Proceedings of ECOS 2002, Berlin (Germany) July 3-5, 2002, Vol. 2, pages 1302-1309

THERMAL PROCESSING OF CHLORINE- AND BROMINE- CONTAINING WASTES

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ABSTRACT

Waste streams that contain large fractions of halogenated compounds, such as poly vinyl chloride (PVC) and brominated flame retardants (BFRs) cannot be incinerated or otherwise thermally treated straightforward. These fractions are unwanted due to high risks of corrosion, dioxins/furans formation, the volatility of metal chlorides and the costs of HCl removal from the flue gases. Also problematic are polymer foams that contain CFC (chlorofluorocarbon)-type ozone depleting substances (ODS).

BFRs are widely used in electronic and electric equipment, furniture and office equipment. While increasing fire safety, BFRs are problematic for thermal treatment of waste streams such as waste electric and electronic equipment (WEEE). They interfere with the recovery of valuable metals from WEEE, besides the risk of ODS emissions such as methyl bromide.

This paper reports from experimental research on combustion of high-PVC solid waste (see also ECOS2000 and ECOS2001), and thermal processing of WEEE aiming at the recovery of valuable metals.

INTRODUCTION

Plastic production is steadily increasing worldwide, faster than options are being developed for recycling wastes that contain large amounts of plastics. Especially for poly vinyl chloride (PVC), mostly used in what are called long-term applications there is therefore a need for new ways of waste processing. Since PVC contains over 50%-wt chlorine (Cl) it is not recommended to burn solid wastes if PVC represents more than, say, 5% of the total weight of the “fuel”. Reasons for this are the potentially high emissions of HCl and associated problems such as corrosion and the risk of dioxins and furans formation. Recently it was reported that around 90% of the plastics in Swedish waste from the building sector was PVC [1], whilst in Finland more than 90% of the chlorine found in the dry fraction of household waste was reported to be PVC [2]. The first part of this paper will address a process for the combustion of high-PVC solid wastes, producing heat while recovering HCl.

Brominated flame retardants (BFRs) are widely used, often together with antimony-based flame retardants, in electronic and electric equipment, furniture and office equipment. While this increases the fire safety for these products, the BFRs are problematic when thermal processes are used during the

treatment of waste streams from these products such as waste electric and electronic equipment, WEEE. Not only do the BFRs negatively effect the incineration of, for example, old furniture: there is a potential for the emission of ozone depleting substances (ODS) such as methyl bromide [3]. Also the formation of brominated analogues of dioxins and furans, PBDD/Fs (poly brominated dibenzo -p- dioxins and - furans) is possible. Finally, they interfere with thermal processes that aim at the recovery of, for example, valuable metals from WEEE waste. The second part of this paper deals with thermal processing of two types of WEEE and the effect of the BFRs present in these wastes.

THERMAL PROCESSING OF PVC-CONTAINING WASTES

The process for two-stage combustion of high-PVC solid waste with HCl recovery [4] is based on experimental findings that PVC can be decomposed into HCl and a low-chlorine or chlorine-free residue by heating to temperatures of around 300-350°C [5-8]. A simplified scheme of the process as it is being assessed and optimised at Helsinki University of Technology is given in Figure 1.

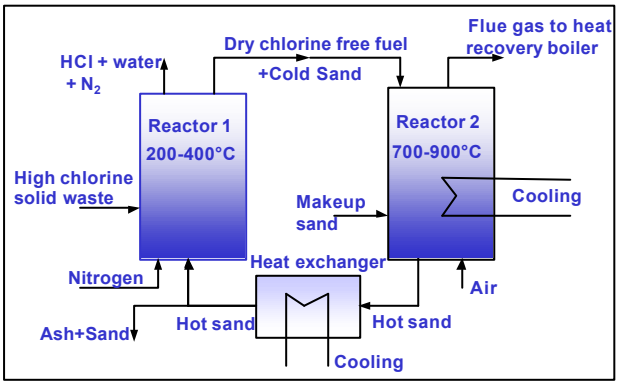


Fig. 1 Two-stage combustion of high-PVC solid waste with HCl recovery: simplified process scheme

High-PVC solid waste is fed to a fluidized bed (FB) pyrolysis reactor, where it is heated up to about 350°C as to release (most of) the hydrogen chlorine (HCl). The gas used for the fluidization in this first reactor is nitrogen (N_2) in order to avoid any risk of dioxins and furans formation.

The gases from the first reactor will contain mainly N_2, HCl, H_2O and small amounts of other gases. The solid residue, which includes the hydrocarbon residue from the PVC plus the rest of the incoming fuel, can be combusted as any other low-chlorine or chlorine-free solid fuel. This is accomplished in the second reactor at around 800°C-850°C without environmental hazard or corrosion problems.

A theoretical study using process simulation software PROSIM showed that the process may have a thermal efficiency of approx. 37%, depending on the pyrolysis temperature, PVC content in the solid waste and the moisture content in the solid waste [9-12]. This efficiency is higher than for a conventional incineration plant that would have approx. 33% thermal efficiency. These calculations were based on wood/PVC fuel mixtures.

A test facility was built at Helsinki University of Technology at Otaniemi, Espoo, based on:

1. kinetic data on de-hydrochlorination for a typical PVC [5,7,8] and on combustion of chars from PVC and wood [6]; and
2. process optimisation calculations for a 40 $MW_{thermal}$ plant design case [9-10], scaled down from 40 MW to 40 kW thermal fuel input.

Reactor 1 is a bubbling FB reactor (inner diameter 0.4 m, height 0.8 m) made of stainless steel ASTM 316. The fluidising medium is nitrogen. This BFB is operated in the temperature range 300 - 400°C: 350°C may be the optimum temperature for producing low-chlorine or chlorine-free fuel in this dehydrochlorination reactor (with a solids residence time of approx. 30 minutes) without significantly pyrolysing any of the other combustible fractions [8]. Silica sand (mean particle size 0.3 mm) is used as bed material.

Reactor 2 is a circulating FB combustor (inner diameter 0.11 m, height 2.3 m) also made of stainless steel ASTM 316. The fluidizing gas is air and the reactor operates at a temperature of 800-850°C. This air will be preheated to approx. 600°C with heating coils until char from the first reactor can provide

sufficient combustion heat. The cooling system of this CFBC is divided into three parts in order to cool separate parts of the reactor when necessary. For process control and data logging, several probes are connected to a computer (PC), *i.e.*19 signals for temperature, 11 for pressure, 5 for flow rate and one signal from a pH meter (see below).

The sand in the CFBC exist gas is collected by a high efficiency cyclone operated with inlet velocity about 15 m/s. The collected sand will be cooled to below 400°C before returning to the BFB by an FB heat exchanger with water. The fluidizing medium is nitrogen gas. This heat exchanger will also act as a non-mechanical valve to prevent any pyrolysis gases from passing to the flue gas exit. A seal pot-type non-mechanical valve between the BFB reactor and the CFBC prevents any flow of air or combustion gases to the BFB.

The pyrolysis gases from the BFB are cooled to 80°C by exchanging heat with water. After that the gases are fed to an NaOH/water solution to separate the HCl from the pyrolysed gas, which mainly contains N_2. The HCl will be neutralized to produce NaCl and water. (For a larger scale process, HCl is to be recovered as hydrochloric acid!) By measuring the pH of the solution the HCl concentration can be followed.

The gases from both FB reactors will be analyzed as well in order to evaluate process efficiency and to see if there is any release of chlorine, HCl or traces of dioxins. Concentrations of HCl and several other species in the pyrolysis gas from the BFB pyrolyser and the flue gases from the CFBC are measured with a Fourier transform infrared (FT-IR) spectrometer (Gasmet Instruments Temet type DX-4000).

Two photographs of the facility are given in Figure 2. At the time of finalising this paper, the performance of the two "loops" in the test rig, *i.e.* 1) pyrolysis reactor / HCl removal from pyrolysis gas / booster blower / pyrolysis reactor, and 2) pyrolysis reactor / combustion reactor / cyclone / heat recovery / pyrolysis reactor are being tested separately. After this,

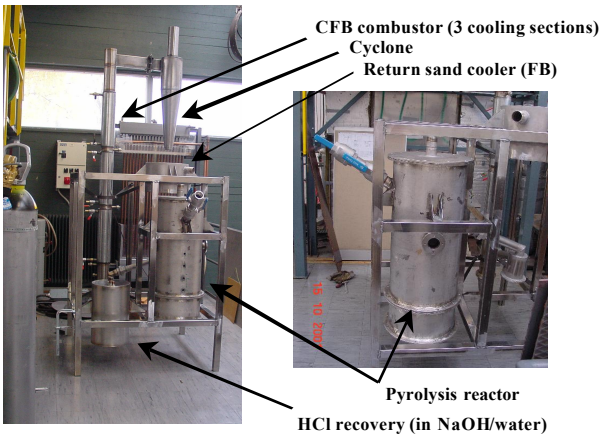


Fig. 2 Impression of the test facility at Helsinki Univ. of Technol. (Oct. 01)

the "loops" will be connected and operated simulataneously. Also, the temperature, pressure and pH measurement equipment is being tested, and the FT-IR gas analyser is being integrated with the test rig. Experiments will be conducted during March-April 2002, with PVC/wood and PVC/coal mixtures.

One last feature that will be studied is that processing of waste streams containing PVC involves also trace elements and heavy metals such as lead (Pb), cadmium (Cd) but also the less harmful calcium (Ca) and zinc (Zn). These are added to PVC for improving its stability against heat, chemicals, ultra-violet irradiation *etc*. Depending on the type of PVC and the other components in the waste mix, metals such as Pb may react with HCl to form volatile metal chlorides or may be trapped by the char. Some work on this was recently published [13] for pyrolysis of mixtures containing PVC at 500-700°C. As to obtain some indication on the amounts of trace elements and heavy metals present in PVC waste, six typical samples were analysed. Results of these analyses are given in Table 1.

Table 1 Chemical composition of six typical waste-PVC fractions (dry)

C %-wt	H %-wt	Cl %-wt	Pb %-wt	Cd %-wt
37 - 41	4.6 - 5.1	46 - 53	0 - 4.0	0 - 0.12

Sn %-wt	Ca %-wt	Zn mg/kg	Ba mg/kg
0 – 0.25	0 – 2.8	0 - 36	0 - 1020

BROMINATED FLAME RETARDANTS, BFRs

Around 350 chemical compounds have been registered as flame retardants of which around 200 find commercial application. A BFR may be defined as "a non-organo phosphoros organic compound where one or more hydrogen atoms are replace by bromine" [14]. This definition excludes ammonium bromide and brominated organophosphates. BFRs contain 50-95 %-wt of bromine, and can be separated into aromatic, aliphatic and cyclo-aliphatic – see several important BFRs in Figure 3. The aromatic BFRs can be divided into three types, *i.e.* polybrominated biphenyl ethers (PBDEs), tetrabromo bisphenol A (TBBPA) and its derivates, and polybrominated biphenyls (PBBs). Of the cycloaliphatic BFRs compounds, hexabromocyclododecane (HBCD) is the most important. Aliphatic BFRs are not used in large amounts since they are less stable than aromatic BFRs; they may be more effective at lower temperatures, however.

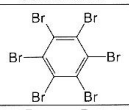
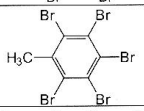
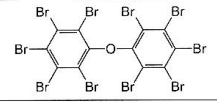
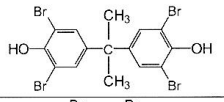
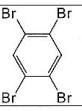
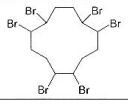
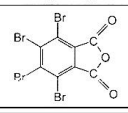
name	structural	total formula
Hexabromobenzene Perbromobenzene		C_6Br_6
Pentabromotoluene		$C_7H_3Br_5$
Perbromodiphenylether Decabromodiphenyl-ether		$C_{12}Br_{10}O$
Tetrabromo-bisphenol A		$C_{15}H_{12}Br_4O_2$
Tetrabromo-benzene		$C_6H_2Br_4$
Hexabromo-cyclodecan		$C_{12}H_{18}Br_6$
Tetrabromo-phthalicacid-anhydride		$C_8Br_4O_3$

Fig. 3 Several brominated flame retardants [15]

BFRs are used in plastics and textiles in order to comply with fire safety regulations. In Western Europe as well as on a global scale, BFRs represented ~15% of the total consumption of flame retardant during the late 1990s. Around 75 % of the BFRs are used in plastics, the other 25 % is used in textiles, rubbers, paint, wood, paper and adhesives. Also important is the distinction between "additive" and "reactive" use, where the latter implies a chemical reaction between the FR and the polymer resin, for example in epoxy resins for printed circuit boards or in rigid polyurethane (PUR) foams. Additive FRs are much less volatile than reactive FRs; FRs such as TBBPA lose their identity when used as a reactive BFR [14].

Since the late 1980s the use of PBDE-type BFRs is declining after several studies pinpointed them as a health and environmental hazard, partly because of their high potential to form polybrominated–p-dibenzodioxins and furans (PBDD/Fs). Their market share was taken over by TBBPA and non-halogenated flame retardants [16]. From the viewpoint of product recycling or chemical recycling, BFR-containing polymers such as PUR foams, extruded polystyrene (XPS) and printed circuit boards and other types of WEEE are considered problematic [16]. On the other hand, BFR-containing wastes are receiving increased attention for combined recovery of bromine (as HBr or NaBr) and energy.

THERMAL PROCESSING OF WASTES CONTAINING BFRs: WEEE

As part of research under an EU 5th framework R&D "Growth" project [17], the thermal decomposition of two types of WEEE was analysed by thermogravimetric analysis (TGA) combined with on-line analysis of the product gases by Fourier transform infrared (FT-IR) analysis.

The experimental set-up is shown in Figure 4. The samples are heated (at 10 K/min) up to 1000 °C in a gas atmosphere that contains a certain amount of oxygen (21 or 2 %-vol) in nitrogen, while the mass is measured as function of time, *i.e.* temperature. At the same time, the concentration of the gases CO_2, H_2O, CO, CH_4, HCN, NO, N_2O, HCl and HBr

is measured using FT-IR, covering the IR spectrum over the range 950-4000 wavenumbers (cm^{-1}).

Two types of typical, BFR containing WEEE materials were analysed: computor monitor housing scrap and electronic circuit board scrap. The results of proximate and ultimate analysis of these two is given in Table 2. Besides a different bromine content the monitor housings have a higher chlorine content and a much lower nitrogen content than the printed circuit boards, the latter due to the presence of ABS (acrylonitrile–butadiene-styrene).

Table 2 Composition of two typical BFR-containing WEEE

%-wt	Scrapped computer monitor housings	Scrapped electronic circuit boards
Moisture	0.1	1.7
Volatiles (dry)	84.7	63.1
Ash (dry)	10.6	20.1
C-fix [a] (dry)	4.7	16.8
C (dry)	75.0	44.2
H (dry)	7.7	5.0
N (dry)	0.9	3.7
O (dry)	7.3	22.0
S (dry)	0.12	0.03
Cl (dry)	**0.21**	**0.02**
Br (dry)	**2.2**	**5.0**
Sb (dry)	0.45	0.02
Si (dry)	0.25	2.9
Cu (dry)	0.14	4.2
Ti (dry)	3.5	n.a.[b]
Others (dry)	2.2	12.9
LHV [c] (dry) (MJ/kg)	22.3	15.8

[a] by difference
[b] not analysed
[c] Lower heating value

The result of the TGA/FT-IR test with the monitor housings is given in Figure 5, showing a mass loss only at temperatures below 700 K, after which approx. 1/3 of the initial mass remains. The corresponding concentration of halogen gases HCl and HBr plus those of the major oxidation products CO_2 and H_2O are

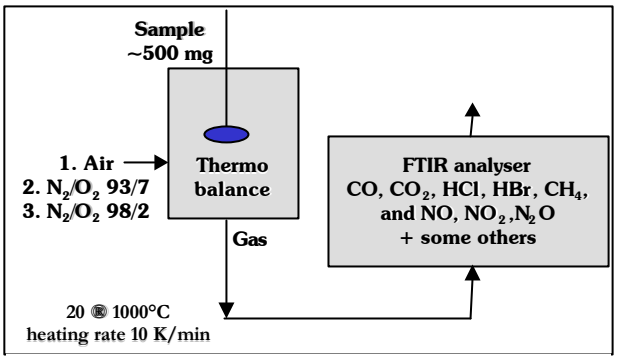


Fig. 4 Experimental set-up for the TGA-FTIR tests

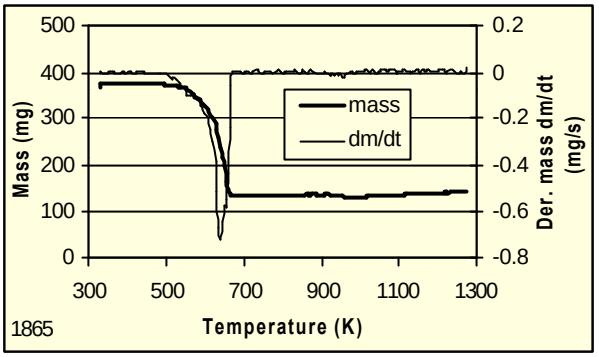


Fig. 5 TGA result from scrapped monitor housings, in air, heating rate 10 K/s

given in Figure 6. A single peak for HCl is seen at 560 K, while the emissions of H_2O and CO_2 peak at 640 K. Clearly, chlorine release occurs much earlier than the main oxidation of the sample.

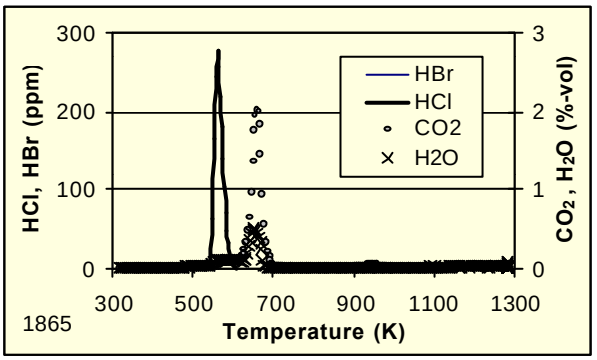


Fig. 6 Concentration of HBr, HCl, CO_2 and H_2O in the product gas from monitor housings, in air, heating rate 10 K/s

Surprisingly enough, the concentration of HBr in the product gases equals zero during the entire test. Discarding the possibility that the Br stays in the sample and will be found in the final residue there are two explanations for

this:

1. Br is released from the sample as a species other than HBr, and this is not hydrolysed to HBr either; or
2. HBr is formed but is immediately oxidised to Br_2 via the "Bromine Deacon reaction"

$$2HBr + ½O_2 \Leftrightarrow Br_2 + H_2O \qquad \textbf{(R1)}$$

It follows from free energy minimisation calculations that the equilibrium constant for reaction (R1) equals

$$ln\, K_p = ln\left[\frac{p_{Br_2} \cdot p_{H_2O}}{\sqrt{p_{O_2}} \cdot p_{HBr}^2}\right] = -8.2556 + \frac{16735}{T} \qquad \textbf{(1)}$$

which with p_{O2} = 0.2 bar and p_{H2O} < 0.05 bar during the test shows that the equilibrium will be very much at the side of Br_2, especially at temperatures below 700 K. Even for a gas with, say, 10 %-vol water the situation would not be very different. This hypothesis may be tested by adding HBr to the inlet gas and verify whether the same result would be obtained. Another option would be to increase the heating rate.

Figure 7 gives the FT-IR spectrum at 367°C, corresponding to the peak in Figure 5. Clearly shown are peaks for CO_2 (2300-2400 cm^{-1}), H_2O (1300-1900 cm^{-1} and 3500-4000 cm^{-1}), CH (~1400 cm^{-1} and 2800-3000 cm^{-1}) and maybe for CH_3Br (~3000 cm^{-1}, ~1300 cm^{-1}, ~1000 cm^{-1}, ~1500 cm^{-1}) [18]. No peaks are seen for HBr (~2550 cm^{-1}) whilst the peak for bromobenzene lies outside the range of measurement (~755 cm^{-1}) [19]. For 287°C, where the peak for HCl is seen in Figure 6, the FT-IR spectrum is shown in Figure 8.

Figure 9 gives the TGA result for scrapped printed circuit boards during heat-up in air at 10 K/min. The corresponding gas analysis for HBr, HCl, H_2O and CO_2 is given in Figure 10. Here, significant mass losses are found at 586 K and 732 K, respectively, corresponding to 35 % of the mass in both stages. While no

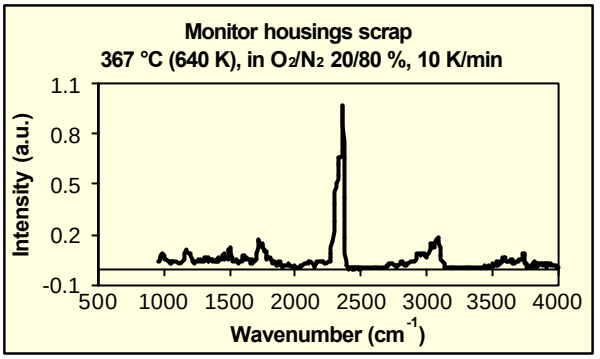


Fig. 7 FT-IR spectrum of the product gas from monitor housings, in air, heating rate 10 K/s, at 367°C

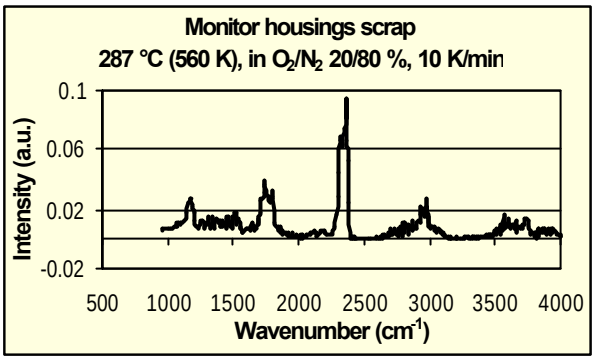


Fig. 8 FT-IR spectrum of the product gas from monitor housings, in air, heating rate 10 K/s, at 287°C

significant further mass loss is recorded above 800 K, Figure 10 shows a release of HCl from this point onwards. Apart from some scattered, small peaks, also here no HBr was detected by the FT-IR.

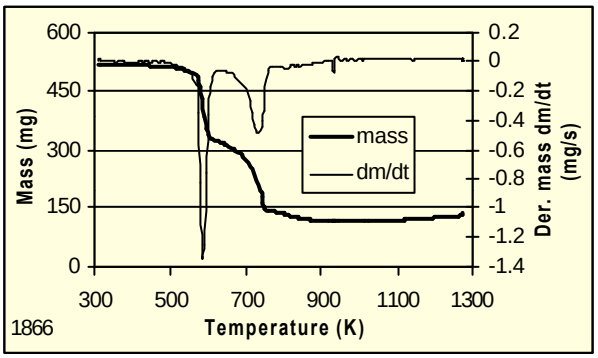


Fig. 9 TGA result from scrapped electronic circuit boards, in air, heating rate 10 K/s

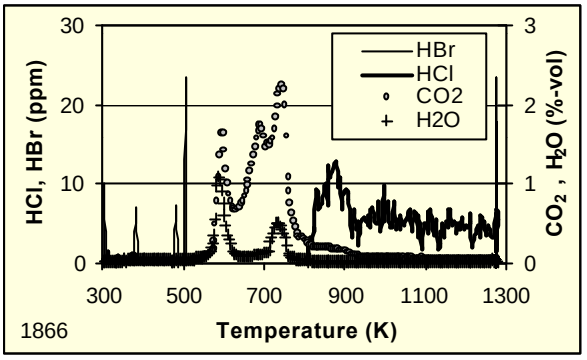


Fig.10 Concentration of HBr, HCl, CO_2 and H_2O in the product gas from scrapped electronic circuit boards in air, heating rate 10 K/s

The FT-IR spectra corresponding to the mass losses at 586 K and 732 K are given in Figures 11 and 12, respectively. Again, the main peak is for CO_2 in both Figures, and

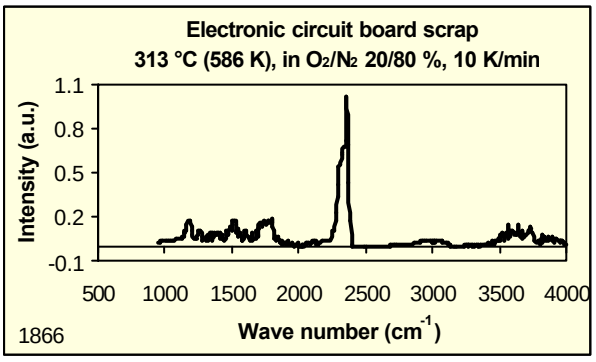


Fig.11 FT-IR spectrum of the product gas from scrapped electronic circuit boards, in air, heating rate 10 K/s, at 313°C

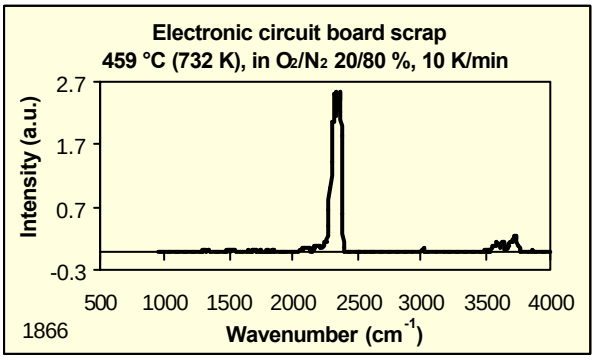


Fig.12 FT-IR spectrum of the product gas from scrapped electronic circuit boards, in air, heating rate 10 K/s, at 459°C

maybe some CH_3Br in Figure 11, at 586 K. Nothing points to presence of HBr in the gas.

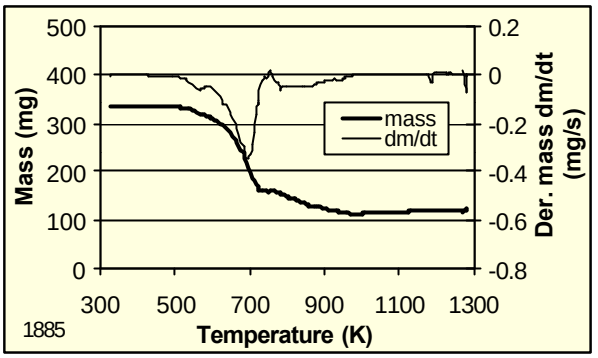


Fig. 13 TGA result from monitor housings in N_2/O_2 98 %/2 %, heating rate 10 K/min

These two tests were repeated in a 98 %/2 % (vol/vol) N_2/O_2 atmosphere: the results from the TGA are given in Figure 13 and 14 for the monitor housings and the electonic circuit boards, respectively. A first result is that the mass loss occurs over wider temperature ranges.

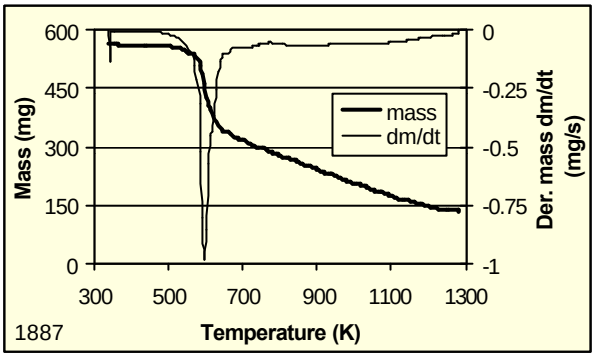


Fig. 14 TGA result from scrapped electronic circuit boards in N_2/O_2 98 %/2 %, heating rate 10 K/min

The monitor housings here show a second mass loss stage above 750 K, whilst no significant amounts of HCl are detected (Figure not given here), as opposed to the peak in Figure 6. The main oxidation of the sample to CO_2 and H_2O is at 500 K and near 800 K. For the electronic scrap, the second peak shown in Figure 9 for air is “smeared out” over the temperature range 700-1300 K in Figure 14. During this test, no HCl was measured by the FT-IR (Figure not given here), whilst a continous release of HBr was

measured between 300 K and 600 K. This sample is oxidised to CO_2 and H_2O mainly at 800-1000 K.

Altogether, there is a significant effect of the presence of oxygen in the surrounding gas. The temperature at which, and in which form, the bromine from the flame retadardant is released is far from clear. One conclusion, though, is that HBr is not the most important bromine species to be considered when considering bromine emissions from thermal processing of waste streams containing brominated flame retardants. Further tests will address the effect of heating rate, gas atmosphere and the effect of bromine "scavengers" such as NaOH.

ACKNOWLEDGEMENTS

The work on PVC-containing wastes is part of the Finnish national research program "Waste to REF and Energy" (1998-2001) and funded by the Finnish Technology Agency TEKES, the Finnish Plastic Industries Federation, Foster Wheeler Energy Oy, Borealis Polymers Oy and received support also from Fortum Foundation. The work on BFR containing materials and WEEE is supported by Ekokem Oy ("apurahoitus 2001") and the EU 5th framework programme "Growth" project Haloclean-conversion, contract no. G1RD-CT-1999-00082 (2000-2002). Prof. Carl-Johan Fogelholm is acknowledged for many useful comments and suggestions.

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