

Emission of brominated pollutants during pyrolysis of WEEE debrominated in subcritical water

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Degradation of brominated flame retardant present in FR-4 printed circuit boards (PCBs) using subcritical water in a high pressure reactor has been investigated. Debromination experiments were carried out in a batch stirred reactor at three temperatures (225°C, 250°C and 275°C) keeping a solid to liquid (S/L) ratio PCB:water=1:5 during 180 min. The results showed that the debromination efficiency was affected by the temperature. Approximately, 18.5% of bromine present in FR-4 printed circuit boards was removed when treatment occurred at 225°C, 37.2 % when occurred at 250°C and 63.6 % at 275°C. Also, the thermal decomposition of the debrominated materials is studied and compared with that of original PCB. Thermogravimetric analyses were also performed at the three different heating rates used, both studying the pyrolysis (inert atmosphere) and combustion (in air). Emissions of PAHs and bromophenols of debrominated materials decreased with the increase of the temperature of treatment, naphthalene and mono- and debrominated phenols being the most abundant compounds, respectively.

In this way, the present work has three main objectives: (1) to evaluate the debromination efficiency of subcritical water treatments on FR-4 printed circuit boards; (2) to study the thermal decomposition of the different debrominated wastes obtained by thermogravimetry; and (3) to carry out a comparison of pollutant emissions during the pyrolysis of PCBs before and after the debromination process, with special care of the brominated pollutants.

The process of debromination, using water as subcritical fluid, was carried out in a high-pressure batch reactor with stirring (volume=1000 mL). The high-pressure reactor belongs to FCF series of Zhengzhou Keda Machinery and Instrument Equipment Co. Ltd. It is constructed of 304 stainless steel. The maximum working pressure is 9.8 MPa and the maximum temperature is 350°C.

The parameters controlling debromination efficiency are temperature, solid/liquid (S/L) ratio and residence time. Xing and Zhang (Xing and Zhang 2013) worked in similar runs, and obtained the maximum debromination rate at 400°C with S/L ratio equal to 1:4 g/mL in 120 min runs. In the present work, debromination runs were carried out at three different temperatures (225°C, 250°C and 275°C) with S/L ratio equal to 1:5 g/mL during 180 min, with the idea that S/L ratio and residence time were not limiting factors in the process. In this way, the pressure reached in the container is that corresponding to the vapor pressure at each temperature, approximately 2.5, 4.0 and 6.0 MPa. Approximately, 100 g of PCB sample were introduced into the reactor in each run.

Thermogravimetric curves of original PCB and debrominated wastes were carried out under dynamic conditions in combustion and pyrolysis with a total flow rate of 100 mL min⁻¹. Dynamic runs were performed at heating rates of 5, 10 and 20 K min⁻¹ for each atmosphere, from room temperature up to 1173 K. For all materials the weight loss curves move to the right (higher temperatures) when increasing heating rate, as expected. This has been observed by many other authors that tried to explain it using different arguments, but the only consideration of the kinetic law should be enough to explain this (Caballero and Conesa 2005; Conesa and Rey 2015; Conesa and Soler 2016). On the other hand, the effect of the presence of oxygen is similar in all materials, accelerating the thermal decomposition (i.e. the curve is observed at lower temperatures compared to the pyrolysis) and producing the oxidation of the final pyrolytic residue. In a previous work (Ortuño, Moltó et al. 2013) it was shown that the decomposition of PCBs in the presence of oxygen presents an increase of the weight, due to the combination of the oxygen with the metal contained in the polymer. In the present situation, an increase in the weight is not observed because the PCB sample used was strictly non-metal contained.

Figure 1 shows the results of the emissions of the 16 priority PAHs during the pyrolysis at 850°C in the horizontal reactor described above. As can be seen in this Figure, the profile of compounds was similar for all samples. The most abundant compounds were naphthalene, followed by acenaphthylene, phenanthrene and fluorene. The results agreed with previous studies where the yields showed a maximum in the pyrolysis at high temperature (850°C) because the pyrolytic reactions are the primary source of PAH formation (Thomas and Wornat 2008) and

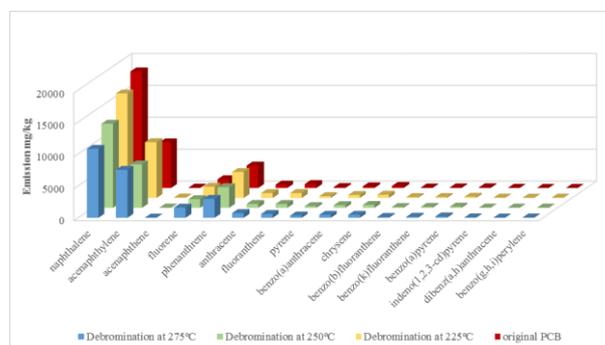


Figure 1. Emission of PAHs during the pyrolysis at 850 °C of the different materials.

the naphthalene was clearly the most abundant PAH formed in the thermal degradation of different materials (Conesa, Font et al. 2009).

The formation of such PAHs seems to be effectively decreased in the subcritical water treatment, as the emission factors decrease when increasing the temperature of the treatment. The emission with the original PCB is similar, somewhat higher, than that detected previously in the pyrolysis at 850 °C of waste PCBs after metal removal (Ortuño, Conesa et al. 2014) and electronic circuit from mobile phones (Moltó, Egea et al. 2011).

Due to the importance of bromine in electronic waste, a more detailed search for brominated compounds has been done within the pyrolysis semivolatile compounds. Three compounds were detected during the decomposition of all samples, as shown in Table 1: 9-bromo-9H-fluorene, bromobenzene and 5-bromobenzofuran. Note that bromobenzene and 5-bromo-benzofuran decreased with an increase of the debromination temperature, whereas there is a slight increase in the production of 9-bromo-PH-fluorene. Bromobenzene was previously detected in higher proportions during the pyrolysis of electronic circuits from mobile phones (with no elimination of the metallic part) (Moltó, Egea et al. 2011).

Table 1. Emission of brominated compounds during pyrolysis at 850°C (mg/kg).

	Original PCB	Debromination at 225°C	Debromination at 250 °C	Debromination at 275 °C
bromobenzene	47,9	48,4	43,1	32,2
Benzofuran, 5-bromo-	8,2	18,7	11,7	10,3
9H-Fluorene, 9-bromo-	35,4	55,2	51,8	48,7
Mono- to penta- bromophenols	26,6	20,1	17,9	14,9

Table 1 shows the total amount of brominated phenols (BrPhs) detected in the pyrolysis runs carried out at 850°C. As can be seen, the total yields of BrPhs decrease with the increase of debromination temperature resulting 14.94 mg/kg for solid residue obtained at 275°C, 17.96 mg/kg for solid residue obtained at 250°C and 20.09 mg/kg for solid residue obtained at 225°C. The total yields of BrPhs of solid residues were all of them lower than the total yield of original PCB (26.59 mg/kg). These results showed that the treatment at high temperature and pressure could to some extent reduce the emissions of brominated compounds in thermal treatments. In previous work (Ortuño, Conesa et al. 2014) the emission of BrPhs in the pyrolysis at 850 °C of waste PCB was much higher, around 800 mg/kg, this fact could be related to the presence of more OH- groups due to the previous treatment with an aqueous solution of HCl and H₂O₂, that was carried out to remove the metal fraction favoring the bromination of phenol.

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