
POLLUTANT FORMATION DURING THE THERMAL DECOMPOSITION OF ELECTRICAL AND ELECTRONIC WASTES

J.A. Conesa*, J. Moltó, R. Font, S. Egea and N. Ortuño

University of Alicante, Department of Chemical Engineering
Ap. 99, E-03080 Alicante (SPAIN)
e-mail:ja.conesa@ua.es Phone: +34-965903400, Fax: +34-965903826

Abstract

In this contribution we present the results of the research done at the University of Alicante in the last four years [1-7] about the thermal decomposition of waste electrical and electronic equipment (WEEE). Several materials have been studied, including PVC and halogen-free wires, printed circuit boards and casing from mobile phones, as well as brominated flame retardants used in the EEE preparation such as TBBPA (tetra-bromo-bisphenol-A). Several experiments were performed in a nitrogen atmosphere (pyrolysis runs) and also in an oxidative atmosphere with different oxygen concentrations. Thermogravimetric runs were used to characterize samples, and a horizontal laboratory reactor was used to study the formation and destruction of pollutants during the thermal decomposition of these samples. More than 150 compounds, including carbon oxides, light hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), chlorophenols (ClPhs), chlorobenzenes (ClBzs) and bromophenols (BrPhs) have been identified and quantified. Furthermore, polychlorodibenzo-p-dioxin and polychlorodibenzofurans (PCDD/Fs), polybromodibenzo-p-dioxin and polybromodibenzofurans (PBDD/Fs), and dioxin-like PCBs produced were analyzed.

Keywords: pyrolysis, combustion, kinetics, electronic, printed circuit board, dioxins, PAHs, mobile phone

1. Introduction

The wire and cable industry manufactures a wide range of products that support a multitude of applications. Some of the major markets are communication cables, power and cable wire, automotive wiring, control and signal cables, and building wiring. Generally wires differ in conducting and isolation materials. The classic conductor material has been copper but aluminum is also used frequently today.

Many wire insulation and covering compositions contain materials, such as lead, halogenated compounds, and other compounds, that impart electrical insulation and fire performance properties. Specifically, fire retardants are used to avoid the propagation of fire. One of the most frequently used types of fire retardant, Halogenated Flame Retardants (HFRs), have been proven to be a hazard to human life and environment, which has led to regulations on their use with the ultimate goal of removing from the market.

Recently, The European Parliament has considered to review the Restriction of Hazardous Substances (RoHS) Directive to include compounds not previously covered by the legislation such as PVC and some HFRs in electronic equipment. The former directive is closely related to the directive on Waste Electrical and Electronic Equipment also known as WEEE directive. WEEE directive promotes the reuse, recycling, and recovery of these wastes as well as the collection of electrical and electronic wastes as a separate waste stream, which enhances the prospects for economic recycling. In this sense, End-Of-Life (EOL) communications and low-

voltage cables are valuable because these consist of approximately 50% copper by weight. The high price of copper ensures that an estimated 95% of EOL cable and wire is recycled.

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.

2. Materials and Methods

Three different types of EEE were used:

- Waste obtained from a mobile phone [1, 4, 5, 7]. The first sample was the printed circuit board alone, including metals (named as EC = Electronic Circuit). The second sample was the case of the mobile phone (named as MC = Mobile Case) and the last sample was obtained by crushing mixture of the circuit board and the case of the phone (named as EW = Electronic Waste).
- Waste from electric PVC and halogen-free wires [2, 6], with and without the presence of the metal conductor
- Brominated flame retardant used in the manufacture of printed circuit boards, in this case TBBPA [3].

3. Results and Discussion

A kinetic model for the pyrolysis and combustion of electronic waste has been obtained [5,7]. One set of parameters can explain all the experiments at the different atmospheres and at the different heating rates used.

At 500 °C in the combustion of the phone case in the laboratory reactor high amounts of PCDD/Fs were obtained, however the pyrolysis of this waste produces a lower emission factor for these pollutants, indicating that for the thermal treatment of this plastic recovered from e-wastes, pyrolysis could be a good option that leads to the formation of gases, oils and chars which can be used as chemical feedstocks or fuels [5].

Comparisons of pollutant emissions have been carried out with the thermal treatment of the mobile phone components at 850 °C, observing the different results and the possible incidence of the flame-retardants and presence of copper. The toxicity of the PCDD/Fs congeners obtained in the combustion of MC is much less than from the other two wastes. Although they are not much greater, this indicates the formation of PCDD/Fs, and consequently the thermal treatment in the industrial process must be more controlled than when burning only MC. Details on the possible organic compounds that can be formed under fuel-rich conditions can be also useful to analyze the performance of industrial processes treating these wastes.

On the other hand, combustion runs of two different wires, one of them halogen-free and another PVC based, have been performed in order to study the pollutant production in different conditions [2, 6]. PAHs, CBs, CPhs, mono to octa-chlorinated dioxins and furans and PCBs were determined for each run. PAHs emission decreases in the presence of the metal conductor, whereas the emission of chlorinated species dramatically increases, by using both kinds of wires. PVC wire presents very much higher emissions than halogenfree wire, and, as expected, the emission of chlorinated species is also much higher. In this sense, total dioxin equivalent toxic emissions were approx. 60 pg g⁻¹ in the case of halogen-free wire, regardless of the presence of metal. For PVC wire the emission was 5690 pg g⁻¹ with no metal and 6 times higher in the presence of copper. PCDD/Fs maximum emissions is of species with a high chlorination degree, except for samples with a high copper and calcium content, where the maximum is displaced to lower chlorine content (2 or 3 chlorine atoms).

Also a kinetic model for the pyrolysis and combustion of PVC and halogen-free electric wires has been obtained. One set of parameters can explain all the experiments at the different atmospheres and at the three different heating rates used. Thermal analysis of different parts of the cable, cover, insulation and

conductive metal, both separately and combined, has allowed for understanding of the interaction between the different materials [2].

Respect to the TBBPA decomposition [3], in the experiments carried out at 850 °C, bromophenols were detected to a lesser extent, in comparison with the experiments at 600 °C. The presence of oxygen does not seem to have a determinant influence in the formation of these compounds. A clear predominance of mono-, di- and tribrominated phenols was observed, particularly those with bromine in the positions 2-, 2,6- and 2,4,6-.

For TBBPA pyrolysis, the main isomers are the tetrabrominated ones, whereas in combustion the hexabrominated furans predominate. The yields obtained in the combustion experiment are nearly four times higher than those from pyrolysis. An overall examination of the degradation products emitted during thermal decomposition of TBBPA has been carried out. More than one hundred semivolatile compounds have been identified with special interest in brominated ones. The levels of PBDD/Fs have been evaluated, detecting amounts close to the ppm range. These results should be considered in the assessment of thermal treatment of materials containing brominated flame retardants, as TBBPA, since the emissions could pose a health and environmental risk.

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