

The Influence of Flame Retarded Plastic Foams upon the Formation of Br Containing Dibenzo-p-dioxins and Dibenzofurans in a MSWI

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1.) Introduction

Flame retarded plastics, especially extruded polystyrene foams (XPS) or rigid polyurethane (PUR) foams have wide application in the building and construction industry for heat insulation. Their final disposal – a problem which will increase during the next decades – requires a thermal treatment in order to destroy the organic matter. The co-combustion of limited amounts in a municipal solid waste incinerator (MSWI) could be a rational disposal route. Before recommending this option, however, two possibly complications causing facts have to be considered. Both types of foams contain

- CFC of in the new formulations HCFC as blowing agents and
- flame retardants, preferably brominated organic compounds.

The total thermal destruction of CFC and HCFC in a MSWI have already experimentally been demonstrated in a test incinerator as well as in a full scale plant ¹⁾.

Flame retarded plastics may increase the inventory of Cl and Br in a MSWI substantially. Especially the behaviour of the latter halogen is not well known. A potential formation of brominated and mixed halogenated dibenzo-p-dioxins or dibenzofurans can be considered. There is evidence that the Br:Cl ratio controls the actual amount of the different species ²⁾. Sampling in Swedish full scale MSWI resulted in only small amounts of brominated aromatic compounds with the brominated and mixed halogenated dioxins and furans always below the detection limit and their total concentrations comprising only a small percentage of the PCDD/PCDF levels ³⁾.

Increases of the PCDD/PCDF levels in the flue gas of a full scale MSWI have been reported for the co-combustion of electronic waste flame retarded by polybrominated diphenylethers ⁴⁾. The results leave some questions concerning their significance. Newer investigations in Dutch incineration plants could not confirm a correlation between Br and the total dioxin formation ⁵⁾. A recently published study upon the role of Br in the de novo synthesis in a model fly ash system could also not detect a promoting effect of Br ⁶⁾.

In order to obtain sound information about the effects of a co-combustion of heat insulating foams the Association of Plastic Manufacturers in Europe (APME), the European Extruded Polystyrene Insulation Board Association (EXIBA), the European Isocyanate Producers Association (ISOPA) and the Forschungszentrum Karlsruhe (FZK) launched a test campaign in the Karlsruhe test incinerator TAMARA.

This paper describes in a comprehensive way the effect of the increased Br inventory of the feed upon the levels of chlorinated, brominated and mixed halogenated dibenzo-p-dioxins and dibenzofurans evaluated from these extensive research programs.

2.) Experimental Performance

The test incinerator TAMARA is a mass burner with a nominal throughput of 200 kg/h of preconditioned waste. The design of the combustion chamber can be changed from the original counter-current into a parallel-flow geometry by the installation of variable roof elements. The XPS tests were conducted using the counter-current design whereas during the PUR tests the parallel-flow configuration was used. In the latter case the residence time of acid gases and alkaline fly ashes is extended and the fly ashes will contain higher amounts of e.g. chlorides or bromides.

The basic fuel burnt in TAMARA is shredded and homogenised household waste which is enriched by 25 % of a pelletized RDF. During the XPS co-combustion trials 3 wt.-% were added as granulate (without blowing gas) and as foams blown with CFC 12 (old formulation) or HCFC 142b/HCFC 22 (new formulation). The combustion temperature was 850 or 950 °C. The CFC 11 blown PUR foams were added at 1 or 2 wt.-%, the combustion temperature was 900 °C. The Cl and the Br concentration of the different feed components is shown in Table 1. The table indicates a high increase of the Cl and Br inventory in the feed during the co-combustion experiments.

Table 1: Analysis of Cl and Br for the basic fuel and the different XPS and PUR species (data in µg/g, * =calculated from (H)CFC inventory)

el.	basic fuel	granulate	XPS (CFC 12)	XPS (HCFC22/142)	PUR A (2 wt.-% Br)	PUR B (4 wt.-% Br)
Cl	5 960±350	43±10	37 900 *	36 750 *	76 000±5 000	72 000±5 000
Br	250±40	7 800±430	25 050±260	25 560±430	22 000±2 000	41 700±4 000

The sampling of the low volatile organic compounds was always performed in the raw gas. During the XPS experiments sampling has been done by FZK using the 'long-term sampler' LPS⁷⁾ and by BASF using the 'PU/Impinger-Hi-Vol' sampling train⁸⁾. Both laboratories analysed for PCDD and PCDF. BASF analysed for chlorinated and bromine containing dibenzo-p-dioxins and -furans.

During the PUR tests the sampling was performed by FZK as well as by GfA (Gesellschaft für Arbeitsplatz- und Umweltanalytik mbH, Münster) and MPU (Mess- und Prüfstelle Technischer Umweltschutz GmbH, Saarbrücken) using two different sampling trains. The GfA train adsorbs low-volatile organic compounds in one single sampling phase⁹⁾. MPU used a sampling train according to the German pre-standard VDI 3499.

The analysis of chlorinated dioxins and furans was done by FZK and by BASF during the XPS respectively by GfA and ITU during the PUR trials. The analysis of the mixed halogenated species has been performed by BASF or GfA and ITU. Clean-up and analysis for bromine containing homologues have been performed according to own protocols¹⁰⁾.

3.) Results

TAMARA allowed stable operation in almost all of the test runs. As a small test incinerator TAMARA suffers from time depending PCDD/F levels in the raw gas, which, however, are reproducible in case the combustion parameters are not changed. This implies to perform a series of reference and co-combustion tests in different weeks at exactly the same time or to calculate the respective reference data from reference tests by means of a time correction formula. The XPS trials followed the first strategy, the PUR tests the second one.

The raw gas levels detected by the different laboratories for the PCDD and PCDF as well as the homologue patterns were always in good agreement and showed no significant influence of the respective feed composition. As an example the total PCDD and PCDF concentrations obtained during the PUR tests are compared to the respective reference test results calculated for in Fig. 1. The levels monitored in TAMARA as well as their variation correspond to the best data reported for full scale facilities and thus confirm the technical relevance of the TAMARA test results.

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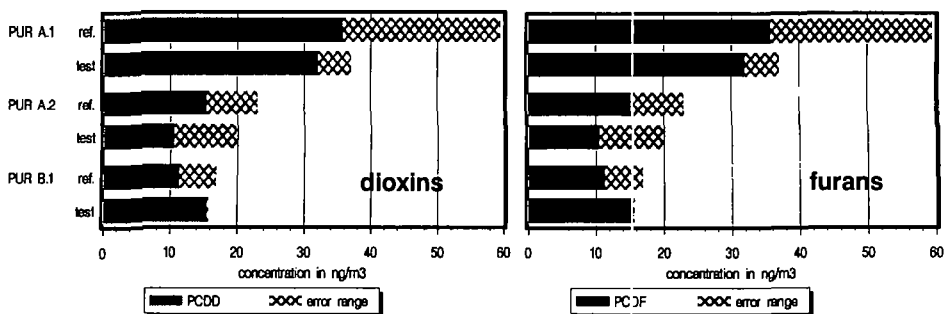


Fig. 1: Comparison of the sum concentrations of PCDD and PCDF in the raw gas during the PUR co-combustion tests with the respective reference data

Whereas the data for PCDD and for PCDF do not show a significant influence of the elevated Br input, the situation seems to change as far as bromine containing species are concerned. It was expected that the excellent consistency of the PCDD/PCDF analytical results would change in the case of species containing bromine due to the limited separation of different chromatographic peaks and to the shortage of certified standards. Hence the results obtained during the PUR trials by both laboratories vary especially in the case of dioxins. The furans which are higher in concentration are more close to each other.

All analyses, however, demonstrate that isomers containing purely bromine are present at very low concentrations only. Out of the mixed halogenated homologues preferentially those containing one bromine are found. Small amounts of two bromine containing species but none with higher numbers of Br atoms could be detected.

Both test campaigns indicate that an additional input of Br into the incinerator does obviously promote the specific formation of mixed halogenated congeners significantly. In Fig. 2 the sum of the Br containing dioxins is plotted as a function of the Br input into the incinerator for all test trials except of those with poor combustion conditions. As a first approach the graph can be interpreted as a straight correlation between both parameters. The data, however, are very low and suffer from high analytical uncertainties.

The same relationship for the bromine containing dibenzofurans is shown in Fig. 3. This graph indicates a correlation at low and approximately constant furan concentrations at high Br input. This behaviour could be explained assuming a similar de novo synthesis for the Br containing compounds as has been found for the formation of chlorinated dioxins and furans ^{11) 12) 13) 14)}.

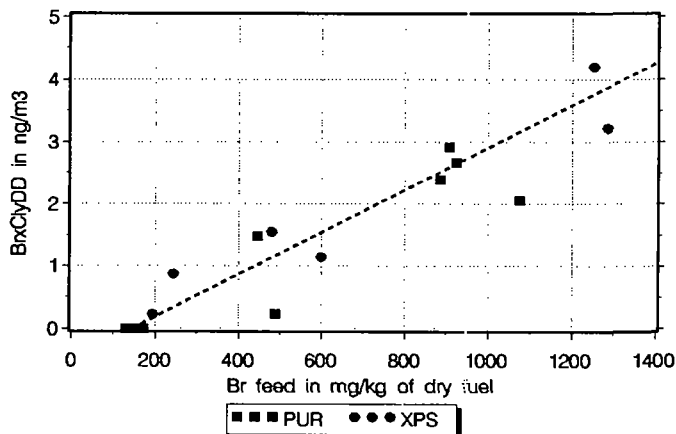


Fig. 2: Raw gas concentrations of Br containing dibenzo-p-dioxins versus Br input

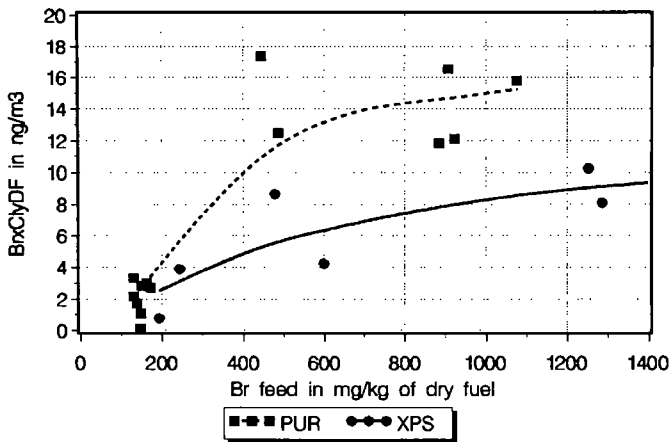


Fig. 3: Raw gas concentrations of Br containing dibenzofurans versus Br input

According to the de novo synthesis mechanism the inventories of active carbon, halogenides and copper in the fly ashes control the formation potential. Hence the relationship of Br containing species and the bromide concentration in the fly ashes should be regarded as has been done in Fig. 4 for the furans. This graph demonstrates that the furan levels show about the same dependence upon the bromide concentration in both test campaigns. The explanation is that the parallel flow configuration established during the PUR co-combustion tests cared for higher transfer of Br into the fly ashes as in the case of the counter-current design used during the XPS tests.

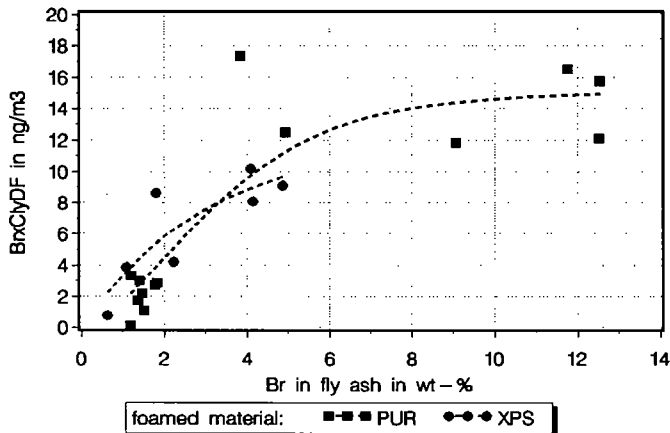


Fig. 4: Raw gas concentrations of Br containing dibenzofurans versus Br in the fly ash

The correlation at low and the saturation at high Br concentrations have to be expected if other parameters influencing the formation reaction stay more or less constant. In the actual case the conclusion can be drawn: the formation of Br containing furans is limited by the availability of carbon in the fly ashes. This is supported by the fact that in a test suffering from poor combustion conditions extremely high concentrations of Br containing furans were analysed.

For evaluating the relevance of the increases the total concentrations of halogenated species of both compound classes has for all test runs been plotted against the Br input in Fig. 5. The typical range of the PCDD/PCDF concentrations in TAMARA is presented as a cross-hatched background area. This visualization indicates that in general the levels of all halogenated dibenzo-p-dioxins and dibenzofurans stay

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well within the band width of PCDD and PCDF concentrations typically found in TAMARA. The outlier is caused by poor combustion conditions.

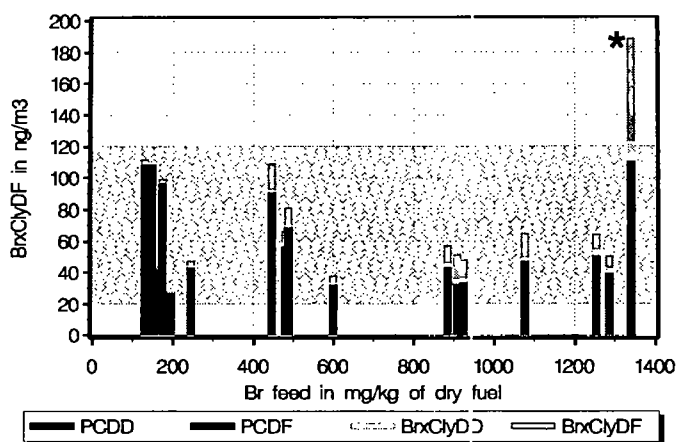


Fig. 5: Sum of halogenated Dibenzo-p-dioxins and Dibenzofurans in all test trials (*: poor combustion conditions)

Furthermore this graph demonstrates that the Br containing dioxins and furans contribute about 20 – 30 % to the total sum of halogenated homologues. The major addition is caused by the furans. If we assume that the toxicity of the bromine containing isomers is close to that of the respective chlorinated ones it can be concluded that the raw gas quality is not significantly altered by the addition of Br containing XPS or PUR foams. This implies that there is no additional risk in the emission if an effective air pollution control system is installed.

4.) Evaluation and Conclusions

During the co-combustion of flame retarded XPS and PUR foams in TAMARA the input of Br into the incinerator was increased by a factor of 6 as a maximum. The most important results of the test trials can be summarized as follows:

- No significant changes in PCDD/PCDF raw gas levels caused by the co-combustion of the foams could be detected.
- Bromine containing dibenzo-p-dioxins and dibenzofurans could be analysed at very low levels. There is a dependence on the bromide concentration in the fly ashes. At Br levels exceeding approx. 5 wt.-% the formation potential of the furans seems to be exhausted and the concentration approximates constant values. A respective behaviour of the dioxins is likely. However, this cannot be corroborated on the basis of our test results due to the very low and scattering data.
- The increase of the total sum of halogenated dioxins and furans was found to be limited to approx. 30 % and did not exceed the concentration range typically found in TAMARA. The implementation of a state-of-the-art air pollution control system guarantees that the co-combustion does not create any emission problem.
- The tests confirm the co-combustion of limited amounts of flame retarded XPS or PUR foams to be an ecologically – as well as economically – compatible disposal route.

5.) References

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