KINETIC ANALYSIS AND POLLUTANT EVOLUTION DURING THERMAL DEGRADATION OF PRINTED CIRCUIT BOARDS CONSIDERING THE EFFECT OF METALS

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Abstract

A kinetic study has been carried out by thermogravimetry in order to compare the thermal behavior of printed circuit boards of mobile phones before and after the removal of the metallic fraction. Experiments were performed in nitrogen atmosphere (pyrolysis runs) as well as in an oxidative atmosphere (10% and 20% oxygen in nitrogen). Several dynamic and dynamic + isothermal runs have been carried out at different heating rates (5, 10 and 20 K min−1), from room temperature to more than 900 K. Moreover, TG–MS experiments were performed (in inert and oxidizing atmosphere) in order to better understand the thermal decomposition of these wastes. Different reaction models are proposed, one for pyrolysis and one for combustion of the two kinds of wastes studied, which proved to simulate appropriately the experimental results at all the heating rates simultaneously.

Regarding the analysis of pollutants evolved, pyrolysis and combustion runs have been carried out at 600 ºC and 850 ºC in a horizontal laboratory furnace in order to analyze a wide range of gases, hydrogen halides, carbon oxides, light hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), chlorinated phenols (ClPhs), chlorinated benzenes (ClBzs) and brominated phenols (BrPhs), among others. Furthermore, polybromo- and polychloro-dibenzo-p-dioxins and furans (PBDD/Fs and PCDD/Fs) and dioxin-like polychlorobiphenyls (PCBs) are being analyzed.

Keywords: *printed circuit boards (PCB), kinetics, pyrolysis, combustion, POPs*

1. Introduction

The increase in electronic waste, including cellular telephones, worldwide is a worrying reality. For this reason, urgent action on the management of these wastes is necessary within a framework that respects the environment and human health.

Printed circuit boards (PCB) are particularly problematic to recycle because of the heterogeneous mix of organic material, metals, and glass fibre [1] and low recycling rates are reported of about 15% [2]. It has been estimated that PCB comprise approximately 6 wt% of all WEEE, representing over 500,000 tonnes of printed circuit boards generated in the EU27 per year [3].

More specifically, the presence of Fe and Cu can catalyze the debromination/hydrogenation reaction, accelerating the formation of chlorinated and brominated dioxins and furans [4]. The present work uses TG and pollutant analysis to compare the thermal behavior of PCB from mobile phones before and after the removal of the metallic fraction.

2. Materials and Methods

Materials

Printed circuit boards of different mobile phones were separated and crushed to fine dust (sample named "PCB"). To remove the metallic fraction, part of the sample was treated with a dilute aqueous solution of HCl and H_2O_2, followed by washing with deionized water and drying at 110 ºC (sample named "metal-free PCB"). Elemental and metal analyses were performed to check the process and can be seen in Table 1 and Table 2.

Table 1. Elemental analysis (wt %).

Sample	C	H	N	S
PCB	20.4	1.9	0.7	0
Metal-free PCB	36.4	3.4	1.4	0

Table 2. FRX analysis (wt %).

Sample	O	Cu	Si	Br	Ca	Al
PCB	24.5	24.2	10.5	5.7	4.5	3.3
Metal-free PCB	21.7	0.5	15.3	12.2	3.8	1.5

Kinetic study

The thermogravimetric study was performed in a Mettler Toledo thermobalance (model TGA/SDTA851e/LF/1600). Dynamic experiments were carried out at different heating rates (5, 10 and 20 K/min), from room temperature to 900 K, covering an extensive range of decomposition. Pyrolysis runs were performed in N_2, whereas two atmospheres were used for the combustion runs: N_2:O_2 4:1 (air) and N_2:O_2 9:1 (poor oxygen conditions).

Laboratory scale reactor

Pyrolysis and combustion runs were carried out at 650 and 850 ºC in order to study the decomposition products under different operating conditions. The experiments were carried out in a tubular quartz reactor located inside a horizontal laboratory furnace (see Figure 1).

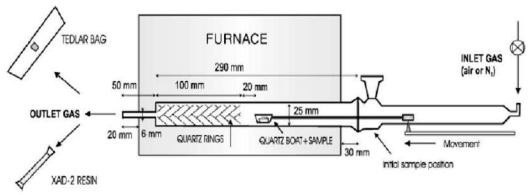

Figure 1. Scheme of the laboratory scale tubular reactor.

The compounds leaving the laboratory reactor were sampled for subsequent analysis. For each experimental condition, four experiments were carried out: in a first run, evolved gas was passed through dilute sulfuric acid and dilute sodium hydroxide solutions which collect the gaseous hydrogen halides and halogens.

In a second run, the non-condensable gases were collected using Tedlar® bags at the outlet of the reactor for a time long enough to collect all the compounds. These samples were analyzed by gas chromatography using different detectors: flame ionization (FID), thermal conductivity (TCD) and mass spectrometer (MS) detectors.

Finally, semivolatile compounds and PBDD/Fs, PCDD/Fs and dioxin-like PCBs were collected in two different experiments with Amberlite® XAD-2 adsorbent resin placed at the outlet of the furnace during the entire experiment. The resin is extracted with appropriate solvents using a DIONEX ASE® 100; then the sample is purified using an automated clean-up system (Power Prep), if necessary, and finally it is concentrated. The samples were analyzed by gas chromatography coupled to low and high resolution mass spectrometry.

3. Results and Discussion

Comparing results for PCB and metal-free PCB samples, in pyrolysis runs (Figure 2), where only the organic polymer decomposes, the final residue is approximately the same for all the runs, although the residue from the non metallic sample is much lower (50 wt% vs. 76 wt%).

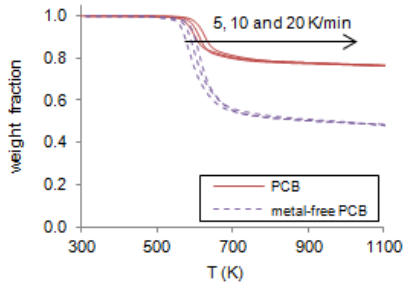

Figure 2. Dynamic runs for pyrolysis.

In the presence of oxygen (Figure 3), the PCB sample presents an oxidation of the metallic compounds and this probably generates a different residue at infinite time. As proposed by Moltó et al. [5], the presence of metals and other compounds catalyzes the decomposition of the organic matter. Also, an increase of weight is observed due to the formation of metallic oxides that lately decompose. Support of this idea is found in the behavior of the non metallic PCB sample, where no weight gain is observed.

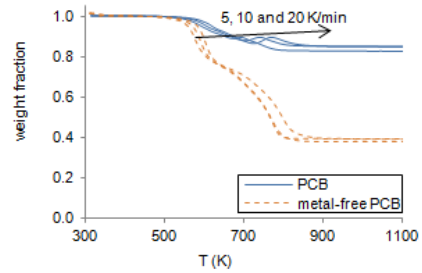

Figure 3. Dynamic runs for combustion in air.

Different kinetic models for the pyrolysis and combustion of these materials have been proposed, for which one set of parameters can explain many experiments under different operating conditions. An acceptable correlation has been obtained for dynamic runs at different heating rates and isothermal runs at distinct temperature operation.

From TG-MS results, for both samples, the main gaseous products are the same in pyrolysis or oxidizing atmosphere: water, CO and CO_2. Moreover, in pyrolysis, methane, ethylene, propylene and phenol are observed, whereas in combustion, only ethylene is detected, indicating that compounds such as methane, propylene and phenol have been oxidized.

Regarding the emission of pollutants from the reactor experiments, analysis and quantification of the different samples is being carried out at the moment.

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