

EFFECT OF TEMPERATURE, ATMOSPHERE AND METALS ON THE THERMAL DEGRADATION OF PRINTED CIRCUIT BOARDS

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Introduction

The permanent expansion of the market of electrical and electronic equipment (EEE) and the shorter innovation cycles, lead to a faster replacement of these appliances, making EEE a fast-growing source of waste (WEEE). As stated in Directive 2012/19/EU¹ on waste electrical and electronic equipment, the content of hazardous components in EEE is a major concern during the waste management phase, and recycling of WEEE is not currently undertaken to a sufficient extent, resulting in a loss of valuable resources.

It has been estimated that printed circuit boards (PCB) comprise approximately 6 wt % of all WEEE, representing over 500 000 tonnes of PCBs generated in the EU per year². Due to the heterogeneous mix of organic material, metals, and glass fiber, printed circuit boards are specially problematic to recycle³ and low recycling rates are reported of about 15 %⁴.

Thermal treatments have been widely investigated as recycling techniques for e-waste, but little attention has been given to the pollutants evolved during these processes. Polymers used in printed circuit boards are either physically blended with or chemically bonded to brominated flame retardants, which may result in emission of brominated organic pollutants during the thermal decomposition of these residues. Moreover, the presence of Fe and Cu can catalyze debromination/hydrogenation reactions, accelerating the formation of chlorinated and brominated dioxins and furans, so further research is needed on the influence of metals in the emissions of halogenated pollutants from PCB waste incineration⁵.

The present work aims to characterize the emissions from pyrolysis and combustion of waste PCB from mobile phones, before and after the removal of the metallic fraction, and at two different temperatures. The study comprises the analysis of gases, halogens and hydrogen halides, carbon oxides, light hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), and brominated phenols (BrPhs), among other semivolatile compounds. Furthermore, polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) have been analyzed.

Materials and methods

Waste printed circuit boards were separated and crushed to fine dust (sample named "PCB", corresponding to the whole printed circuit boards). To remove the metallic fraction, part of the sample was treated with a H₂O:HCl:H₂O₂ (2:1:1 vol.) solution, followed by washing with deionized water and drying at 110 °C (sample named "nmf-PCB", corresponding to the non metallic fraction). Elemental and metal analyses (see Table 1) were performed to check the process and characterize the samples.

Using a tubular quartz reactor located inside a horizontal laboratory furnace (see Figure 1), pyrolysis and combustion runs were carried out at 600 and 850 °C, in order to study the decomposition products under different operating conditions. In this reactor, the sample is placed in a quartz boat (holder) which is introduced inside the furnace at 1 mm/s, performing the sampling of the gases at the reactor outlet. Sample amounts used correspond to slightly substoichiometric oxygen conditions (oxygen defect), favoring the formation of compounds of incomplete combustion, in order to simulate the system operation under adverse conditions and poor combustion (75 mg of "PCB" and 40 mg of "nmf-PCB").

Table 1. Composition (wt %) of printed circuit boards (PCB) and non metallic fraction (nmf-PCB).

Sample	PCB	nmf-PCB
Elemental analysis:		
C	20.4	36.4
H	1.9	3.4
N	0.7	1.4
S	-	-
X-Ray Fluorescence analysis:		
O	24.5	21.7
Cu	24.2	0.50
Si	10.5	15.3
Br	5.7	12.2
Ca	4.5	3.8
Al	3.3	1.5
Pb	0.9	0.03
Sn	1.4	0.5
Ni	0.3	0.1
Ba	0.2	0.7
P	0.4	0.5

(-): not detected

For each experimental condition, four different runs were carried out on each sample, as well as a blank run, due to the different sampling and analysis techniques used to quantify the following groups of compounds:

- Hydrogen halides and halogen gases were collected by passing the evolved gases through two consecutive impingers containing diluted solutions of H₂SO₄ and NaOH, according to U.S. EPA method 26⁶. The solutions were analyzed by ion chromatography.

- Gases and volatile compounds were collected in Tedlar[®] bags and analyzed by gas chromatography coupled to thermal conductivity (TCD), flame ionization (FID) and mass spectrometer (MS) detectors.

- Semivolatile compounds were adsorbed on Amberlite[®] XAD-2 resin at the outlet of the reactor and extracted with dichloromethane/acetone (1:1 vol.) by accelerated solvent extraction (Dionex ASE[®] 100). These compounds, including polycyclic aromatic hydrocarbons (PAHs), were analyzed by HRGC-MS in SCAN mode, according to U.S. EPA method 8270D⁷, while bromophenols were analyzed in SIR mode. An Agilent HP5-MS (30 m x 0.25 mm i.d. x 0.25 μm) was used as chromatographic column.

- PBDD/Fs were collected with the same sorbent resin in a separate run. The resin was extracted with dichloromethane and toluene in two subsequent steps using a Dionex ASE[®] 100; then the samples were purified using an automated clean-up system (Power Prep[®]), and finally concentrated. The samples were analyzed by gas chromatography coupled to high resolution mass spectrometry (HRGC-HRMS), according to the standard method for its chlorinated analogues⁸. A Restek TRB-Meta X5 chromatographic column (15 m x 0.25 mm x 0.25 μm) was used for the analysis. Recoveries of the ¹³C-labeled PBDD/Fs were between the acceptable limits, except for ¹³C-OBDD/F, which are not reported.

Throughout the experimental process (sampling, extraction, purification, concentration and analysis) the samples were protected from light, in order to prevent photodegradation of the brominated compounds.

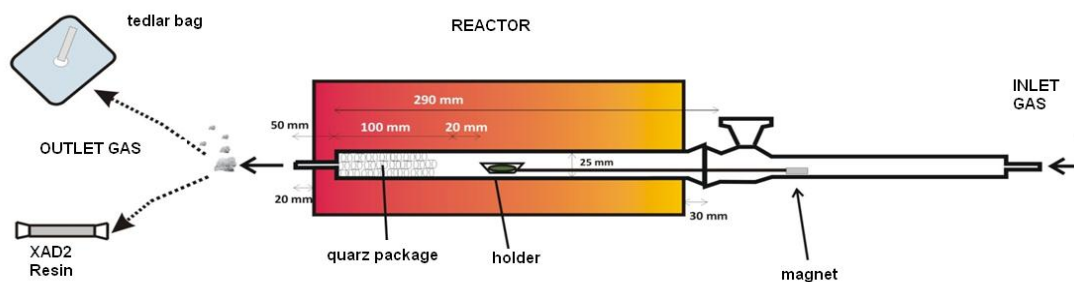


Figure 1. Scheme of the laboratory scale tubular reactor.

Results and discussion

Table 2 shows the results of the majority compounds obtained in the analyses of gases, volatile and semivolatile compounds of the two samples in pyrolysis (P) and combustion (C) runs at 600 and 850 °C.

Apart from CO and CO₂, HBr was the main gas emitted from the decomposition of printed circuit boards. Minor quantities of Br₂, HCl and Cl₂ were also detected in all runs. Inorganic bromine emissions accounted for 24 - 37 % of initial bromine content for sample “PCB” and 39 - 53 % in the case of “nmf-PCB”, showing an increase with temperature and a less accused dependence on the presence of oxygen.

Among light hydrocarbons, the most abundant were methane, ethylene, propylene, benzene and toluene, with similar trends for both samples. These compounds are easily oxidized in combustion runs, hence yields were higher in pyrolysis runs, and increased in the run at 850 °C.

Phenol, benzofuran and styrene were the majority semivolatile compounds, emitted in all experiments, except in combustion at 850 °C. Both samples followed similar trends, with the highest semivolatile yields observed in the pyrolysis run at 600 °C. Yields are higher for the decomposition of the non-metallic fraction, and this can be due to the fact that the polymer content in sample “nmf-PCB” is approximately twice the polymer content from sample “PCB”.

Table 2. Gases, volatile and semivolatiles compounds from pyrolysis (P) and combustion (C) of printed circuit boards (PCB) and non metallic fraction (nmf-PCB).

EXPERIMENT	P600		C600		P850		C850	
SAMPLE	PCB	nmf-PCB	PCB	nmf-PCB	PCB	nmf-PCB	PCB	nmf-PCB
COMPOUND	mg compound/kg sample (ppm)							
Gases and volatile compounds								
Inorganic bromine:								
HBr	14900	46300	12700	45900	20200	58100	11800	59600
Br ₂	1200	1600	1000	3700	1100	2800	6700	5800
Carbon oxides:								
CO	-	-	88980	288030	-	-	94840	295630
CO ₂	18510	51230	441580	594950	31940	57470	677440	506180
R _{CO} = CO/(CO+CO ₂)	0%	0%	17%	33%	0%	0%	12%	37%
Main light hydrocarbons:								
methane	3570	8540	2910	8310	10980	23310	30	30
ethylene	1370	2340	930	1540	3550	6430	-	-
propylene	2070	4310	310	340	1140	2030	-	-
benzene	1060	1910	650	1290	13790	24470	-	-
toluene	1050	1600	-	1070	3350	7240	-	-
Semivolatile compounds and PAHs								
Main 16 priority PAHs:								
naphthalene	39	73	28	57	5790	11320	1	3
acenaphthylene	3	-	2	2	2170	6240	-	-
fluorene	22	62	-	-	750	1450	-	-
phenanthrene	9	21	6	17	1470	3080	-	-
Other semivolatiles:								
styrene	780	1050	40	90	1670	2910	-	-
phenol	27740	53660	7380	24200	2800	6620	-	-
benzofuran	1990	2700	680	1350	2390	3640	-	-

(-): not detected or < 1 ppm

Only in the pyrolysis at 850 °C were all 16 priority PAHs detected, and also with the highest yields. In general, the most abundant were naphthalene, acenaphthylene, fluorene and phenanthrene.

Emissions of bromophenols are shown in Figure 2, with maximum formation at 600 °C in oxygen presence. Mono-, di- and tribrominated isomers predominate, more specifically, formation of isomers with a bromine atom in ortho/para positions is favored (2-, 4-, 2,4-, 2,6- and 2,4,6-BrPh), which concur with the most abundant isomers found during thermal degradation of tetrabromobisphenol A⁹, commonly used as flame retardant in printed circuit boards.

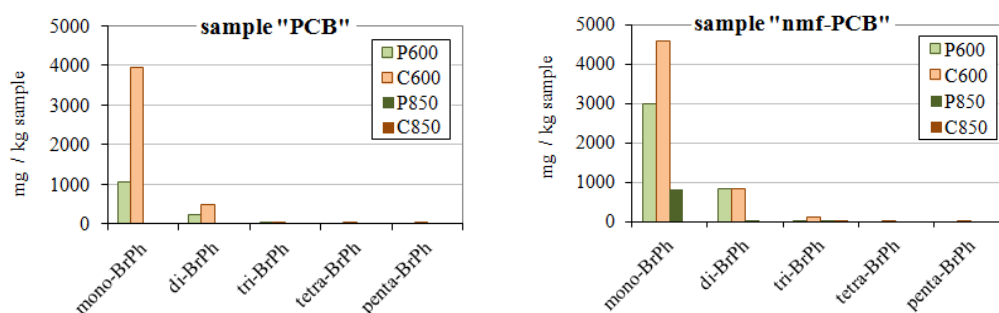


Figure 2. Yields of brominated phenols in pyrolysis (P) and combustion (C) at 600 and 850 °C of two samples: printed circuit boards (“PCB”) and non-metallic fraction (nmf-PCB).

The emissions of 2,3,7,8-substituted PBDD/Fs are shown in Figure 3. In pyrolytic conditions, yields were relatively low and similar regardless of the temperature. In combustion at 850 °C the emissions were 3 times higher than in pyrolysis, whereas in combustion at 600 °C, a significant increase was observed (60-fold for sample “PCB” and 10-fold for “nmf-PCB”).

Both samples exhibited similar isomer profiles, with 1,2,3,4,6,7,8-HpBDF as the most abundant isomer among furans and 1,2,3,4,6,7,8-HpBDD among dioxins. However, 2,3,4,7,8-PeBDF and 1,2,3,4,7,8-HxBDF are the

furans that contribute most to the toxicity of the emissions, while 2,3,7,8-TBDD and 1,2,3,7,8-PeBDD are the ones that enhance toxicity the most.

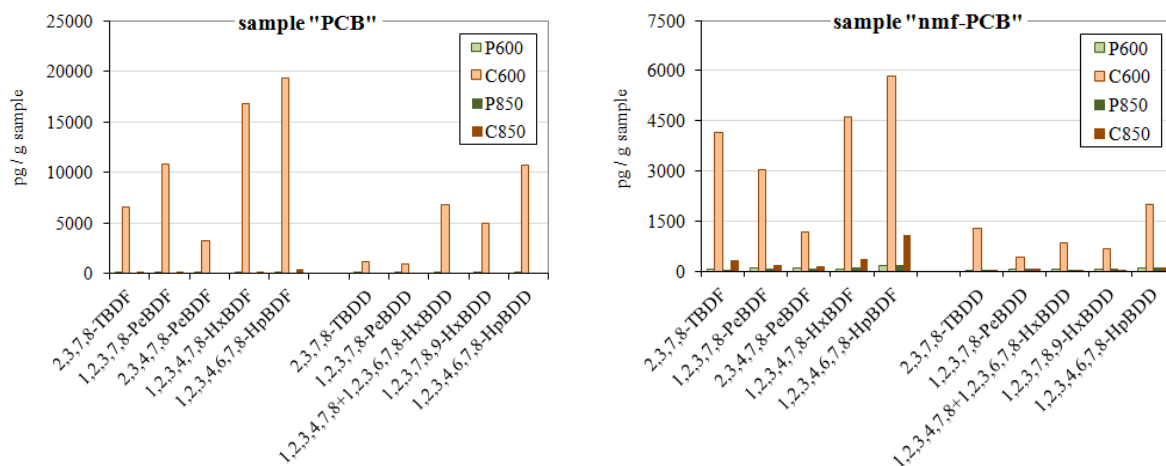


Figure 3. Yields of 2,3,7,8-brominated dioxins and furans in pyrolysis (P) and combustion (C) at 600 and 850 °C of two samples: printed circuit boards (“PCB”) and non-metallic fraction (nmf-PCB).

Emissions and levels of toxic equivalents of PBDD/Fs were higher in combustion than in pyrolysis runs, since oxygen promotes the radical halogenation reactions and leads to an increase in PBDD/F formation, particularly furans.

It is known that metals catalyze the surface-mediated reaction of precursors, such as brominated phenols, that lead to PBDD/Fs formation⁵, as it was observed for sample “PCB”, but the effect of the metal presence is only observed in the run with maximum formation.

As a general conclusion from the different results obtained for both samples, it is shown that yields of the different compounds emitted depended more on operating conditions (temperature and oxygen ratio), but also on the nature of the material or the presence of metals. Therefore, a strict control of operating conditions is required in order to minimize pollutant emissions from thermal recycling of this kind of wastes.

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