

# FORMATION OF DIOXIN IN A MODIFIED LABORATORY-SCALE FLUIDIZED-BED REACTOR DURING A LONG-TERM MSW COMBUSTION EXPERIMENT

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### Introduction

The 5 kW laboratory-scale fluidized-bed reactor at the Umeå University enables studies of the formation of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), as well as related pollutants such as polychlorinated biphenyls (PCB), polychlorinated benzenes (PCBz), polychlorinated phenols (PCPh), and polycyclic aromatic hydrocarbons (PAH). Reactions occurring both in the combustion and post-combustion zones can be studied under simplified but 'real' combustion conditions, while reducing the experimental costs compared with full-scale experiments. The laboratory-scale reactor has been used in a number of combustion research experiments of very varying character. The solid fuel used was in several studies artificial MSW [1], in some cases with additives such as brominated flame retardants [2], but also biofuel [3], and automotive shredder residue [4]. However, due to heavy usage and increased demands on functionality and process monitoring the reactor was in need of renovations and improvements.

The aim of this study was to evaluate the performance of the laboratory-scale fluidized-bed reactor after the modifications, regarding combustion and temperature conditions, and levels of mono- to octachlorinated PCDD/F, tri- to decachlorinated PCB, and hexachlorinated benzene (hxCBz). Furthermore, even to compare the concentrations of the chloroorganic compounds at different operating times, temperatures and residence times, with the intention to show the stability and how to obtain reproducibility in the reactor.

### Materials and Methods

The design of the fluidized-bed laboratory-scale reactor was previously described by Wikström et al. [5]. The reactor consists of four parts: a bed section, a freeboard section, a convector section and an air pollution control (APC) system. The convector section allows sampling at different temperatures and residence times. The laboratory-scale reactor is equipped with electrical heaters, one at the bed, two at the freeboard and four at the convector section, to prevent unwanted temperature variations and to achieve stable temperature conditions faster [6]. The laboratory-scale reactor has been modified in a number of ways; new thermocouples, new injection ports and improved fuel feeding device. Also new equipment was installed; zirconium dioxide cell measuring oxygen, Gas Analyzer based on a Fourier-Transform Infrared (FTIR) enabled on-line monitoring of H<sub>2</sub>O, CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>2</sub>, CO, NO, HCl, NH<sub>3</sub>, N<sub>2</sub>O, and CH<sub>4</sub> and a new Operating system using the software LabVIEW 7 Express. All modifications allowing a more controllable combustion and temperature conditions.

Three combustion experiments were conducted in replicate on separate days, using the same fuel, same temperature conditions and the same O<sub>2</sub> content. The MSW fuel combustion was executed for 11 hours (experiment 3), during the combustion three parallel flue gas samples were collected for one hour at the temperatures 600, 300 and 200°C, for every other hour starting after two hours. The two replicate experiments were performed during 7 hours of MSW combustion, and sampling occurred only during the last hour (experiment 1 and 2). The fuel used was an artificial municipal solid waste. Sampling of flue gases was performed according to standard method [7] using the cooled probe polyurethane foam plug (PUFP) sampling technique. Spiking, filtration, extraction and clean-up of flue gas and ash samples were performed according to standard methods described elsewhere [8].

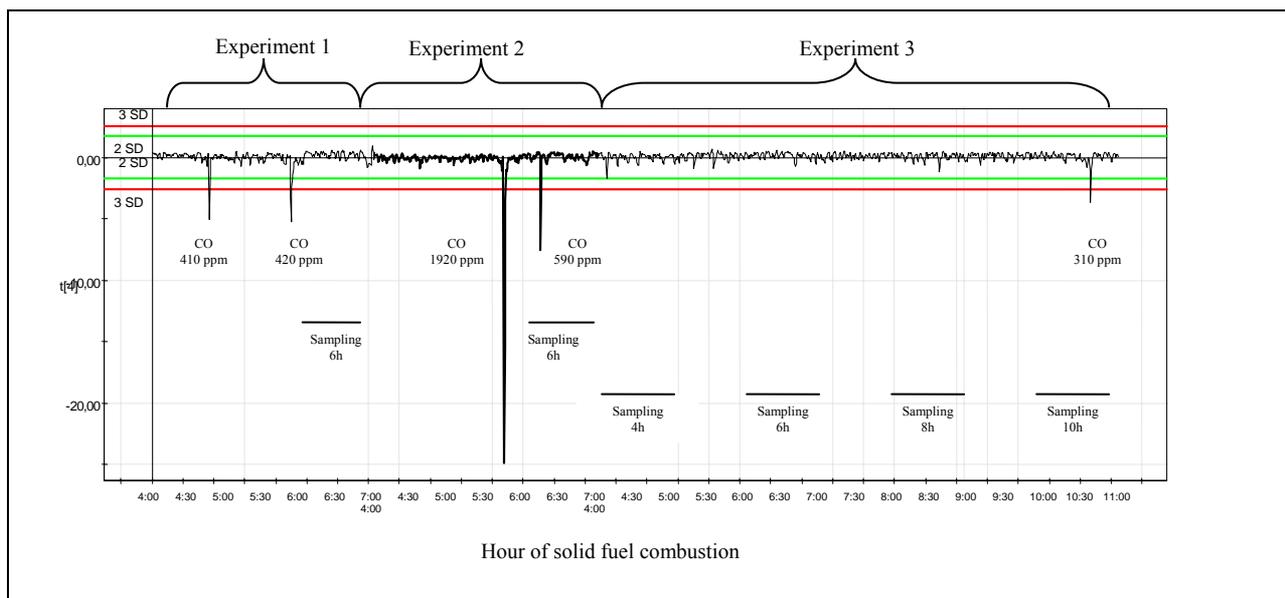
**Results and Discussion**

The combustion conditions were in general very stable and similar during and between experiments, without any trends or patterns (Table 1), confirming that the improved fuel feeding device performs satisfactory. The combustion process during experiment 3 is still stable after 11 hours of combustion, however it takes approximately four hours of solid fuel combustion before the process has obtained stability. Some sudden changes occur during all three experiments (Figure 1); the deviations from the outer control limit in experiments 1 and 2 were due to changes in the CO level (CO peaks).

**Table 1.** Combustion conditions, in dry gases, and temperatures,  $\pm 1$  standard deviation, during sampling. The  $NH_3$ ,  $SO_2$  and  $CH_4$  levels were  $<1$  ppm during all three experiments.

	EXP 1 6 Hours	EXP2 6 Hours	2 Hours	4 Hours	EXP3 6 Hours	8 Hours	10 Hours
<b>O<sub>2</sub> (vol%)</b>	11.0	10.6	11.2	11.4	11.0	10.8	10.3
<b>CO<sub>2</sub> (vol%)</b>	9.2	9.1	8.9	8.9	9.2	8.7	8.8
<b>H<sub>2</sub>O<sup>a</sup> (vol%)</b>	7.8	7.9	7.7	7.7	7.9	7.5	7.7
<b>CO (ppm)</b>	4.3	9.8	2.4	1.7	1.3	2.4	6.7
<b>HCl (ppm)</b>	245	258	264	259	263	240	245
<b>NO (ppm)</b>	357	632	356	354	375	357	355
<b>NO<sub>2</sub> (ppm)</b>	23	23	20	21	23	23	24
<b>N<sub>2</sub>O (ppm)</b>	197 <sup>b</sup>	50	55	51	51	50	44
<b>Bed Temp. (°C)</b>	820 $\pm$ 9	834 $\pm$ 13	829 $\pm$ 8	829 $\pm$ 11	834 $\pm$ 9	826 $\pm$ 10	833 $\pm$ 11

<sup>a</sup> Wet gas, <sup>b</sup> This higher level, compared to EXP 2 and 3, may be due to calibration error



**Figure 1.** Combustion conditions in a multivariate control chart for experiment 1, 2 and 3, from 4-7 hours and 4-11 hours of solid combustion respectively. The chart describes the variation from the average variable with 2 and 3 standard deviations as inner and outer control limits. Combustion parameters  $NH_3$ ,  $SO_2$ ,  $CH_4$ , and  $N_2O$  were excluded.

## Thermal processes

The temperature conditions were very similar during all combustion experiments (Table 1). All the temperatures in the laboratory-scale reactor were stable after three hours of solid fuel combustion and five hours of electrical heating; the largest variation could be seen in the bed temperatures. The residence time of the flue gas were 8.1, 12.7 and 16.7 seconds to the temperatures 600, 300 and 200°C respectively; calculated from the elementary content of the fuel, air supply, local temperatures and the volume of the laboratory-scale reactor.

No trends or patterns can be seen for the chlorinated compounds over time during long-term performance (Table 2); they neither increase nor decrease, which holds for all three temperatures (600, 300 and 200°C, respectively). PCDD/F homologues display the typical profile dominated at 200°C by hexa- and heptaCDD [9,10], and tetra- and pentaCDF [11,12], respectively (Figure 2), while at 600°C PCDD/F profiles are dominated by the lowest chlorinated homologues (mo- and diCDD/F). The same increase in the total content and formation with temperature and residence time could be seen for the replicates (experiments 1 and 2). Even the average PCDD/F homologue profiles were the same between combustion experiments. The hxCBz appear to form between 300 and 200°C. For the  $\Sigma$ DIN-PCB [13] no clear trend can be observed according to temperature and residence time. The results from the long-term performance indicate that the ash deposits in the convector section do not emit additional chloroorganic compounds.

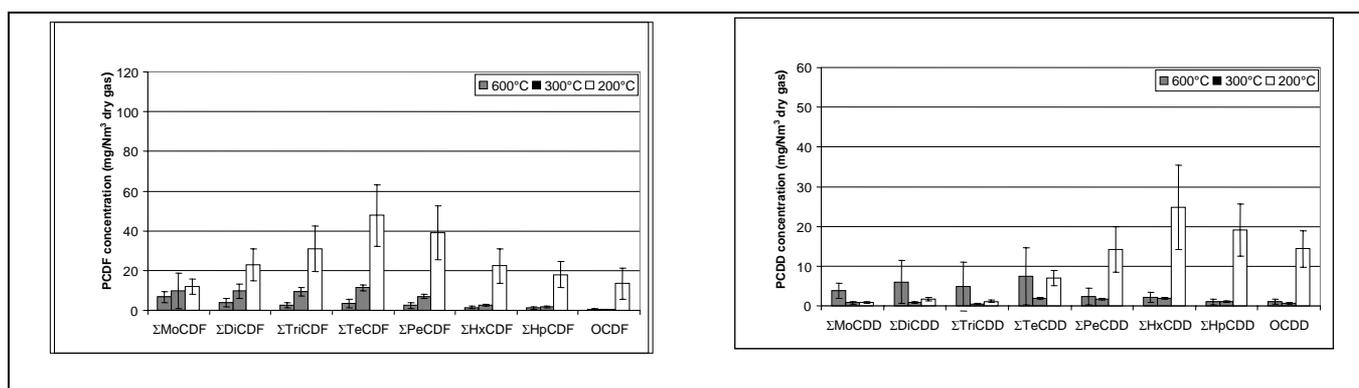
**Table 2.** Total concentrations of mono- to octachlorinated PCDFs and PCDDs (ng/Nm<sup>3</sup> dry gas).  $\Sigma$ DIN-PCB includes PCB congeners 28, 52, 101, 138, 153, and 180. PCB numbering according to IUPAC.

	Sample info		$\Sigma$ PCDF	$\Sigma$ PCDD	$\Sigma$ DIN-PCB	HxCBz
	°C	Hours				
EXP 1	600	6	73	109	28	707
	300	6	108	9.2	23	821
	200	6	289	88	32	3561
EXP 2	600	6	28	5.3	19	35
	300	6	96	12	11	370
	200	6	457	165	36	2557
EXP 3	600	2	17	13	20	50
	300	2	155	16	24	411
	200	2	204	58	17	804
	600	4	9.1	7.4	18	41
	300	4	40	9.3	15	95
	200	4	183	80	23	966
	600	6	18	15	16	31
	300	6	39	9.3	18	115
	200	6	139	54	11	569
	600	8	26	58	16	46
	300	8	47	10	7.9	142
	200	8	185	74	133	778
	600	10	30	27	13	40
	300	10	77	8.8	50	178
	200	10	218	72	24	855

The difference between experiments was in the concentrations of the PCDD, PCDF and hxCBz. No clear differences between experiments in the  $\Sigma$ DIN-PCBs could be noted. The difference in concentration of the PCDD/F between

## Thermal processes

combustion experiments indicates that this combustion system is very sensitive to disturbance. The main factor that differs between combustion experiments is the CO-levels, or specifically number of CO peaks. Although the combustion system itself is stable and able to yield reproducible combustion data, the reactions taking place in the flue gases during cooling are easily affected even by small variations of the fuel load. For this reason, constant manual monitoring of O<sub>2</sub> concentration in the convector, and, when needed, adjustments of air flow, is imperative. Flue gas samples should be collected no sooner than after 3.5-4 hours of MSW fuel combustion, when combustion conditions and temperatures are stable.



**Figure 2.** PCDF and PCDD homologue profiles; average during the long-term performance (experiment 3), sampled at 4-10 hours of MSW fuel combustion. Error bars represent  $\pm 1$  standard deviation.

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