste and Biomass Valorization*, **1**, 107-120.

Wu H., Shen Y., Harada N., An Q., Yoshikawa K., (2014), Production of Pyrolysis Oil with Low Bromine and Antimony Contents from Plastic Material Containing Brominated Flame Retardants and Antimony Trioxide, *Energy and Environment Research*, **4**, 105–118.

Zhu H.M., Jiang X.G., Yan J.H., Chi Y., Cen K.F., (2008), TG-FTIR analysis of PVC thermal degradation and HCl removal, *Journal of Analytical and Applied Pyrolysis*, **82**, 1-9.