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Thermogravimetric kinetic analysis and pollutant evolution during the pyrolysis and combustion of mobile phone case

R. Font, J. Moltó *, S. Egea, J.A. Conesa

Chemical Engineering Department, University of Alicante, P.O. Box 99, 03080 Alicante, Spain

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ABSTRACT

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. Mobile phone components can be physically segregated through grinding at the dismantling sites, in order to reuse or reprocess (via chemical or physical recycling) the recovered plastics and valuable metals.

A kinetic study of the thermal decomposition of a mobile phone case has been carried out under different conditions by thermogravimetry. Several experiments were performed in a nitrogen atmosphere (pyrolysis runs) and also in an oxidative atmosphere with two different oxygen concentrations (10% and 20% oxygen in nitrogen). Dynamic runs and dynamic + isothermal runs have been carried out to obtain much decomposition data under different operating conditions. Moreover some TG–MS runs were performed in order to better understand the thermal decomposition of a mobile phone case and identify some compounds emitted during the controlled heating of this material. A scheme of two independent reactions for pseudocomponents has been proposed for the pyrolysis process. For the combustion runs, the scheme proposed includes two pyrolytic reactions competing with other two reactions with formation of an intermediate residue, and finally the reaction of oxidation/burning of the intermediate residue.

Furthermore, pyrolysis and combustion runs at 500 °C in a horizontal laboratory furnace were carried out. More than 50 compounds, including carbon oxides, light hydrocarbons, and polycyclic aromatic hydrocarbons (PAHs) have been identified and quantified. The main semivolatile compounds detected were phenol and styrene. Furthermore, polychlorodibenzo-p-dioxin and polychlorodibenzofurans (PCDD/Fs) and dioxin-like PCBs produced were analyzed. In the combustion run, PCDDs were obtained in higher amounts than PCDFs and HxCDD was the most emitted homologue.

1. Introduction

Technological innovation with the expansion of markets contributes to accelerating the replacement of electrical and electronic products, which leads to the generation of a large amount of waste arising from these products. This amount has been steadily increasing in recent years and the European Commission estimates that each European citizen presently produces about 14 kg year^{-1} of “technological wastes” (de Marco et al., 2008).

While most of these wastes, including mobile phones, personal computers, audio and video equipment, currently enter the solid waste stream and end up in municipal landfills or municipal waste combustors, a small but growing portion is directed for recycling (Gullett et al., 2007). E-waste is chemically and physically distinct from other forms of municipal or industrial waste; it contains both valuable and hazardous materials that require special handling and recycling methods to avoid environmental contamination and detrimental effects on human health (Robinson, 2009).

About 50–80% of the e-waste collected for recycling in industrialized countries end up in recycling points in China, India, Pakistan, Vietnam and Philippines, taking advantage of the lower labor costs, and less stringent environmental regulations in these countries (Wong et al., 2007). Unfortunately, open burning of this kind of waste is the usual technique employed to recover the valuable parts and this method has little regard for workers’ safety and for environmental protection (Cobbing and Amsterdam, 2008).

The Electrical and Electronic Equipment Waste Directive (European Commission, 2003) promotes the re-use, recycling and recovery of such electrical and electronic waste. Economic and environmentally appropriate valorisation routes for e-wastes with high plastics contents have to be identified. In this way, several test programs have been developed in Europe. The European Flame Retardants Association (EFRA), the plastics producing industry federation PlasticsEurope, and Umicore Precious Metals Refining carried out a full scale trial to assess the technical feasibility of including mixed e-wastes in the feed to an integrated metals

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* Corresponding author. Tel.: +34 96 590 38 67; fax: +34 96 590 38 26.
E-mail address: julia.molto@ua.es (J. Moltó).

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smelter and found that Hoboken smelter plant has the ability to treat e-wastes in conformity to applicable legislation, serving as energy source and reducing agent (Brusselaers et al., 2006). In the context of a European project ''Halocleanapplication'', a pilot plant of two gas tight rotary kilns has been developed to convert electronic scrap into gaseous hydrogen bromine, a nearly debrominated oil and a residue, that contains the noble metals in a more concentrated form, being the three fractions suitable for further usage (Balabanovich et al., 2005). Another interesting project has been developed in Karlsruhe Research Centre where trials conducted at pilot plant scale have demonstrated that e-wastes co-combustion with municipal solid wastes allows the economic feasibility of recovering bromine or hydrogen bromide when suitable wet scrubbing systems are employed (Vehlow et al., 2003).

Up to now the attention has been mainly focused on the recoverable metals, while there is not a clear alternative for recycling the miscellany of non-metallic compounds (plastics, rubbers, etc.) present in electronic wastes. Thermal treatment of these materials could be an alternative for treating these wastes. Thermal treatment comprises different processes such as direct combustion, co-combustion with organic wastes, pyrolysis and gasification.

There are other interesting contributions in literature considering pyrolysis and/or combustion of electronic wastes. Some of them, related to this paper, are presented:

- Balart et al. (2006) carried out an interesting kinetic analysis of the pyrolysis of polymeric mixtures, obtaining variations of apparent activation energies and reaction orders versus composition, but they do not propose a mathematical equation for simulating the process.
- de Marco et al. (2008) pyrolyzed different types of e-wastes, including mobile phones, studying the different solid, liquid and gas yields. No pollutants were determined.
- Gullett et al. (2007) analyzed the air emissions and residual ash from open burning of insulating wire and circuit board. For the circuit board, the average PCDD/Fs were 92 ng TEQ kg^{-1}. No data were obtained for mobile phone cases.
- Hall and Williams (2007) investigated the pyrolysis of three plastic fractions from e-wastes, one of them (with acrylonitrile–butadiene–styrene – ABS) had a similar composition similar as the mobile case studied. Elemental analysis and composition of gas, liquid and solid were determined. No PCDD/Fs were analyzed.

In a previous work, the thermal degradation of a mobile phone (printed circuit board + case) and printed circuit board alone have been investigated. Kinetics and emissions from the controlled heating of these materials were studied (Moltó et al., 2009). In order to study the feasibility of thermal treatment of plastics recovered from mobile phones, the thermal decomposition and the pollutants emitted at different conditions were studied for a mobile phone case. The conclusions obtained can be significant for other fractions from e-wastes, containing the same type of polymer. On the other hand, there are some interesting aspects that must be analyzed, because emissions of chlorinated pollutants, such as polychlorodibenzo-p-dioxin and polychlorodibenzofuran (PCDD/F) from separated fractions can be greater than from the whole waste, as occurs in this mobile case.

2. Experimental section

2.1. Raw material

The material studied was the case obtained from an obsolete mobile phone. Prior to the runs the material was crushed to fine dust using a vibratory disc mill by Herzog, HSM100 model (Osnabrück, Deutschland). Some characteristics of the mobile phone case are presented in Table S-1. CHNS analysis was carried out in a Perkin–Elmer 2400 (Perkin–Elmer, Beaconsfield, UK) and net calorific value determined in an AC-350 calorific bomb (Leco Corporation, St. Joseph, MI). Semi-quantitative analysis of the rest of the elements was measured using a Philips TW 1480 automatic sequential spectrometer X-ray Fluorescence (Philips Co, Ltd.). Carbon content is high, which is consistent with the nature of the sample. High quantities of titanium and iron oxides can also be observed; both are usual additives employed as pigments to provide color and opacity to products such as plastics.

In order to obtain information about functional groups, and therefore identify the polymer present in the case, a FTIR analysis was carried out in a Bruker IFS FT-IR spectrometer and in reference to the results obtained by Balart et al. (2006), it can be concluded that the case is an acrylonitrile–butadiene–styrene (ABS)/polycarbonate (PC) blend. This mixture shows very effective flame retardant properties upon the addition of conventional halogen and/or non-halogen flame retardant agents, and this is the main reason of their wide use in electrical appliances. Fig. S-1 of the Supporting Information shows the FTIR spectrum of the phone case.

2.2. Thermobalance

The apparatus used to study the thermal decomposition of the material was a Mettler Toledo thermobalance model TGA/SDTA851e/LF/1600, with 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.

Pyrolysis (N_2) and combustion runs, N_2:O_2 4:1 (normal conditions) and N_2:O_2 9:1 (poor oxygen conditions), were carried out. 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.

In order to check the good performance of the thermobalance, an additional experiment with a heating rate of 5 K min^{-1} using Avicel PH-105 microcrystalline cellulose was carried out. The kinetic values obtained showed good agreement with the results presented by Gronli et al. (1999) in their round-robin study of cellulose pyrolysis kinetics by thermogravimetry.

The TG–MS runs were carried out in the same thermobalance previously indicated coupled to a Thermostar 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, 13–18, 25–32, 35–46, 50–52, 55–58, 60, 65, 68, 73, 78, 91, 96, 105, 106. In the TG–MS experiments, the gases employed were He and He:O_2 (4:1). The response of the different ions was divided by that of helium ($m/z = 4$) and subtracted from that corresponding to the beginning of the run.

2.3. Laboratory reactor

Furthermore, combustion and pyrolysis runs were carried out in a laboratory reactor in order to study the pollutants emitted at 500 °C. This temperature was chosen to study slow thermal