

Stockholm  
2016

# Literature review on flame retardants in WEEE

BY  
ANNELIES NIJS

SUPERVISORS: WEIHONG YANG  
PANAGIOTIS EVANGELOPOULOS

DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING,  
ROYAL INSTITUTE OF TECHNOLOGY (KTH)

## **ABSTRACT**

As electrical appliances and electronic equipment (EEE) keep growing in popularity, they keep being replaced by newer and better devices. Consequently also its waste keep growing, known as WEEE. One of the biggest environmental issues connected to this e-waste is the presence of flame retardants in most plastics. A big fraction of flame retardants are brominated, which can form toxic dioxins and furans when incinerated. Not only brominated flame retardants influence behaviour of WEEE in different processes. The different kinds of common flame retardants in EEE are mapped, discussed how they work and how they behave in different recycling processes. A life cycle analysis on brominated and halogen free flame retardants is given.

A lot of existing research was collected. Regulations that have been instituted to control hazardous emissions seem to be working. A perfect solution is at the moment not yet existing and a lot more research is needed.

# TABLE OF CONTENTS

---

Abstract .....	1
1 Introduction .....	1
2 Methods.....	2
3 Results.....	2
3.1 Different types of flame retardants .....	2
3.1.1 Halogenated Flame retardants.....	3
3.1.2 Halogen free flame retardants .....	4
3.2 Behaviour in recycling .....	5
3.2.1 Pyrolysis.....	7
3.2.2 Dehalogenation processes .....	7
4 Sustainability analysis .....	9
4.1 Production.....	10
4.2 Use.....	11
4.3 End of life .....	12
4.4 Discussion.....	13
5 Conclusion.....	13
6 References .....	14

# 1 INTRODUCTION

---

As technology keeps improving the production of electric and electronic equipment (EEE) keeps rapidly growing. Old equipment gets discarded and replaced in an increasing pace and this causes an impressive amount of waste EEE (WEEE). United Nations University (UNU) estimated in 2014 a yearly global e-waste production of approximately 40 million tons (Baldé, et al., 2015).

This WEEE is both an environmental problem and an opportunity. A lot of valuable materials, mainly metals, are used in EEE and can be recycled. For example, 10% of all gold fabrication goes into electronics (GFMS Ltd, 2010). Knowing that in mobile phones approximately 300 g/t of gold is present (Hagelüken & Corti, 2010), while in the highest grade gold ore only 44,1 g/t can be found (Basov, 2015), the economic opportunities become clear.

Unfortunately a lot of this waste isn't properly collected and treated. UNU says only 6.5 Mt of that 40 Mt was reported to be collected by official take-back systems. A lot of the waste ends up in a storage room of the final owner or gets thrown away in household waste, ending up in incineration or landfills. Of the e-waste that is collected, there is high recycling rates of approximately 85%. These high numbers are focused on the metal recycling. It is estimated that under 25% of the plastic fraction is recycled (J. Baxter, et al., 2015). To comply with legislation and maintain sustainability also plastics should be recycled in the future, not only the valuable metals.

Different reasons exist to why this fraction of recycled plastics is so low. Firstly, during the use and recycling of the product the polymers are degraded, this can result in undesirable properties. Plastics, unlike metals, cannot be recycled indefinitely due to this degradation issue. Secondly, there is a high diversity within the plastic fraction of polymers with different additives, contaminants and molecular weights. This complicates the recycling process and quality of the product. Existing techniques to break down polymers to chemical building blocks out of which new material can be made are not being used because of a lack of input. Plastic waste streams are too diversified. Thirdly, there is the presence of hazardous additives. Cadmium is being used in pigments and halogen flame retardants are often present. This paper will look into how the presence of flame retardants influences the recycling process.

Plastic materials are quite flammable, so to not form a fire hazard towards the customer flame-retardants are added. Electrical components can build up heat or short-circuits can occur, so several sources of ignition are present. Most used plastics in electric equipment like ABS, HIPS, SB, PC will burn when ignited and sometimes even keep burning after the ignition source is removed. Polyphenylether (PPE) can be accepted as self-extinguishing, due to the tendency of PPE to carbonize when being exposed to heat.

In a society where sustainability is rising, recyclability is a very important aspect. When designing a new product, companies should consider what happens with their product after its lifetime. Regulations are instituted to control this and to protect the environment and human health. The directive 2015/863/EU (RoHS) by the European parliament prohibits the use of multiple hazardous substances. The maximum concentration value tolerated of Cadmium is 0,01%. The use of lead, mercury, hexavalent chromium, polybrominated biphenyls (PBB) and polybrominated diphenyl

ethers (PBDE) is restricted to 0,1 weight percent in EEE. After 22 July 2019 also DEHP, BPP, DBP and DIBP will be added to this list of restrictions.

As an increasing amount of problems is found with currently used flame retardants, more research is needed on the exact behaviour of established flame retardants and on possible alternatives. An overview will be given of different flame retardants that can be found at present, how their flame retardance effect works and how they behave in the environment. Subsequently the recycling processes of e-waste are discussed and how flame retardants influence these. Pyrolysis will be discussed in more detail.

## 2 METHODS

---

First a research was executed to what flame retardants are used in electronic appliances. Both those that were popular in the past and the emerging ones are important, since they all end up in waste treatment. An understanding of how they work is acquired and most importantly, what problems have been reported. It was checked if any regulations exist on the use of certain substances and the influence of those.

Next it was important to know how flame retarded polymers are recycled and how they behave in these processes.

Finally a sustainability analysis is performed using life cycle analysis.

## 3 RESULTS

---

### 3.1 DIFFERENT TYPES OF FLAME RETARDANTS

Flame retardants are added to plastics because of their inherent flammability. Their interaction with fire can happen in different stages. The American Chemistry Council defines three key ways (American Chemistry Council, 2016):

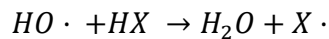
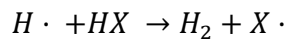
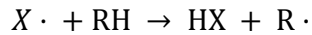
- Disrupting the combustion stage of a fire.
- Limiting the decomposition process by forming a physical insulation layer between the material and the fuel source
- Emitting water, nitrogen or other inert gases to dilute the concentration of flammable gases and oxygen.

Flame retardants are either additive or reactive, where the reactive kind is chemically bonded to the material. Additive flame retardants, like PBDEs, leach more easily into the environment.

An overview of the different types of flame retardants where their mechanism is explained, some concrete examples and if any environmental or health issues have been reported.

### 3.1.1 Halogenated Flame retardants

Halogenated flame retardants work by vapour phase inhibition. They function by capturing free radicals, preventing flame propagation. When heated they release Br or Cl radicals which react with hydrocarbon molecules from the smoke, forming the hydrogen halides HBr or HCl. If antimony trioxide ( $\text{SbO}_3$ ) is used as synergist antimony halides are formed instead. These halides then react with the  $\text{H}\cdot$  and  $\text{OH}\cdot$  radicals present in the flame, forming an inactive molecule and again halogen radicals. Since these halogen radicals are less reactive as  $\text{H}\cdot$  and  $\text{OH}\cdot$  they don't have enough potential to propagate the combustion reactions. As halogen size grows this mechanism becomes more efficient, so bromine is more efficient than chlorine.



As these flame retardants are designed to be stable up to very high temperatures they are not very degradable, making them persistent substances in the environment. This is why multiple flame retardants ended up in the Stockholm convention list of persistent organic pollutants (POP). These substances all possess the following 4 properties (Secretariat of the Stockholm Convention Clearing House, 2008):

- Persistent: stay intact for long periods instead of breaking down into safer chemicals
- Transported over far distances, thus dispersed over the whole world.
- Bio-accumulative: builds up in the fatty tissue of living organisms. The concentrations get higher at the top of the food chain.
- Toxic to humans and wildlife.

On the original list of the Stockholm convention in 2001 the only flame retardant mentioned was polychlorinated biphenyl (PCB). In 2009 some brominated flame retardants (BFR) were added, including hexabromocyclododecane (HBCD) and different bromodiphenyl ethers (BDE) like hexaBDE, heptaBDE which are components of octaBDE. Also tetraBDE and pentaBDE are defined as POP's.

The evidence of environmental issues of BFRs is plentifully available. High levels of PBDEs have been found in the blood of workers in an electronics-dismantling plant (A. Sjödin, et al., 1999). A Swedish study that tracked PDBE concentrations in breastmilk from 1996 to 2010 showed a general decreasing trend, which shows that restrictions of these substances are doing their work (P. O. Darnerud, et al., 2015).

When subjected to thermal stress, some BFR's will form polybrominated dioxins and furans (PBDD/F). So incineration or even recycling of plastics containing BFR can cause the formation of PBDD/F. Also chlorinated flame retardants and chlorinated polymers like PVC can act as precursors to the formation of chlorinated dioxins/furans (PCDD/F). Both halogenated dioxins and furans are highly toxic, and research is showing mixed dioxins/furans have at least similar toxicity (Fernandes, et al., 2010).

There is a big variety of halogenated flame retardants which will not all be discussed here. One of the earliest flame retardants is polychlorinated biphenyl (PCB) which was used because of its high chemical stability. After the discovery of its toxicity it was banned and manufacturers started using its brominated counterpart, PBB. Also the use of this flame retardant was restricted after a tragic accident in 1973 (Fries, 1985). The following popular flame retardants were polybrominated diphenyl ethers (PBDE). In 2004 PentaBDE and OctaBDE were banned in the EU and later recognized as POPs, although the use of PBDEs is declining some manufacturers still use them and they can plenty be found in WEEE.

Tetrabromobisphenol-A (TBBPA) is considered an alternative to PBDEs and is nowadays widely used. When used in epoxy resins, TBBPA reacts with epichlorohydrin. The concentration can go up to 20% bromine (European Chemicals Bureau, 2006). These kind of epoxy resins are used for printed circuit boards, thus very common in electronic equipment. The most commonly used laminate is the FR4-type and contains around 9-10% bromine on a laminate weight basis (Leisewitz, et al., 2001). Since TBBPA is reactively fixed in the resin, no bromine migration happens during normal conditions. Bromine release can be expected as soon as the base material starts to decompose, which is above 300°C. Because of this cross-linking the formation of dioxins and furans by TBBPA is lower than by PBDE (Leisewitz, et al., 2001). Other currently used BFRs are hexabromocyclododecane (HBCD) and decabromodiphenyl ethane (DBDPE) (Birnbaum & Bergman, 2010).

### 3.1.2 Halogen free flame retardants

As a result of all the environmental problems with halogenated flame retardants a lot of alternatives came into the market. A small overview will be given.

#### Phosphorous flame retardants

Most phosphorous flame retardants (PFRs) interact with the fire in the condensed phase. They release phosphoric acid when heated, which will promote the charring of the material, forming a (carbon) barrier between the material and the heat source. These flame retardants work best with polymers containing oxygen like polyesters, polyamides etc.

PFRs can also volatilize and form active radicals ( $\text{PO}_2\cdot$ ,  $\text{PO}\cdot$  and  $\text{HPO}\cdot$ ) who act as scavengers for  $\text{H}\cdot$  and  $\text{OH}\cdot$  radicals. An example of a flame retardant that works in the vapour phase is triaryl phosphate.

They can be both reactive and additive, sometimes a combination is used.

Phosphorous flame retardants can be divided into organic and inorganic compounds. Organics PFRs that are used in electronic application include phosphates, phosphinates, phosphonates, and phosphine oxides. Organic phosphorous flame retardants are reported to have a bad effect on the properties though. Many organic phosphorus compounds tend to act as a plasticizer, a synergist like antimony trioxide (ATO) or aluminium trihydrate needs to be added to reach the flame retarding requirements, and the water absorbing property of the material is increased by adding organic phosphorus compounds (Sakon, et al., 1989). All these factors are to be taken into consideration when designing a plastic component with organic PFR.

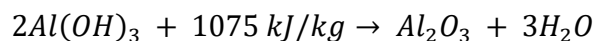
An example of an inorganic PFR is red phosphorus, which shows great flame retarding capability. Its drawbacks are the colour restrictions and concerns about its long-term stability. Red phosphorus flame retardants would react with moisture to form toxic phosphine gases so they are stabilized with various organic or inorganic substances. However Rinkagaku Kogyo states in their patent (Sakon, et al., 1989) that its use is limited to certain fields and does not meet the requirements for use in high performance electronic components.

Because the volatility of PFRs is higher than those of BFRs higher concentrations are found in the environment. Concentrations of PFRs have recently been measured in free-range chicken eggs from e-waste recycling sites (X. Zheng, et al., 2016).

Cl-containing PFRs are reported to be carcinogenic (Veen & Boer, 2012). Tricresyl phosphate (TCP) also has negative human health effects and TPHP, DCP and TCP are considered toxic. Resorcinol-bis-diphenylphosphate (RDP), Bisphenol A bis(diphenylphosphate) (BDP) and melamine polyphosphate could be, environmentally speaking, good alternatives for BFRs.

### **Mineral flame retardants**

Metal hydroxides like aluminium trihydroxide (ATH) or magnesium dihydroxide (MDH) react with fire via a condensed phase mechanism. Decomposition happens through a highly endothermic reaction. For ATH this happens at approximately 220°C following this reaction:



For Mg(OH)<sub>2</sub> the reaction is similar and more endothermic, with temperatures needed above 300°C. The released water molecules quench its surroundings and the formed steam dilutes the burnable gases. The formed metal oxides form a protective layer on the polymer surface, protecting it against continued decomposition and reducing the release of toxic gases (Rakotomalala, et al., 2010).

A high amount is necessary to achieve flame retardant effects, which can strongly influence the properties of the polymer. Despite these amounts, no environmental problems arise. Generally ATH does not interfere with recycling (Leisewitz, et al., 2001).

Zinc stannate (ZS) and zinc hydroxystannate (ZHS) have a purpose as a non-toxic synergist to replace ATO in halogen-containing polymers like PVC to improve the fire retardancy and reduce smoke emissions. They are also applied as partial replacements for fillers like ATH and MDH. Coated variants of these fillers can be used at lower concentrations to achieve similar flame retardant properties (Cusack & Hornsby, 1999).

## **3.2 BEHAVIOUR IN RECYCLING**

All WEEE recycling techniques usually start with a manual disassembly step. Hazardous materials, glass, batteries, PCBs and parts like plastic or metallic covers are dismantled and sorted. Next comes a size reduction step by mechanical shredding, crushing and grinding with the purpose of liberating all different materials. These small particles are then separated by density difference,



particle size and magnetic and electrical properties. Here will be discussed what happens with the plastic fractions.

If pure plastic recycling is desirable, good separation of the different kinds is crucial. A great deal can be achieved by simple density-separation. For further separation an interesting process is the Creasolv® process, which uses selective extraction to obtain very pure plastics. Furthermore plastics with and without flame retardants can be separated and removal of BFRs is proclaimed (Mäurer, 2016). It would be advantageous if waste plastics can easily be identified when collected, facilitating separation for recycling.

Some plastics, like thermosets and composites, cannot be recycled as the same material. They can be downcycled and used in another purpose. One company uses the separated plastic fraction (including flame retardants) of PCBs as a supplement in manufacturing of flame-retarded duroplastic products (Leisewitz, et al., 2001).

Sometimes plastic fractions will end up in the metals recycling route. The behaviour of plastics, and more specifically flame retardants during hydrometallurgy has barely been analysed. Zhong et al. studied the reactions of tetrabromobisphenol A with three different acid leaching reagents (Y. Zhong, et al., 2014).

Pyrometallurgy is a classic and easy technique to recover metals by concentrating the desired metals in a metallic phase and rejecting the other materials in a slag or gas phase. Drawbacks of this technique are the potential loss of some metal fractions and the formation of toxic gases because of the polymers present. These polymers are not recovered but used as fuel in the furnace to reduce the costs of the process. Traditional smelters can therefore not be used when polymers are present, state-of-the-art smelters are used with systems containing washers, adiabatic coolers and scrubbers. During combustion the formation of dioxins should be avoided. McKay (McKay, 2002) presents some guidelines for the operating conditions:

- Combustion temperature should be above 850°C to destroy any dioxins/furans in the feed. For effective and complete combustion of particulate carbonaceous material a temperature above 1000°C is necessary.
- A high enough residence time is necessary to ensure complete destruction. The higher the temperature, the shorter the residence time can be. At 850°C a residence time of 2 s is advised.
- Excess oxygen can be used to ensure complete destruction of any fuel particulates.
- Turbulence should be high enough in the combustion chamber, with the highest efficiency for a Reynolds number of 50 000 or larger.
- There is a critical temperature zone, between 250°C and 450°C, in which dioxin formation rate is at a maximum. Rapid cooling or quenching is demanded to get through this zone as quick as possible.
- Air pollution control by scrubbing, using a bag-filter or by activated carbon injection.

The process that will be looked into deeper here is pyrolysis. This because it is considered to be the process with most promising outcomes for recycling of plastics (M.P. Luda, et al., 2005) (Brebü & Sakatu, 2006). It produces valuable chemicals or fuels and remaining metals can easily be

recycled from the solid fraction. The energy consumption is quite low as only  $\pm 10\%$  of the waste plastics' energy is used to convert the scrap into petrochemical products (Uddin Md. A. , et al., 2002). Also the amount of harmful gasses is a lot lower than during incineration.

### 3.2.1 Pyrolysis

Pyrolysis is a process that happens at intermediate temperatures in an inert atmosphere. It can be used to separate organic and inorganic matter, with most organic material starting to decompose around  $300^{\circ}\text{C}$ . At the end of the process, a solid, gaseous and liquid fraction is left.

A lot of study has been done about the pyrolysis of WEEE, including the effect of different polymers present and different dehalogenation techniques (Uddin Md. A. , et al., 2002) (T. Bhaskar, et al., 2004). A complete examination of TBBPA behaviour during thermal decomposition is done by Ortuno et al. (Ortuno, et al., 2014). They show that the amount of furans is almost 50 times higher after combustion compared to pyrolysis. Brominated dioxins are in the ppb range for pyrolysis and ppm for combustion. Antimony-oxide, a synergist often used with BFRs also has an impact on the reactions during thermal degradation and debromination (Bhaskar T., et al., 2003).

The main operating variables are temperature and residence time. With high temperature ( $>600^{\circ}\text{C}$ ) more simple and small molecules are formed, while at lower temperatures ( $\sim 400^{\circ}\text{C}$ ) liquid products are dominant. Temperature is the most important parameter, the time is dependant of the reaction temperature. Short residence times favour the formation of primary products like monomers, for more thermodynamically stable products a longer reaction time is needed. Same result is obtained by using respectively low pressure for primary products and high pressure for complex, liquid products (Buekens, 2006).

The solid fraction is mainly chars and will contain all inorganic matter, like the metals that were present. The gases contain a lot of energy which can be used to power the pyrolysis plant. The liquid fraction could have future application as energy fuels, but because of the flame retardants in the plastics a large number of brominated compounds are present. Therefore dehalogenation is a crucial step, either before the decomposition, during the pyrolysis process or successively by upgrading the pyrolysis oils.

### 3.2.2 Dehalogenation processes

#### *Dehalogenation before the decomposition*

A two-stage process is applied for the pyrolysis process. In the first stage halogenated compounds are liberated at a low temperature ( $\sim 300^{\circ}\text{C}$ ). A higher temperature is consequently used in the second stage to decompose the material and form oils with reduced or no halogens present. A drawback of this technique might be the higher costs.

Grause et al. (Grause G., et al., 2015) describe how organic bromine (decaBDE) gets converted into inorganic bromide by a solution of NaOH in ethylene glycol. The bromine content in HIPS goes down to 0.02 wt% when this reaction is accomplished in a ball mill reactor. The polymer matrix

stays intact during this process and the thermal stability even goes up, which brings interesting opportunities for mechanical recycling of HIPS instead of feedstock recycling.

Another method to debrominate HIPS is given by (Brebu & Sakatu, 2006) which uses ammonia treatment at 450°C. The Br compounds are converted into inorganic NH<sub>4</sub>Br powder, which can be followed by bromine recovery. Approximately 60-70 wt% of the organics are recovered as oils rich in benzene derivatives and suitable for feedstock recycling. Ammonia is however not strong enough to remove the aromatically bonded bromine, which means the degradation oil is not completely bromine-free.

### ***Dehalogenation during the decomposition***

Parameter control and additives or catalysts help in dehalogenation during pyrolysis. As discussed for combustion, a longer residence time allows for destruction of the halogenated compounds.

Lai et al. (Lai, et al., 2007) discuss 2 factors that inhibit the formation of PBDD/Fs. First it is seen that when pyrolysis temperature was increased from 850°C to 1200°C the PBDD/F concentration and emission factor decreased approximately 50%. The other factor was the addition of CaO, which is hypothesised to react with HBr to form CaBr<sub>2</sub>.

Uddin et al. (Uddin Md. A. , et al., 2002) compared the normal thermal degradation of HIPS-Br mixed with PVC with the catalytic degradation of the same material, using different amounts of an iron oxide carbon composite catalyst. Halogenated organic compounds react into hydrocarbons and hydrogen halides by catalytical dehydrohalogenation. When no halogens are left in the liquid fraction after pyrolysis, it is a feasible fuel oil or can be used as chemical feedstock.

*Table 1: Products obtained during thermal and catalytic degradation (vapor phase) of HIPS-Br/PVC(4/1) at 430 °C: catalyst: TR-00301 (Uddin Md. A. , et al., 2002)*

METHOD	YIELD OF DEGRADATION PRODUCTS (WT%)			LIQUID PRODUCTS		TOTAL HALOGEN IN OIL	
	Liquid (L)	Gas (G) <sup>a</sup>	Residue (R)	Cnp <sup>b</sup>	Density (g/cm <sup>3</sup> )	Br (ppm)	Cl (ppm)
<b>THERMAL</b>	48	21	31	10.4	0.92	55	4300
<b>CAT 1 G</b>	44	12	44	9.3	0.87	910	1870
<b>CAT 2 G</b>	37	12	51	9.3	0.84	0	840
<b>CAT 4 G</b>	38	14	48	9.4	0.83	0	0
<b>CAT 8 G</b>	34	13	53	9.0	0.78	0	0

<sup>a</sup>G=100-(L+R)

<sup>b</sup> Average carbon number of liquid products.

Table 1 shows the result of this study. As the amount of catalyst added goes up, the halogens present in the liquid disappear. Additionally, with more catalyst higher molecular weight compounds get cracked. The oil density goes down, the fraction of oil also becomes smaller.

### *Upgrading of oils after pyrolysis*

Thermal and catalytic hydrogenation can be used to upgrade the liquids. Vasile et al. (C. Vasile, et al., 2007) reports that after hydrogenation most oxygen containing compounds are converted in aromatic hydrocarbons. Simultaneously the hazardous oxygen containing compounds, nitrogen, halogens and sulphur are eliminated. They also mention that the upgraded oils contain a very high amount of aromatics, making them a good feedstock for producing basic aromatics.

Another process route is hydrodehalogenation. This happens when the pyrolysis oils react with hydrogen-donating media in the presence of catalysts. Hydrogen halides are formed and a hydrogenated liquid.

## **4 SUSTAINABILITY ANALYSIS**

---

A way to determine which flame retardant is the best option is necessary. A life cycle assessment (LCA) is a great way. An LCA provides knowledge of the environmental impact in all life cycle stages. It follows the product from the cradle to the grave. It has a holistic focus on the product and takes as much as possible into consideration.

A lot of LCA studies is available on electronic appliances. Most of these will not go into the waste treatment problems very deeply. Also often it is assumed that the plastics used are simple polymers, ignoring used additives.

When analysing flame retardants the following stages should be looked at:

- Synthesis/production
- Transport/storage
- Use: eventual fire
- End of life

The goal of performing an LCA on this subject is to collect knowledge on the environmental effects of different kind of flame retardants. This way the alternatives with lowest overall environmental impact can be found. The analysis happens for different stages of the flame retardants' life cycle, by seeing which stage has the biggest impact right now it can help showing where the room for improvement is biggest. For each step the inputs and outputs have to be considered. Inputs being resources like raw materials and energy, outputs being emissions or by-products.

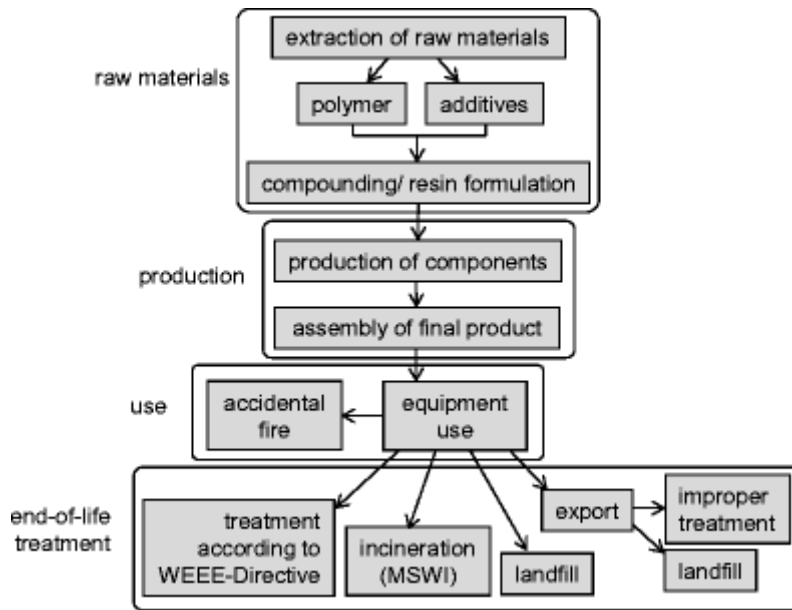


Figure 1: Life cycle of flame retarded polymers in EEE (Jonkers, et al., 2016)

In this paper a review of the work of (Jonkers, et al., 2016) will be given. In Figure 1 it is shown which phases they studied. They compared the environmental impact of laptops with either brominated flame retardants (BFRs) or with halogen free flame retardants (HFFRs).

#### 4.1 PRODUCTION

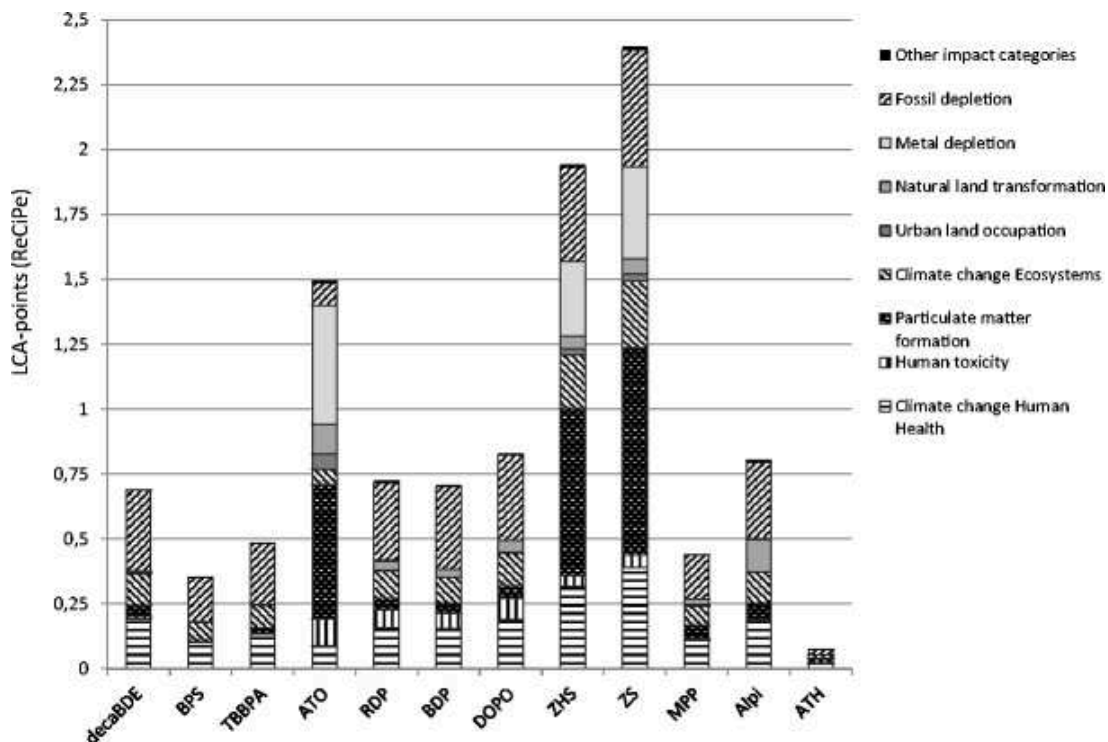


Figure 2: Environmental impact for the production of 1kg flame retardant. ReCiPe Single Score technique (Jonkers, et al., 2016)

Figure 2 shows the environmental impact for the production of several flame retardants. The mineral flame retardants, like antimony trioxide (ATO) and Zinc Stannates (ZS) score highest. This is because heavy metals are emitted during the mining phase.

During production of phosphorous flame retardants like RDP, BDP and DOPO there is emission of white phosphorus.

For most of the FRs the score is mainly determined by the energy use during the production stage. If fossil fuels are being used it will result in relatively high scores.

Although the difference in score seems huge when looking at these scores for the separate flame retardants, it is important to bear in mind that they are used in different quantities and in different polymer systems. That's why it is practically more interesting to look at the production of the polymer with flame retardant like in Figure 3. For each polymer a version is shown without flame retardant, with a BFR and with a HFFR. Now the differences are a lot smaller. This is not only because the production of the polymer has the biggest contribution, but also because the FRs with high impacts are used at lower loading rates.

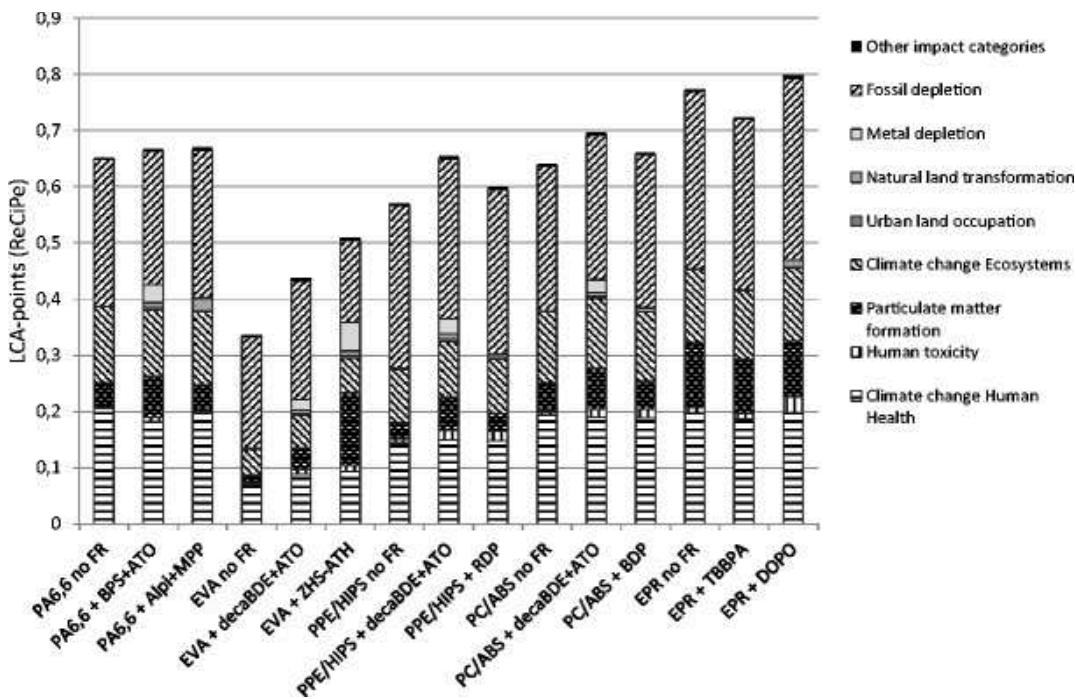


Figure 3: Environmental impact for the production of 1kg flame retarded polymer.

## 4.2 USE

In the usage phase there can be environmental impact in 2 ways. In case of normal usage the FRs can volatilize from the material. BFRs perform badly when talking about human toxicity and freshwater ecotoxicity, while HFFRs perform bad for terrestrial and marine ecotoxicity.

The other way is in case of accidental fire. BFRs cause a relatively high score for terrestrial ecotoxicity due to emission of ATO. Also they have a higher rate of smoke emission which causes more particulate matter formation. HFFRs on the other hand cause more CO<sub>2</sub> emissions, this way contributing more to climate change.

Depending on what field is being looked at BFR or HFFR score better, when looking at a single score result for the usage phase the BFR scenario scores a bit higher and thus has a higher environmental impact.

### 4.3 END OF LIFE

Four end-of-life options are considered in this LCA (Jonkers, et al., 2016):

- Collection and treatment according to the WEEE directive
- Disposal with municipal waste, followed by incineration in a municipal solid waste incinerator (MSWI)
- Disposal with municipal waste, followed by landfill dumping
- Export, followed by substandard waste treatment

It is very hard to determine the percentages of the waste ending up in the different treatment systems, since different stakeholders report very different numbers. The final assumptions made for this LCA are that almost half is handled according to the WEEE directive, 12% is incinerated, 25% is landfilled and that leaves 19% exported.

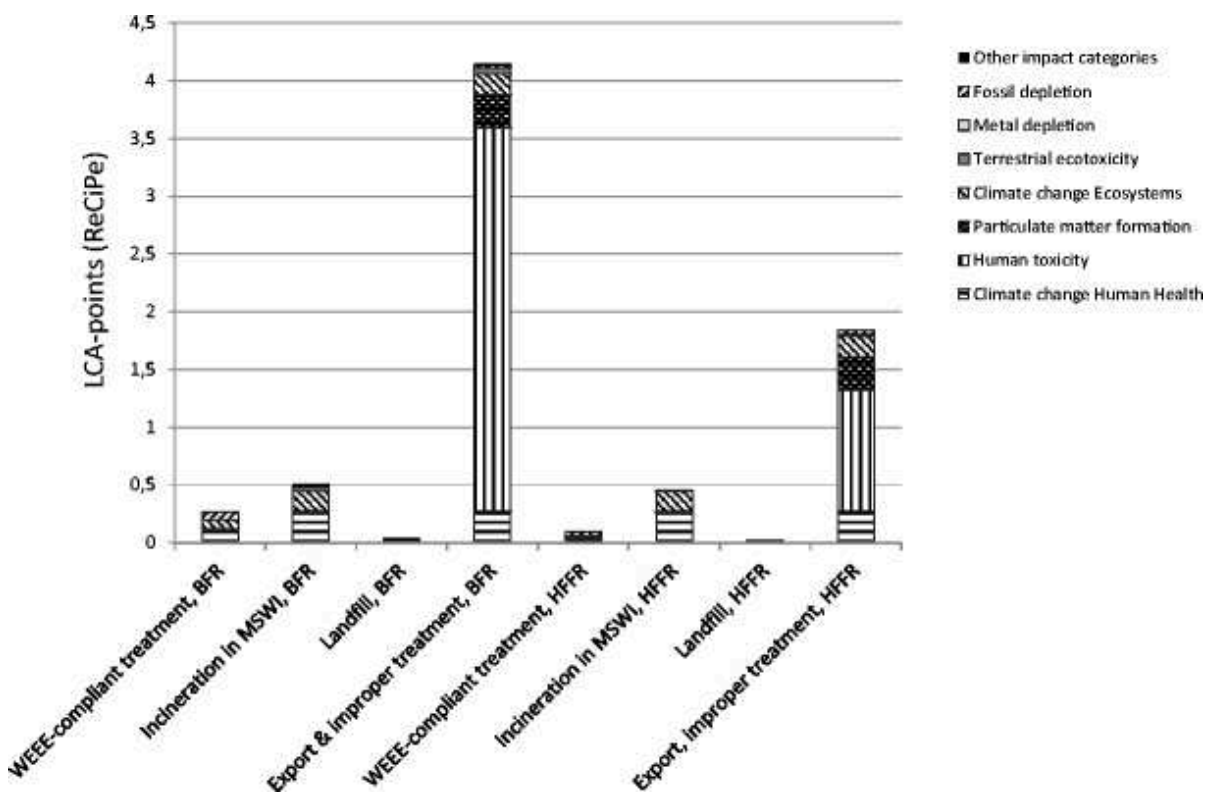


Figure 4: Environmental impact for the end-of-life treatment of 1 laptop. Comparison of laptop with BFRs and one with HFFRs in different end-of-life treatments

Figure 4 shows the LCA scores for the waste treatment options for a complete laptop with either BFRs or HFFRs. The BFR scenario scores highest for all toxicity impact categories, with the biggest cause the formation of dioxins. In the HFFR scenario, toxicity is due to the emissions of lead, arsenic, hydrogen fluoride, PAHs and other chemicals.

## 4.4 DISCUSSION

There are different processes in the life cycle of an electronic appliance that are influenced by flame retardants. The highest impacts come from the production phase of the flame-retarded polymer and from improper waste treatment. The probability of accidental fire is low and the contribution to the environmental impact by volatilization in the use phase is also low.

For the improper waste treatment phase the largest contribution is made by human toxicity. For all other phases it is climate change, fossil depletion and particulate matter formation that dominate, mainly because of fossil energy consumption.

Even though volatilization has a low impact on the complete life cycle, it is one of the most important exposure routes for humans.

Generally there is a very small difference in the LCA scores of the BFR and HFFR containing laptops. The largest differences are in the human toxicity and the improper treatment phase, which might be one of the most important ones though.

So generally the HFFR route has a higher impact on climate change, but BFR are more dangerous to our health. Even when the WEEE is being treated according to the WEEE directive, the impact for the BFR route is higher than for HFFRs.

## 5 CONCLUSION

---

In this report the different flame retardants that can be found in e-waste and will end up as waste in the future were mapped. Not only is it important to look into alternatives for these substances, but to keep evaluating the risks of old and new substances. Even in a perfect world where all new products from now on no longer contain hazardous substances, there is still a massive amount of old products in landfills waiting to be recycled. Environmental effects should be monitored and informal recycling activities in developing countries should be better controlled.

A lot of research has been done on most brominated flame retardants like PDBEs, TBBPA. New flame retardants are introduced to the market to replace the old and environmentally unfriendly ones, but they can sometimes also turn out to be an environmental hazard. Regulations that have been instituted to control hazardous emissions seem to be working. Studies on different materials should not only cover their environmental behaviour but also their behaviour during recycling processes. As sustainability becomes more and more important and landfill mining is rising it is important to come up with optimally functioning processes.

When comparing brominated flame retardants with halogen free flame retardants in a life cycle analysis it again becomes clear how all of them have benefits and concerns. Generally for human health it would be better to stop using brominated flame retardants.

The biggest take-away we learn is that there is still a vast amount of research to be done.



## 6 REFERENCES

---

- A. Sjödin, et al., 1999. Flame retardant exposure: polybrominated diphenyl ethers in blood from Swedish workers. *Environ Health Perspect.*, 107(8), pp. 643-648.
- American Chemistry council, 2016. *Flame retardants*. [Online]  
Available at: <https://flameretardants.americanchemistry.com/default.aspx>  
[Accessed 13 November 2016].
- Baldé, C., Wang, F., Kuehr, R. & Huisman, J., 2015. *The global e-waste monitor - 2014*, Bonn, Germany: United Nations University, IAS - SCYCLE.
- Basov, V., 2015. *The world's highest grade gold mines - mining.com*. [Online]  
Available at: <http://www.mining.com/the-worlds-highest-grade-gold-mines/>  
[Accessed 13 november 2016].
- Bhaskar T., et al., 2003. Effect of Sb<sub>2</sub>O<sub>3</sub> in brominated heating impact polystyrene (HIPS-Br) on thermal degradation and debromination by iron oxide carbon composite catalyst (Fe-C). *Applied Catalysis B: Environmental*, 43(3), pp. 229-241.
- Birnbaum, L. S. & Bergman, Å., 2010. Brominated and Chlorinated Flame Retardants: The San Antonio Statement. *Environ Health Perspect.*, 118(12), pp. A514-A515.
- Brebu, M. & Sakatu, Y., 2006. Novel debromination method for flame-retardant high impact polystyrene (HIPS-Br) by ammonia treatment. *Green Chemistry*, 8(11), pp. 984-987.
- Buekens, A., 2006. Introduction to feedstock recycling of plastics. In: *Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels*. Chichester, UK : John Wiley & Sons, pp. 2-40.
- C. Vasile, et al., 2007. Feedstock recycling from plastics and theromsets fraction of used computers. II. Pyrolysis oil upgrading. *Fuel*, Volume 86, pp. 477-485.
- Cusack, P. A. & Hornsby, P. R., 1999. Zinc stannate-coated fillers: Novel flame retardants and smoke suppressants for polymeric materials. *Journal of Vinyl and Additive Technology*, 5(1), pp. 21-30.
- European Chemicals Bureau, 2006. European Union Risk Assessment Report 2,2',6,6'-tetrabromo-4,4'-isopropylidenediphenol (tetrabromobisphenol-A or TBBP-A) Part II - Human Health. 63(EUR 22161 EN).
- Fernandes, A. et al., 2010. *Investigation into the Occurrence of Mixed Halogenated Dioxins, Furans and Biphenyls in Food*, York: Food and Environment Research Agency .
- Fries, G., 1985. The PBB episode in Michigan: an overall appraisal.. *Crit Rev Toxicology*, 16(2), pp. 105-156.
- GFMS Ltd, 2010. *Gold Survey 2016*, London: Thomson Reuters.

- Grause G., et al., 2015. A novel process for the removal of bromine from styrene polymers containing brominated flame retardant. *Polymer Degradation and Stability*, Volume 112, pp. 86-93.
- Hagelüken, C. & Corti, C., 2010. Recycling of gold from electronics: Cost-effective use through 'Design for Recycling'. *Gold Bulletin*, 43(3), pp. 209-220.
- J. Baxter, et al., 2015. *WEEE plastics recycling*, Denmark: Nordic council of Ministers.
- J. DiGangi, et al. , 2010. San Antoni Statement on Brominated and Chlorinated Flame Retardants. *Environ Health Perspective*, 118(12), pp. A516-A518.
- Jonkers, N., Krop, H., van Ewijk, H. & Leonards, P. E., 2016. Life cycle assessment of flame retardants in an electronics application. *Int J Life Cycle Assess*, 21(2), pp. 146-161.
- Lai, Y. C., Lee, W. J. & Wangli, H., 2007. Inhibition of polybrominated dibenzo-p-dioxin and dibenzofuran formation from the pyrolysis of printed circuit boards. *Environ. Sci. Technol.*, Volume 41, pp. 957-962.
- Leisewitz, A., Kruse, H. & Schramm, E., 2001. *Substituting Environmentally Relevant Flame Retardants: Assessment Fundamentals*, Berlin: Federal Environmental Agency (Umweltbundesamt).
- M.P. Luda, et al., 2005. WEEE recycling: Pyrolysis of fire retardant model polymers. *Waste management*, 25(2), pp. 203-208.
- Mäurer, A., 2016. *High quality recycling of plastics using the CreaSolv® Process*. [Online] Available at: <https://www.ivv.fraunhofer.de/en/forschung/verfahrensentwicklung-polymer-recycling/hochwertiges-kunststoffrecycling.html> [Accessed 18 november 2016].
- McKay, G., 2002. Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: review. *Chemical Engineering Journal*, 86(3), pp. 343-368.
- Ortuno, N., Molto, J., Conesa, J. A. & Font, R., 2014. Formation of brominated pollutants during the pyrolysis and combustion of tetrabromobisphenol A at different temperatures. *Environmental Pollution*, Volume 191, pp. 31-37.
- P. O. Darnerud, et al. , 2015. Time trends of polybrominated diphenylether (PBDE) congeners in serum of Swedish mothers and comparisons to breast milk data. *Environmental Research*, Volume 138, pp. 352-360.
- Rakotomalala, M., Wagner, S. & Döring, M., 2010. Recent Developments in Halogen Free Flame Retardants for Epoxy Resins for Electrical and Electronic Applications. *Materials*, 3(8), pp. 4300-4327.
- Sakon, I., Sekiguchi, M. & Kanayama, A., 1989. *Red phosphorus flame retardant and nonflammable resinous composition containing the same*. US, Patent No. 5026757.

Secretariat of the Stockholm Convention Clearing House, 2008. *What are POPs?*. [Online] Available at: <http://chm.pops.int/TheConvention/ThePOPs/tabid/673/Default.aspx> [Accessed 15 november 2016].

T. Bhaskar, et al., 2004. Pyrolysis studies of f PP/PE/PS/PVC/HIPS-Br plastics mixed with PET and dehalogenation (Br, Cl) of the liquid products. *Journal of Analytical and Applied Pyrolysis*, 72(1), pp. 27-33.

Uddin Md. A. , et al., 2002. Dehydrohalogenation during pyrolysis of brominated flame retardant containing high impact polystyrene (HIPS-Br) mixed with polyvinylchloride (PVC). *Fuel*, 81(14), pp. 1819-1825.

Veen, I. v. d. & Boer, J. d., 2012. Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis.. *Chemosphere*, 88(10), pp. 1119-1153.

X. Zheng, et al., 2016. Phosphate flame retardants and novel brominated flame retardants in home-produced eggs from an e-waste recycling region in China.. *Chemosphere*, Volume 150, pp. 545-550.

Y. Zhong, et al., 2014. Kinetics of tetrabromobisphenol A (TBBPA) reactions with H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HCl: Implication for hydrometallurgy of electronic wastes. *Journal of Hazardous Materials*, Volume 270, pp. 196-201.