

DIFFERENT FORMATION MECHANISMS OF DIOXINS IN COMBUSTION SYSTEMS WHEN CHLORINE OR BROMINE IS PRESENT.

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Introduction

Several combustion methods emit organic pollutions via the stack or in the ash fractions. Especially halogenated aromatic compounds as polychlorinated biphenyles (PCBs), chlorinated dioxins (PCDDs and PCDFs) and brominated flame retardants have been considered as environmental threats.

EU and other countries have regulated the emission to air of some of these pollutants. However, the regulation is based on toxic dioxin equivalents (TEQs) approaches that do not include brominated and mixed brominated chlorinated compounds in their calculation. Studies have shown that these congeners are as toxic as the pure chlorinated ones.

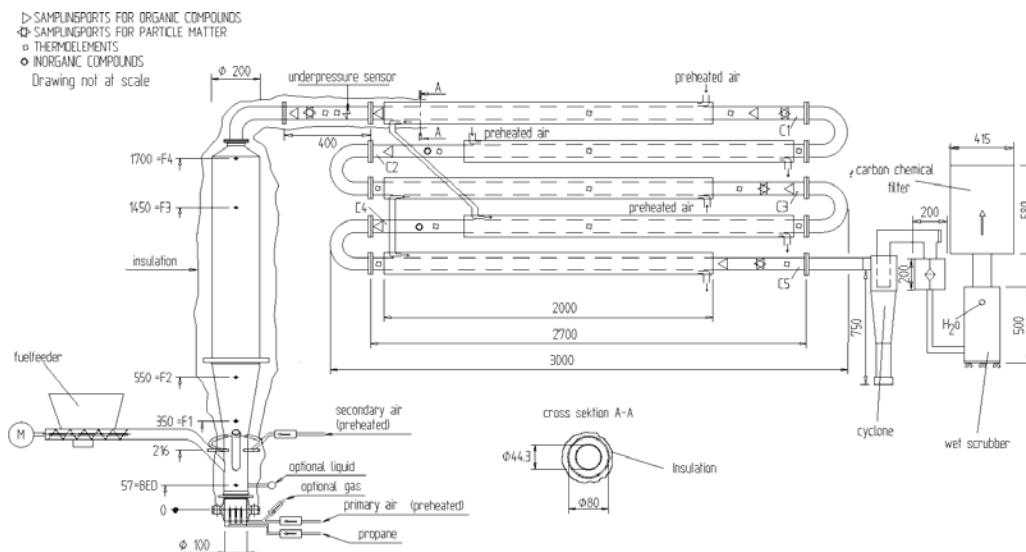
Polyhalogenated dibenzo-p-dioxins, PXDD (X=Br,Cl), and polyhalogenated dibenzofurans, PXDF (X=Br,Cl), are formed in combustion processes when both bromine and chlorine are present. It is since earlier experiments known that PCDD/F are mainly formed during flue-gas cooling in the temperatures between 400 and 250 °C. It is also known that CuCl₂ is an important catalyst, either as a direct chlorinating agent or as a Cl-converter from HCl to Cl₂ in the Deacon-process. It is likely to believe that PCDD/F and PXDD/F follow the same or similar formation pathways. Chlorine and bromine have several similar properties, but in combustion they possess some important differences that might effect the formation of PXDD/F. The two major differences are 1) More Br₂ is formed compared to Cl₂ calculating on molar basis. 2) Br-C bond is weaker than the Cl-C bond.

The first might promote PXDD/F formation and the second promote PXDD/F debromination. In addition to Br₂ and Cl₂, also BrCl will be present in hot flue-gas.

In this study we have investigated the formation pathway of halogenated dioxins and related compounds when chlorine, bromine or mixed chlorine bromine containing fuel fractions are combusted during controlled conditions.

Methods and Materials

The PXDD/F formation is studied in the Umeå pilot-scale combustion reactor see Figure 1. This is a 5-kW fluidized-bed reactor that can be operated with different temperatures in the post-combustion zone. The reactor consists of a vertical combustion zone 0.1 m id, 2.5 m in height and a horizontal convector for flue-gas cooling, 15 m long. A fuel was prepared with equal bromine and chlorine levels on molar basis. This high bromine level is probably very unusual in real life, but is an advantage for bromine - chlorine comparison. During combustion 3 parallel samples were taken at three different locations in the convector part; namely at 600, 250 and 150°C. These flue-gas samples were analyzed for PCDD/F, PXDD/F and PBDD/F.

Figure 1: The Umeå pilot reactor**Results and Discussion**

All the bromine-chlorine containing fuels formed PBCDD/Fs as well as PCDD/Fs and PBDD/Fs when burned in the reactor. The chlorine containing fuels formed PCDD/Fs (Figure 2). The levels of halogenated dibenzofurans were much higher than the levels of the corresponding dioxins. This is consistent with results of previous studies of PCDD and PCDF formation from MSW (1). A minor decrease in the levels of PCDD and PCDFs was observed with bromine addition. The decreases were similar for all the congener groups analysed, so the PCDD and PCDF congener patterns do not show any obvious variations over the range of experiments (Figure 2). This indicates that both furans and PCDD precursors undergo similar halogenation reactions. All brominated fuels formed TeBCDD and TeBCDF during the combustion experiments. No obvious differences in TeBCDD, TeBCDF or PCDD/F formation could be seen between the different bromine fuels (added as different types of brominated flame retardants). This is in analogue with the results from the studies by Wikström and Marklund (2) who found that the origin of the chlorine did not influence PCDD/F formation in combustion processes. As no brominated flame retardants were found in the flue gas. This indicates that the brominated flame retardants were destroyed in the combustion zone, and there was a formation of new brominated organic compounds there or in the cooling zone. There are no obvious trends of increased or decreased TeBCDD/F or PCDD/F levels for fuels with high respectively low levels of the same flame retardant (fuels B, C, D and E) (Figure 2). However, with both bromine levels and chlorine in the fuel, the mixed bromo/chloro dioxins and dibenzofurans were the most abundant congeners. A Gaussian-like distribution was seen over the range from TeCDD/F, MoBrTriCIDD/F, DiBrDiCIDD/F, TriBrMoCIDD/F to the TeBDD/F congener groups. Compared to the TeCDF formation in chlorine environment the DiBrDiCIDD formation was 10 times higher than expected, but based on TeBDF formation in bromine environment the DiBrDiCIDD were as expected. A striking difference between the halogens is that more TeBDFs are formed than TeCDFs on a molar basis. This can be seen both within the results for the mixed halogen fuels (B, D, C, E and F) and also in a comparison of the single halogen fuels A and G. Enhanced bromination has been reported

earlier by Sidhu (3) in the formation of PBCDD/F in thermal reactions with halogenated phenols. This is presumably due to the presence of Br₂ and BrCl in the combustion zone and the flue gases, which allows bromination of the dioxin precursors and dibenzofuran skeletons without the presence of a catalyst. This increases the reactivity of bromine and boosts the rates of formation of PBDD/F relative to the chlorine analogues, which require a catalyst to enhance the conversion of HCl into Cl₂. BrCl is a very effective brominating agent, via both radical and substitution pathways. In the hydrogen substitution mechanism a chloride scavenges a hydrogen, due to chlorides greater electro negativity, and the bromine substitute the hydrogen atom.

$$R1R2C-H + BrCl \rightarrow R1R2CBr + HCl$$

Conclusions

Formation of brominated aromatic compounds are more enhanced than the chlorinated analogues in flue gases. As HBr easier disassociate into Br[•] the need of catalytic size to convert HBr is not needed. That implies higher yields of these compounds. The HBr level is the limited factor in gas phase bromination of aromatic compounds not the amount of catalytic sites as for chlorination reactions. This explain why we have higher level of bromine than chlorine in our results (Figure 3). A Br – Cl exchange on the molecule or an enhanced formation of Cl radicals from Br-Cl can explain the higher chlorination level of the aromatic compounds in the flue gas when bromine is present in the fuel (Figure 3).

These results show a difficulty to combust fuels containing bromine as the emissions of toxic halogenated aromatic compounds increase. There is also an analytical problem as we can only find a small fraction (the pure chlorinated compounds) of the toxic pollutants if we use normal standardization methods to quantify PCBs and dioxins in the flue gas.

Figure 2. TeXDF profiles in pico moles/ m³ from all experiments (sample 2) as the sum of congener groups.

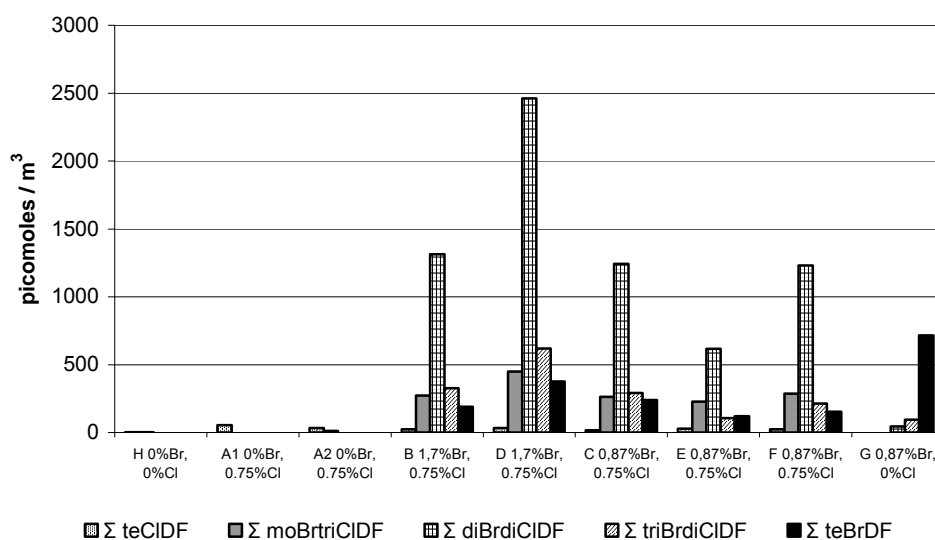
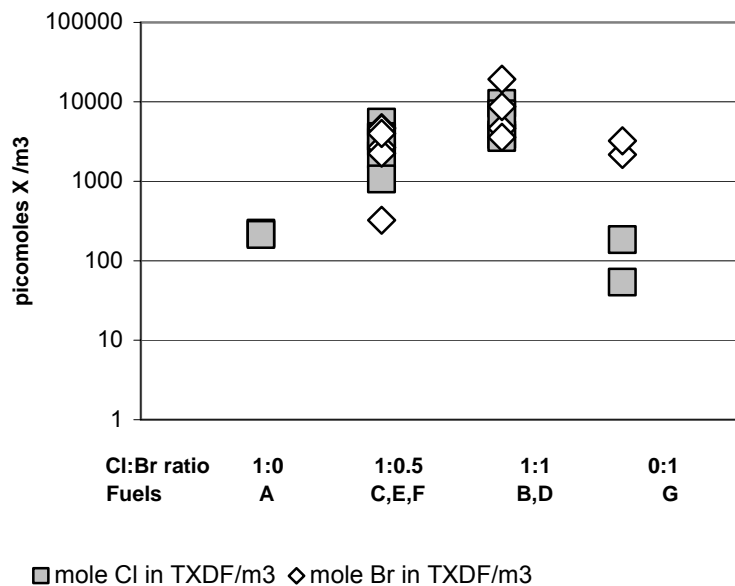


Figure 3. Sum of pico moles of X (X=Br, Cl) incorporated into TeXDF for different Br and Cl fuel combinations.



References

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3. Sidhu, S.; Maqsood, L. and Dellinger, B. (1995) *Combust.Flame*. **100** (11), 20.