DECOMPOSITION OF TWO TYPES OF ELECTRIC WIRES
CONSIDERING THE EFFECT OF THE METAL IN THE
PRODUCTION OF POLLUTANTS

Juan A. Conesa*, Silvia Egea, Julia Moltó, Nuria Ortuño and Rafael Font

Department of Chemical Engineering. University of Alicante. P.O. Box 99, 03080 Alicante (Spain). Phone: + (34) 96 590 38 67 Fax: + (34) 96 590 38 26

*Corresponding author. Email: ja.conesa@ua.es
DECOMPOSITION OF TWO TYPES OF ELECTRIC WIRES CONSIDERING THE EFFECT OF THE METAL IN THE PRODUCTION OF POLLUTANTS

ABSTRACT
Combustion runs at 700 °C in a horizontal laboratory furnace were carried out on two different electric wires (PVC and halogen-free wire). Tests were performed in the presence and in the absence of the metal conductor of the wires. The analyses of the polycyclic aromatic hydrocarbons (PAHs), chlorobenzenes (CBzs), chlorophenols (CPhs), mono- to octa-chlorodibenzo-p-dioxin and dibenzofurans (PCDD/Fs), and dioxin-like PCBs are shown. Regarding semivolatile compounds, PAHs production decreases in the presence of metal, while a higher amount of chlorinated compounds are emitted. Respect to the PCDD/Fs, the PVC wire in the presence of metal presents the highest emission, with a much more emission of furans than dioxins. The maximum emission is with 2 or 3 chlorine atom PCDD/Fs. PCBs emission correlates with PCDD/F production and represents 3-4% of total toxicity, determined by using WHO2005 factors.

KEYWORDS: WEEE, cables, dioxins, PAHs, PCBs, combustion.
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 aluminium 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 retardants, 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 considerate 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 (2003). 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 percent copper by weight. The high price of copper ensures that an estimated 95 percent of EOL cable and wire is recycled.
In traditional metal recycling, physical techniques are used to separate metals and plastics. The result of this operation is a waste formed by a single mixed fraction of different polymers (PVC, PE, LLDPE, HDPE, PP, etc). Until now plastic fractions of EOL cables have been landfilled because it was considered as a waste product with low value; however, today it is known that this waste has a great value and it is suitable for recycling, by material, chemical or energy recovery. In all cases previous polymer separation is advisable. Material recovery is an attractive option for PVC; whereas either material or energy recovery are equally attractive for polyolefin waste (Hagstrom et al., 2006).

Thermal treatment of PVC wastes it is a problematic way of recovery. Besides hydrogen chloride, chlorinated aromatic compounds are evolved during pyrolysis or combustion of PVC, such as chlorobenzenes (CBzs), chlorophenols (CPhs), chlorobiphenyls (PCBs) and, polychlorodibenzo-p-dioxins and polychlorodibenzofurans (PCDD/Fs) (Aracil et al., 2005). This could be especially alarming when the process is uncontrolled. Illegal recycling, open burning at landfills or accidental fires involves a serious damage to health and to environment. Moreover, when copper is present during combustion process, a catalytic formation of chlorinated compounds and dioxins, both in gas and solid phases, from phenols have been observed (Stanmore, 2004; Ryu et al., 2005; Ryu, 2008; Altarawneh et al., 2009).

Behaviour of cables and wires considering their heat release has been previously studied (Hirschler, 1994), showing that cables with excellent fire performance can be made by using a variety of materials, so that it would seem to follow that it is important to specify fire performance and leave material choice to manufacturers.
There is not extensive information of the emissions from thermal degradation processes of electric wires in oxidative atmosphere, and less in the presence of conductive metal (Chaala et al., 1997; Thibert and Gautier, 1999; Gullett et al., 2007; Kantarelis et al., 2009). The present work aims to extend the information in this issue providing the basis for the analysis of environment impact and development of new products, taking special interest on the effect of the metal on the decomposition and the previsible differences between PVC and halogen-free wires.

2. MATERIAL AND METHODS

2.1 Electrical Wires

Supplied by General Cable, Co., two kinds of commercial cables have been employed in this work. The first one is a common wire (designed as P), with PVC cover and reticulated polyethylene as insulation. The second one is a special fire-resistant and halogen-free wire (designed as H). Figure 1 shows the scheme of electrical wire, the composition of the two materials used and the weight percentage of each part. As we can see in Figure 1, the material used in the cover (or jacket) of the halogen free wire is a mixture of polyethylene, a thermoplastic elastomer, and aluminium trihydroxide (PE-TPE-ATH). Elemental analysis of the wires and some more details can be found in a previous work (Conesa et al., 2010). To ensure the homogeneity, the samples were crushed (1-3 mm) using a laboratory blender by DINKO, 8010 model (DINKO, Barcelona, Spain).

In order to study the effect of the presence of copper during the decomposition, for each kind of wire two different samples were prepared: one consisting of the plastic parts, named P1+P2 and H1+H2, and the other one representing the entire wire named P1+P2+P3 and H1+H2+H3, where P3 and H3 refers to the metal (see Figure 1).

2.2 Experimental system
Experiments were performed in a moving tubular reactor which consists in a quartz tube (10 mm wide), where the material is introduced uniformly along. This tube is introduced in a horizontal furnace, maintained at the desired temperature, at constant velocity using a horizontal actuator. Figure SM-1 (Supplementary Information) shows a scheme of the experimental system. More details of the equipment can be found elsewhere (Barneto et al., 2009; Conesa, 2011). In all runs the temperature of the oven was 700 °C. Synthetic air was introduced parallel to the sample, with gas flowing at 300 mL/min (measured at 1 atm and 20 °C). All runs were performed under fuel-rich atmosphere, with an oxygen ratio of 0.5 (ratio between actual and stoichiometric oxygen (Conesa et al., 2007; Conesa et al., 2009)).

The outlet gas stream was sampled to analyze semivolatile compounds such as PAHs, CPhs and CBzs, PCDD/Fs, and dioxin-like PCBs. Emitted gases were collected using a poliaromatic Amberlite® XAD-2 resin as sorbent (Supelco, Bellefonte, USA) placed at the outlet of the furnace during the whole experiment. Before the decomposition runs, a control containing no sample was carried out using the same experimental conditions (blank).

Amberlite® XAD-2 resin was extracted in toluene by Accelerated Solvent Extraction (ASE-100, Dionex-Thermo Fisher Scientific Inc., California, USA) and the extracted solution was divided as follows: approximately 30 wt. % was employed to analyze PAHs (US-EPA 8270D method), CPhs and CBzs; the rest (over 70 wt. %) was used for the analysis of PCDD/Fs and “dioxin-like” PCBs (EPA 1613 and 1668A methods).

PAHs, CPhs and CBzs were analyzed by GC–MS in SIM mode (Agilent GC 6890N/Agilent MS 5973N, Agilent Technologies, USA) using the isotope dilution method. CPhs and CBzs were also specifically analyzed in SIM mode with mixture
standards containing all isomers, following an analogous procedure to that of the 16 PAHs. Additionally, the identification of each isomer was confirmed by checking the ratio between the areas of the primary and the secondary ions, since they are known due to presence of $^{35}\text{Cl}$ and $^{37}\text{Cl}$.

For the analysis of PCDD/Fs and “dioxin-like” PCBs, cleanup was performed using the Power Prep system (FMS, Inc., Boston, MA) with three different columns: silica, alumina, and activated carbon (FMS, Inc., Boston, MA). The analysis was completed by HRGC/HRMS. For HRGC, an Agilent HP5890 gas chromatograph equipped with programmable temperature vaporization (PTV) inlet with a septumless head was used. For HRMS, a Micromass Autospec UlitmaNT mass spectrometer (Micromass, Waters, UK) with a positive electron impact (EI+) source was employed. All congeners of dioxins and furans were determined, from mono- to octachlorinated species.

The standards used for the analysis of 16 PAH were supplied by Dr. Ehrenstorfer-Schäfers (Augsburg, Germany) and the standards of CPhs, CBzs, PCDD/Fs and “dioxin-like” PCBs were obtained from Wellington Laboratories (Ontario, Canada). All the solvents for organic trace analysis were purchased form Merck (Germany).

3. RESULTS AND DISCUSSION

Table 1 shows the results on the emission of PAHs for the four runs done in the laboratory reactor. Note that these results are expressed in mg/(kg of consumed material), i.e., considering only the plastic fractions in the basis; if the whole weight is considered in the weight base, emission of runs P1+P2+P3 and H1+H2+H3 will be approximately halved (composition is shown in Figure 1). In the first column (Table 1) we can see the results for the combustion of the halogen free wire with no metal, the
second column is in the presence of metal, and third and fourth columns are the ones obtained with the PVC wire.

The main PAHs emitted in all cases are naphtalene and acenaphtylene. It seems in both cases that the presence of metal reduces the production of this kind of pollutants, probably due to the catalysis of cracking reactions that produces low molecular weight compounds. Also it is possible that the presence of metal catalyses chlorination reactions as will be presented later. The emission of each of the species shown in Table 1 is decreased almost in the same proportion for each one of the wires, being approximately a 80% of the emission in the absence of the metal in the case of halogen-free wire, and a 6% in the case of PVC wire.

Previous works (Andersson et al., 2004) analyzed the pollutants derived from combustion of electric wires under well-ventilated and vitiated conditions, at small and large scale, but unfortunately the experimental conditions of the runs performed were not well controlled and a clear conclusion was not found. The authors find emissions of total PAHs equivalent to approximately 50-250 mg/kg for PVC and halogen-free wires, finding an increase in PAHs production for vitiated atmosphere (poor oxygen availability) using the PVC wire but not in the case of halogens-free wire.

The total emission of CBzs and CPhs is presented in Table 2. The emission of each isomer analysed is presented in Tables SM-1 and SM-2 (Supplementary Information), for CBzs and CPhs respectively. For both kind of compounds the formation is much more important for the PVC wire, and is enhanced in the presence of metal. This would explain, at least partly, the decrease in PAHs shown before. Transformation of PAHs to chlorinated species has been already reported at temperatures between 300 and 1000 °C (Zhang et al., 2011). Both wires present a much more emission of CPhs than CBzs.
Furthermore, the highest chlorobenzene emission is in the mono-chlorobenzene species, and 3,4-dichlorophenol in the case of chlorophenols. Chlorinated phenols are known to be the most direct precursors of the formation of PCDD/Fs congeners (Ballschmiter et al., 1988; Born et al., 1989; Sidhu et al., 1995), and these are among the most abundant aromatic compounds found in municipal solid waste incineration emissions (Tuppurainen et al., 2000). On the other hand, many authors have confirmed the formation of chlorinated compounds and dioxins, both in gas and solid phases, from phenols when there is an oxidative atmosphere and in the presence of copper chloride (Stanmore, 2004; Ryu et al., 2005; Ryu, 2008; Altarawneh et al., 2009).

Figure 2 presents the distribution of the congeners contributing to the toxicity of the PCDD/Fs emission in the four experiments, with H and P wires in the presence or absence of metal. Data in Figure 2 has been calculated by using I-TEQ factors ($f_i$) and normalizing the contribution of each congener to the total toxicity:

$$\text{% PCDD/Fs toxicity congener } i = \frac{f_i C_i}{\sum_{i=1}^{17} f_i C_i} \times 100$$

where $C_i$ represents emission of toxic congener $i$.

Some points should be noted. On the one hand, the distribution of congeners depends on the material but rarely on the presence of metal. In this sense, the major contribution to the total toxicity is from 2,3,7,8-tetrachlorodibenzofuran in the case of H wire and 2,3,4,7,8-pentachlorodibenzofuran in the combustion of PVC. On the other hand, it is important to note that in the runs performed, furans contribute much more to the toxicity than dioxins. Specifically, congener 2,3,4,7,8-pentachlorodibenzofuran has been found to be the most represented in industrial incinerators emissions (Fiedler et al., 2000). Another work (Li et al., 2008) determined the concentrations and profiles of PCDD/Fs,
PCBs and polybrominated diphenyl ethers (PBDEs) in the ambient air of an e-waste dismantling area, in the southeast of China; and they found that congener 2,3,4,7,8-pentachlorodibenzofuran contributed dominantly to the total I-TEQs in all the samples analyzed.

Concerning the total toxicity, not the congener distribution, the values obtained for halogen free wire were 65 pg WHO/g in the case of no metal (sample H1+H2) and 61 pg WHO/g in the presence of the metal (sample H1+H2+H3); for PVC wire the emission was 5690 pg WHO/g in the run performed with no metal (P1+P2), and 33840 pg WHO/g in the presence of the metal (P1+P2+P3). In this way, it is clear that halogen-free wire does not produce a high amount of these pollutants, independent of the presence or absence of metal. On the other hand, PVC wire emission is almost 100 times the one observed in H wire, and there is a great increase in the presence of the copper metal. Note that the level of PCDD/Fs emission is expressed in pg/g that is one million times lower than the results presented for PAHs and CBzs and CPhs.

In their study, (Andersson et al., 2004) find a emission of dioxins equivalent to approximately 70-1400 pg WHO/g, with a clear increase in the case of PVC wires. Conesa et al. (2009) compared the emissions of PCDD/Fs (pg I-TEQ/g) during the combustion at 850 °C in fuel-rich conditions with a similar horizontal reactor to that used in the present work for different wastes. Combustion of waste oil and electronic circuits (Moltó et al., 2011) generates similar PCDD/F amount than combustion of halogen-free wire. In the case of PVC wire, the level of PCDD/Fs found is closer to that obtained for PVC wastes or some types of sewage sludges. It must be emphasized that PVC wire in the presence of the metal presents a worrying huge emission of these dangerous pollutants.
The data of the production of PCDD/Fs in the laboratory horizontal reactor cannot, obviously, be directly extrapolated to a real scale fire, bearing in mind that the results would differ depending on the temperature and oxygen availability. In this sense, it is difficult to estimate the actual pollutant production in an open fire; the paper by (Andersson et al., 2004) presents a very interesting research with real fires that, as mentioned, is in accordance with results presented here. Also the work of (Hull et al., 2008; Blomqvist et al., 2012) presents a number of large-scale fire experiments comparing the emission found with that of open burning fires.

As has been already commented, not only toxic congeners were determined, but all congeners from mono to octachlorinated PCDD/Fs. Figure 3 shows the total emission of dioxins and furans in all four runs. In this Figure, 1F makes reference to monochlorofurans, 1D to monochlorodioxins, 2F represents dichlorofurans… and so on. It is clear that the emission with PVC in the presence of metal is much more important than the other three runs. It is also important to note that there are much more furans than dioxins. This is due to the major thermal stability of the furans (Xhrouet et al., 2001; Conesa et al., 2002), considering that the runs were performed at 700 °C. Note than, although it is not shown in the tables, in all the runs, the sum of toxic dioxins and furans represents less than 0.8 % of the total emission of dioxins and furans.

Also note that the maximum is at 2 or 3 chlorine atoms PCDD/Fs in the case of PVC wire decomposition in the presence of metal. This can be explained by the presence of copper and calcium in the composition of the sample (Conesa et al., 2010). Some studies showed that high calcium and copper levels, together with elevated temperatures, promote degradation of high chlorinated PCDD/Fs (Weber et al., 2002; Lundin et al., 2011).
In the PVC combustion with no metallic part, we can again find much more furans than dioxins, but the maximum is displaced to more chlorinated species. This is expected because, at high temperature and in presence of abundant chorine, the most chlorinated isomers are usually the most stable compounds (Christmann et al., 1989; Kim et al., 2004; Conesa et al., 2005).

Figure 3 also shows that during the halogen-free wire decomposition it is almost not produced congeners of more than 3 chlorine atoms, and also that there are much more emission of furans than dioxins.

From the data presented, we can calculate the average number of chlorines in the emission both for dioxins and furans. Calculation results indicate that both dioxins and furans behave in a similar way, with average chlorination degree of dioxins slightly higher than that of furans.

Finally Figure SM-2 (Supplementary Information) shows the emission of PCBs. This time the y-axis in figure is done in logarithmic scale because again there is much higher emission in the case of PVC wire. The number of chlorines of these molecules goes from 4 to 6 so a conclusion on the chlorination degree is difficult. It is interesting to point out that the formation of PCBs is completely correlated with the formation of dioxins and furans, in such a way that PVC wire emission is almost 100 times the one observed in H wire, and there is a magnification in the presence of the copper metal. The contribution of PCBs to total toxicity is in all cases between 3 and 4 %, considering the toxicity calculated according to WHO-TEF-2005 values (Van den Berg et al., 2006), this is because the I-TEQ does not consider the dioxin-like PCBs.

In previous studies (Moltó et al., 2011) there were performed combustion runs of electronic circuits. In this study the emission of PCDD/Fs was much higher at 850 °C
than at 500 °C. This behavior was studied in detail (Conesa et al., 2005) with a different material, meat and bone meal, where it was found that the maximum PCDD/Fs production is at intermediate temperatures of approx. 700 °C.

The results obtained in this work show the importance of avoiding the open burning of this kind of wastes, usually carried out in developing countries to recover the valuable parts of the electric wires.

4. CONCLUSIONS

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. PAHs, CBs, CPhs, mono to octa-chlorinated dioxins and furans and PCBs where 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 halogen-free wire, and, as expected, the emission of chlorinated species is also much higher. In this sense, total dioxin equivalent toxic emissions where approx. 60 pg/g in the case of halogen-free wire, regardless of the presence of metal. For PVC wire the emission was 5690 pg/g 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).

5. ACKNOWLEDGMENTS
Support for this work was provided by the Generalitat Valenciana (Spain) with projects PROMETEO/2009/043/FEDER, and by the Spanish MCT CTQ2008-05520.

REFERENCES


CAPTIONS

Tables
Table 1. Emission of 16 EPA priority PAHs in the four runs performed.

Table 2. Total emission of chlorobenzenes (CBzs) and chlorophenols (CPhs) in the four runs performed.

Figures
Figure 1. Scheme of the electrical cables, their composition (supplied by manufacturer) and % weight of each part.

Figure 2. Toxic congener profiles in the emission of PCDD/Fs for H (halogen-free) and P (PVC) wires.

Figure 3. Mono to octachloro dioxins and furans in the emission for H (halogen-free) and P (PVC) wires.
Table 1. Emission of 16 EPA priority PAHs in the four runs performed (emission/kg plastic fraction).

<table>
<thead>
<tr>
<th>Compound</th>
<th>H1+H2</th>
<th>H1+H2+H3</th>
<th>P1+P2</th>
<th>P1+P2+P3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg compound/kg consumed material</td>
<td>mg compound/kg consumed material</td>
<td>mg compound/kg consumed material</td>
<td>mg compound/kg consumed material</td>
</tr>
<tr>
<td>naphthalene</td>
<td>142.6</td>
<td>102.8</td>
<td>410.0</td>
<td>39.8</td>
</tr>
<tr>
<td>acenaphthylene</td>
<td>54.8</td>
<td>42.4</td>
<td>113.3</td>
<td>3.83</td>
</tr>
<tr>
<td>acenaphthene</td>
<td>2.26</td>
<td>2.35</td>
<td>6.61</td>
<td>nd</td>
</tr>
<tr>
<td>fluorene</td>
<td>nd</td>
<td>4.86</td>
<td>34.1</td>
<td>0.71</td>
</tr>
<tr>
<td>phenanthrene</td>
<td>19.1</td>
<td>13.7</td>
<td>89.1</td>
<td>3.37</td>
</tr>
<tr>
<td>anthracene</td>
<td>2.29</td>
<td>1.25</td>
<td>13.0</td>
<td>nd</td>
</tr>
<tr>
<td>fluoranthene</td>
<td>6.01</td>
<td>4.86</td>
<td>28.8</td>
<td>0.93</td>
</tr>
<tr>
<td>pyrene</td>
<td>12.7</td>
<td>10.8</td>
<td>36.2</td>
<td>0.67</td>
</tr>
<tr>
<td>benzo(a)anthracene</td>
<td>1.19</td>
<td>0.90</td>
<td>5.48</td>
<td>0.20</td>
</tr>
<tr>
<td>chrysene</td>
<td>3.50</td>
<td>3.07</td>
<td>10.6</td>
<td>0.73</td>
</tr>
<tr>
<td>benzo(b)fluoranthene</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>benzo(k)fluoranthene</td>
<td>4.69</td>
<td>5.80</td>
<td>13.0</td>
<td>nd</td>
</tr>
<tr>
<td>benzo(a)pyrene</td>
<td>1.94</td>
<td>2.85</td>
<td>1.39</td>
<td>nd</td>
</tr>
<tr>
<td>indeno(1.2.3-cd)pyrene</td>
<td>1.14</td>
<td>1.09</td>
<td>0.43</td>
<td>nd</td>
</tr>
<tr>
<td>dibenz(a,h)anthracene</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>benzo(g,h,i)perylene</td>
<td>2.69</td>
<td>3.13</td>
<td>2.08</td>
<td>nd</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>255.14</strong></td>
<td><strong>199.9</strong></td>
<td><strong>764.37</strong></td>
<td><strong>50.2</strong></td>
</tr>
</tbody>
</table>
Table 2. Total emission of chlorobenzenes (CBzs) and chlorophenols (CPhs) in the four runs performed (emission/kg plastic fraction).

<table>
<thead>
<tr>
<th></th>
<th>$H_1+H_2$</th>
<th>$H_1+H_2+H_3$</th>
<th>$P_1+P_2$</th>
<th>$P_1+P_2+P_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBzs</td>
<td>0.051</td>
<td>0.044</td>
<td>0.444</td>
<td>20.8</td>
</tr>
<tr>
<td>CPhs</td>
<td>12.1</td>
<td>13.5</td>
<td>43.0</td>
<td>141.9</td>
</tr>
</tbody>
</table>
Figure 1. Scheme of the electrical cables, their composition (supplied by manufacturer) and % weight of each part.

<table>
<thead>
<tr>
<th>Part</th>
<th>PVC cable (P) wt.-%</th>
<th>Halogen free cable (H) wt.-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (Cover)</td>
<td>P1: PVC, 41 %</td>
<td>H1: Thermoplastic polyolefin (PE-TPE-ATH), 36 %</td>
</tr>
<tr>
<td>2 (Insulation)</td>
<td>P2: Reticulated polyethylene, 9%</td>
<td>H2: Silicone rubber, 20 %</td>
</tr>
<tr>
<td>3 (Conductor)</td>
<td>P3: Copper, 50 %</td>
<td>H3: Copper, 44 %</td>
</tr>
</tbody>
</table>
Figure 2. Toxic congener profiles in the emission of PCDD/Fs for H (halogen-free) and P (PVC) wires.
Figure 3. Mono to octachloro dioxins and furans in the emission for H (halogen-free) and P (PVC) wires.