Science of the Total Environment 499 (2014) 27–35

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Pollutant emissions during pyrolysis and combustion of waste printed circuit boards, before and after metal removal

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HIGHLIGHTS

- Thermal decomposition of printed circuit boards (with and without metals) is studied.
- Important differences were found at the different experimental conditions.
- Emission of brominated pollutants is much higher than that of chlorinated.
- Metal enhances emission of halogenated compounds.
- An increase in the temperature produces the destruction of pollutants.

ARTICLE INFO

Article history:
Received 9 July 2014
Received in revised form 9 August 2014
Accepted 12 August 2014
Available online 29 August 2014

Editor: Adrian Covaci

Keywords:
Printed circuit board
WEEE
Pyrolysis
Combustion
Dioxin

ABSTRACT

The constant increase in the production of electronic devices implies the need for an appropriate management of a growing number of waste electrical and electronic equipment. Thermal treatments represent an interesting alternative to recycle this kind of waste, but particular attention has to be paid to the potential emissions of toxic by-products. In this study, the emissions from thermal degradation of printed circuit boards (with and without metals) have been studied using a laboratory scale reactor, under oxidizing and inert atmosphere at 600 and 850 °C. Apart from carbon oxides, HBr was the main decomposition product, followed by high amounts of methane, ethylene, propylene, phenol and benzene. The maximum formation of PAHs was found in pyrolysis at 850 °C, naphthalene being the most abundant. High levels of 2-, 4-, 2,4-, 2,6- and 2,4,6-bromophenols were found, especially at 600 °C. Emissions of PCDD/Fs and dioxin-like PCBs were quite low and much lower than that of PBDD/Fs, due to the higher bromine content of the samples. Combustion at 600 °C was the run with the highest PBDD/F formation: the total content of eleven 2,3,7,8-substituted congeners (tetra- through heptaBDD/Fs) was 7240 and 3250 ng WHO_{2005}-TEQ/kg sample, corresponding to the sample with and without metals, respectively.

1. Introduction

Waste from electrical and electronic equipment (WEEE) is growing significantly and causing a huge environmental problem if not dealt with in an appropriate way, besides the enormous resource impact of electrical and electronic equipment (EEE) production (UNEP, 2009). Currently, the available data on e-waste are poor; United Nations University's estimations of the current e-waste arisings across the EU amount to around 8.3–9.1 million tonnes for 2005 (UNU, 2007). The same study forecasts a 2.5–2.7% annual growth for total WEEE (household and non-household), reaching about 12.3 million tonnes by 2020 in these countries.

Printed circuit boards (WCB) are one of the most complex constituents of WEEE, with a mixture of both valuable and/or hazardous elements. Metals represent up to 40% in weight (including Cu, Al, Fe, Sn, Co, In, Sb and precious metals like Ag, Au, Pd and Pt), ceramic material up to 30% (mainly SiO_2 and Al_2O_3), and plastic content corresponds to the remaining 30% (Li and Zeng, 2012). In addition, tetrabromobisphenol A (TBBPA) is predominantly used as reactive flame retardant in rigid FR-4 printed circuit boards, incorporated through chemical reactions with the epoxy resin (US EPA, 2009).

According to Guo et al. (Guo et al., 2009), the WCB components are usually divided into metallic fractions (MFs) and non-metallic fractions (NMFs), which consist of metals (mainly copper) in the first case and a mixture of reinforcing materials, thermosetting resins, brominated flame retardants (BFR) and other additives in the second case.

Extensive investigation has been carried out on pyrolysis as a recycling technique for waste WCB without previous separation of the metallic and non-metallic fractions. Chiang et al. (Chiang and Lin, 2014; Chiang et al., 2010) carried out the pyrolysis of crushed WCB between 200 and 500 °C and analyzed the composition of residue, liquid

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http://dx.doi.org/10.1016/j.scitotenv.2014.08.039
0048-9697/

and gaseous fractions. Chien et al. (Chien et al., 2000) studied the distribution of Br in pyrolysis products by using a fixed-bed reactor at 350–800 °C and thermogravimetry, and found that it mainly evolved as HBr and bromobenzene in the product gas. De Marco et al. (de Marco et al., 2008) conducted pyrolysis experiments at 500 °C on four different WEEE samples (polyethylene wires, table phones, mobile phones and printed circuit boards), with a focus on the solid and liquid fractions. Guo et al. (Guo et al., 2014) studied the pyrolysis of large-size FR-4 WCB at 500 °C in a fixed-bed reactor at 500 °C, obtaining 71.6 wt% of solid residue, 18.2 wt% of tar and 10.17 wt% of gas. Other authors (Hall and Williams, 2007a, 2007b; Quan et al., 2010) reported on the pyrolysis at high temperature (700–800 °C) as a feasible way to recover the organic, metallic and glass fiber material from circuit boards from different appliances (televisions, computers, and mobile phones). Jie et al. (Jie et al., 2010, 2008) performed the pyrolysis of WCB from waste personal computers, at temperatures between 300 and 700 °C for 30 min, and suggested that the resulting pyro-oils and gases could be used as fuels or chemical material resource. Long et al. (Long et al., 2010) proposed a combination of vacuum pyrolysis and mechanical processing using a pilot-scale fixed bed reactor to recycle the different fractions of waste WCB (i.e. organic resins, copper and glass fiber).

Watanabe et al. (Watanabe et al., 2008) and Sakai et al. (Sakai et al., 2001) conducted combustion experiments of waste WCB in a pilot-scale incinerator equipped with a flue gas treatment system. They observed the formation of brominated, chlorinated and mixed halogenated dioxins and furans, although the overall destruction rate was higher than 90% in flue gas at the final exit.

Concerning the thermal treatment of metal-free samples from waste WCB, some authors analyzed the pyrolysis and/or combustion products. Blazsó et al. (Blazsó et al., 2002) studied the potential of different inorganic solids of basic character as dehalogenation agents in the pyrolysis of electronic scrap (an electronic junction and a printed circuit board without metals) at 450 and 600 °C. Barontini et al. (Barontini and Cozzani, 2006; Barontini et al., 2005) used thermogravimetric analysis and a laboratory-scale fixed-bed reactor to study the thermal degradation patterns of metal-free samples from epoxy resin circuit boards, both in inert and oxidizing atmospheres. The findings of these works were compared with those corresponding to the degradation of a TBBPA containing paper-phenol laminate by Grause et al. (Grause et al., 2008), who pyrolyzed the sample both in a thermogravimetric analyzer and in a quartz glass reactor (40–1000 °C). Quan et al. (Quan et al., 2012) used TG-FTIR (thermogravimetry with Fourier transformed infrared) and Py-GC/MS (Pyrolysis with gas chromatography and MS detector) techniques to analyze the pyrolysis of metal-free WCB waste at 600 °C.

Despite the considerable amount of research carried out on the decomposition and products obtained during thermal treatment of used WCB, less attention has been paid to the toxicity of the gaseous products emitted. There can be a potential for emissions of brominated dioxins and furans or other by-products when products containing TBBPA are combusted during end-of-life processes (US EPA, 2009). Only some authors (Duan et al., 2011, 2012; Gullett et al., 2007; Lai et al., 2007) characterized the emission of PBDD/Fs (brominated dioxins and furans) from pyrolysis or combustion of such wastes, and, as stated by Duan et al. (Duan et al., 2011), further research is needed on the influence of metals in the emissions of halogenated pollutants from WCB waste incineration.

Our group has already reported on the combustion and pyrolysis emissions from obsolete mobile phones, including printed circuit boards, mobile cases and a mixture of both materials (Moltó et al., 2011, 2009), but analyzing only the chlorinated compounds, including PCDD/Fs. The aim of the present study is to characterize the emissions from thermal degradation of waste WCB in an exhaustive way, especially regarding the potential formation of PBDD/Fs and the influence of the metal presence. In this way, the study comprises the analysis of gases, halogens and hydrogen halides, carbon oxides, light hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), chlorinated phenols (ClPhs), chlorinated benzenes (ClBzs) and brominated phenols (BrPhs), among other semivolatile compounds, as well as polybromo- and polychlorodibenzo-p-dioxins and furans (PBDD/Fs and PCDD/Fs) and dioxin-like polychlorobiphenyls (dl-PCBs).

2. Materials and methods

2.1. Material

Printed circuit boards from 10 different waste mobile phones (approximately 100 grams) were separated and crushed to fine dust (sample named “WCB”, corresponding to the whole printed circuit boards), using a vibratory disc mill by Herzog, HSM 100 (Osnabrück, Germany). In order to obtain a metal-free fraction, a part of “WCB” sample was treated with a dilute aqueous solution of HCl and H_2O_2, followed by washing with deionized water and drying at 110 °C (sample named “nmf-WCB”, corresponding to the non-metallic fraction).

The characterization of both samples and a thermogravimetric study about the thermal decomposition of these samples under inert and oxidative atmospheres was previously published (Ortuño et al., 2013). Using a CHNS analyzer, a carbon content of 20.4 and 36.4 wt% was found for the “WCB” and the “nmf-WCB”, respectively. The effectiveness of the acid washing treatment was confirmed by X-ray fluorescence, with the “WCB” sample showing a copper content of 24.2 wt% versus 0.50 wt% for the “nmf-WCB”. Not only Cu, but also Ca, Al, Pb, Sn, Ni and Fe showed a significant decrease in the “nmf-WCB” and, as a consequence of the removal of the metallic content, the concentration of the remaining elements increased. It must be emphasized that the amounts of Br and Cl, change from 5.7 and 0.13 wt% in the “WCB” sample to 12.2 and 1.04 wt% in the washed sample (Ortuño et al., 2013).

2.2. Experimental setup

Pyrolysis and combustion runs were conducted with both samples at two different temperatures (600 and 850 °C), using a tubular quartz reactor located inside a horizontal laboratory furnace described in detail elsewhere (Aracil et al., 2005a). For each run, synthetic air (combustion runs) or nitrogen (pyrolysis runs) was introduced in parallel flow with respect to the sample, at a constant flow of 300 mL/min (1 atm, 20 °C). With this gas flow rate, the gas residence time at the nominal temperature was calculated to be 4.9 s at 600 °C and 3.5 s at 850 °C. The higher temperature (850 °C) was chosen because the EU incineration directive (European Council, 2000) sets a minimum of two seconds at this temperature for the post-combustion zone of an incinerator, whereas the lower temperature (600 °C) is enough to achieve the thermal decomposition of the samples (Ortuño et al., 2013) and represents low temperature zones in the combustion chamber.

The sample was placed in a holder (quartz boat), which was introduced into the reactor at a constant speed (1 mm/s), once the set temperature had been reached, and maintained inside the reactor for 10 min, while the compounds leaving the laboratory reactor were sampled for subsequent analysis. A packing of quartz rings was placed at the end of the reactor to avoid gas bypass, ensure good mixing of the gases from the primary decomposition of the samples and allow further reactions (Aracil et al., 2005b).

A bulk air ratio was defined (Aracil et al., 2010) as the ratio between the actual oxygen flow and the stoichiometric oxygen flow necessary for complete combustion. The chosen sample amounts correspond to an air ratio of 0.95, slightly substoichiometric oxygen conditions, favoring the formation of compounds of incomplete combustion, in order to simulate the operation of the system under adverse conditions and poor combustion. This corresponds to 75 mg of “WCB” and 40 mg of “nmf-WCB”.