

FORMATION OF NON- TO OCTACHLORINATED PCDD/F DURING MSW COMBUSTION IN A LABORATORY-SCALE FLUIDIZED-BED REACTOR

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Introduction

During MSW incineration, PCDD and PCDF are unintentionally formed, and since PCDD/Fs generally are chemically stable environmental contaminants which may be long-range transported from combustion sources to almost all areas of the globe, the most reasonable control strategy for reducing PCDD/F emissions is to minimize their formation rather than to collect and destroy them after formation. Knowledge of PCDD/F formation mechanisms allows development of practical remediation measures such as inhibition technologies, waste sorting, waste pre-treatment, and catalytic destruction.

In thermal processes, PCDD/Fs are primarily formed in the post-combustion zone at approximately 200-400°C. The general opinion is that PCDD/Fs in the waste are destroyed in the high-temperature region of modern incinerators, however the relative importance of the two classic theories, precursor and de novo formation, is still highly controversial. Nevertheless, there is no doubt that both pathways occur during PCDD/F formation under realistic conditions, but to which extent, and which pathway is dominating?

The laboratory-scale fluidized-bed reactor at Umeå University was used to study formation of non- to octachlorinated PCDD and PCDF during combustion of an artificial MSW, and parallel flue gas samples were collected at different temperatures during flue gas cooling. The main objective was to study reactions occurring in the post-combustion zone within the temperature interval of 600-200°C, and to evaluate homologue profiles and congener distribution patterns.

Materials and Methods

A standardized, artificial MSW fuel was incinerated in the laboratory-scale fluidized-bed combustion reactor at Umeå University (Figure 1), which is constructed as to simulate a full-scale MSW combustor. The reactor system consists of four sections: a bed section, a freeboard section, a convector (post-combustion zone), and an air pollution control device. At the beginning of the first convector unit and at the end of each unit there are sampling ports (P1-P7), which enable sampling of flue gases and particles at various residence times. A detailed description of the reactor was given by Wikström et al.¹ and Aurell et al.²

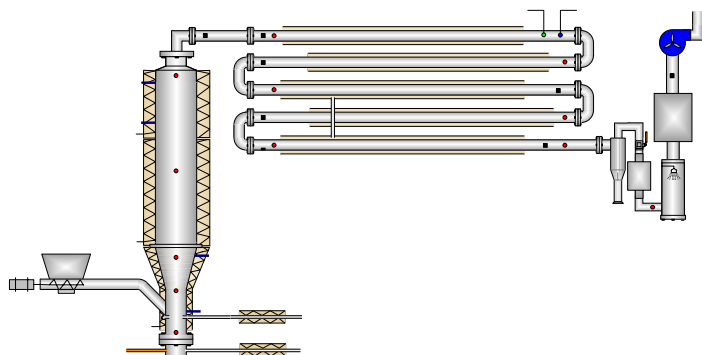


Figure 1. The laboratory-scale fluidized-bed reactor, not in scale. Sampling ports are denoted P1-P8, electrical heaters H1-H9, thermocouples T1-T12, and injection ports I1-I4. A FTIR gas analyzer and a zirconium dioxide cell oxygen measuring probe are connected to the end of the first convector section. The air pollution control device consists of A) cyclone, B) metal- and textile filter, C) wet scrubber, and D) active carbon filter. The positions where flue gas samples have been collected in this study are marked P2, P4, and P7.

Three replicate combustion experiments were performed using the same fuel, same temperature gradients, and with sampling at the same positions at the same time each experiment, in order to study PCDD/F formation pathways in the post-combustion zone. The combustion experiments were conducted on separate days, with one day in between for cleaning. MSW fuel was combusted for 7 hours at an average fuel feeding rate of approximately 0.67 kg/h or 3.6 kW/h. Primary air flow was set to 74 l/min, and secondary air flow was 22 l/min. During the last hour of each combustion experiment, three parallel flue gas samples were collected for one hour at sampling ports P2, P4 and P7 (Figure 1), corresponding to flue gas temperatures of approximately 600, 300 and 200°C, respectively. Sampling, extraction, clean-up and determination of mono-octaPCDD/F was performed according to methods described elsewhere^{2,3}. Clean-up of nonchlorinated dibenzo-*p*-dioxin (DD) and dibenzofuran (DF) was performed according to the hexaCBz clean-up procedure described by Aurell et al.²

Results and Discussion

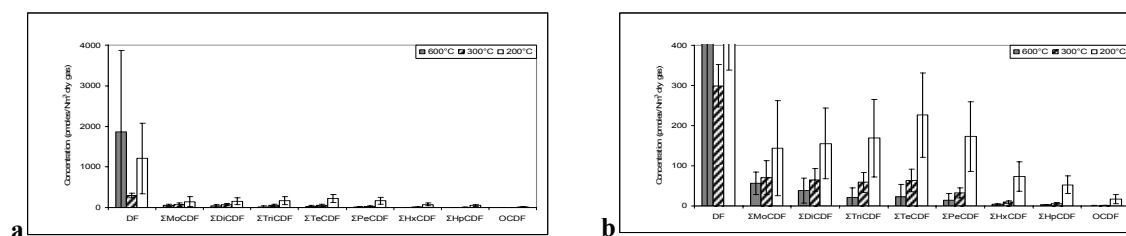
Total concentrations of non- to octachlorinated PCDF and PCDD were increasing with decreased temperature and increasing residence time in the convection section (Table 1), and are distinctly higher in the samples collected at 200°C, indicating an extensive formation of these compounds in the low-temperature region of the convector.

Table 1. Total levels of non- to octachlorinated PCDD/Fs, in pmoles/Nm³ dry gas.

Sampling Temperature	EXP 1			EXP 2			EXP 3		
	600°C	300°C	200°C	600°C	300°C	200°C	600°C	300°C	200°C
Σ PCDF	1176	741	2059	5444	359	4177	604	411	821
Σ PCDD	319	48	283	19	37	426	60	43	142

The large increase in PCDD/F concentrations observed between 300 and 200°C is very interesting since it suggests an extremely narrow temperature window for formation of PCDFs as well as PCDDs. However, the levels of PCDD/Fs formed are not as important for mechanistic studies as the homologue profiles and congener distribution patterns. The levels and homologue profiles often differs between different combustion sources and combustion conditions, while the congener distribution patterns have shown to be very constant^{4,5}. Also, the toxicities of the different PCDD/F congeners varies, with the 2,3,7,8-substituted congeners being the most toxic. Thus, it is important to understand not only the basis for the relative abundance of homologues and the various degrees of chlorination, but also the distribution of individual congeners in the flue gases.

Evaluating the homologue profiles, a shift in degree of chlorination was noticed, towards a profile dominated by higher chlorinated congeners (Figure 2). This shift was very distinct for the PCDD homologues, and less pronounced for the PCDFs, which may support the hypothesis of separate formation pathways for the two groups of compounds. The levels of PCDFs were significantly higher than the PCDD-levels resulting in a PCDF:PCDD ratio $\gg 1$, which according to Huang and Buekens⁶, is characteristic for a formation pathway dominated by the de novo synthesis of PCDD/Fs.



Thermal processes

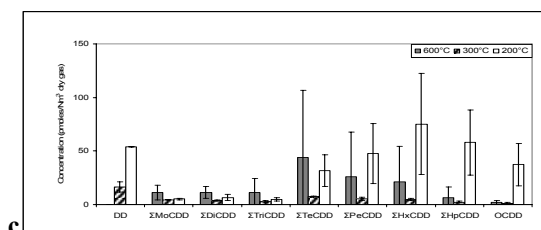


Figure 2. Homologue profiles of PCDF (a) with a closer detail of mo-oCDF (b), and PCDD (c). Error bars represent ± 1 standard deviation.

Figures 3 and 4 show the congener distribution patterns of the PCDFs and PCDDs, respectively. The dominating PCDF congeners within each homologue group are mainly chlorinated in the lateral positions (2,3,7,8-positions), namely 2-moCDF, 2,4-diCDF, 2,3,4-, 2,3,8-triCDF, 2,3,4,8-teCDF, 1,2,3,7,8-peCDF, 1,2,3,4,7,8-hxCDF and 1,2,3,4,6,7,8-hpCDF. The preferred chlorination of carbon 6 in hxCDF is not unexpected since it is more available than carbon 9, the other remaining carbon, located in the bay of the dibenzofuran backbone. The chlorination patterns of PCDDs are not as clear as for PCDFs, but the domination of lateral chlorination seems to be less pronounced. However, the results are less reliable for PCDDs since concentrations in the high temperature samples were generally below or close to the detection limit.

In addition, PCDD/F vapor pressures were evaluated, being a measure of solubility in air, which provides an indication of the volatility of the specific compound. The vapor pressures of dioxins are strongly dependent on number of chlorine substituents for fixed temperatures. However, the differences between vapor pressures of different isomers with equal molecular weight are much smaller⁷. Most PCDD/Fs display vapor pressures ranging between 1×10^{-2} and 1×10^{-6} Pa at ambient temperatures, and are thus classified as semi-volatile organic compounds. However, the vapor pressure is highly temperature dependent and at elevated temperatures the vapor pressure increases to levels exceeding 1×10^{-2} Pa, which is the lower limit for volatile organic compounds, making the PCDD/Fs more likely to be present in the gas phase than adsorbed to particles. Between 250 and 125°C, the vapor pressure decreases by a factor of approximately 1000, meaning that in the convector section a substantial condensation of PCDD/Fs onto particles is likely occurring, which enables particle-mediated formation and/or chlorination, and might partly explain the large increase in PCDD/F concentrations at 200°C compared to 300°C, as well as the shift in homologue profiles. Nevertheless, comparisons between combustion experiments are uncertain since there is always an interaction between the compound and the surface, as well as other organic compounds, but also since the available amount of particle surface is of high importance.

In conclusion, the total levels of PCDD and PCDF were distinctly higher in the flue gas samples collected at the lowest temperature in the convector (200°C) compared to at 600°C, and the homologue profiles shift towards the higher chlorinated homologues. This indicates an extensive secondary formation of organic carbon structures in the convection section, combined with additional chlorination reactions of the already formed organic compounds. Chlorination of PCDFs was mainly directed to the lateral positions, resulting in higher total toxicity of the combustion by-products.

References

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Thermal processes

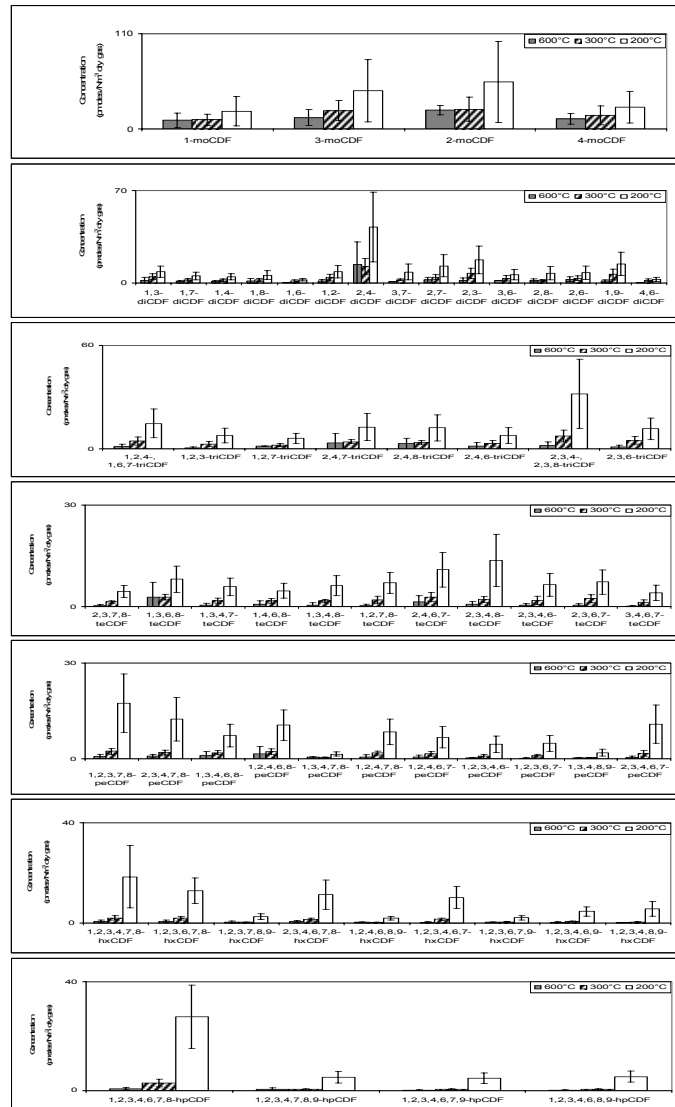


Figure 3. Congener distribution patterns of PCDFs. Error bars represent ± 1 standard deviation.

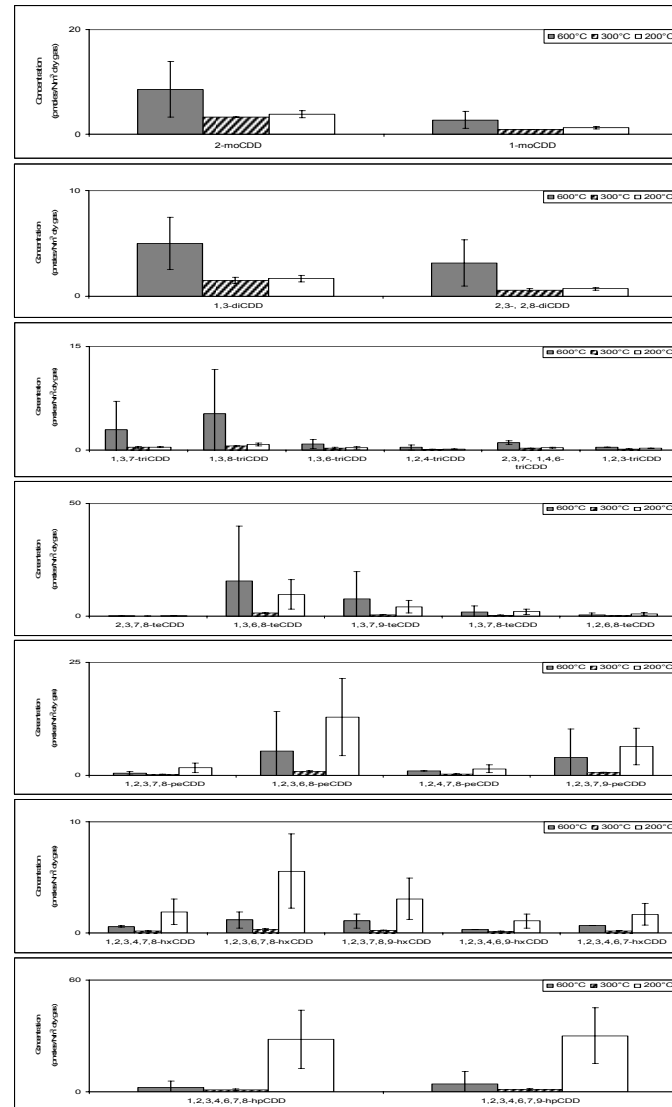


Figure 4. Congener distribution patterns of PCDDs. Error bars represent ± 1 standard deviation.