

# WASTE MANAGEMENT OF PLASTICS CONTAINING BROMINATED FLAME RETARDANTS

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## **Abstract**

Bromine is used as the building block for some of the most effective flame retarding agents available to the plastics industry today. They are used to protect against the risk of accidental fires in a wide range of electrical and electronic equipment (EEE). Brominated flame retardants (BFRs), as all flame retardants, act to decrease the risk of fire by increasing the fire resistance of the materials in which they are applied. There is a perception that BFRs affect adversely the end-of-life management of plastics through formation of brominated dioxins and furans (PBDD/F). In fact, there exists a wide range of data and practical experience demonstrating that the end-of-life management of plastics containing BFRs is fully compliant with legislation setting the strictest limit values for PBDD/F and is fully compatible with an integrated waste management concept.

## **Mechanical Recycling**

Several recycling studies have shown that plastics containing specific BFRs can be mechanically recycled and have demonstrated that the strict polybrominated dibenzodioxin and dibenzofuran (PBDD/PBDF) limit values of the German „*Dioxin Ordinance*“ (Chemikalienverbots-Verordnung) can be met if recycling is done properly [1]. The following table gives an overview of selected BFR-polymer systems which were tested on PBDD/F concentrations after multiple recycling processes. Some of these results have been confirmed by other publications [1]. Table 1 shows the results of selected studies.

A study which investigated the system DecaBDE/HIPS did look as well into the possibility of debromination of the flame retardant DecaBDE. It was found that this substance does not degrade down to the lower brominated diphenyl ethers (see table 2).

**Table 1:** PBDD/F congeners determined in recycled HIPS and ABS plastic.

PBDD/F Species	HIPS/DecaBDE 5 x recycled	ABS/BEO 4 x recycled	ABS/TBBPA 4 x recycled	Limit values
Dimensions	µg/kg	µg/kg	µg/kg	µg/kg
Sect. 4 2,3,7,8-TetraBDD .	n.d.	n.d.	n.d.	
1 1,2,3,7,8-PentaBDD	n.d.	n.d.	n.d.	
2,3,7,8-TetraBDF	n.d.	n.d.	n.d.	
2,3,4,7,8-PentaBDF	n.d.	n.d.	n.d.	
Sum of the 4 PBDD/F	0.06	n.d. (< 0.06)	n.d. (< 0.09)	1
1,2,3,4,7,8-/1,2,3,6,7,8HexaBDDb	n.d.	n.d.	n.d.	
1,2,3,7,8,9-HexaBDD	n.d.	n.d.	n.d.	
1,2,3,7,8-PentaBDF	0.06	n.d.	n.d.	
Sum of the 8 PBDD/F	0.12	0.16	0.23	5

**Table 2:** Analytical results of lower brominated diphenyl ethers in the recyclate after 5 x recycling of DecaBDE/HIPS [1].

Sample characterization	High Impact Polystyrene (HIPS)		
	Analysis 1	Analysis 2	Mean Value
Sample No.			
Unit	µg/kg		
3,4,4'-Tribromodiphenylether	n.d. (< 5)	n.d. (< 5)	n.d. (< 5)
Total Tribromodiphenylether	A	A	A
2,4,4',6-Tetrabromodiphenylether	n.d. (< 8)	n.d. (< 8)	n.d. (< 8)
2,3',4',6-Tetrabromodiphenylether	n.d. (< 8)	n.d. (< 8)	n.d. (< 8)
2,2',4,4'-Tetrabromodiphenylether	n.d. (< 8)	n.d. (< 8)	n.d. (< 8)
2,3',4,4'-Tetrabromodiphenylether	n.d. (< 8)	n.d. (< 8)	n.d. (< 8)
3,3',4,4'-Tetrabromodiphenylether	n.d. (< 8)	n.d. (< 8)	n.d. (< 8)
Total Tetrabromodiphenylether	A	a	A
2,3',4,4',6-Pentabromodiphenylether	n.d. (< 9)	n.d. (< 9)	n.d. (< 9)
2,2',4,4',5-Pentabromodiphenylether	n.d. (< 9)	n.d. (< 9)	n.d. (< 9)
2,2',3,4,4'-Pentabromodiphenylether	n.d. (< 9)	n.d. (< 9)	n.d. (< 9)
Total Pentabromodiphenylether	A	a	A
2,2',4,4',5,5'-Hexabromodiphenylether	n.d. (< 10)	n.d. (< 10)	n.d. (< 10)
Total Hexabromodiphenylether	A	a	A
2,3,3',4,4',5,6-Heptabromodiphenylether	n.d. (< 180)	n.d. (< 180)	n.d. (< 180)
Total Heptabromodiphenylether	A	a	A

n.d. = not detected at the indicated detection limit    a = no PBDPE congener detected

Furthermore, it was demonstrated that brominated dioxin/furan (PBDD/F) exposure at the workplace during recycling [1] or recovery [2] is of no concern. The results of a further report [3] came to comparable conclusions regarding the processing of plastics containing specific BFRs. In a study done by the University of Erlangen comparing the situation at the workplace for extrusion and injection molding during recycling runs, no significant increase in the concentrations between first and second recycling pass are observed. The values for injection molding are slightly lower during the second recycling pass. Also the concentrations in the exhaust gases (sampling point 3 and 6) decrease in the second recycling run. This may be due to the loss of volatile compounds during the first recycling pass. Even the exhaust gases are meeting the workplace exposure limits. Table 3 shows

that the limit value of 50 pg ITE / m<sup>3</sup> is not exceeded at any sampling point by any compound, even if the full limit of detection is included in the calculation [4].

**Table 3:** Workplace exposure during HIPS/DecaBDE processing (limit value=50 pg ITE/m<sup>3</sup>).

Report Sample No. <sup>1</sup>	Air Volume [m <sup>3</sup> ]	Sampling site	ITE <sup>8</sup> PBDF/Ds excl. LOD [pg/m <sup>3</sup> ]	ITE <sup>8</sup> PBDF/Ds incl. 1/2 LOD [pg/m <sup>3</sup> ]	ITE <sup>8</sup> PBDF/Ds incl. LOD [pg/m <sup>3</sup> ]
R1 EX WP 2.1	26,24	1	0.25	0.33	0.40
R1 EX WP 2.2	26,26	2	0.09	0.17	0.25
R1 EX EG 3	9,82	3	4.95	4.95	4.95
R1 IM WP 5.1	33,12	4	0.66	0.73	0.80
R1 IM WP 5.2	33,08	5	0.83	0.90	0.98
R1 IM EG 6	13,94	6	2.84	2.90	2.95
R2 EX WP 8.1	27,28	1	0.44	0.56	0.67
R2 EX WP 8.2	27,24	2	0.13	0.22	0.30
R2 EX EG 9	11,4	3	0.72	1.14	1.55
R2 IM WP 11.1	37,40	4	0.15	0.22	0.29
R2 IM WP 11.2	37,40	5	0.07	0.14	0.21
R2 EX EG 12	16,84	6	0.26	0.41	0.57

<sup>1</sup> R = Recycling run; EX = Extrusion; WP = Workplace air; EG = Exhaustgas; IM = Injection molding

Japanese publications [5, 6, 7] show, that BFRs are the only flame retardants in their study that meet the needed flammability standards and physical properties after multiple recycling tests. Even after 5 recycling processes the recyclate had V-O classification. A study by the Swedish National Testing and Research Institute [8] with DecaBDE/HIPS confirmed V-O rating after 5 recycling steps and a simulated aging process.

### **Bromine Recovery**

Studies have been carried out to investigate the potential of a sustainable production of bromine. The objective is to recover the bromine from plastic waste from electrical and electronic equipment (WEEE) or other plastic waste streams containing bromine. The volumes available correspond to ca. 11,000 tonnes of bromine/year from WEEE [9, 10]. To improve the economic benefit, additional feed streams, like plastics from automotive shredder residues (ASR), packaging material with bromine residues and other bromine containing wastes could also be considered. After adding the BFRs containing plastics into a thermal process it is possible to recover the bromine to produce the raw material bromine for producing again BFRs or an HBr 48% solution for reuse in the chemical industry. This is a potentially important step to close the bromine loop, to enable a sustainable production of

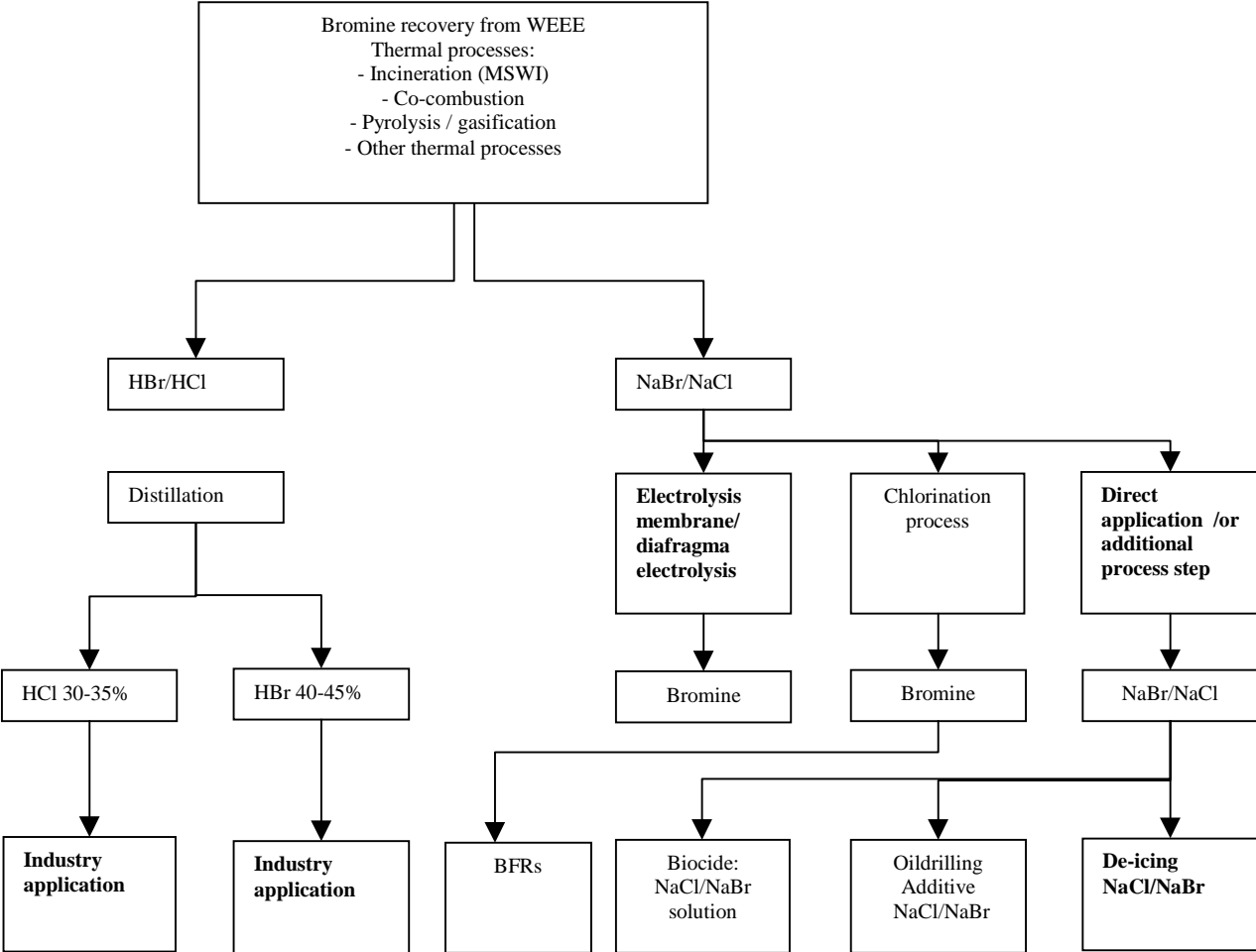
bromine and to avoid potential releases of bromine containing substances through improper and uncontrolled disposal.

To evaluate the technical and economic feasibility of recovering bromine or Hydrogen Bromide (HBr) two pilot trials were conducted. For co-combustion with municipal solid waste the TAMARA pilot plant (FZK, Karlsruhe) was used [11]. To simulate a pyrolysis/gasification process ECN Holland had been selected to run the Pyromate Process (Gibros/PEC) [12]. For the co-combustion process the released HBr out of the waste from E&E was collected into two scrubbers with caustic and a bypass scrubber which was run acidic. Via a bypass system in the TAMARA pilot plant a simulation of wet scrubbing with water to recover the HBr as an acid was set up.

Despite the mentioned thermal processes, also other processes like smelters have the potential to recover bromine from WEEE. Another thermal process is a copper smelter process in Germany which is planning to built a smelter for printed wiring boards, including a bromine recovery unit in the form of HBr 47%. The sampled bromine-rich residues from the co-combustion and bromine feedstock recycling trials are currently under evaluation to find the optimal recovery process. A basic process study, including an ASPEN+ computer simulation has been carried out, which enables the separation the HBr from the other components to get a 48%-HBr solution. Due to the sulphates or sulphuric acid (pH-dependent), the yield of HBr recovery was lower than expected. The option is to install an additional distillation column to recover also this part of the HBr. The potential occurrence of HF could influence the material of construction to build this unit, directly linked to the scrubber system of the thermal process. At the end the following streams are produced: a mixture of HCl-HF, HBr-48% and a small stream of sulphuric acid contaminated with HBr.

The process of recovering bromine is not influenced by the presence of fluorine or chlorine (HF, HCl). The bromine recovery was tested with chlorine, as this is the standard process worldwide. The main process steps are a chlorination step plus a steaming out tower to concentrate the bromine. With this process yields of >90% can be reached. The recovered bromine can be re-used as raw material. An alternative option to produce bromine if chlorine is not available on site, could be the use of peroxide within the HBr-stream. Figure 1 is providing an overview of potential options of a bromine recovery process and possibilities of closing the bromine cycle.

**Figure 1:** Potential options for the bromine recovery process and closing the bromine cycle.

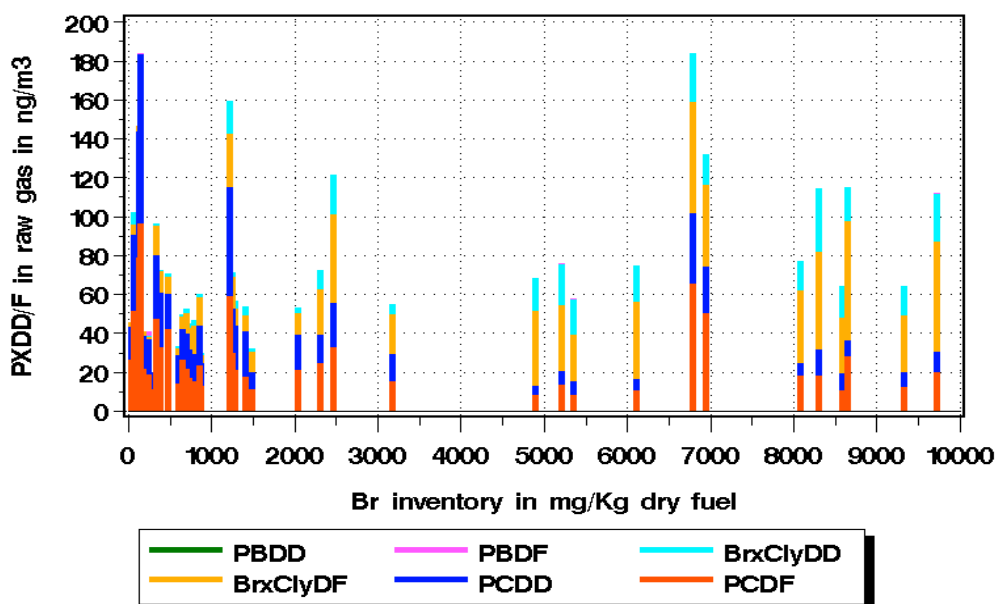


**Combustion**

BSEF has cooperated with Forschungszentrum Karlsruhe and various industry partners under the umbrella of the APME (Association of Plastic Manufacturers in Europe) to undertake a number of research programs. The aim of these was to investigate the co-combustion of plastic waste streams together with municipal solid waste. Plastics containing brominated flame retardants were fed to the pilot plant, TAMARA, with 250 kg/h feed to simulate full scale incinerators [11]. Different plastics such as those used in TV monitors and printed wiring boards were use as starting material. In one of these tests [11], in which the Br content of the fuel was increased to approximately 10 g/kg dry waste, results confirmed that up until a level of 3 g, no detectable amounts of elementary Br<sup>2</sup> could be detected in the raw gas, post incineration. These tests and various other incineration and pyrolysis test [14] and combustion studies [11, 15, 16] have demonstrated that waste from E&E equipment and insulation foams can be safely added to today’s municipal solid waste

(MSW) to generate in an environmentally sound manner useful energy when incinerating BFR-containing materials. PBDD/F formation is not altered by the presence of the bromine-containing waste, and remains well within emission standards in these processes. The OECD [17] came to the same conclusion regarding the insignificance of dioxin/furan formation when incinerating BFRs. The OECD noted that the highest formation rates for brominated dioxins/furans from PBDEs during laboratory experiments [18] were associated with low temperatures and pyrolytic conditions. Modern waste-to-energy facilities are specifically designed to avoid these conditions. A report from the European Commission [19] came to the same results. Figure 2 shows the results from incineration of plastics containing BFRs collected during the last years in the Tamara pilot plant.

**Figure 2:** Sum of PXDD/F vs. Bromine inventory in the Tamra 2 study [11].



## Conclusions

It can be concluded that plastics containing brominated flame retardants are compatible with an integrated waste management concept. Studies show that recyclates from **mechanically recycled** plastics containing BFRs are in compliance with strict PBDD/PBDF limit values when handled properly and that recyclates keep their properties and meet the fire safety standards (for example V-0) after multiple recycling processes. Several **combustion** studies have demonstrate that BFR containing plastics can be safely added to today's municipal solid waste to generate in an environmentally sound manner useful energy when incinerating BFR-containing materials. PBDD/F formation is not altered by the presence of the bromine-containing waste, and remains well within emission standards in these processes. **Bromine recovery** from WEEE plastics containing brominated flame retardants is technically, economically and ecologically feasible [13]. Using co-combustion techniques or

pyrolysis/gasification, it is in either case possible to recover bromine for re-use as raw materials. For co-combustion processes the advantage is that existing modern incinerators can be used where a bromine recovery unit will be added to the scrubber system. Using pyrolysis/gasification processes or a smelter process, a dedicated unit can be built where a more concentrated bromine stream can be recovered. The consequence will be an increase in the logistics costs. Co-feed with ASR is possible as plastics from WEEE do have similar characteristics. A bromine recovery unit will become economical with a capacity above 500 mtons/year, depending on the local situation. There is the potential for recovering up to 10.000 metric tons of bromine yearly in Western Europe, and with this, resources can be saved and the bromine cycle can be closed.

Besides mechanical recycling and energy recovery of plastics, bromine feedstock recycling could play an important role in a waste management concept for plastics containing brominated flame retardants [13].

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