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Analysis of Products from the Pyrolysis of Plastics Recovered from the Commercial Scale Recycling of Waste Electrical and Electronic Equipment

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Abstract

Three plastic fractions from a commercial waste electrical and electronic equipment (WEEE) processing plant were collected and investigated for the possibility of recycling them by batch pyrolysis. The first plastic was from equipment containing cathode ray tubes (CRTs), the second plastic was from refrigeration equipment, and the third plastic was from mixed WEEE. Initially, the decomposition of each of the plastics was investigated using a TGA linked to a FT-ir spectrometer which showed that the CRT plastic decomposed to form aliphatic and aromatic compounds, the refrigerator plastic decomposed to form aldehydes, CO_2, aromatic, and aliphatic compounds, and the mixed WEEE plastic decomposed to form aromatic and aliphatic compounds, CO_2, and CO. Each plastic mixture was also pyrolysed in a batch reactor to determine the halogen and metal content of the pyrolysis products, additionally, characterisation of the pyrolysis oils was carried out by GC-MS and the pyrolysis gases by GC-FID and GC-TCD. It was found that the halogen content of the oils was relatively low but the halogen and metal content of the chars was high. The pyrolysis oils were found to contain valuable chemical products and the pyrolysis gases were mainly halogen free, making them suitable as a fuel.

Keywords: Pyrolysis, Electrical and Electronic Equipment; waste

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1. Introduction

It has been reported that 939,000 tonnes of waste electrical and electronic equipment (WEEE) was disposed of in the UK in 2003 of which 143,000 tonnes (3 million units) was refrigeration equipment and 96,000 tonnes (4 million units) was equipment that contained cathode ray tubes (CRT's) [1]. Refrigerators and CRT's contain many materials that can already be recycled, such as glass and metals, but the plastic fraction is currently more difficult to dispose of.

The recent EC Waste Electrical and Electronic Equipment Directive [2] aims to promote the re-use, recycling and recovery of such electrical and electronic waste. Included in the category of waste electrical and electronic equipment are; household appliances - e.g. refridgerators, washing machines, microwave ovens, irons, toasters, hair dryers etc.; information technology and telecommunications equipment - e.g. personal computers, printers, telephones, mobile phones, calculators, mainframe computers etc.; consumer equipment - e.g. radios, television sets, video recorders, musical instruments, etc.; lighting equipment - e.g. fluorescent lamps, sodium lamps, metal halide lamps etc.; electrical and electronic tools - e.g. electrical drills, electrical saws, sewing machines etc.; toys - e.g. electric trains, car racing sets, video games, etc.; medical equipment systems - e.g. radiotherapy equipment, dialysis equipment, analysers, freezers etc.; monitoring and control instruments - e.g. smoke detectors, heating regulators, thermostats etc.; automatic dispensers - e.g. hot drink dispensers, cold drink dispensers, automatic dispensers for solid products etc.

The Directive requires Member States of the European Union to set up collection systems where the consumer will be able to return the equipment free of charge. The Directive therefore requires the separate collection of electrical and electronic waste as a separate waste stream, which enhances the prospects for economic recycling. The waste is then required to be transferred to an authorised treatment facility where any potentially hazardous components and materials are removed. This collection and treatment process produces various fractions suitable for recycling, amongst which is the plastic fraction.

Pyrolysis is an established process that can potentially be used to convert plastics to more valuable chemicals and fuels [3-6]. Pyrolysis is the thermal degradation of the plastic polymer to produce a char, oil and gas, all of which have potential as useful end products. There have been many studies on the pyrolysis of pure plastic materials [7, 8] and mixtures of pure plastic which simulate those representative of real world samples such as municipal solid waste plastics [4, 9-11]. However, there are few studies detailing the product characteristics from the pyrolysis process of real world waste plastics [12, 13]. In addition, there are no studies that the authors are aware of that investigate the detailed yield and composition of the pyrolysis products from real world waste electrical and electronic equipment.

In this work, the pyrolysis of three WEEE plastics that we collected at a commercial WEEE recycling plant has been investigated. The three plastics were pyrolysed in a fixed bed reactor that was heated to 600 °C at a heating rate of 10 °C min^{-1}. The resulting oils were characterised by GC-MS and the pyrolysis gases were characterised using GC-FID and GC-TCD. The ash and halogen content of the plastics and the pyrolysis products was also determined. Thermogravimetric analysis linked to Fourier Transform infra-red spectrometer was used to help characterise the pyrolysis oils of the three different plastics.

2. Experimental

2.1 Materials

Three samples of waste electrical and electronic equipment were collected and used for the investigation; equipment containing cathode ray tubes (CRTs); plastic from refrigeration equipment; and mixed WEEE. The first plastic was collected from a cathode ray tube (CRT) recycling plant; computer monitors and television sets are recycled by removing the plastic outer casing before separation of the glass screen from the electronic components. The glass and circuit boards are separated for recycling while the plastic fraction is ground into small pellets and then sold for low level recycling applications. A representative 1 kg sample of the plastic pellets was taken. This was carefully sampled using a multiple grab procedure to ensure that it was a representative sample of the CRT plastic waste.

The second plastic was collected from a refrigeration-unit recycling plant. Whole fridges and freezers have their compressors removed before they are transported into two shredders (coarse and fine shredding) before the different WEEE fractions are separated. The ferrous metals are removed by electromagnets, the foam insulation is removed by air blowing, and the non-ferrous metals and plastics are separated by a cyclone. The CFC's released during the shredding of the fridges and freezers are destroyed by catalytic conversion to HCl and HF. A representative 1 kg sample of the shredded plastic was taken using the standard sampling procedure. The sample also contained a significant proportion of non-ferrous metal pieces due to inefficiencies in the separation process. The third plastic was a mixture of all WEE plastics taken from a separate process line. Again, care was taken to ensure that the sample of mixed WEE plastic was representative of the material produced from the recycling process plant.

The three plastics were supplied in 5-10mm diameter fragments and about 500g of these fragments were ground to sub 2mm particles to increase the homogeneity of the samples. For the fixed bed reactor experiments, a 600µm-1mm fraction of the plastics was used and for the analytical analysis of the plastics, a 38-180µm fraction of the plastics was used.

The elemental analysis of the plastics was determined using a CE Instruments Flash EA 1112 elemental analyser. The system combusts the sample at 1000 °C and analyses the combustion gases of the sample to determine, carbon, hydrogen, nitrogen and sulphur composition. Oxygen is analysed separately by the instrument.

The halogen content of the plastics was determined using bomb calorimetery according to EPA method 5050. The bomb was loaded with 1g of sample and a small volume of alkali solution before being charged with pure oxygen. Upon combustion of the sample, the halogens are released and are dissolved in the alkali solution. Once the bomb had cooled it was thoroughly rinsed with more alkali solution. The halogen content of the alkali solution was then determined using a Dionex DX100 ion chromatograph fitted with a Dionex AS4A column. The efficiency of the system was checked by combusting materials with known chlorine and bromine contents.

The ash content of the plastic was determined by using the standard method EN ISO 3451-1:1997. A known mass of plastic was combusted in an ashing furnace at 600°C; this temperature was chosen to minimise the loss of any volatile metal halides. The mass of ash was determined by repeatedly weighing the ashing crucible until a constant mass was achieved.

2.2 TGA-FT-ir

A Stanton and Redcroft TGA was linked to a Nicolet 560 FT-ir and used to analyse the thermal decomposition of each of the plastics. 30 mg of sample was placed in the TGA cell and then ramped to 600°C at a rate of 20°C min^{-1} in an atmosphere of nitrogen. The evolved gases were swept into the FT-ir sample cell where they were scanned every 60 seconds. The FT-ir spectral library was used for identification of the evolved gases. The large sample size was used to ensure a good response on the FT-ir and to try to ensure repeatability between samples by decreasing the heterogeneity of the samples.

2.3 Fixed Bed reactor

Each of the three plastics was pyrolysed in a fixed bed reactor. The reactor measured 260mm in length by an internal diameter of 44.5mm and was externally heated by a 1.5kW tube furnace (figure 1). A crucible that contained 10g of plastic sample was placed in the reactor at the start of the experiment and the reactor was then sealed and purged with nitrogen before being ramped to 600°C at a rate of 10°C min^{-1}.

After exiting the fixed bed reactor, the pyrolysis gases and oils passed through a water cooled condenser and then two dry-ice cooled condensers that collected any oils and waxes released during the pyrolysis process. In addition, a glass wool trap was used to remove any oils or waxes that were not trapped by the condensers. Any inorganic gaseous halogens were collected by bubbling the pyrolysis gases through an alkali solution, the fluorine, chlorine, and bromine concentration of the alkali trap solution was analysed off-line using a Dionex DX100 ion chromatograph fitted with a Dionex AS4A column. The organic and permanent gases were sampled from the pyrolysis gases by drawing off gas samples into a syringe at pre-arranged intervals. The organic gases were analysed using a Varian 3380 GC fitted with a stainless steel 2m by 8mm column packed with n-octane Porasil C of 80-100 mesh size and a FID detector. The permanent gases were analysed by a second Varian 3380 GC fitted with twin TCD detectors, one for N_2, CO, O_2, and H_2 and one for CO_2.

The mass balance was calculated by weighing the mass of char and oil produced and analysing the pyrolysis gases by ion chromatography, GC-FID, and GC-TCD. The mass of each gas was then determined and contributed to the mass balance of the experiment, rather than calculated as ‘mass of gas by difference’. Each plastic was tested at least twice.

The pyrolysis oils were recovered from the water-cooled condenser, only a small amount of oil was collected by the dry-ice cooled condensers and the glass wool trap, and was analysed by GC-MS and GC-FID. The GC-MS was a Shimadzu QP2010 fitted with a 30m RTX-5 column. The injector temperature was 285°C and the oven was held at 40°C for 15 minutes, then ramped to 280°C at 5° C/min, and then held for 15 minutes. The mass spectrometer electron energy was 70eV and the ion source and coupling temperatures were 220°C and 300°C respectively. The GC-FID was a Varian 3380 fitted with a Varian CP-sil 5CB column (15m x 0.25mm x 0.25µm). The injector and FID temperatures were 290°C and 300°C respectively and the oven was held at 40°C for 15 minutes, then ramped to 280°C at 5° C/min, and then held for 15 minutes.

The GC-MS was used to determine the compounds present in each of the pyrolysis oils and the GC-FID was calibrated to determine the concentration of the benzene, toluene, ethylbenzene, styrene, cumene, phenol, and alpha-methylstyrene in each oil. The concentration of the other compounds present in the oil was determined by comparing the peak area of styrene on the GC-MS plot (for which the concentration was known from the GC-FID) with the peak area of the un-calibrated compounds. The ash content of the oils was determined using EN ISO 6245:2002. A known mass of oil was burnt in a crucible and the remaining char was ashed in an ashing furnace at 600°C. The mass of ash could then be determined by mass difference. The halogen content of the oils was determined by EPA method 5050, as described above.

The pyrolysis chars were recovered from the reactor after it had cooled and were examined by scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDX) to determine elemental composition using a CamScan 4 SEM-EDX. The halogen content of the chars was determined by bomb calorimetery (EPA method 5050) but unfortunately, the ash content of the chars could not be properly determined due to iron deposits from the reactor crucible adhering to the char.

3. Results and discussion

3.1 Composition of the waste plastics

The chemical composition of the materials (table 1) showed that none of the plastics contained large quantities of bromine with the maximum being 0.1% in the mixed WEEE plastic. The mixed WEEE plastic also contained the highest concentration of fluorine, 0.31%, while the refrigeration plastic and the cathode ray tube (CRT) plastic contained less than 0.01% fluorine. Chlorine was present in significant quantities in the CRT plastic and the refrigeration plastic, which contained 1.3% chlorine. Chlorine was probably a component of the plastics due to the presence of PVC, which is widely used in domestic appliances [14]. The halogen concentration of the plastics is significant because 2.5% of all electronic and electrical equipment plastics contain toxic brominated flame-retardants such as polybrominated diphenyl ethers or polybrominated biphenyls [15] that can be released during pyrolysis. Halogens present in plastics can also form extremely toxic polyhalogenated dibenzo dioxins and furans either during the pyrolysis itself or during any subsequent combustion of the pyrolysis products [14, 16, 17]. Hydrogen halides can also be released during pyrolysis, or subsequent combustion of the pyrolysis products, when halogens are present in the plastic wastes [18]. Hydrogen halides are extremely corrosive and require special flue gas treatment.

The three plastics contained 71.4 – 81.6 % carbon and 6.3 – 7.5 % hydrogen and no sulphur. The CRT plastic contained by far the highest concentration of nitrogen (5.5%) reflecting the fact that acrylonitrile – butadiene – styrene (ABS) co-polymer is often used for CRT cases [19]. The nitrogen concentration of the plastics is significant because toxic nitrogen compounds such as hydrogen cyanide and ammonia can be formed during pyrolysis [20] and if any of the nitrogenated pyrolysis products are to be used as a fuel then the nitrogen compounds can form NO_x, which is a greenhouse gas, during combustion [21]. The oxygen content of all three plastics was significant with the mixed WEEE plastic containing the highest concentration of oxygen (13.5%).

WEEE plastic has been reported to contain 3-5% ash [22]. The plastics used in this study all contained at least 1.3% ash (table 1). The CRT and mixed WEEE plastics had no visible metal pieces so it can be assumed that all of the metals were contained within the polymer as fillers. The refrigerator plastic contained metal pieces that were a consequence of inefficiencies in the separation of the different components of the shredded refrigeration units, but the polymers themselves most likely also contained metal fillers. Metal fillers in polymers have been shown to have a significant impact on the pyrolysis of plastics [23-25].

3.2 TGA-FT-ir investigation of the waste plastics

Each of the three plastics was heated on a thermogravimetric analyser (TGA) to 600°C at a ramp rate of 20°C min^{-1} in an atmosphere of nitrogen and the volatile products were analysed by Fourier transform infra-red spectrometry (FT-ir) as they were evolving. Figure 2 shows a 'waterfall' plot of the FT-ir spectra during the pyrolysis of the CRT plastic. The waterfall plot simply shows all the FT-ir spectra stacked behind each other according to the time of the FT-ir scan. Figure 2 shows spectra that are typical of mono-substituted hydrocarbons and aliphatic hydrocarbons. For example, the peaks between 3010-3110 cm^{-1} are typical of C-H stretches in aromatic rings and the C-H out-of-plane deformation vibrations at 694 and 757 cm^{-1} are typical of mono-substituted aromatics. The peaks around 1597 and 1491 cm^{-1} can be assigned to C=C bonds. The peaks between 2850 – 2970 cm^{-1} can be attributed to methyl and methylene groups while the peak at 1458 cm^{-1} could be caused by methylene group in-plane deformation. The peaks at 911 and 968 cm^{-1} could be caused by $CH=CH_2$ groups. The decomposition of CRT began after 18.6 minutes and ended after 32.6 minutes and aromatic and aliphatic material was released for the whole of this time.

Figure 3 shows the waterfall plot from the pyrolysis of the refrigeration plastic which starts with the release of aldehydes (possibly formaldehyde) after 11.5 minutes. The presence of aldehydes was determined by the presence of peaks in the region of 2802, 2720-2740, and 1740 cm^{-1}. After 15 minutes, the release of aldehydes ceased and the release of CO_2 occurred until 20 minutes, which can be seen in, figure 3 as the peaks at 2357, 2308, and 674 cm^{-1}. After 20 minutes, the release of mono substituted aromatics and aliphatics was recorded; the release of aliphatics almost ceased after 27 minutes but the release of aromatics continued until 39 minutes. The presence of aromatics was determined by the presence of C-H group stretches at 3010-3110 cm^{-1} and C-H out-of-plane deformation vibrations at 694 and 758 cm^{-1}, which are typical of mono substituted aromatics. The aliphatics were identified by the methyl and methylene C-H stretches at 2850-2970 cm^{-1}. The variety of the different phases in pyrolysis of the refrigeration plastic would suggest that the raw plastic is a very heterogeneous mix of different polymers.

Figure 4 shows the waterfall plot for the pyrolysis of the mixed WEEE plastic. The decomposition of the mixed WEEE plastic begins with the release of aldehydes, identified by the peaks at 2802 and 1740 cm $^{-1}$, after 18.1 minutes and then, after 20 minutes, the release of mono-substituted aromatic hydrocarbons (3010 – 3110 cm $^{-1}$), aliphatic hydrocarbons (2850 – 2970 cm^{-1}), CO_2 (2357, 2308, and 674 cm^{-1}), and CO which was identified by the double peak centred around 2144 cm^{-1}. Analysis of the TGA trace showed that mass loss ceased after 26 minutes but from the FT-ir waterfall plot it can be seen that CO_2 is still being released. However, CO_2 gives a very strong response on FT-ir spectrometers so it is probable that only very small amounts of CO_2 are actually being released after 26 minutes. Similarly, between 20 and 26 minutes in figure 4 it appears that the CO_2 release is greater than the release of organics, but this is probably not the case due to the strong response of CO_2.

Each plastic was analysed at least twice on the TGA-FT-ir and in general, good repeatability occurred. However, some differences could sometimes be seen. For instance, the two mixed WEEE plastic experiments showed near identical TGA plots, but the FT-ir waterfall plots showed that more aliphatic material was released in the early stage of decomposition and less CO_2 was released in the later stages of decomposition in one sample compared to the other.

3.3 Product yield and composition

Table 2 shows the product yield from the fixed bed pyrolysis of the waste plastic samples. The CRT plastic pyrolysed to form an average of 14.5% char, 83.9% oil, and 1.4% gas, the refrigeration plastic pyrolysed to form an average of 20.4% char, 76.5% oil, and 3.0% gas, and the mixed WEEE plastic pyrolysed to form an average of 21.1% char, 70.6% oil, and 7.8% gas. The total mass balance can be misleading for the char because the plastics all contained significant quantities of ash and the vast majority of the ash was retained by the pyrolysis char. In particular, the refrigeration plastic contained large amounts of aluminium because the process of separating the non-ferrous metals from the plastics at the recycling plant was not efficient. Therefore, the organic char was calculated to be 13.2% for the CRT plastic, 6.6% for the refrigeration plastic, and 17.8% for the mixed WEEE plastic. All of the pyrolysis oils had a very low viscosity and were brown in colour. The char resulting from the pyrolysis of the refrigeration plastic was dark grey and had a rough surface, whereas the chars from the pyrolysis of the CRT and mixed WEEE plastics were black and glassy in appearance.

Each of the chars was examined by scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDX) to determine the elemental composition of the chars. The char from the pyrolysis of the CRT plastic (figure 5) was found to contain magnesium, aluminium, calcium, titanium, chromium, and nickel as well as oxygen and carbon. The iron could be contamination from the reactor crucible. The CRT derived pyrolysis char contained pores ranging from 0.01-0.1mm in diameter. The char from the pyrolysis of the refrigeration plastic (figure 6) contained magnesium, aluminium, silicon, titanium, oxygen, and carbon and large quantities of chlorine and calcium, presumably in the form of calcium chloride. The very small amount of carbon detected in the refrigeration pyrolysis char by the SEM-EDX system reflects the very low amount of organic char compared to inorganic ash. The SEM images of the refrigeration char showed the presence of pores ranging from 0.01-0.5mm in diameter. The char from the pyrolysis of the mixed WEEE plastic (figure 7) contained magnesium, aluminium, silicon, calcium, titanium, and zinc as well as carbon and oxygen. The SEM imaging of the mixed WEEE char showed that there were two distinct types of char – a smooth surfaced char that contained some pores in the region of 0.1mm and some rough surfaced char that was more porous.

The mass composition of the pyrolysis gases (on a nitrogen free basis) is shown in table 3. The CRT pyrolysis gas was composed mainly of CO_2, methane, and butene/butadiene (which co-eluted on the GC). Nearly half the pyrolysis gas released by the refrigeration plastic was CO_2 with significant proportions of methane and H_2 present. Over half the pyrolysis gas released from the mixed WEEE plastic was carbon dioxide with a significant proportion of CO present. The pyrolysis gases of all three plastics contained all the C_1-C_4 alkanes and alkenes but generally no pattern could be observed as to the relationship between the proportion of the alkanes and alkenes.

Gas samples were taken at pre-determined intervals from the fixed bed reactor so the evolution of the gases as the tests progressed could be plotted. Figure 8 shows the major gases released during the pyrolysis of the CRT plastic. Gas evolution from the CRT plastic began at 365 °C with the release of CO_2 and butene/butadiene and peaked at 555 °C. The maximum CO_2 release occurred at approximately 610 °C, the same temperature at which CO and H_2 evolution peaked; H_2 release is not shown in figure 8. The evolution of butene/butadiene peaked at approximately 445 °C before gradually decreasing. The release of methane did not begin in any great quantity until 515°C and peak methane production occurred at 555 °C. Ethane, ethene, propane, propene, and butane followed the same evolution pattern as methane during the pyrolysis of the CRT plastic.

Figure 9 shows the evolution of the major gases during the pyrolysis of the refrigeration plastic, there were three peaks in total gas production at 405 °C, 560 °C, and 600°C. The first peak in gas evolution started at just 255°C and was almost entirely due to the release of CO_2; CO_2 release peaked at 405 °C and again at 560 °C. The evolution of CO followed the same profile as CO_2 but CO release did not begin in any great quantity until 355 °C. The release of CO_2 peaked twice, suggesting that the first stage might have been the direct evolution of CO_2 from the polymers and the second stage might have been due to the partial combustion of the polymer by evolved oxygen. The refrigeration plastic contained 4.7% oxygen (table 1). The release of methane began at 360 °C and peaked at 560 °C, the profile of ethane, ethene, propene, and butane release followed that of methane. The profile of methane release exactly matched that of the second stage of CO_2 release, adding weight to the suggestion that the second CO_2 peak was caused by oxidation. The profile of propane release during the pyrolysis of the refrigeration plastic was similar to that of methane but at low temperatures (360 -510 °C) more propane than methane was being released, which is unusual. Butene/butadiene release peaked three times at 455°C, 560 °C, and 600°C with the maximum being at 560 °C. The third peak in the total gas release (at 600°C) was due to the third peak in butene/butadiene release (figure 9).

The gas evolution profile during the pyrolysis of the mixed WEEE plastic is shown in figure 10, the total gas release began at 405°C and peaked at 505°C with another minor peak at 605 °C. The mixed WEEE plastic pyrolysed to form a large quantity of gas (table 2) and the majority of this gas was CO_2 (table 3). In figure 10, it is clear that the CO_2 release occurs very rapidly as the major peak of gas release is very sharp. The profile of CO_2 (and CO) release was the same as the profile of the total gas release mentioned above. The release of methane from the mixed WEEE plastic peaked at 555°C with a minor peak at 605 °C and butene/butadiene was released in two stages, peaking at 455°C and 605 °C. The release of the minor hydrocarbon components from the mixed WEEE plastic was much more complicated than from the other two plastics so their profile has been plotted in figure 11. During the mixed WEEE plastic pyrolysis the release of hydrogen peaked twice at 600°C, once after 60 minutes and once at 70 minutes, before gradually decreasing. Ethene release peaked at 505 °C and 600°C (70 minutes) and ethane release peaked at 555°C. The release of propene from the mixed WEEE plastic peaked at 555°C and 605 °C (70 minutes) and propane release peaked at 555°C. The release of butane peaked at 455°C. It is interesting that the release of the alkene gases both peaked twice while the release of the alkane gases only peaked once.

Each of the pyrolysis oils was analysed by GC-MS and GC-FID to determine the composition of the oils. The components identified in each oil are shown in tables 4 to 6 and the corresponding GC-MS chromatograms are shown in figure 12 to figure 14. The components listed are all those that were identified by the GC-MS with a similarity index (SI) of 90% or greater or those components which gave particularly large peaks but which could only be identified with an SI of less than 90%.

The composition of the oil resulting from the pyrolysis of the CRT plastic is shown in table 4. Most of the CRT pyrolysis oil was composed of styrene (19.3%) and benzenebutanenitrile (10.3%); other significant components were ethylbenzene, alpha-methylstyrene, 1,3-diphenylpropane, and toluene. The vast majority of the oil was composed of aromatic components many of which were nitrogenated or oxygenated. The CRT plastic had the largest nitrogen content of any of the plastics (5.5%) and this is reflected in the large number of nitrogenated components in the oil, i.e. benzenebutanenitrile accounted for 15.3% of the nitrogen in the CRT plastic waste. No halogenated compounds could be positively identified in the pyrolysis oil of the CRT plastic but some compounds were identified with an SI of less than 90%, they were 1-chloro-6-phenylhexane, 5-chloro-3-phenyl isoxazole, 2-bromo-1-methyl-1-phenylcyclopropane, and 1-bromo-3-methylbenzene.

GC-MS analysis of the refrigeration plastic pyrolysis oil (table 5) showed that styrene was by far the most prominent compound (39.9%) with other significant compounds being ethylbenzene (8.6%), toluene (4.6%), 1,3-diphenylpropane (3.5%), and alpha-methylstyrene (2.7%). The refrigeration plastic pyrolysis oil contained a particularly large number of diphenyl containing compounds as well as mono-substituted decanoates. Only one halogenated compound, (1-Chloroethyl)benzene, could be identified in the oil with an SI of >90% but 3-chloro-3-methylheptane, pentadecyl trichloroacetate, 1-chloroheptacosane, 2-bromo-1-methyl-1-phenylcyclopropane, and decyl 2-bromopropanoate could be tentatively identified in the oil.

The components identified in the mixed WEEE plastic pyrolysis oil are listed in table 6. The largest component of the mixed WEEE plastic oil was phenol (21.4%) followed by 4-isopropylphenol (8.8%), styrene (5.9%), diphenyl carbonate (2.4%), and bisphenol A (2.3%). Bisphenol A is a component of polycarbonates and epoxy resins and in this instance probably came from polycarbonates. The mixed WEEE plastic contained particularly high concentrations of oxygen (table 1), which resulted in the formation of large concentrations of phenol. The phenol in the oil accounted for 18.8% of the oxygen present in the mixed WEEE plastic waste. No halogenated compounds were identified in the mixed WEEE pyrolysis oil with an SI of greater than 90% but Hexadecyl chloroacetate and (4-chlorobutyl)benzene could be tentatively identified in the oil.

3.4 Halogens and metals in the pyrolysis products

The halogen content of the chars and oils, as measured by EPA method 5050, are shown in table 7; when comparing the halogen concentrations measured by bomb calorimetery and those observed by SEM – EDX it should be noted that the lower detection limit of the EDX is 1%. The halogen content of the gases is shown in table 3. It should also be noted that due to the low levels of halogens in the plastics it was not possible to carry out a full halogen balance because halogens that became concentrated in the char, oil, or gas came within the detection limits of EPA method 5050 when they weren’t in the raw plastic.

The only measurable halogen in the CRT plastic was chlorine. When the CRT plastic was pyrolysed to 600°C in the fixed bed reactor, the pyrolysis char contained 0.76% chlorine and 0.82% bromine; the CRT pyrolysis oil and gases contained very low concentrations of halogens. Bromine was measurable in the char but not in the raw plastic because it became concentrated in the char. SEM – EDX analysis of the CRT char showed the presence of calcium so it possible that calcium chloride and calcium bromide were formed during the pyrolysis of the CRT plastic which would explain the high concentration of halogens in the char.

The refrigeration plastic pyrolysed to produce chars with high chlorine and bromine content, 6.8% and 0.83% respectively. The refrigerator plastic pyrolysis oil contained only small amounts of bromine but significant quantities of chlorine (0.96%). The refrigerator plastic pyrolysis gas also contained 0.3% chlorine and 0.1% fluorine (table 3). The char and oil produced during the pyrolysis of the mixed WEEE plastic contained very low concentrations of halogens (table 7) the most significant of which was the fluorine present in the char (>0.13%). No halogens were measured in the pyrolysis gases of the mixed WEEE plastic.

The ash content of each pyrolysis oil was determined by firstly igniting a known mass of each oil and then burning off the remaining char in an ashing furnace. It was found that the pyrolysis oils of the mixed WEEE plastic and the CRT plastic contained 0.2 wt% ash while the refrigeration plastic contained 0.1 wt% ash. It has been reported that the presence of chlorine and bromine has a significant impact on the volatility of metals contained within plastics during thermal decomposition of the polymers [14, 26] and this probably explains the presence of metals in the pyrolysis oils.

The pyrolysis of the three plastic wastes that were collected from commercial WEEE recycling plants has demonstrated that there is potential for using pyrolysis to recycle WEEE plastics. The halogen content of the pyrolysis oils was much lower than in previous studies where model halogenated polymers have been pyrolysed [27-29]. This was mainly due to the low halogen concentration in the three plastic fractions compared to pure model polymers but also because the metal content of the chars may have scrubbed the halogens from the volatile pyrolysis products. The by-product of this scrubbing action was an increased halogen content in the chars. The halogen content of the oils could probably be reduced further by the addition of a sorbent to the reaction crucible; the use of sorbents for bromine scavenging has been investigated elsewhere [30].

The composition of the oils varied greatly between the three different plastics. However, all three pyrolysis oils contained valuable products such as toluene, styrene, phenol, bisphenol A, and diphenyl carbonate. The low halogen content of the pyrolysis oils also means that the oils could be suitable for combustion as a fuel. The pyrolysis chars may pose more of a problem to use commercially than the oils because they contain both high halogen and high ash concentrations. The metal fraction of the char is potentially valuable and the mechanisms for recycling metals are well established. If the majority of the halogens are present in the chars as metal halides, it may be possible to separate the halogens from the organic fraction of the char but organic halogens will be more difficult to remove from the char. The pyrolysis gases could be used as a fuel relatively easily, potentially in the pyrolysis process as process fuel. Any hydrogen halides, of which there were few, can easily be removed from the pyrolysis gas stream by wet, semi-dry, and dry scrubbing systems that are currently used on municipal waste incinerators exhaust gases [31] leaving behind an organic gas fraction that can be burnt without the risk of forming toxic halogenated organics. Halides recovered by scrubbing systems would also have commercial value.

4. Conclusions

Three waste plastics were collected from a waste electrical and electronic equipment (WEEE) processing plant and then homogenised before being pyrolysed on a TGA-FT-ir to gain an initial insight into their decomposition characteristics. The three different plastic wastes were the plastic fraction of cathode ray tube (CRT) containing equipment such as televisions and computer monitors, the plastic fraction of refrigeration equipment, and a plastic fraction of mixed WEEE. On the TGA-FT-ir the CRT plastic pyrolysed to form mono-substituted aromatics and aliphatics, the refrigerator plastic pyrolysed to form aldehydes, CO_2, mono-substituted aromatics, and aliphatics, and the mixed WEEE plastic pyrolysed to form aliphatics, mono-substituted aromatics, CO_2, and CO.

The three plastic wastes were pyrolysed in a batch reactor that was heated to 600°C at a heating rate of 10°C min^{-1}. The major pyrolysis product of each plastic was pyrolysis oil with only small amounts of gas being produced. Each of the pyrolysis oils was characterised by GC-MS, which showed that all the oils contained mainly aromatic compounds and both nitrogenated and oxygenated compounds; very few organic halogens were found in the pyrolysis oils. The pyrolysis oils contained relatively low concentrations of halogens. The pyrolysis chars were high in both metal and halogen content but it is possible that both the metals and halogens could be separated from the organic char.

Acknowledgements

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Table 1 Elemental composition of the three plastic wastes collected from a commercial WEEE processing plant

	CRT	Refrigeration	Mixed WEEE
N	5.5	1.8	0.8
C	81.6	71.4	75.7
H	7.5	7.0	6.3
S	0.0	0.0	0.0
O	3.9	4.7	13.5
F	>0.01	>0.01	0.31
Cl	0.26	1.30	>0.01
Br	>0.01	>0.01	>0.10
Ash	1.3	13.8	3.3

Table 2 Mass balances when each plastic was pyrolysed in the fixed bed reactor to 600°C

Wt%	CRT Expt 1	CRT Expt 2	Refrigeration Expt 1	Refrigeration Expt 2	Mixed WEEE Expt 1	Mixed WEEE Expt 2
Char	15.2	13.7	19.3	21.5	20.7	21.4
Oil	83.2	84.5	77.1	75.9	71.3	69.9
Gas	1.2	1.6	3.3	2.6	7.7	7.9
TOTAL	99.6	99.7	99.7	100.0	99.7	99.2

Table 3 Mass composition of the gases produced by each plastic during batch pyrolysis on a nitrogen free basis

Wt%	CRT	Refrigeration	Mixed WEEE
H2	5.1	10.3	1.0
CO	6.1	7.4	14.7
CO2	24.4	47.1	64.7
Methane	20.1	10.6	6.4
Ethene	6.7	3.1	1.2
Ethane	10.3	3.8	1.0
Propene	6.7	5.0	1.1
Propane	4.0	3.4	0.5
Butene/Butadiene	14.9	7.5	8.9
Butane	1.8	1.3	0.5
Cl	0.0	0.3	0.0
Br	0.0	0.0	0.0
F	0.0	0.1	0.0
S	0.0	0.1	0.0

Table 4 Composition of the oil resulting from pyrolysis of the CRT plastic

RT (min)	SI (%)	CAS #	Name	Concentration (%)	Peak #
GC-FID only		71 - 88 - 3	Benzene	0.2	
5.1	97	108 - 88 - 3	Toluene	3.2	1
10.5	98	100 - 41 - 4	Ethylbenzene	8.3	2
13.7	98	100 - 42 - 5	Styrene	19.3	3
17.2	98	98 - 82 - 8	Cumene	1.7	4
19.6	94	103 - 65 - 1	propylbenzene,	0.1	
21.4	95	98 - 83 - 9	α-Methylstyrene	6.8	5
23.8	95	611 - 15 - 4	1-ethenyl-2-methylbenzene,	0.1	
27.2	97	95 - 87 - 4	2,5-dimethylphenol,	0.9	6
27.4	91	768 - 00 - 3	(E)-2-Phenyl-2-butene	>0.1	
28.4	95	140 - 29 - 4	Benzyl nitrile	0.1	
28.5	90	2177 - 47 - 1	2-Methylindene	0.1	
29.3	96	1823 - 91 - 2	α-methyl-benzeneacetonitrile	0.2	
33.3	91	5590 - 14 - 7	2-Phenylcyclopropanecarbonitrile	0.2	
34.4	99	2046 - 18 - 6	Benzenebutanenitrile	10.3	7
34.9	93	5590 - 14 - 7	2-Phenylcyclopropanecarbonitrile	0.1	
35.3	93	10340 - 49 - 5	(1-methyl-3-butenyl)benzene	1.2	8
36.7	93	5590 - 14 - 7	2-Phenylcyclopropanecarbonitrile	0.3	
39.2	96	103 - 29 - 7	Bibenzyl	0.1	
39.9	93	5814 - 85 - 7	1,2-Diphenylpropane	>0.1	
42.3	97	1081 - 75 - 0	1,3-Diphenylpropane	4.1	9
42.4	93	132 - 75 - 2	1-Naphthaleneacetonitrile	0.3	
42.7	92	29881 - 14 - 9	1,2-Diphenylcyclopropane	0.2	
42.8	90	7614 - 93 - 9	1,3-Diphenyl-1-butene	0.2	
42.9	96	1520 - 44 - 1	(3-Phenylbutyl)benzene	0.5	
43.6	95	103 - 30 - 0	(E)-Stilbene	0.1	
44.1	90	29881 - 14 - 9	1,2-Diphenylcyclopropane	1.3	10
44.5	95	1083 - 56 - 3	1,4-Diphenylbutane	0.2	
45.0	90	7614 - 93 - 9	1,3-Diphenyl-1-butene	0.3	
45.5	92	7614 - 93 - 9	1,3-Diphenyl-1-butene	0.4	
47.4	95	629 - 79 - 8	Hexadecanenitrile	0.6	
49.1	92	35465 - 71 - 5	2-Phenylnaphthalene	0.1	
51.3	69	-	unknown	1.8	11
52.4	92	92 - 06 - 8	m-Terphenyl	0.1	
52.5	73	-	unknown	1.5	12
64.4	93	612 - 71 - 5	1,3,5-Triphenylbenzene	0.1	
			Total	**64.8**	

Table 5 Composition of the oil resulting from pyrolysis of the Refrigeration plastic

RT (min)	SI (%)	CAS #	Name	Concentration (%)	Peak #
5.1	97	108 - 88 - 3	Toluene	4.6	1
10.5	98	100 - 41 - 4	Ethylbenzene	8.6	2
13.8	98	100 - 42 - 5	Styrene	39.9	3
17.2	98	98 - 82 - 8	Cumene	0.7	4
19.1	92	611 - 15 - 4	2-Methylstyrene	>0.1	
19.6	94	103 - 65 - 1	Propylbenzene	0.1	
21.4	95	98 - 83 - 9	α -Methylstyrene	2.7	5
23.8	96	637 - 50 - 3	Propenylbenzene	0.2	
25.4	95	672 - 65 - 1	(1-Chloroethyl)benzene	0.1	
26.3	91	935 - 67 - 1	(1-methoxy-1-methylethyl)benzene,	1.1	6
27.4	90	2039 - 89 - 6	2,5-Dimethylstyrene	>0.1	
29.8	90	91 - 20 - 3	Naphthalene	>0.1	
34.3	95	2046 - 18 - 6	Benzenebutanenitrile	1.1	7
35.3	92	10340 - 49 - 5	(1-methyl-3-butenyl)benzene	0.1	
36.9	94	101 - 81 - 5	Diphenylmethane	0.1	
39.2	95	103 - 29 - 7	Bibenzyl	0.1	
39.9	95	5814 - 85 - 7	1,2-Diphenylpropane	0.1	
41.3	82	55191 - 25 - 8	(1,1-dimethylnonyl)benzene,	0.5	8
42.3	97	1081 - 75 - 0	1,3-Diphenylpropane	3.5	9
42.7	90	29881 - 14 - 9	1,2-Diphenylcyclopropane	0.1	
42.8	91	7614 - 93 - 9	1,3-Diphenyl-1-butene	0.3	
42.9	93	1520 - 44 - 1	(3-Phenylbutyl)benzene	0.4	
43.6	94	103 - 30 - 0	(E)-Stilbene	0.1	
43.7	79	3128 - 88 - 9	1,2-Diphenyl-1-isocyanoethane	1.6	10
44.1	90	29881 - 14 - 9	1,2-Diphenylcyclopropane	0.7	
44.5	92	1083 - 56 - 3	1,4-Diphenylbutane	0.2	
45.0	90	7614 - 93 - 9	1,3-Diphenyl-1-butene	0.3	
45.1	96	0 - 00 - 0	2,4-Diphenyl-4-methyl-1-pentene	0.6	
45.5	92	7614 - 93 - 9	1,3-Diphenyl-1-butene	0.9	11
47.9	90	112 - 39 - 0	Methyl hexadecanoate	0.2	
49.1	95	35465 - 71 - 5	2-Phenylnaphthalene	0.3	
51.7	94	112 - 61 - 8	Methyl octadecanoate	0.1	
52.4	93	92 - 06 - 8	3-Phenylbiphenyl	0.1	
57.1	78	-	unknown	2.4	12
58.4	96	27554 - 26 - 3	Isooctyl phthalate	0.6	
58.9	84	-	unknown	1.3	13
60.9	90	1165 - 53 - 3	1,3,4-triphenylbenzene	>0.1	
64.5	96	612 - 71 - 5	1,3,5-Triphenylbenzene	0.3	
			Total	**74.9**	

Table 6 Composition of the oil resulting from the pyrolysis of the mixed WEEE plastic

RT (min)	SI (%)	CAS #	Name	Concentration (%)	Peak#
GC-FID		71 - 88 - 3	Benzene	0.1	
5.1	97	108 - 88 - 3	Toluene	0.8	1
10.6	98	100 - 41 - 4	Ethylbenzene	1.0	2
13.7	98	100 - 42 - 5	Styrene	5.9	3
17.3	94	98 - 82 - 8	Cumene	0.2	
21.4	95	98 - 83 - 9	α -Methylstyrene	1.0	
22.0	99	108 - 95 - 2	Phenol	21.4	4
23.7	91	527 - 84 - 4	1-Methyl-2-iso-propylbenzene	>0.1	
29.4	95	123 - 07 - 9	4-Ethylphenol	0.7	
31.2	98	99 - 89 - 8	4-Isopropylphenol	8.8	5
33.2	97	98 - 54 - 4	4-(1,1-Dimethylethyl)phenol	0.3	
33.5	92	4286 - 23 - 1	p-Isopropenylphenol	1.7	6
34.3	94	2046 - 18 - 6	Benzenebutanenitrile	1.1	
42.3	96	1081 - 75 - 0	1,3-Diphenylpropane	0.7	
43.2	93	102 - 09 - 0	Diphenyl carbonate	2.4	7
44.2	78	73669 - 43 - 9	3,5-Diethyl-2-phenylpyridine	1.4	8
45.5	91	7614 - 93 - 9	1,3-Diphenyl-1-butene	0.2	
46.6	92	599 - 64 - 4	4-(Dimethylphenylmethyl)phenol	1.3	
49.0	85	-	unknown	1.9	9
50.1	62	-	unknown	1.6	10
52.7	96	80 - 05 - 7	Bisphenol A	2.3	11
56.4	95	115 - 86 - 6	Triphenyl phosphate	1.3	12
58.4	94	27554 - 26 - 3	Isooctyl phthalate	0.1	
58.9	84	-	unknown	0.7	13
64.5	94	612 - 71 - 5	1,3,5-Triphenylbenzene	0.3	
			Total	**57.6**	

Table 7 Halogen concentration of the chars and oils resulting from the pyrolysis of all three plastics at 600°C

		Halogen concentration in the pyrolysis chars and oils (%)		
		F	**Cl**	**Br**
Char	**CRT**	>0.01	0.76	0.82
	Mixed WEEE	>0.13	>0.07	>0.09
	Refrigeration	>0.01	6.80	0.83
Oil	**CRT**	>0.01	>0.05	>0.01
	Mixed WEEE	>0.01	>0.06	>0.09
	Refrigeration	>0.01	0.96	>0.06

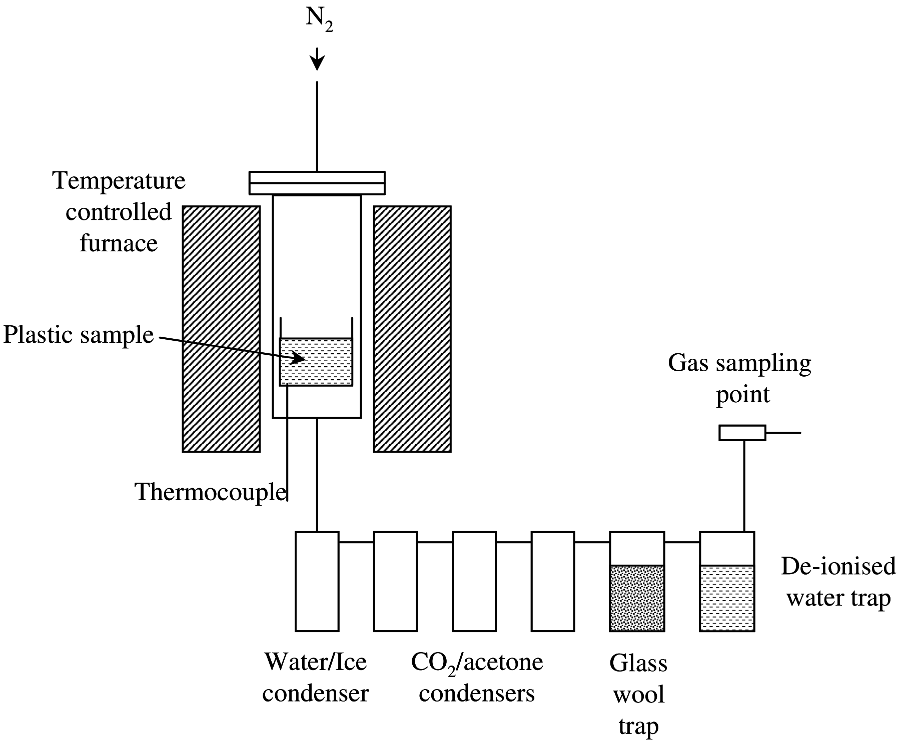

Figure 1 Schematic of the fixed bed reactor

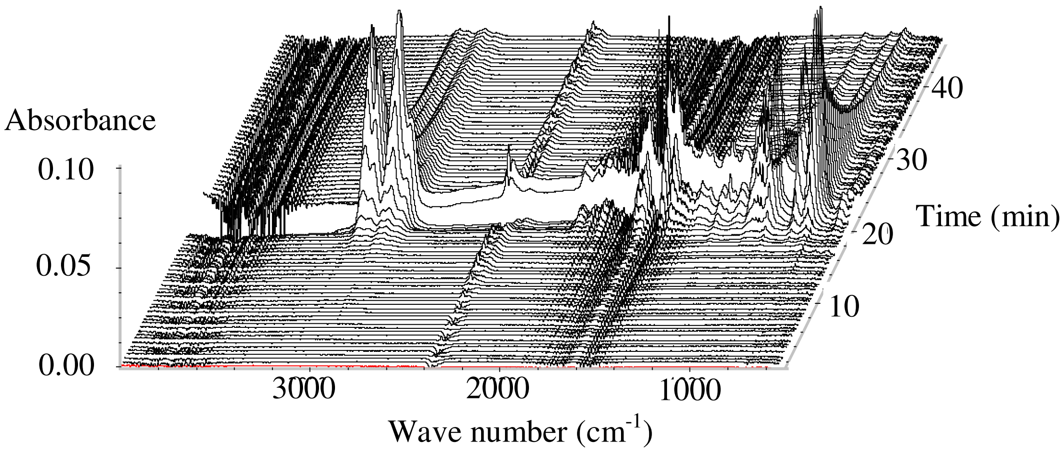

Figure 2 TGA-FT-ir analysis of the CRT plastic

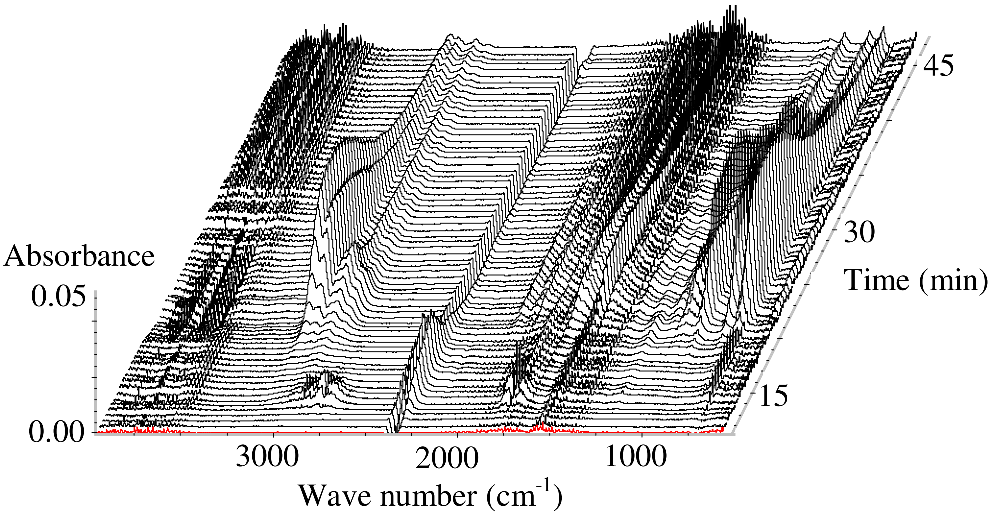

Figure 3 TGA-FT-ir analysis of the Refrigeration plastic

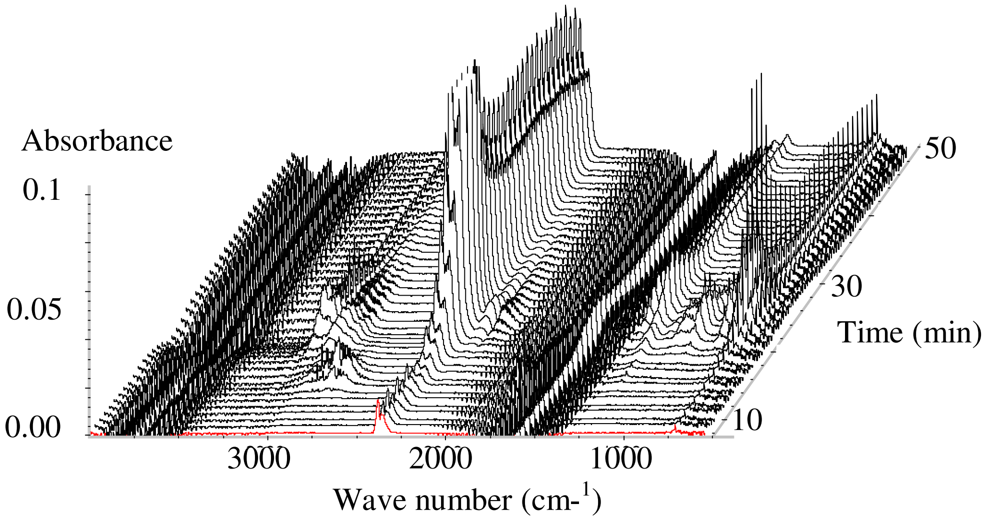

Figure 4 TGA-FT-ir analysis of the mixed WEEE plastic

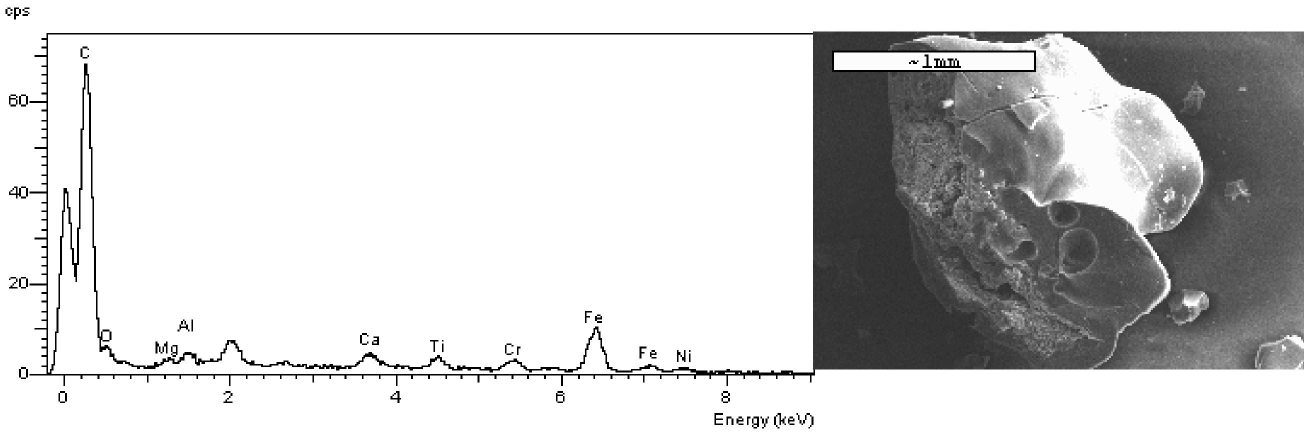

Figure 5 SEM-EDX analysis of the CRT pyrolysis char

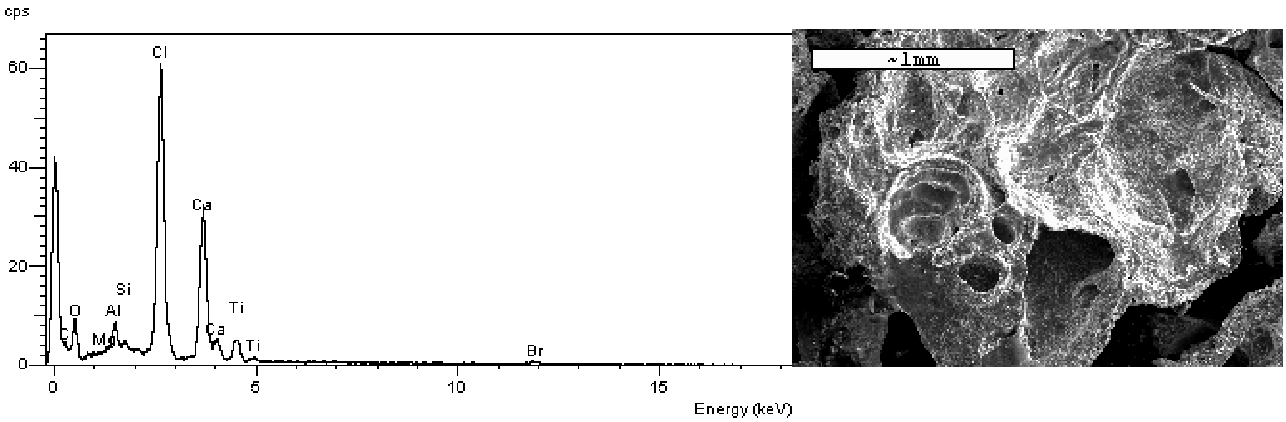

Figure 6 SEM-EDX analysis of the Refrigeration plastic pyrolysis char

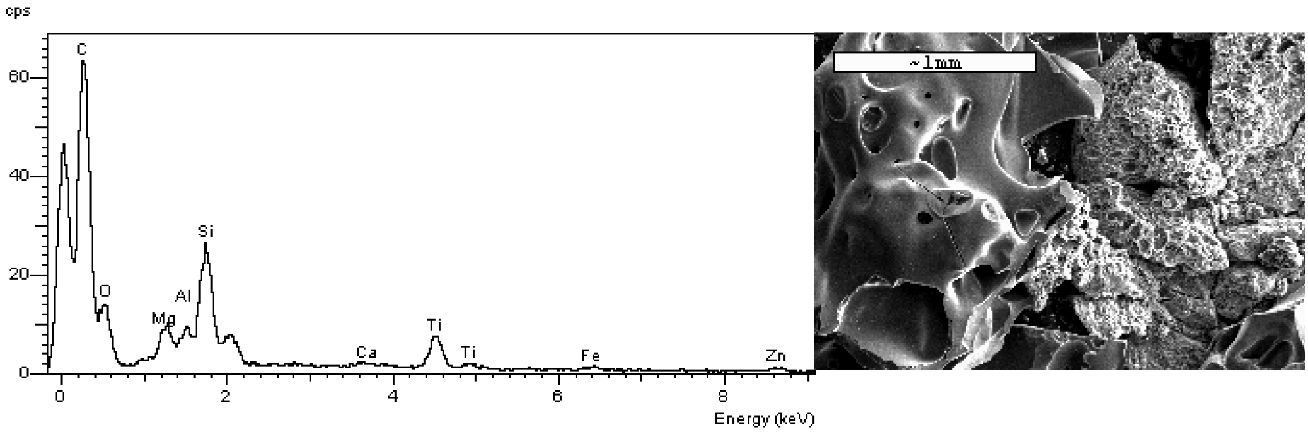

Figure 7 SEM-EDX analysis of the mixed WEEE plastic pyrolysis char

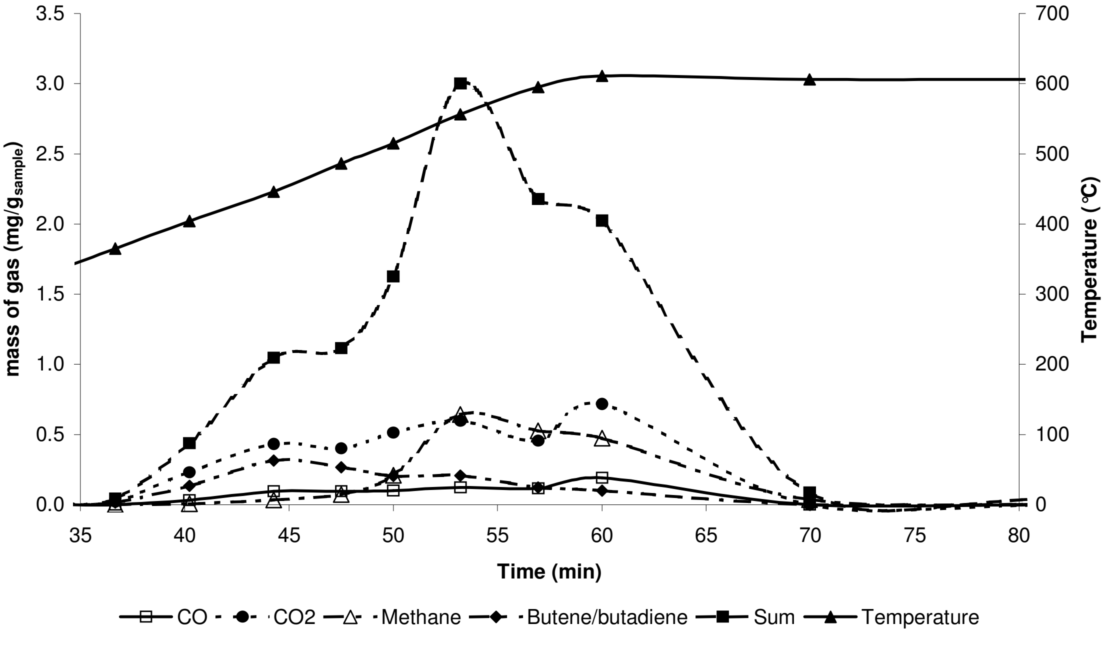

Figure 8 Profile of the release of gases during the batch pyrolysis of CRT plastic in a fixed bed reactor

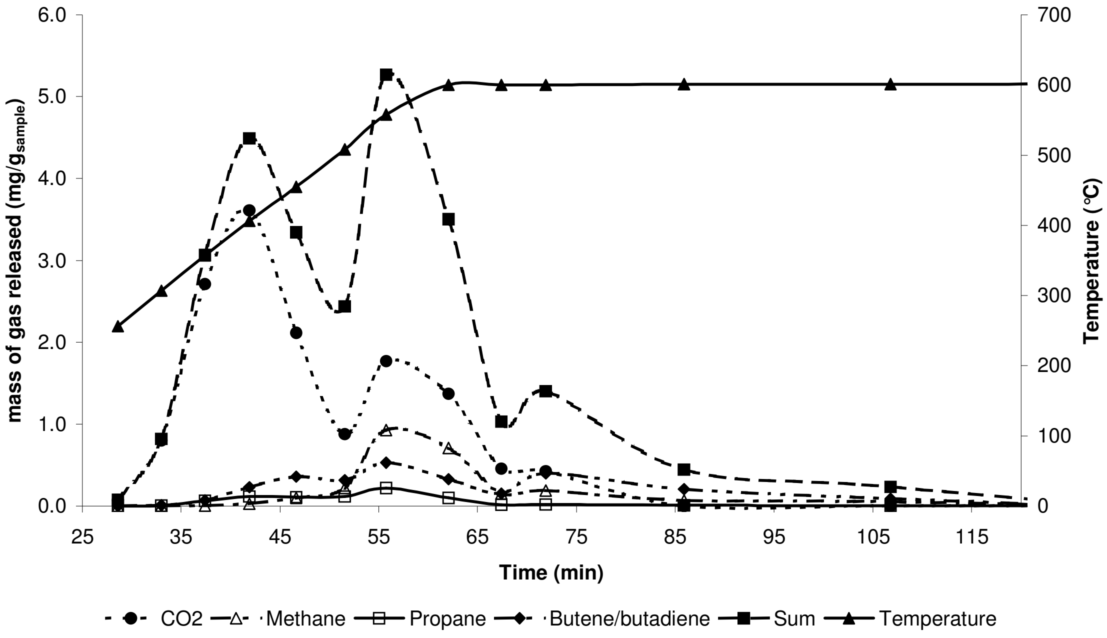

Figure 9 Profile of the release of gases during batch pyrolysis of the refrigeration plastic in a fixed bed reactor

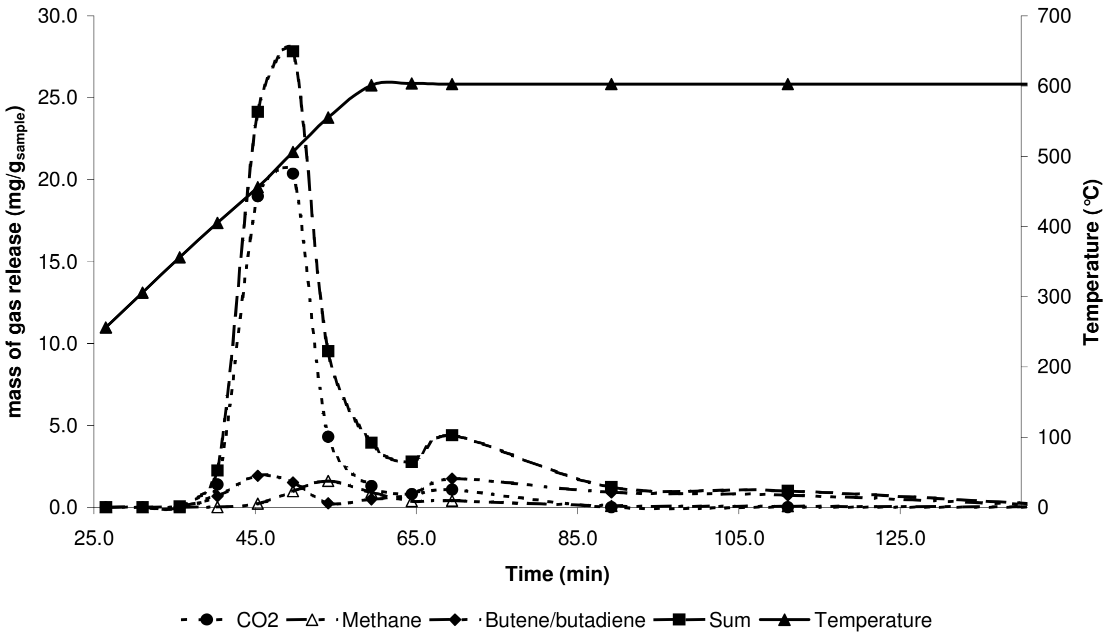

Figure 10 Profile of the gases released during batch pyrolysis of the mixed WEEE plastic in a fixed bed reactor

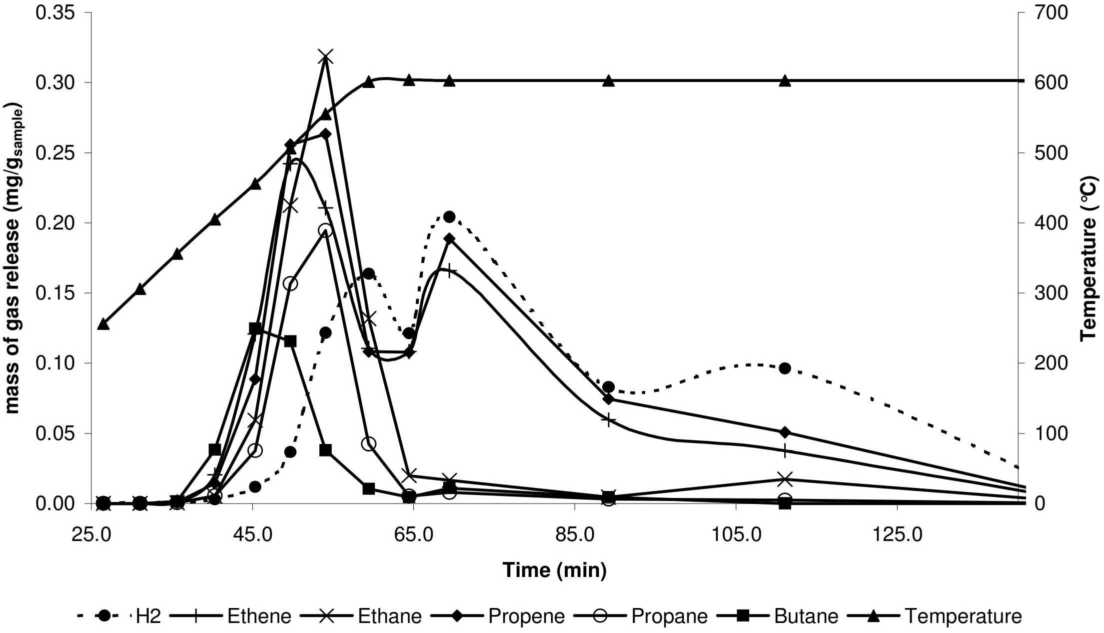

Figure 11 Organic gases released during the batch pyrolysis of the mixed WEEE plastic in a fixed bed reactor

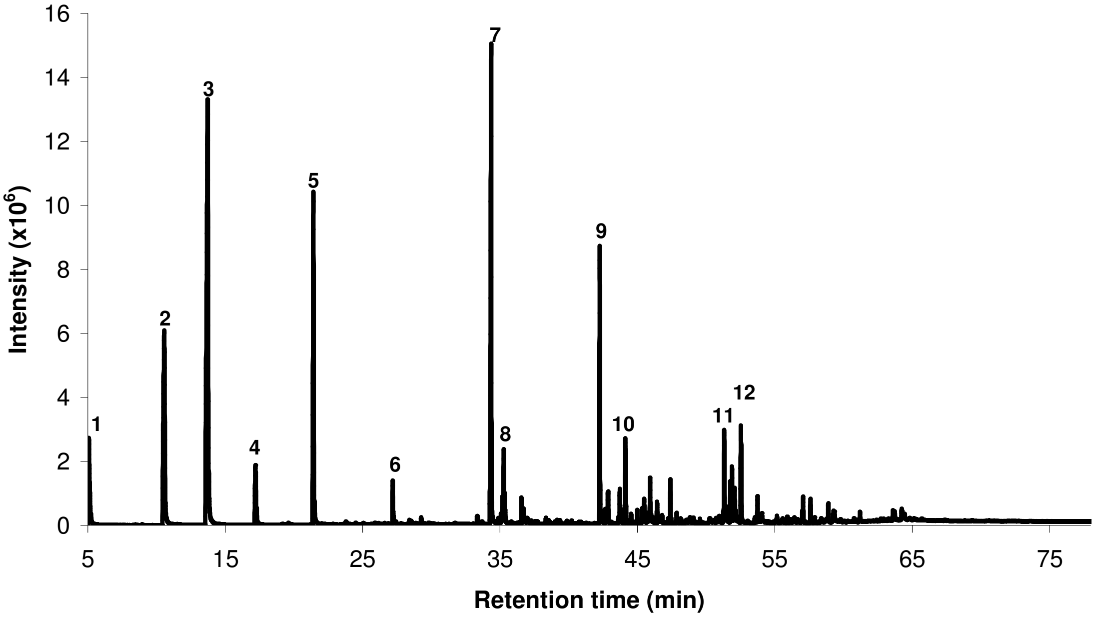

Figure 12 GC-MS analysis of the oil resulting from the pyrolysis of the CRT plastic in a fixed bed reactor

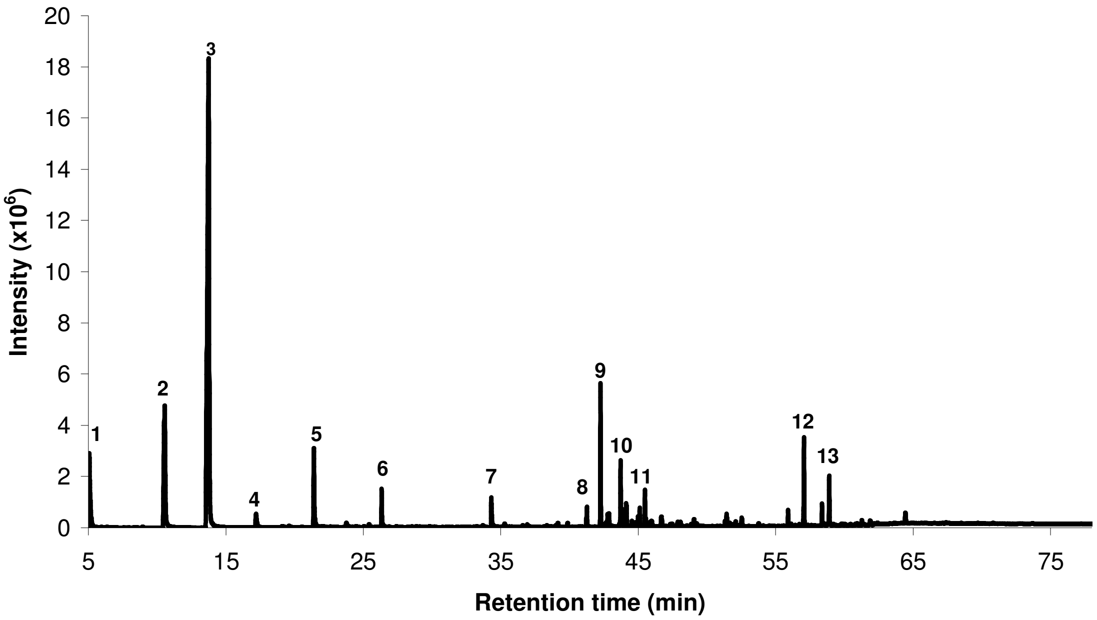

Figure 13 GC-MS analysis of the oil resulting from the pyrolysis of the Refrigeration plastic in a fixed bed reactor

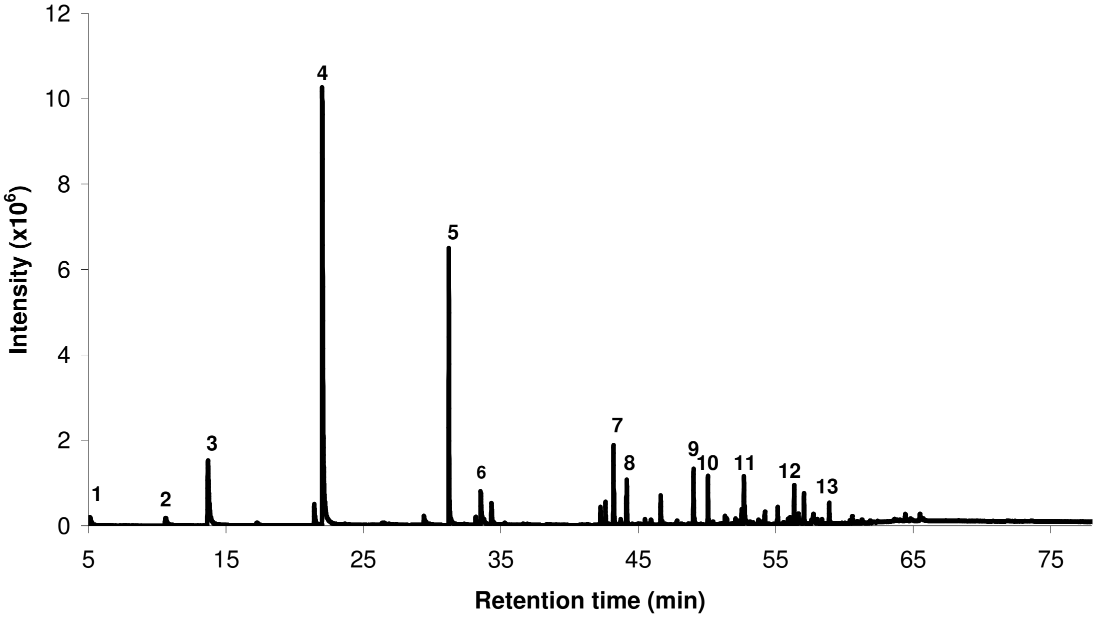

Figure 14 GC-MS analysis of the oil resulting from the pyrolysis of the mixed WEEE plastic in a fixed bed reactor