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PROCESSING WASTE PRINTED CIRCUIT BOARDS FOR MATERIAL RECOVERY

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ABSTRACT

Purpose We have investigated the use of pyrolysis for the processing of waste printed circuit boards (PCBs). The aim was to make the process of separating the organic, metallic, and glass fibre fractions of PCBs much easier and therefore make recycling of each PCB fraction more viable.

Design/methodology/approach The PCBs were pyrolysed in a fixed bed reactor at 850°C. The organic fraction released by the boards was analysed by a variety of gas chromatography techniques. The residue that remained after pyrolysis was analysed by ICP-MS to determine the type of metals that were present.

Findings When PCBs were heated to 800°C in an oxygen free atmosphere, the organic fraction decomposed to form volatile oils and gases leaving behind the metal and glass fibre fraction of the boards. The pyrolysed boards were very friable and the different fractions (metal components, copper power boards, glass fibre, etc) could be easily separated. The recovered metals could then be recycled by traditional routes with particular emphasis being placed on the recovery and recycling of rare and precious metals. The organic oils and gases which are produced during pyrolysis of PCBs can either be used as a chemical feedstock or as a fuel.

Research limitations/implications The research was only carried out on a very small scale so an investigation into scale-up must be performed.

Practical implications By using pyrolysis, the organic and metallic fraction of printed circuit boards can be separated and recycled.

Originality/value This paper presents a novel method for resource recovery from PCBs.

Keywords: printed circuit board, recycling, pyrolysis, materials recovery

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1. INTRODUCTION

Member states of the European Union are now required to separately collect and process waste electrical and electronic equipment (WEEE) by the WEEE Directive (European Commission, 2003). Under the WEEE directive, waste printed circuit boards must be processed and recycled in an environmentally sustainable manner. The heterogeneous nature of printed circuit boards means that they are particularly problematic to recycle resulting in recycling rates as low as 15% in the UK in 2002 (Goosey and Kellner, 2002). Currently, the majority of waste printed circuit boards are either incinerated or are sent to landfill with no resource recovery (Fisk et al., 2003).

Ideally, a process would be developed whereby both the organic and metallic fraction of printed circuit boards can be recovered and this might be possible by using pyrolysis. Pyrolysis is a process whereby organic materials are heated to high temperatures in the absence of oxygen and has been intensively investigated in recent years as a means of recycling plastics (Kaminsky et al., 2004; Hall and Williams, 2006a; Hall and Williams, 2006b; Bhaskar et al., 2007; Hall and Williams, 2007a; Hall and Williams, 2007b) including polymers that are mixed with glass fibres (Cunliffe et al., 2003). Under pyrolysis conditions, organic materials decompose to form gases, oils, and chars that can subsequently be used for chemical feedstock or fuel. When pyrolysis is applied to printed cicuit boards, the organic resin should decompose to form an oil and gas which will volatilise and then flow out of the reaction chamber leaving behind the metallic and glass fibre fractions of the circuit boards and a small amount of char. The removal of the organic resin from the circuit boards will mean that they can be easily dismantled and furthermore the high temperatures used in the pyrolysis process will melt the solder which is used to attach the electrical components to the boards making the process of dismantling the boards even easier. Therefore, the pyrolysis of printed circuit boards will lead to the recovery of organic oil and gas, which can be used as a fuel of chemical feedstock, while simultaneously separating the metallic and glass fibre fractions from the organic fraction.

In this work we have used a laboratory-scale batch reactor to investigate the pyrolysis of several different printed circuit board wastes. We have quantified both the organic and metallic pyrolysis products and reported on the ease with which the metal and glass fibre components can be separated from the pyrolysis char compared to the relative difficulty of removing metal components directly from printed circuit boards. We have also reported on the effect of pyrolysis on the brominated and phosphated flame retardants that are routinely used in printed circuit boards.

2. EXPERIMENTAL

2.1 MATERIALS

The circuit boards from a range of televisions, computers, and mobile phones were selected and the batteries were removed. The boards were then broken into pieces that were 1.5 – 2 cm^2, which was the maximum size that would fit into the fixed bed reactor. The small pieces of board from each category were mixed together so that the experiments would be carried out on a wide selection of different boards. The boards from the computers and mobile phones were nearly all multilayered with a high fraction of glass fibre but some of the computer boards were single layered; nearly all the television boards were single layered.

The computer circuit boards had a global composition of 32 wt% metal and glass and 68% organic material and the television circuit boards had exactly the same composition. The mobile phone circuit boards were somewhat different and contained 83 wt% metal and glass and 17 wt% organic material.

2.2 FIXED BED REACTOR

The three categories of printed circuit board were individually pyrolysed in a fixed bed reactor that measured 260mm in length by 44.5mm in diameter (Figure 1). The reactor crucible was loaded with 20g of sample and the reactor was then sealed and purged with nitrogen. Once the reactor had been purged it was heated to 800ºC at a heating rate of 10ºC/min and then held at temperature for 135 minutes to ensure that the pyrolysis process was complete.

The volatile pyrolysis products exited the reactor and the pyrolysis oils were collected by a train of water-cooled and ice-cooled condensers. At regular intervals throughout the experiment samples of the pyrolysis gases were taken by gas-tight syringes which were analysed off-line for C_1 – C_4 hydrocarbons, CO_2, CO, and H_2 by gas chromatography. The pyrolysis gas was also bubbled through an alkali solution which was then analysed off-line by ion chromatography to determine the concentration of halogens in the gas.

The pyrolysis oils were mainly collected by the first water-cooled condenser and contained a significant quantity of water which was removed using a centrifuge. The dry pyrolysis oils were characterised using gas-chromatography with mass spectrometry (GC-MS), gas chromatography with flame ionisation detection (GC-FID) and gas chromatography with electron capture detection (GC-ECD). The GC-MS was used to determine the type of compounds present in the pyrolysis oil, the GC-FID was used to quantify the identified compounds, and the GC-ECD was used to determine and quantify the halogenated compounds present in the pyrolysis oil.

The pyrolysis residues was collected from the reactor crucible after the reactor had cooled and were initially examined by scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX). The residues were also ashed at 600°C according to EN ISO 3451-1:1997 and the resulting metals were analysed using ICP-MS. The friability of the pyrolysed boards was tested by hand.

3. RESULTS AND DISCUSSION

3.1 PRODUCT YIELD

The product yields from the pyrolysis of the three different types of printed circuit boards are shown in figure 2. The repeatability of the experiments was good when the heterogeneous nature of the samples was taken into consideration. The mass balance for the pyrolysis of the mobile phone boards was very high but some mass losses occurred during the pyrolysis of the computer and television circuit boards. It is thought that the mass losses are mainly due to the formation of water which was not all collected by the condenser train. There were also some organic compounds present in the pyrolysis gas that could not be identified and these will also have contributed to the lower mass balances when the computer and television boards were pyrolysed.

The computer printed circuit boards pyrolysed to form an average of 68.9 wt% residue, 22.7 wt% oil, and 4.7 wt% gas. Pyrolysis of the television circuit boards led to an average mass balance of 60.0 wt% residue, 28.5 wt% oil, and 6.5 wt% gas and pyrolysis of the mobile phone circuit boards led to an average mass balance of 82.2 wt% residue, 15.2 wt% oil, and 2.3 wt% gas.

The composition of the pyrolysis gases is shown in figure 3. CO_2 and CO were the most abundant pyrolysis gases due to the decomposition of the epoxy group. The printed circuit boards from mobile phones formed less CO_2 and more CO than the printed circuit boards from the computers and televisions. Hydrocarbon gases made up a significant proportion of the pyrolysis gases and hydrogen was also present. The pyrolysis gases contained only very low levels of halogen gases, which is an advantage if the gases are used as a fuel because hydrogen halides are very corrosive and may also be involved in the formation of dioxins and furans.

3.2 PYROLYSIS RESIDUE

The pyrolysis residues were recovered from the crucible of the fixed bed reactor once the reactor had cooled. All of the residues contained a small amount of organic char as well as the metal components of the printed circuit boards. The friability of the pyrolysed cicuit boards was tested by attempting to separate the metallic, glass fibre, and char fractions by hand; in all cases this was easily accomplished, demonstrating that the pyrolysis process greatly increased the ease with which the different fractions of printed circuit boards could be separated.

The residue produced by the pyrolysis of the computer printed circuit boards was a mixture of flexible, glass fibre containing boards and brittle boards that contained no glass fibre (Figure 4). Both types of pyrolysed computer board could easily be broken and the copper track and power boards, electrical components, and glass fibre separated. The glass fibre was covered in a layer of char, giving it a black appearance but the copper track was relatively clean. Most of the electrical components were intact, including the microchips.

The residue from the pyrolysis of the television boards was very brittle and the electrical components could easily be separated from the residue (Figure 5). In fact, the residue was so brittle that some of the electrical components had come loose during the pyrolysis process. The television circuit boards did not contain any glass fibre.

The residue from the pyrolysis of the mobile phone boards consisted of flexible pieces of pyrolysed boards, the copper power boards and track, large electrical components, and glass fibre (Figure 6). The different fractions of the pyrolysed mobile phone boards were easy to separate with the exception of some of the small electrical components which could not be separated from the copper power boards.

To characterise the metals, each of the pyrolysis residues was ashed and the resulting metals were acid digested and then analysed by ICP-MS, the results are presented in figure 7. The most abundant metal in all the residues was copper, but high concentrations of calcium, aluminium, lead, iron, barium, nickel, magnesium, sodium, silver, and zinc were also found in the residues. Gold was detected in the computer and mobile phone residues but not in the television residues and virtually no cadmium or mercury was detected in any of the boards. Gallium was found in all of the residues, but only in low concentrations.

In addition to the ICP-MS analysis, the pyrolysis residues were also examined by SEM-EDX. As well as the metals shown in figure 7, bromine, carbon, oxygen, phosphorous, silicon, and tin were all found to be present in the residues. The carbon was the pyrolysis char and the silicon and oxygen were contained in the glass fibres. Bromine and phosphorous were probably present due to the decomposition of flame retardants and fillers, the brominated compounds most likely formed metal bromides during the pyrolysis process while the phosphated compounds probably formed elemental phosphate. The residues from the pyrolysis of the computer printed circuit boards also contained scandium and sulphur and the residues from the pyrolysis of the television printed circuit boards contained vanadium.

The friable, pyrolysed circuit boards obviously contained a wide variety of different metals which would require further separation and processing if they were to be recycled. Cui and Forssberg (2003) carried out a review of the mechanical recycling options for waste electrical and electronic equipment in which they discussed several options for the separation of small metal particles. The separation of metals after the oxidisation of the organic fraction of printed circuit boards has also been reported (Lee et al., 2005).

3.3 PYROLYSIS OIL

The pyrolysis oil produced by each type of printed circuit board was characterised using GC-MS, GC-FID, and GC-ECD. Figure 8 shows the concentration of phenol, substituted phenols, phosphates, and bromophenols in the pyrolysis oil. According to the GC-MS data, the unidentified fraction of the pyrolysis oil mainly consisted of benzofurans and phenols that could not be positively identified and therefore could not be properly quantified.

The pyrolysis oils mainly consisted of compounds that can be attributed to the decomposition of bisphenol A epoxy resin or epoxy novolac resin. Phenol was the most abundant product, followed by 4-(1-methylethyl)phenol which must occur due to the splitting of the bisphenol A structure. The further breakdown of 4-(1-methylethly)phenol led to the presence of 4-methylphenol and 4-ethylphenol in the pyrolysis oils. Despite the high temperatures used in the pyrolysis process the bisphenol A structure did not completely break down as all the pyrolysis oils contained some bisphenol A as well as some p-hydroxydiphenyl. The pyrolysis oils also contained 2-methylphenol, 2,6-dimethylphenol, and 2-ethylphenol, which are typical of the compounds produced during the pyrolysis of epoxy novolac (Bradna and Zima, 1991). Overall, we were able to quantify 42.1 wt% of the computer pyrolysis oil, 21.4 wt% of the television pyrolysis oil, and 60.7 wt% of the mobile phone pyrolysis oil.

The type of organic resin used probably had an impact on the composition of each pyrolysis oil but the degree of curing applied to epoxy resins has also been shown to affect their pyrolysis products (Bradna and Zima, 1991; Balabanovich et al., 2004). Additionally, basic metals have been reported to affect the amount of bromophenols formed during the pyrolysis of brominated epoxy resin (Blazso et al., 2002). Various other authors have also reported on the effect of metals on the pyrolysis of polycarbonate of bisphenol A and epoxy resin (Blazso, 1999; Sivalingam and Madras, 2004).

Printed circuit boards regularly contain the flame retardant tetrabromobisphenol A (TBBPA) as part of the polymer matrix. During pyrolysis of all the printed circuit boards it was found that the pyrolysis oils contained both TBBPA and its pyrolysis products such as 2,4-dibromophenol. The thermal decomposition and pyrolysis of TBBPA has been discussed in detail by other authors (Barontini et al., 2004a; Barontini et al., 2004b; Marsanich et al., 2004) but it is sufficient to say that at high temperature a competition exists between the evaporation and pyrolysis of TBBPA which results in both TBBPA and its pyrolysis products being present in the pyrolysis oil.

A number of phosphated compounds were found in the pyrolysis oils, the most abundant of which was triphenyl phosphate. Triphenyl phosphate is used as a flame retardant additive (Danish Environmental Protection Agency, 1999) but it also the pyrolysis product of several other flame retardants including bisphenol A bis(diphenyl phosphate) (Balabanovich, 2004), triphenyl (diphenoxyphosphinyl)phosphorimidate (Fukushima et al., 1998), and tetraphenyl imidodiphosphate (Shimasaki et al., 1992). The highest concentrations of triphenyl phosphate occurred in the oil resulting from the pyrolysis of the television printed circuit boards with a significant concentration also being present in the oil produced by the pyrolysis of the computer boards (Figure 8). Very little triphenyl phosphate was identified in the mobile phone pyrolysis oil.

In addition to triphenyl phosphate, the oils resulting from the pyrolysis of the computer and mobile phone boards contained the plasticizer cresyl diphenylphosphate. The pyrolysis oil from the computer printed circuit boards also contained two isomers of cresyl phosphate, which is used as a plasticizer in PVC and polystyrene. The GC-MS analysis of the pyrolysis oils identified several other phosphated compounds apart from those mentioned above, but unfortunately the appropriate standards were not available to confirm their identification. Phosphated flame retardants are mainly used in thermoplastics so their presence in the pyrolysis oil of printed circuit boards is probably due to the pyrolysis of plastic components that were attached to the boards, rather than the pyrolysis of the boards themselves.

4. CONCLUSIONS

Printed circuit boards are particularly problematic to recycle because they consist of a heterogeneous mixture of organic, metallic, and glass fibre material. In this paper we have demonstrated that pyrolysis can be used to recover all three materials from printed circuit boards. Untreated printed circuit boards are practically impossible to dismantle safely, however, the pyrolysis process separates the majority of the organic material from the inorganic material and produces a residue which can easily be separated into metals, glass fibre, and any remaining organic material. The pyrolysis process also produces organic gases which can be used as a fuel to provide the heat necessary for the pyrolysis of printed circuit boards. The pyrolysis process produces an oil which contains high concentrations of valuable phenol as well as lower concentrations of other valuable chemicals such as TBBPA and triphenyl phosphate. The fractions of the pyrolysis oil that have no intrinsic value can either be fed into the refinery process or used as a fuel. The isolated metals can be recycled following traditional routes for scrap metals. The use of pyrolysis to treat waste printed circuit boards has the potential to recover valuable resources rather than further diminishing virgin supplies.

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PROFILES

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William Hall is a Research Fellow in the Energy and Resources Research Institute at the University of Leeds where he carries out research into waste incineration and pyrolysis. Most of his current research is centred on using pyrolysis to simultaneously recycle flame retarded plastics while destroying the toxic brominated flame retardants and he has published several papers on this subject in the last few years. William is also working on the pyrolysis of municipal solid waste, refuse derived fuel, and medical waste. He holds a PhD in Environmental Engineering and a BSc in Fuel and Combustion Science from the University of Leeds.

Figure 1 Schematic diagram of the fixed bed reactor

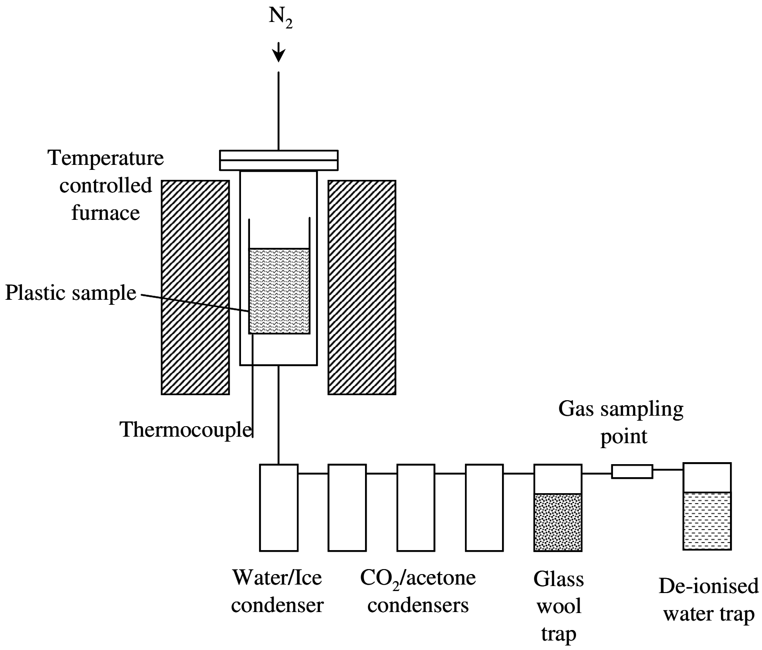

Figure 2 Mass balances when each type of printed circuit board was pyrolysed in the fixed bed reactor (wt%).

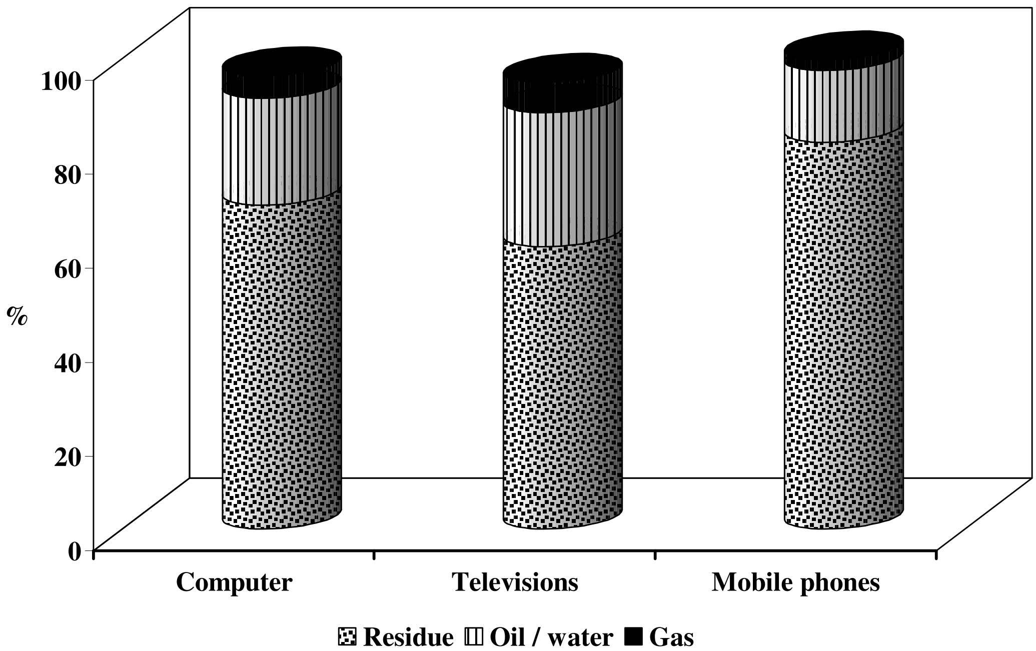

Figure 3 Mass composition of the pyrolysis gases produced by each type of circuit board on a nitrogen free basis (wt%)

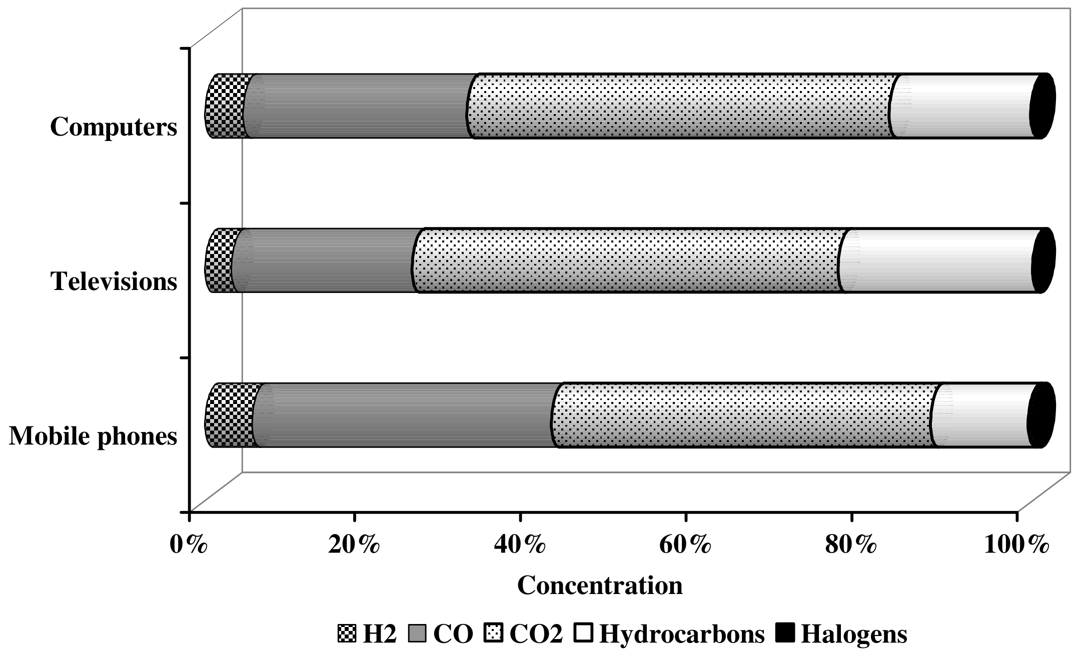

Figure 4 The effect of pyrolysis on printed circuit boards taken from computers. The untreated boards (top left) pyrolyse to form a friable residue (top right) that can easily be separated into the copper power boards and components (bottom left) and glass fibre (bottom right).

Figure 5 The effect of pyrolysis on printed circuit boards taken from televisions. The untreated boards (top left) pyrolyse to form a friable residue (top right) that can easily be separated into char (bottom left) and electrical components (bottom right).

Figure 6 The effect of pyrolysis on printed circuit boards taken from mobile phones. The untreated boards (top centre) pyrolyse to form a friable residue (bottom left) that can easily be separated into the copper power boards and glass fibre (bottom right).

Figure 7 An analysis of the major metals as a percentage of the pyrolysis residue for each type of circuit board

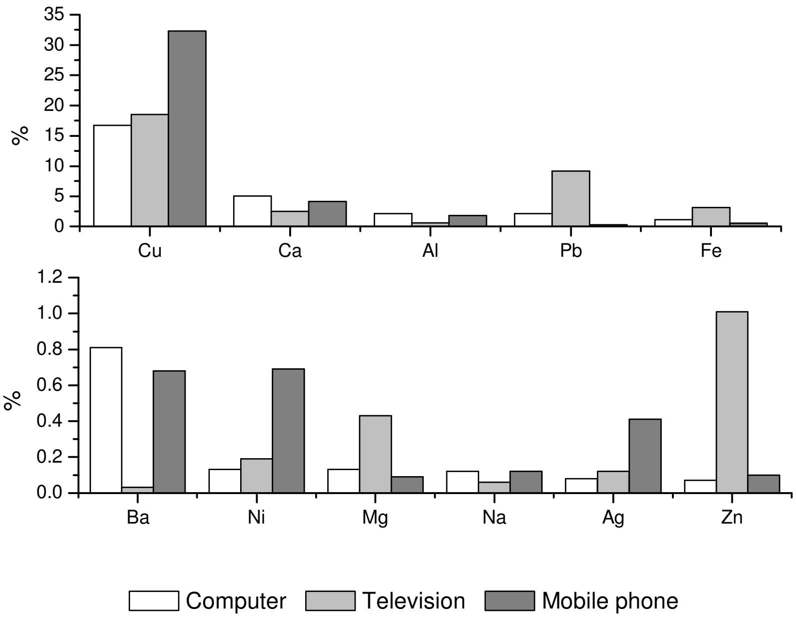

Figure 8 Quantification of the major products in the oil resulting from the pyrolysis of printed circuit boards at 800°C in a fixed bed reactor