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Pyrolysis and combustion of electronic wastes

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ABSTRACT

The decreasing costs and increasing availability of electronic products of all kinds, including mobile phones, audio and video equipment, and personal computers and their accessories, coupled with advances in technology that rapidly make these products obsolete, foretell a growing disposal problem.

The materials employed in the present work were a mobile phone (printed circuit board + casing) and printed circuit boards alone. Pyrolysis and combustion runs at 500 °C in a horizontal laboratory furnace were performed, and the analyses of the gas and semivolatile fractions (including dioxins and furans and “dioxin-like” PCBs) are shown. The mobile phone and printed circuit boards were analysed for PCDD/F and “dioxin-like” PCB content in order to establish the level of pollutant in the samples themselves.

Some TG–MS experiments were carried out in order to better know the thermal decomposition of electronic wastes and identify some compounds emitted during the controlled heating of these materials. Furthermore, a kinetic study of the thermal decomposition of the electronic circuit (EC) both in nitrogen and nitrogen:oxygen atmospheres using different heating rates is presented.

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1. Introduction

One of the facts that indicate the development of society is the fast electrical and electronic equipment change in people's lives. The decreasing costs and increasing availability of electronic products of all kinds, including mobile phones, audio and video equipment, and personal computers and their accessories, coupled with advances in technology that rapidly make these products obsolete, produce a large amount of electronic wastes in the trash. In Europe the increase of this waste is three times faster than that of municipal wastes and by year 2015 this growth can reach 12 millions of tonnes [1].

The latest Electrical and Electronic Equipment Waste Directive [2] promotes the re-use, recycling and recovery of these waste as well as the collection of electrical and electronic wastes as a separate waste stream, which enhances the prospects for economic recycling.

These new wastes present a growing disposal problem owing to the substances included that may cause serious damage to the environment and have adverse effects on human health. Therefore, the management of this waste must be done properly [3].

Due to the high amount of valuable metals that these products contain they can be considered as an important source of recycling. But sometimes this “recycling” consists of the rudimentary

operation of open burning of the electronic circuits (ECs) and equipment to remove the polymeric fraction and obtain the metals [4]. This uncontrolled combustion produces the emission of large amounts of pollutants to the atmosphere, some of them (PCDD/Fs, PCBs, and PAHs) with high toxicity for the environment and human lives [5].

Brominated flame-retardants are widely used in electronic products [6], mainly tetrabromobisphenol A (TBBPA) and its derivatives and the thermal decomposition of these wastes can produce high amounts of brominated compounds. Some of these pollutants have structures similar to dioxins and furans (PBDD/Fs) but their toxicity has not been extensively studied and scientists have reached no agreement about this. Birnbaum and Staskal published an extensive review about the few data of toxicity and they concluded that, according to the available literature, the health effects of the brominated dioxins are similar to that of the chlorinated homologues [7].

Some authors have studied the debromination of flame-retardants in combustion processes to try to minimize the emissions of brominated compounds. Zeolites and inorganic bases are used to reduce these emissions [8–11]. Blazsó and Czégény [8] used some molecular sieves in the pyrolysis of polycarbonate blended with TBBPA and epoxy resin containing TBBPA. They obtained an important decrease in TBBPA emissions and found that in some cases, TBBPA splits into phenols and bromophenols. These same authors copyrolyzed printed circuit boards with some solids with basic character obtaining the debromination of bromophenyl groups and a decrease in the yields of bromostyrenes [9]. Lai et al.

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used CaO to adsorb the HBr emitted in the combustion of ECs and to inhibit the PBDD/F synthesis [10]. Finally Hall and Williams used zeolites in the pyrolysis of two flame-retarded plastics and found a positive effect in the removal of volatile organobromine compounds [11].

In this work, a study of the thermal decomposition and the pollutants emitted at different combustion and pyrolytic conditions has been carried out with mobile waste. A special effort has been made to identify brominated compounds in the combustion gases.

2. Experimental

2.1. Raw materials

Two different materials were used to study the pollutant emissions. On the one hand, the printed board of a mobile phone was separated and crushed to fine dust; on the other hand, the circuit board and the case of the mobile were crushed together. These two samples were named EC and electronic waste (EW), respectively.

Elemental analysis of the major components was carried out in a Perkin-Elmer 2400. The concentration of the rest of the elements was measured using a model TW 1480 automatic sequential spectrometer X-ray Fluorescence that gives semi-quantitative results. Tables 1 and 2 show the results of the EC (showing high amounts of silicon and copper compounds) and EW (showing high amounts of carbon, since the main component is the polymer of the case, acrylonitrile-butadiene-styrene/polycarbonate).

2.2. Thermobalance

A Mettler Toledo thermobalance model TGA/SDTA851e/LF/1600 was used for TG experiments. This apparatus has a horizontal furnace and a parallel-guided balance. The position of the sample does not change during the measurement, and flow gas perturbation and thermal buoyancy are minimized. The sample temperature is measured with a sensor placed just under the sample holder.

The pyrolysis runs were performed with a N_2 atmosphere, whereas two atmospheres were used for the combustion runs: $N_2:O_2$ 4:1 (normal conditions) and $N_2:O_2$ 9:1 (poor oxygen conditions). The flow rate was 100 ml min^{-1} .

Dynamic experiments were carried out at different heating rates between 5 and 20 K min^{-1} , from room temperature to a final temperature higher than 1000 K, covering in this way an extensive range of decomposition. Isothermal experiments started with a constant heating rate until the set temperature was obtained, and then the final temperature was maintained constant throughout the pyrolysis or combustion process for around or more than 120 min. The sample mass used was around 5 mg in all cases, and under these conditions, it has been tested that the heat transfer effects are very small.

An experiment with a heating rate of 5 K min^{-1} using Avicel PH-105 microcrystalline cellulose was carried out additionally. This experiment was used to check the good performance of the

Table 2
Fluorescence analysis of the materials used.

Wt.%	EW	EC
CuO	10.14	18.74
SiO ₂	9.60	32.41
Br	2.34	4.57
CaO	1.92	6.83
TiO ₂	1.23	1.78
SnO ₂	1.03	1.94
Al ₂ O ₃	0.90	8.33
Fe ₂ O ₃	0.79	0.64
SO ₃	0.36	0.30
Sb ₂ O ₃	0.25	0.00
NiO	0.17	1.10
BaO	0.16	1.92
As ₂ O ₃	0.10	0.00
I	0.08	0.00
ZnO	0.08	0.21
Ag ₂ O	0.07	0.63
Au	0.06	0.00
MgO	0.06	0.00
Nd ₂ O ₃	0.05	0.11
P ₂ O ₅	0.05	0.34
Cl	0.04	0.00
Cr ₂ O ₃	0.03	0.07
SrO	0.02	0.12
Bi ₂ O ₃	0.02	0.00
ZrO ₂	0.01	0.18
Nb ₂ O ₅	0.01	0.00
K ₂ O	0.00	0.16
MnO	0.00	0.24
PbO	0.00	0.91

thermobalance. The kinetic values obtained showed good agreement with the results presented by Grønli et al. [12] in their round-robin study of cellulose pyrolysis kinetics by thermogravimetry.

The TG–MS runs were carried out in a TGA/SDTA851e/LF/1600 with TG-ATD coupled to a Thermostat GSD301T Pfeiffer Vacuum MS apparatus with the following operating conditions: sample mass around 10 mg, heating rate 30 K min^{-1} , ionization 70 eV, SIR detection of several ions: 4 (helium), 18 (water), 28 (carbon monoxide), 44 (carbon dioxide), 80 and 82 (hydrogen bromide), 94 and 96 (bromomethane, bromophenol).

The kinetic study was carried out with the EC because this is a material with high content of copper, and consequently it is very different from other polymeric wastes that have been more extensively studied in literature. There are some authors that have studied the thermal decomposition in TGA runs and their results are compared with our results in the following sections.

2.3. Combustion and pyrolysis runs

The combustion of these samples was carried out in a horizontal laboratory furnace with a tubular quartz reactor located inside. The sample is placed in a holder and a small engine introduces it inside the reactor. A detailed description of the system can be found elsewhere [13].

The furnace conditions in the combustion and pyrolysis of the samples were 773 K, a flow of 300 ml min^{-1} (air or nitrogen) and a feeding velocity of 1 mm s^{-1} . This temperature was chosen to study a slow thermal treatment, where the compounds emitted have no chance to crack in secondary products; thus, the actual operating conditions of open fires is simulated. Bearing in mind the thermogravimetric study, all the volatile fractions must have disappeared at $500\text{ }^\circ\text{C}$; so it should be a temperature high enough to study the pollutant emissions. The sample mass in all the runs was 100 mg.

Volatile and semivolatile compounds and dioxins, furans and dioxin like PCBs were analysed. The first ones were collected in

Table 1
Ultimate analysis of the materials used.

Wt.%	EW	EC
C	63.0	16.9
H	5.7	1.5
S	0.0	0.04
N	1.7	0.0
O and ash	29.6	81.5

Tedlar bags and analysed in two gas chromatographs, one with a thermal conductivity detector (TCD) and the other with a flame ionization detector (FID). Semivolatile compounds were collected in an adsorbent XAD-2 resin, extracted with solvent and analysed with GC–MS by the isotope dilution method.

Finally, dioxins and furans and dioxin-like PCBs were collected with similar resin and subjected to all the extraction and clean-up steps that US-EPA recommends (EPA 1613 and 1668A methods). These compounds were analysed in an HRGC–HRMS and quantified with the isotope dilution method. The steps were the following: addition of internal standard, toluene extraction, addition of clean-up standard, acid/base back-extraction, silica/alumina/active carbon clean-up, concentration and analysis by HRGC/HRMS. The automatic Power-Prep/FMS system was used for the clean-up. This is a relative new system with good results in recovery and repeatability [14]. Different runs were done for the three groups of compounds.

3. Results and discussion

3.1. Thermogravimetric results of EC

Fig. 1 shows the TG plots for EC pyrolysis (nitrogen) at heating rates of 5, 10 and 20 K min^{−1}. In figure, the weight fraction represents the residual mass fraction of the solid, that is the sum of the residue formed and the non-reacted initial solid. For a run, the value of increment of temperature, on the right Y-axis, is also plotted in a convenient scale, from −10 K for a strong endothermic process to +10 K corresponding to a strong exothermic process. It can be observed that there is an initial small endothermic peak due to the vaporization of the moisture and a second exothermic peak at around 1000 K.

Fig. 2 shows the DTG curve for a pyrolysis run (in order to observe the fractions that can be taken into account in the decomposition). It can be deduced that there is an initial large peak followed by a small band or wide peak, which means that at least two fractions must be considered in the decomposition.

Three isothermal experiments were carried out in pyrolytic conditions. These experiments started with a heating rate until the desired temperature was reached, and then the final temperature was maintained constant throughout the pyrolysis process. These final temperatures were selected according to the temperatures

Fig. 1. Electronic circuit pyrolysis at several heating rates: 5, 10, and 20 K min^{−1}. Experimental TG curves (the calculated curves overlap the experimental ones).

Fig. 2. Weight fraction and its derivative from a pyrolysis run.

with the highest weight loss in dynamic runs. Fig. 3 shows the experimental TG values for three runs that overlap to the calculated ones in accordance with the model presented.

Fig. 4 shows the experimental TG plots of combustion runs (N₂:O₂ 4:1) at three heating rates (5, 10, and 20 K min^{−1}). The ΔT corresponding to the DTA analysis is also plotted and an initial very small endothermic peak (evaporation of the moisture) is observed. Afterwards, a small exothermic band due to oxidative pyrolysis appears, and later a significant exothermic process takes place in the last part of the decomposition due to strong oxidation.

Fig. 5 shows the weight fraction and its derivative for a dynamic run of combustion, indicating that the simulation is not easy, because many processes are involved.

Fig. 6 shows the experimental results of five isothermal combustion runs obtained with different operating conditions.

Figs. 7 and 8 show the experimental results for dynamic and isothermal runs in a 9:1 N₂:O₂ atmosphere.

Finally, TG–MS results are presented in Figs. 9 and 10 for EW and EC. The evolution of some masses corresponding to brominated

Fig. 3. Isothermal pyrolysis. Experimental and calculated TG curves.

Fig. 4. Electronic circuit combustion at 5, 10 and 20 K min⁻¹. Experimental TG curves (the calculated curves overlap the experimental ones).

compounds were followed but only bromomethane was detected. The emission of bromomethane is later than that of CO and CO₂ because the decomposition of the material occurs at lower temperature and bromine is emitted by the flame-retardants. Hydrogen bromide was only detected at very low concentration.

Kowalska et al. [15] studied the pyrolysis of three types of printed circuit boards by thermogravimetry. The results showed that the decomposition took place mainly in the range 300–400 °C (573–673 K), and at temperatures above 400 °C, there was a slow decomposition. The decomposition main range of the residues studied in this paper is a little wider (573–750 K). On the other hand, Hall and Williams [16] presented a TG pyrolysis run of mixed waste electrical and electronic equipment. In this case the decomposition took place in the range 400–550 °C (673–823 K), a little wider than that of the residues considered in this paper. Barontine and Cozzani [17] used the TG for simulating pyrolysis

Fig. 6. Isothermal combustion. Experimental and calculated TG curves.

and combustion of dynamic runs, using electronic boards. The shape of the curves and the decomposition ranges were similar to those presented in this paper. Neither isothermal runs nor kinetic models are presented in all these references.

3.2. Pyrolysis model

Three fractions have been considered in the kinetic model proposed for the pyrolysis of the EC, because with two fractions the correlations obtained were not satisfactory:

$$w_{s10} \text{Solid}_1 \xrightarrow{1} (w_{s20} - v_{1\infty}) \text{Residue}_1 + v_{1\infty} \text{Volatiles}_1$$

Fig. 5. Weight fraction and its derivative from a combustion run.

Fig. 7. Dynamic TG runs of oxidative pyrolysis (N₂:O₂ 9:1) at several heating rates: 5, 10, and 20 K min⁻¹.

Fig. 8. Isothermal TG runs in a N₂:O₂ 9:1 atmosphere at several heating rates: 5, 10, and 20 K min⁻¹.

In the previous reactions, Solid₁, Solid₂ and Solid₃ refer to the different fractions of the original material, “Volatiles_{*i*}” include the gases and volatiles evolved in the corresponding reactions (*i* = 1–3), and “Residue_{*i*}” is the possible residue formed in the decomposition of each Solid_{*i*} (*i* = 1–3). On the other hand, the small letters represent the yield coefficients representative of each reaction and consequently, it is considered that they do not change with time or with the extension of the reaction. Each fraction has a yield coefficient that represents the maximum mass fraction obtainable by each reaction. In this way, $v_{i\infty}$ is the yield coefficient for the Volatiles_{*i*} that coincides with the maximum mass fraction of volatiles that can be evolved at infinite time.

The conversion degree for each reaction is defined as the ratio between the mass fraction of solid reacted at any time ($w_{s_{i0}} - w_{s_i}$) and the corresponding initial fraction of this component $w_{s_{i0}}$, or the

Fig. 9. TG/MS of electronic waste in pyrolysis conditions with a heating rate of 30 K min⁻¹.

Fig. 10. TG/MS of electronic circuit in pyrolysis conditions with a heating rate of 30 K min⁻¹.

ratio between the mass fraction of volatiles obtained at any time during which the reaction is taking place (V_i) and the corresponding yield coefficient $v_{i\infty}$, so

$$\alpha_i = \frac{w_{s_{i0}} - w_{s_i}}{w_{s_i}} = \frac{V_i}{v_{i\infty}} \quad i = 1-3 \quad (1)$$

where $w_{s_{i0}}$ is the weight fraction of each Solid_{*i*} that is in the original material, and consequently

$$\sum_{i=0}^3 w_{s_{i0}} = 1 \quad (2)$$

From the mass balance between products and reactants and the conversion degrees, the kinetic equations for the pyrolysis runs can be expressed as follows:

$$\begin{aligned} -\frac{d(w_{s_i}/w_{s_{i0}})}{dt} &= \frac{d(V_i/v_{i\infty})}{dt} = \frac{d\alpha_i}{dt} = k_i \left(\frac{w_{s_i}}{w_{s_{i0}}} \right)^{n_i} = k_i (1 - \alpha_i)^{n_i} \\ &= k_i \left[1 - \frac{V_i}{v_{i\infty}} \right]^{n_i} \end{aligned} \quad (3)$$

with the kinetic constants following the Arrhenius equation:

$$k_i = k_{i0} \exp\left(-\frac{E_i}{RT}\right) \quad i = 1-3 \quad (4)$$

By integration of these equations, it is possible to calculate α_1 to α_3 at each time if the temperature program is known; the relationship between α_i values and the weight fraction measured in the thermobalance (w) is related with the total volatile fraction obtained (V) by

$$w = 1 - V = 1 - F_V(v_{1\infty}\alpha_1 + v_{2\infty}\alpha_2 + v_{3\infty}\alpha_3) \quad (5)$$

In the previous equation, a correcting factor F_V has been introduced due to the fact that the samples can have a slight but significant different content of inert material. In all the cases the values F_V considered are between 0.83 and 1.05.

In order to obtain a single set of parameters, the dynamic runs and the isothermal runs were correlated with the same set of parameters. The calculated values were obtained by integration of the differential equations presented in the kinetic model, with the Euler method, but considering and testing that the intervals of time were small enough, so the errors introduced are negligible. The optimization method of the Solver function in a spreadsheet Excel was used to minimize the differences between experimental and calculated weight loss values and their derivatives. The objective function (OF) to minimize was the sum of the square differences

between experimental and calculated total volatile V and their derivatives multiplied by a factor in order to make the two terms similar, although this factor was changed in order to obtain acceptable correlations:

$$OF = \sum_{m=1}^M \sum_{j=1}^N (V_{m,j}^{\text{exp}} - V_{m,j}^{\text{cal}})^2 \quad (6)$$

where M is the number of runs and N is the number of points in each run.

The model validity was tested calculating the variation coefficient (VC):

$$VC = \frac{\sqrt{OF/(N_{\text{total}} - P)}}{\bar{V}_{\text{exp}}} \times 100 \quad (7)$$

where N_{total} and P are the number of data and parameters fitted, respectively, and $\bar{V}_{\text{exp}}$ is the average of the experimental values of weight fraction corresponding to the volatiles evolved. In order to scale parameter fitting, and according to the procedure suggested by Martín-Gullón et al. [18], the optimization was performed in terms of a 'comparable kinetic constant' K_i^* instead of optimizing k_{0i} . This constant is calculated at a temperature around the maximum decomposition rate (T_{max}). Value 0.64 was obtained from the optimization program for decreasing the great interrelation between the pre-exponential factor, the apparent energy and reaction order. Since K_i^* , E_i and n_i are optimized, the pre-exponential factor k_{0i} is deduced from the following expression:

$$K_i^* = k_i(0.64)^{n_i} = k_{0i} \exp\left(\frac{-E_i}{RT_{\text{max}}}\right) (0.64)^{n_i} \quad (8)$$

The kinetic parameters obtained are shown in Table 3. The calculated values are also shown in Figs. 2 and 3 overlapping the experimental curves (in the case of Fig. 1, the calculated values are also very close to the experimental ones). The mean variation coefficient, considering the weight fraction of volatiles evolved is 2.5%, which is a small value, indicating that the correlation is satisfactory. The kinetic parameters must be considered as correlation ones.

Fig. 11 shows the contribution of each reaction in the decomposition process. It can be observed that there are two main fractions (1 and 2).

Table 3
Kinetic parameters obtained for the pyrolysis and combustion models of the EC.

Reaction	Weight fraction	k (s^{-1})	E (kJ/mol)	n	b (for O_2)
Pyrolysis					
1	0.116	6.254×10^{11}	162.3	0.33	–
2	0.099	1.385×10^{28}	354.4	8.00	–
3	0.118	4.561	86.8	6.00	–
VC (%)	2.5				
Combustion					
1	0.116	6.254×10^{11}	162.3	0.33	0
2	0.099	1.385×10^{28}	354.4	8.00	0
3	0.118	5.137×10^3	86.8	6.00	0
1cp	0.008	3.060	34.5	1.41	2.3
2cp	0.016	1.125×10^{13}	147.3	2.54	2.3
1c	0.108	4.248×10^5	124.9	0.01	2.3
2c	0.083	4.987×10^{12}	173.2	2.06	2.3
4	0.016	2.286×10^9	133.7	0.82	0.47
5	0.016	5.141×10^{21}	272.8	0.19	0.47
VC (%)	2.7

Fig. 11. Evolution of the weight fraction of volatiles for each reaction in a pyrolysis TG run.

3.3. Combustion model

Different kinetic models have been tested to correlate the experimental data of combustion. After considering many schemes of parallel + series + competitive reactions, the following one was selected. This model considers five initial solid fractions. There are two reactions considered for the oxidation of metallic fractions, where the sample increases its weight due to the formation of oxides, and three pyrolytic reactions, two of them which compete with other two reactions that lead to the formation of a residue that is oxidized at high temperatures. The scheme obtained is the following one:

- (1) Organic matter decomposition: Three pyrolytic reactions, two of them competing with other two reactions:

Pyrolytic reactions

Competitive (oxidative) pyrolysis with formation of an intermediate residue

- (2) Oxidation of the intermediate residue

It must be emphasized that $v_{1cp\infty}$ and $v_{2cp\infty}$ can be greater or lower than $v_{1\infty}$ and $v_{2\infty}$. In the case of the model obtained after correlation of the data, $v_{1cp\infty}$ and $v_{2cp\infty}$ were lower than $v_{1\infty}$ and $v_{2\infty}$, ($v_{1c\infty} + v_{1cp\infty}$) equals $v_{1\infty}$ and ($v_{2c\infty} + v_{2cp\infty}$) equals $v_{2\infty}$. This means that the competitive reactions partially oxidize the two fractions and then the oxidized residues decompose to achieve total yields of volatiles equal to those from the direct pyrolysis.

- (3) Metal oxidation: two fractions are considered where there is an increase of weight.

The kinetic equations, considering conversion degrees are the following:

$$\frac{d\alpha_i}{dt} = k_i(1 - \alpha_i)^{n_i} \quad \text{for } i = 3, 4 \text{ and } 5 \quad (18)$$

$$\frac{d\alpha_i}{dt} = k_i(1 - \alpha_i - \alpha_{icp})^{n_i} \quad \text{for } i = 1 \text{ and } 2 \quad (19)$$

$$\frac{d\alpha_{icp}}{dt} = k_{icp}(1 - \alpha_i - \alpha_{icp})^{n_{icp}} \quad \text{for } icp = 1cp \text{ and } 2 \quad (20)$$

Note that reactions 1 and 1cp and 2 and 2cp are competitive. On the other hand, there are also two consecutive reactions as a consequence of the oxidation of the intermediate residue, so

$$\frac{d\alpha_{ic}}{dt} = k_{ic}(\alpha_{icp} - \alpha_{ic})^{n_{ic}} \quad \text{for } ic = 1c, 2c \quad (21)$$

For reactions 1, 2 and 3, the pre-exponential factors do not depend on the concentration of oxygen. For reactions 1 and 2, the same set of values k_{oi} , E and n as those obtained from the correlation of the pyrolysis runs have been assumed. For reaction 3, the same values of E and n as the pyrolysis run have been assumed, but the pre-exponential factor has been deduced for the correlation of the combustion data, taking the same value for the two atmospheres considered $N_2:O_2$: 4:1 and 9:1.

For the remaining reactions, the dependence of oxygen has been considered with the following expressions:

$$k = k^* \left[\frac{p_{O_2}}{0.20} \right]^b \quad (p_{O_2} \text{ in atm}) \quad (22)$$

where the pre-exponential factor k^* is directly proportional to the oxygen pressure, and p_{O_2} is the partial pressure of oxygen in atm, and logically k equals k^* when working with $N_2:O_2$ 4:1 atmosphere (p_{O_2} equals 0.20 atm). The values of coefficient b have been obtained for each reaction.

The total weight fraction and the volatile weight fraction V are related with the conversion degrees by

$$w = 1 - V$$

$$= 1 - F_p(v_{1\infty}\alpha_{1\infty} + v_{2\infty}\alpha_{2\infty} + v_{3\infty}\alpha_{3\infty} + v_{1cp\infty}\alpha_{1c\infty} + v_{2cp\infty}\alpha_{2cp\infty} + v_{1c\infty}\alpha_{1c\infty} + v_{2c\infty}\alpha_{2c\infty}) + F_M(v_{4\infty}\alpha_{4\infty} + v_{5\infty}\alpha_{5\infty}) \quad (23)$$

where $v_{i\infty}$, $v_{ic\infty}$ and $v_{icp\infty}$ represent the maximum values in accordance with the scheme of reactions proposed, and F_p and F_M are respectively, weight factors corresponding to the polymeric

Fig. 12. Evolution of the weight fraction of volatiles for each reaction in a combustion TG run.

fraction that can decompose and to the metal fraction that can be oxidized. In this case, this weight factor obtained also by optimization varies in a wide interval, although most of the values are between 0.8 and 1.2. It must be emphasized that these factors are included considering that each sample can contain different quantities of fractions that can be decomposed or oxidized. In duplicated runs, it has been tested that the volatile mass evolved at infinite time in TG runs can be very different from one sample to another.

The contribution of the different reactions is presented in Fig. 12, where the main fraction corresponds to reaction 3, although the system is complex.

The kinetic parameters obtained, are also shown in Table 3, and are valid for the two atmospheres and for dynamic and isothermal runs. In Figs. 4–8, the calculated values are also plotted together with the experimental ones. It can be observed that the curves are close together, although there are some peaks that cannot be reproduced with the model proposed. It is possible that the presence of metals and other compounds can catalyze the decomposition rate of the organic matter and/or the organic matter can get oxidized, increasing the weight, decomposing immediately and decreasing again. In any case, the model obtained can be satisfactory for analyzing the decomposition and for simulation. The variation coefficient is 5.8%, which indicates that the correlation is acceptable. The values of activation energy are logical and similar to other values obtained in the thermal decomposition of other materials, but it must be reminded that these parameters are only valid for correlation. It is curious that the weight fraction of volatiles calculated as increase in the oxidation of the metal fractions is equal to 0.16, probably corresponding to the oxidation of Cu to Cu₂O and Cu₂O to CuO. A detailed study of the oxidation/decomposition considering the diffusion of oxygen together with the decomposition of the solid material is outside the objectives of this paper and would not be probably useful taking into account the heterogeneity of the sample.

It must be emphasized that the samples used were milled to fine dust, because in a group of previous TG runs made to carry out this study with a particle size of 1–2 mm, a great variation of the final residue was observed. In the pyrolysis runs, where only the

organic polymer decomposes, the final residue is approximately the same for all the runs, and the correction factors are very close to unity. In the combustion runs, there is an oxidation of the metallic compounds and this probably generates a different residue at infinite time. Under these restrictions, it is not possible to deduce if the heating rate has any influence on the final residue. Although an effort was done to obtain homogeneous sample, the results indicate that the sample of fine dust was not uniform enough to obtain logical variations on the final residue, and/or there is another type of interactions not considered in this paper.

4. Pollutant emissions in ECs and mobile waste

Runs were carried out at 500 °C in a poor oxygen atmosphere in order to study the evolution of compounds when the decomposition temperature is not very high and there is no good mixing with air. In accordance with the TG data, at 500 °C (773 K) the decomposition is nearly completed, so the results obtained mainly show the primary products and direct derivatives that are formed in the decomposition.

4.1. Gases and volatile compounds

The results of the gases in combustion and pyrolysis are shown in Table 4.

The analysis of the gases in the TCD chromatograph gives information about the combustion process. The parameter RCO % in the table is the ratio between $\text{CO}/(\text{CO} + \text{CO}_2)$, and the combustion conditions can be related to this value. High values mean a pronounced oxidative pyrolysis and the values decrease when the oxygen in the environment increases.

Table 4

Gases and volatile emissions in pyrolysis and combustion experiments. nd means lower than detection limit.

	Sample (mg/kg)			
	Pyrolysis 500 °C		Combustion 500 °C	
	EW	EC	EW	EC
CO ₂	40000	6000	210000	90000
CO	nd	nd	39000	24000
RCO (%)			15	21
Methane	1308	332	1687	576
Ethane	291	81	157	51
Ethylene	325	136	512	127
Propane	148	31	62	18
Propylene	338	269	337	191
Isobutane	nd	nd	16	nd
Acetylene	nd	nd	20	24
Butane	nd	nd	nd	nd
<i>trans</i> -Butene/1-butene	82	nd	nd	nd
<i>trans</i> -2-Butene	247	21	163	nd
Isobutene	229	21	nd	nd
<i>cis</i> -2-Butene	38	5	nd	nd
Isopentane	15	nd	nd	nd
<i>n</i> -Pentane	37	13	440	nd
Propyne	545	nd	nd	nd
1,3 Butadiene	nd	nd	nd	nd
1-Pentene	47	2	nd	nd
2-Butyne	4	nd	nd	nd
1-Butyne	nd	nd	nd	nd
Hexane	46	nd	nd	nd
1-Hexene	59	nd	nd	nd
<i>cis</i> -2-2-Hexene	5	nd	nd	nd
Heptane	14	nd	nd	nd
Benzene	207	85	18	68
1-Heptene	47	nd	nd	nd
Isooctane	nd	nd	nd	nd
Toluene	2866	267	nd	268
Xylene (<i>o</i> -, <i>m</i> -, <i>p</i> -)	737	183	nd	207

The emission of volatile compounds is quite related with to the polymer quantity in the samples. Electronic waste emits higher amounts of volatile compounds than circuits in the same conditions owing to the origin of the sample. Pyrolysis runs give higher concentrations and wider distribution of different compounds but with reference to the emission of the most toxic compounds (benzene, xylene, etc.) the behaviour of the EC is similar.

Methane is the main compound in all the runs, although a high yield of toluene is obtained in the pyrolysis of electronic waste.

4.2. Semivolatile compounds

Brominated compounds are used in printed board as flame-reardant agents and the combustion of these types of compounds produce the emission of other bromine compounds with unknown grades of toxicity. In the semivolatile compounds there are three groups of compounds identified: polycyclic aromatic hydrocarbon compounds (PAH), brominated compounds and other aromatic compounds.

4.2.1. PAH

The sixteen polyaromatic compounds established by US EPA as priority PAHs were searched in the four runs but only naphthalene and in one case phenanthrene were identified.

4.2.2. Brominated compounds

A group of these compounds was identified and quantified in all the chromatograph time windows. TBBPA is a flame-reardant mainly used in printed circuit boards synthesized by bisphenol A in a not very selective process. For this reason its use can be the responsible for finding other bromobisphenols and bromophenols in the gases and other bromoaromatic compounds in the EC samples but not in waste samples. Bromobenzene, bromodioxin, dibromophenols and other bromo-chlorinated compounds have been identified. Some of these compounds have been identified by other authors such as Csoma et al. [19] and Barontini and Cozzani [20]. The latter authors found most of these brominated compounds in the primary thermal decomposition pathways of TBBA. Hall and Williams [18] did not find brominated compounds in the semivolatile fraction of plastic WEEE pyrolysis, but the amount of bromine in their samples was much lower than that found in the other studies.

4.2.3. Other aromatic compounds

Around 140 semivolatile compounds were identified as reaction products and the main ones were styrene, phenol and bisphenol A with the higher levels in the pyrolysis of electrical waste, which agrees with the results for volatile compounds. The Kovats and Lee index [21] was used to sort the compounds obtained, and the quantification was carried out using an internal standard. The list of all the compounds identified and quantified is presented in Table 5.

4.3. PCDD/F and dioxin-like-PCB

The combustion under irregular conditions of polymer metals-halogen materials can be the source of dioxin and furan emissions. In this case, where the bromine is a main element in the elemental analysis of the samples, polybrominated dibenzodioxins can be more important than the chlorine isomers. Some authors are studying the relation between PBDD/F emissions and some brominated compounds that are identified as precursors in the formation of these dioxins [17–22]. Following the studies of these authors, the identification of dibromophenol and tribromophenol,

Table 5

Emission of semivolatile compounds in combustion and pyrolysis runs. nd means lower than detection limit.

Compound (mg/kg)	Pyrolysis 500 °C		Combustion 500 °C	
	EW	EC	EW	EC
Cyclohexene 4 ethenyl	235	nd	nd	nd
Pyridine 4 methyl	nd	84	nd	nd
Ethylbenzene	1456	20	311	nd
<i>p</i> -Xylene	126	nd	21	nd
Styrene	42332	108	8749	17
Benzene, methoxy-	nd	nd	nd	5
Dimetilpirazine	nd	83	nd	nd
<i>p</i> -Benzoquinone	nd	nd	nd	9
Benzene (1-methylethyl)	202	54	29	nd
Bromobenzene	nd	nd	15	nd
Allylbenzene	nd	nd	42	nd
Benzene cyclopropyl	257	nd	nd	nd
Benzene propyl	158	nd	21	nd
Benzene 1ethyl 2 methyl	28	nd	nd	nd
Trimetilpiridine	nd	nd	nd	nd
Benzaldehyde	12	nd	651	nd
Ethoxy-benzene	nd	nd	nd	11
Benzene 1ethyl 4 methyl	31	nd	nd	nd
Benzene 123 trimethyl	81	41	nd	nd
Phenol	26611	17801	3382	3601
Alfa methyl styrene	6112	nd	1296	nd
Benzonitrile	104	nd	57	nd
<i>p</i> -Methylstyrene	nd	nd	22	nd
Benzoofuran	nd	313	39	131
2 Propenyl benzene	209	nd	nd	nd
Para cymene (4-isopropiltoluene)	nd	58	nd	nd
Indane	37	nd	nd	nd
Benzeneacetaldehyde	nd	nd	423	nd
Benzene 3 butenyl	107	nd	nd	nd
2 Methyl phenol	402	468	34	133
<i>p</i> -Cymenene	nd	nd	32	nd
3-Hexenedinitrile	nd	nd	12	nd
1,2 Diethylbenzene	nd	21	nd	nd
2-Bromophenol	nd	328	nd	122
4-Bromophenol	nd	103	nd	nd
<i>p</i> -Alliltoluene	nd	20	nd	nd
Styrene, 7,8-oxyde-	nd	nd	57	nd
Acetophenone	72	nd	69	nd
Methyl phenol	719	nd	26	69
Benzene, 1-ethenyl, 3-ethyl-	nd	nd	nd	29
Dihydrobenzofuran	nd	18	nd	nd
Benzene 1 ethenyl 4 ethyl	2960	1126	nd	nd
<i>p</i> -Ethylstyrene	1052	391	nd	nd
<i>m</i> -Ethylstyrene	nd	nd	94	nd
Trimethyl benzene	nd	9	nd	nd
3 Methyl benzonitrile	80	nd	nd	nd
Dimethyl phenol	nd	44	nd	25
Methyl benzofuran	24	195	18	88
Benzene 1 ethenyl 4 methoxy	34	58	36	nd
Acetic acid, 2-methylphenyl ester-	nd	nd	nd	10
Adamantane 1,3 dimethyl	202	nd	nd	nd
2 Ethyl phenol	73	72	nd	58
Benzeneacetonitrile	nd	nd	41	nd
Benzil nitrile	141	nd	nd	nd
2,4 Xylenol	nd	87	nd	nd
Methyl indene	80	41	16	nd
4 Ethyl phenol	626	155	6	nd
2,3 Dimethylbenzonitrile	64	nd	nd	nd
1,3 Dihydro naphthalene	30	nd	nd	nd
Phenol, 2-bromo-4-methyl-	nd	nd	nd	5
2 Propenenitrile 2 phenyl	60	nd	nd	nd
Naphthalene	56	58	9	1
2-Ethylbenzofuran	nd	nd	nd	1
246 Trimethyl phenol	71	17	nd	nd
Benzoofuran, 4,7-dimethyl-	nd	nd	nd	3
23 Dihydrobenzofuran	37	nd	14	nd
2-Propanone, 1-phenoxy-	nd	nd	nd	34
Phenol 4 (1methyl ethyl)	5191	2237	nd	nd
Phenol 4 ethyl 3 methyl	34	27	nd	nd
2-Coumaranone	nd	nd	nd	22
Benzenopropanonitrile	48	nd	10	nd

Table 5 (Continued)

Compound (mg/kg)	Pyrolysis 500 °C		Combustion 500 °C	
	EW	EC	EW	EC
2 Propyl phenol	60	nd	nd	nd
Isoquinoline	44	nd	10	24
2- <i>n</i> Propilfenol	nd	56	nd	nd
1 <i>H</i> Indene 1,1, dimethyl	19	45	nd	nd
Phenol <i>p</i> - <i>tert</i> -butyl	2556	50	320	nd
<i>p</i> -Isopropenylphenol	10663	nd	nd	nd
Tetrametil benzene	nd	53	93	nd
Benzenebutanenitrile	4224	nd	nd	nd
Methylnaphthalene	nd	nd	8	nd
Benzenebutanenitrile	nd	nd	595	nd
Benzenamine, 4-bromo, 2-6-dimethyl-	nd	326	nd	27
1 Phenyl 1 heptyne	19	nd	nd	nd
Bencene acetaldehyde alpha methyl	134	nd	nd	nd
Ethanone 1 (2-hydroxi phenyl)	170	53	nd	nd
1,1'-Biphenyl	nd	nd	18	nd
Phenol, 2,6-dibromo-	nd	nd	nd	24
2,4-Dibromophenol	nd	55	nd	6
2 Bromo 14 dioxin	nd	18	nd	nd
4 <i>H</i> -1-Benzopyran-4-one-	nd	nd	nd	30
1,4-Benzediol, 2-bromo-	nd	nd	nd	3
Cyclopropanecarbonitrile, 2-Phenyl- <i>trans</i> -	nd	nd	23	nd
Acetophenone, 4'-hydroxy-	nd	nd	nd	110
phenol 35 bis (11dimethylethyl)	47	nd	nd	nd
4,5-Dibromobenzocyclobutene	nd	nd	10	nd
1 <i>H</i> -Isoindole-1,3(2 <i>H</i>)-dione	nd	nd	nd	19
Benzoimide	nd	35	nd	nd
Ethanone, 1-(3-bromo-4-hydroxyphenyl)-	nd	nd	nd	29
1,1'-Biphenyl, 4-methyl-	nd	nd	nd	9
<i>o</i> -Phenylphenol	nd	19	nd	nd
2-Nafthalenecarbonitrile	nd	nd	15	nd
Bibenzyl	44	nd	nd	nd
Dibenzofuran	nd	11	nd	13
4 (Methylthio) acetophenone	nd	14	nd	nd
2-Propanol, 1-chloro-3-phenoxy	nd	nd	nd	13
3,6-Dibromo-2,5-xylidine	nd	194	nd	12
1,3 Diphenylpropane	527	nd	118	nd
1-Naphtaleneacetonitrile	nd	nd	11	nd
Brominated compound	14	nd	nd	nd
57 Dibromo 23 dihydro 2 methylbenzofuran	nd	32	nd	nd
Phenanthrene	2	nd	nd	nd
<i>p</i> -Hydroxybiphenyl	nd	nd	nd	181
1,2 Diphenylethylene	nd	nd	12	nd
<i>m</i> -Phenylphenol	nd	553	nd	nd
1,2-Dimethylcyclopropene	nd	nd	42	nd
3 Phenol benzofuran	nd	18	nd	6
1 Methoxy 4 pyrrolidinonaphthalene	nd	71	nd	nd
2-Aminoquinolene	486	nd	nd	nd
1,3-Butadiene, 1,4-diphenyl-, (E,E)-	nd	nd	9	nd
Para-alfa-cumilfenol	151	5	nd	nd
2 methyl 4'methoxy 1,1' biphenyl	nd	42	nd	nd
[1,1'-Biphenyl]-4,4'-dicarbonitrile	nd	nd	9	nd
2-Phenylnaphtalene	nd	nd	16	nd
2-Propanol-1,3-diphenoxy	nd	nd	nd	9
2-Benzylnaphtalene	nd	nd	11	nd
2(4'Hydroxyphenyl)2-(4etoxiphenyl)propane	374	24	8	nd
1 <i>H</i> -Pyrrolo[2,3- <i>b</i>]pyridine, 4-methyl-2-phenyl	nd	nd	6	nd
<i>m</i> -Terphenyl	nd	nd	12	nd
Bisphenol A	11258	1018	28	265
2-(4'-Hydroxyphenyl)-2-(4'-methoxyphenyl)propane	nd	nd	nd	11
Brominated compound	nd	nd	nd	119
Bromobisphenol A	nd	432	nd	nd
Hexametilbenzofenone	104	nd	nd	nd
2-Bromo-3'-methoxyacetophenone	nd	33	7	nd
Acridine, 4,5-dibromo-9-chloro	nd	nd	nd	25
Thieno[3,2-<i>c</i>]pyridine, 3-bromo-	nd	nd	34	9
Dibromobisphenol A	nd	157	nd	nd
Tribromobisphenol A	nd	43	nd	nd

In bold, brominated compounds.

Table 6

PCDD/F and PCB emission in pyrolysis and combustion runs. nd means lower than detection limit.

	pg who2005 TEQ/g		EW comb	EC comb	EW pyr	EC pyr
	EW	EC				
2378-TCDF	0.0034	0.0584	0.2326	0.1064	nd	0.8387
12378-PeCDF	0.0124	0.0009	0.1860	nd	0.3769	0.4452
23478-PeCDF	0.0672	0.0805	0.9302	0.7181	6.7839	3.4839
123478-HxCDF	0.0379	0.0411	0.2326	0.3191	1.5913	1.0645
123678-HxCDF	0.0276	0.0379	0.6202	0.4255	3.4338	0.8710
234678-HxCDF	0.0534	0.0505	0.9302	0.1596	3.4338	1.3871
123789-HxCDF	0.0448	0.0095	1.8605	nd	2.0101	0.6774
1234678-HpCDF	0.1005	0.0205	0.1318	nd	0.5863	0.2774
1234789-HpCDF	0.0238	0.0017	0.0155	nd	0.1340	0.0677
OCDF	0.5791	0.0030	0.0135	0.0050	0.0153	0.0056
2378-TCDD	nd	0.1421	0.7752	0.7979	nd	13.5484
12378-PeCDD	0.1034	0.0474	nd	nd	nd	3.2258
123478-HxCDD	0.0362	0.0063	0.3101	nd	2.0938	0.3871
123678-HxCDD	0.0121	0.0174	nd	0.0798	2.5126	0.4516
123789-HxCDD	0.0379	0.0079	nd	0.1330	1.0888	0.2581
1234678-HpCDD	0.0076	0.0062	0.3023	0.1702	0.2010	0.1710
OCDD	0.0040	0.0015	0.0049	0.0017	nd	0.0116
Total PCDD/F	1.1514	0.5328	6.546	2.916	24.262	27.172
PCB-81	0.0003	0.0000	0.0012	0.0004	0.0023	0.0005
PCB-77	0.0010	0.0002	0.0039	0.0016	0.0090	0.0031
PCB-123	0.0000	nd	0.0003	0.0001	0.0005	0.0025
PCB-118	0.0003	0.0009	0.0084	0.0032	0.0085	0.0001
PCB-114	0.0000	0.0000	0.0004	0.0002	0.0004	0.0008
PCB-105	0.0001	0.0003	0.0023	0.0006	0.0027	nd
PCB-126	0.0776	0.0253	0.0775	0.0532	1.5913	0.4516
PCB-167	0.0000	0.0001	0.0008	0.0004	0.0011	0.0004
PCB-156	0.0000	0.0002	0.0023	0.0008	0.0011	0.0003
PCB-157	0.0000	nd	0.0004	0.0001	0.0007	nd
PCB-169	0.0093	0.0014	0.1628	0.0798	0.7789	0.2323
PCB-189	0.0000	0.0003	0.0005	0.0002	0.0016	nd
Total PCB	0.0885	0.0287	0.2609	0.1406	2.3979	0.6917
Total PCDD/F + PCB	2.602	0.603	6.806	3.057	26.659	27.864

can anticipate the emissions of PBDD/Fs. In this work, the analysis of PBDD/F was not possible. For this reasons the precursors and other brominated products have been identified as possible surrogates.

On the other hand, polychlorinated dioxins and furans and dioxin like PCBs were analysed in the raw samples and in the combustion and pyrolysis runs. The results are shown in Table 6. The level of the content in the raw material is similar to those obtained in other domestic samples, food or environmental samples, and this level is the same order than those found for other authors in open-burning systems [4].

The profiles of the PCDD/F analysis are shown in Figs. 13 and 14. In electronic waste samples the main PCDD/Fs are the most chlorinated ones, in combustion and pyrolysis runs the trend is the

same and the raw material has 98% abundance of OCDF. In ECs the trend is similar but the raw material has a wider distribution of isomers although the main one is OCDF.

Figs. 15 and 16 show the PCB results. Combustion runs are very similar in both cases but pyrolysis runs have different isomers. The more toxic ones, PCB-126 and PCB-169, are emitted mainly in pyrolysis runs.

The level of toxic equivalents obtained in dioxin analysis is curiously higher in pyrolysis runs than in combustion ones. The trend of PCDD/Fs and PCBs yields is similar, but the toxicity obtained for the pyrolysis runs is higher.

In order to analyse if the emission factors of 3–27 pg/g are low or high, these results can be compared with those found by Aracil

Fig. 13. Comparison of PCDD/F in emissions and electronic waste.

Fig. 14. Comparison of PCDD/F in emissions and electronic circuit.

Fig. 15. Comparison of PCB in emissions and electronic waste.

Fig. 16. Comparison of PCB in emissions and electronic circuit.

et al. [23] who obtained levels of PCDD/F in PVC combustion of 4000 pg I-TEQ/g and Moltó et al. [24], who found 14 pg I-TEQ/g in the combustion of polyester fabrics. It can be observed that the emission factors of dioxins in the thermal treatment of electronic wastes are low, and with adequate operating conditions, there would probably be no risk of emissions of PCDD/F. But these results do not indicate something similar about PBDD/F. On the contrary, the expected yields are estimated to be high.

5. Conclusions

On the one hand a single set of parameters has been used to correlate dynamic and isothermal runs to obtain two kinetic models, one for pyrolysis and other for combustion of EC. It has been tested that an acceptable correlation can be obtained for dynamic runs at different heating rates and isothermal runs at distinct temperature operation.

On the other hand, the emissions of the pyrolysis and combustion of two types of materials, EC and electronic waste have been studied. More than 100 semivolatile compounds have been identified with special interest in brominated ones. The levels of PCDD/Fs and dioxin-like-PCBs have been evaluated and compared with the levels in raw material concluding that there are no high emission factors. Nevertheless, the emissions of PBDD/Fs have not been analysed but the identification of other brominated compounds can indicate the emission of this group of dioxin homologues. Some studies with open burning [4] and pyrolysis of electronic waste [25] reveal the high emissions of PBDD/Fs, in order to 50–500 times higher than those of the homologues of PCDD/Fs. For these reasons, the conclusion about the thermal treatment of this kind of waste in no optimal conditions is that the emissions can be a healthy and environmental hazard that must be subjected to strong studies and controls.

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