

POLYBROMINATED FLAME RETARDANTS - POSTERS

PXDD AND PXDF FROM COMBUSTION OF BROMOFLAMERETARDENT CONTAINING MSW

Gunilla Söderström and Stellan Marklund

Umeå University, S-901 87 Umeå, Sweden

Introduction

The formation of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) from combustion of municipal solid waste (MSW) has been and is continuously investigated. The basic reason behind the formation is the presence of chlorine, both in inorganic and organic form. Mechanisms forming PCDD's and PCDF's in combustion are probably also due to the formation of polyhalogenated dibenzo-p-dioxins (PXDD) and polyhalogenated dibenzofurans (PXDF), X=Br, Cl. The physico-chemical properties of bromine and chlorine are though slightly different and formation rates can therefore differ. The increased use of brominated flameretardents in various products is giving an increased amount of bromine in MSW. PXDD's and PXDF's are thus becoming more likely to be found in MSWI fluegas and ash. The increased use of brominated flameretardents follows the development of electronic equipment and higher demands on fire safety. Sooner or later flameretarded products ends up as waste or recycling material. A new law in Sweden prohibits combustible waste to be left on waste deposits. A result if this decision is that more waste will then be incinerated, also flameretarded waste. Incineration is used in some methods for metalrecycling of electronic waste. In this case bromine levels can be relatively high and PXDD and PXDF are likely to be formed.

The aim of this study was to investigate the formation of PXDD and PXDF when brominated flameretardents are co-combusted with MSW. The halogen levels were set as a worse case scenario with high levels of bromine where amounts of chlorine and bromine are equal on molar basis. Chlorine levels were set considering a chlorine content of 0.75% w/w, a normal level in Swedish/ European MSW. Altogether three bromine levels were chosen on molar basis ¹⁾ equal amounts of Br and Cl ²⁾ Br levels half of Cl ³⁾ only Cl, no Br. The flameretardents used were Decabromodiphenyl ether (DeBDE), Hexabromocyclododecane (HBCD) and Tetrabromobisphenol-A (TBBP-A). These three are amongst the most commonly used bromo flameretardents today. Incineration studies of these flameretardents has earlier shown formation of polybrominated dibenzo-p-dioxins (PBDD's) and polybrominated dibenzofurans (PBDF's)^{1,2}. Most earlier studies has used fuels with few components, i.e. mainly the flameretardent. In this study we have used a pilot-scale fluidized bed reactor to imitate the conditions in a full-scale MSWI-plant. The fuel compositions are described below in table 1.

Methods and Materials

Fuels The fuel base was pellets of a standardized MSW ³. This fuel contains paper, plastics, organic matter and metals. The chlorine content is 0.75% with equal amounts of organic and inorganic chlorine. One fuel used as reference contained almost no chlorine. Pellets were coated

POLYBROMINATED FLAME RETARDANTS - POSTERS

with selected flameretardent. DeBDE and HBCD came from Fluka, TBBP-A from Riedel de Haën, all of technical grade.

Fuel name	Description	Br:Cl ratio molarbasis
A	MSW Mix 0,75% Cl, organic Cl : inorganic Cl 1:1	0:1
B	DeBDE "high" = Fuel A + 1,7 % w/w Br	1:1
C	DeBDE "low" = Fuel A + 0,87% w/w Br	1:2
D	HBCD "high" = Fuel A + 1,7 % w/w Br	1:1
E	HBCD "low" = Fuel A + 0,87% w/w Br	1:2
F	TBBP-A "low" = Fuel A + 0,87% w/w Br	1:2
G	TBBP-A "low", 0%Cl = Fuel H + 0,87% w/w Br	1:0
H	halogen free MSW	0:0

table 1

"High"; Br level = chlorine on molar basis

"Low"; Br level = of chlorine level on molar basis

Combustion The pilotscale fluidized bed incinerator at Environmental chemistry, Umeå University was used for these experiments. It has been thoroughly described by Wikstrom⁴. It has an effect of 5kW and in this case it was operated with aprox. 1 kg fuel/hour. Combustion temperature 800-850 °C. Samples taken in convector midsection at aprox 300°C. Between experiments, the reactor and convector were cleaned in order to minimize memory effects. One experiment was performed for each fuel, except for fuel A which was performed twice.

Sampling Organic compounds were sampled 2 and 3 hours after combustion of solid fuel had started. Stable organic compounds were sampled with a train designed for PCDD/F sampling. The sampling train is also suited for sampling other organic compounds like PCB, PBCDD/F. This sampling train is one of the european cerified train⁵ and further described by Marklund⁶. O₂ levels were analysed in outgoing gas after the pump to ensure that no air leaks diluted the samples. Before sampling the train was "spiked" with 13C-labelled TeBDE, PXDD:s, and PXDF:s.

Analytical procedure Condensate and impinger solutions were particle filtrated and extracted with a SPME-disc (Supelco). The particlefilters, SPME-disc and polyurethanefoam adsorbent were further extracted with toluene in Soxhlet. Before extraction the samples were spiked with more 13C-labelled congeneres The extracts from Soxhlet were concentrated and cleaned with a silica multilayer column, an alumina oxide column and finally a carbopack column. After clean-up, tetradecane and syringe-spike was added. The samples were then analyzed on a VG 250-S HRGC/HRMS. Te/PeBCDD and Te/PeBCDF were analyzed on a SP2330 coloumn. Possible interference of brominated diphenylethers was checked and excluded.

Calculations has been performed both on weight and molar basis. The lack of PXDD and PXDF standards prevents isomer-specific analysis. Results are therefore focused on total sums of TeXDD's and TeXDF's.

POLYBROMINATED FLAME RETARDANTS - POSTERS

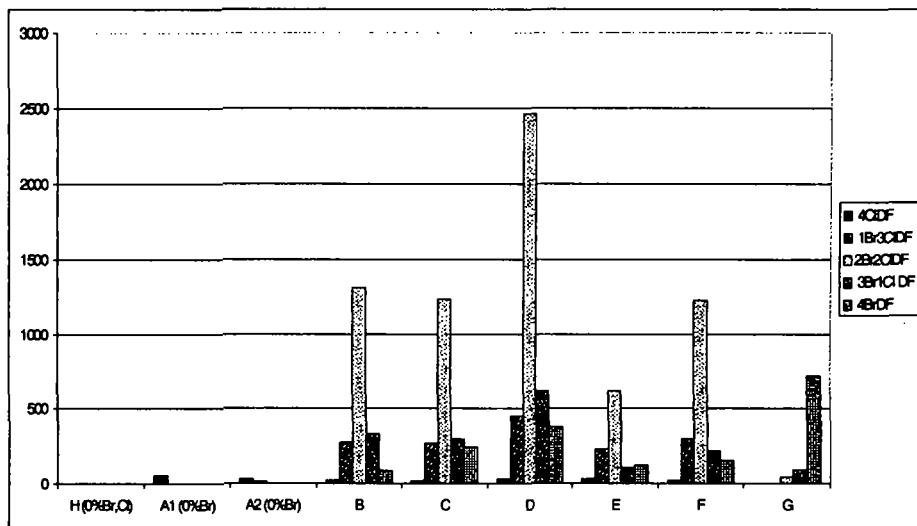


Figure 1, Sum TeXDF, pico mole / m³ 10% CO₂

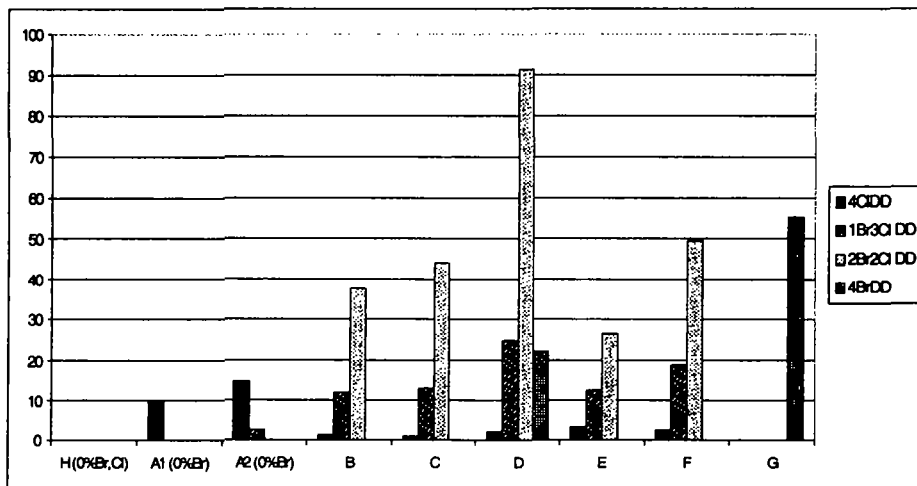


Figure 2, Sum TeXDD, pico mole / m³ 10% CO₂

Results and Discussion

Figures 1 and 2 shows the results from analysis of TeXDD and TeXDF. In the case when no chlorine was present (fuel G), mainly TeBDF's were formed. Minor amounts of 2Br2CIDF's and 3Br1CIDF's could also be found, probably an effect of small amounts of chlorine from paper in the fuel. The two combustions of fuel A indicates good reproducibility. As expected, the zero halogen level fuel, H, gave no significant amounts of PXDD's or PXDF's. All bromoflamerardents in these combustion runs formed TeXDD's and TeXDF's when co-

ORGANOHALOGEN COMPOUNDS

POLYBROMINATED FLAME RETARDANTS - POSTERS

combusted with MSW. This correlates with other studies^{1,2}. As in most MSWI cases, more TeXDF's than TeXDD's were formed. More TeBDF's than TeCDF's were formed, both on weight and molar basis comparison. The halogen form X₂ can be an important parameter for increased PXDD and PXDF formation. Bromine is more likely to form Br₂ than chlorine to form Cl₂ in combustion. This can explain the difference between TeCDF and TeBDF. The distribution of Br and Cl in TeXDF can be described statistically. There are 38 possible TeCDF isomeres, 140 of 1Br3ClDF's, 210 of 2Br2ClDF's, 140 of 3Br1ClDF's and 38 of TeBrDF's, i.e ratio aprox. 2:7:10:7:2. This description does not consider any physicochemical differences between Br and Cl. The ratio between the theoretic distribution and what is formed in this study (figures 1 and 2) shows that theoretic distribution is followed in the experimintents. Although, 2Br2ClDF formation is favoured beyond the statistical distribution. An isomere specific analysis could reveal if 2378-isomeres (most toxic) are formed. In this case we find possible peaks, but coelution might occur. The results indicates that formation of TeBDD and TeBDF is not strongly dependent on the chemical structure of the flameretardent incinerated. This is probably due to an almost complete fragmentation in the combustion zone and rebuilding in convector zone. It is not possible to directly translate the results to a fullscale plant and emissions to surroundings. A full-scale plant is usually equipped with flue-gas cleaning devices which might alter the composition. The findings of PXDD and PXDF on soil in Japan by Watanabe⁷ can possibly be related to the formation in our study.

Acknowledgement

The Nordic Council of Minister is acknowledged for supporting and financing this project.

References

1. Luijk, R. (1993) Formation of polyhalogenated dibenzo-p-dioxins and -dibenzofurans during thermal degradation processes (*Thesis*)
2. Dumler, R., Thoma, H., Lenoir, D., Hutzinger, O.. (1989) *Chemosphere* 19,12
3. Wikström, E., Löfvenius, G., Rappe, C., Marklund, S.. (1996) *Environmental Science and Technologie*, 30, 5
4. Wikström, E., Andersson, P., Marklund, S.. (1998) *Review of Scientific Instruments*. 69, 4
5. EN 1948-1:1996
6. Marklund, S., Söderström, G., Ljung, K., Rappe, C., Kraft, M., Hagenmaier, H.. (1992) *Waste Manegement and Research*. 10
7. Watanabe, I., Ugawa, M.. (1999) *Organohalogen Compounds*. 43