SHORT TERM *DE NOVO* FORMATION OF PCDD/PCDF AND CORRELATION TO POLYCHLORINATED BENZENES AS SURROGATES

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Introduction

Numerous studies in laboratory pilot incinerators focus on the understanding of formation mechanism of PCDD/PCDF. The optimum temperature for *de novo* synthesis in laboratory fixed bed experiments is around 300°C to 370°C[1-3]. However the formation rates in these *de novo* experiments seem not sufficient to explain the actual amount of PCDD/PCDF generated in incinerators. Recently, studies using an entrained flow reactor with a methane combustion carbon source and fly ash showed[4,5] relatively high *de novo* formation rates of PCDD/PCDF. The observed PCDD/PCDF emission was explained by a short term *de novo* synthesis in the second range. On the other hand, other experiments, also using an entrained flow reactor indicated the occurrence of memory effects of PCDD/PCDF formation on the fly ash adsorbed to the furnace wall in the hour range.[6] In this respect it was not clear to which extent the fly ash adsorbed on the furnace wall might have affected the calculated rates in the experimental set-up of the previous experiment.[4,5] Therefore we wanted to clarify the possibility of short term *de novo* synthesis of PCDD/PCDF using an experimental set-up excluding adsorption and memory effects and evaluate the temperature range in which short term formation may occur. Additionally we evaluated the correlation of PCDD/PCDF and polychlorinated benzenes (PCBz) during the *de novo* experiments with respect to the use of PCBz as indicator compounds.

Materials and Methods

Model fly ash was prepared by dry mixing of silica with 0.5 % copper (as $CuCl_2 \cdot (H_2O)_2$) and 0.2 % soot. The soot was originally derived from pyrolysis of refused derived fuel (RDF) in a laboratory fluidized bed incinerator. The reactor consisted of an open quartz ampoule (25 cm; 1.5 cm id.). The reactor was placed into an oven vertically (TMF 2000, Eyela, Japan) and preheated to the respective temperatures of the experiments. The entire model fly ash (50 mg) was fed into the reactor at the start of the respective experiment. Pre-tests with a temperature sensor at the bottom of the reactor (within the ash) showed a decrease of 10-15 °C when dropping the fly ash into the furnace. Within approximately 3 seconds the sensor was back to the set temperature indicating a heat-up time of the fly ash in this time range. After the respective reaction time, the fly ash was removed by turning the reactor and quenching the fly ash on a cold plate.

Results and discussion

Short term *de novo* synthesis of PCDD/PCDF was already observed within 10 seconds at 350 °C (Figure 1). Increasing the temperature to 400 °C, the formation of chlorinated aromatics tremendously increased and showed a maximum formation at 500 °C within the 10 seconds residence time. At the 300 °C (10 seconds) PCDD/PCDF were not detected whereas a maximum yield of 6520 ng/g PCDF and 675 ng/g PCDD was formed on the model fly ash via "conventional" *de novo* synthesis within 60
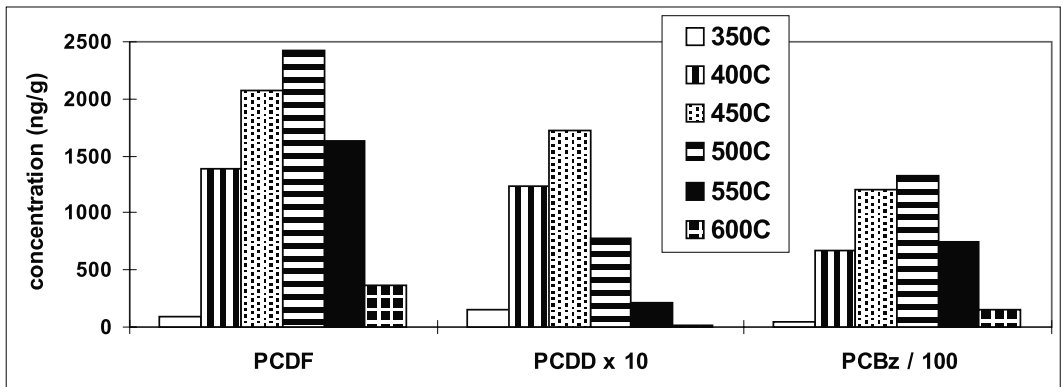
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Figure 1. Temperature dependence of formation of PCDD, PCDF and PCBz in short term *de novo* synthesis (10 seconds).

minutes (300 °C).

We investigated the time dependence of PCDD/PCDF formation at 500 °C (Figure 2). Already after 3 seconds[1] residence time 1870 ng/g PCDF were detected. Within 10 seconds the maximum PCDF amount was formed (2420 ng/g). Prolonging the experimental time to 60 seconds resulted in a decrease of PCDF (1850 ng/g) and after 5 minutes only 750 ng/g PCDF were detected (Figure 2). The observed time and temperature dependence of PCDD/PCDF can be explained by the dual property of fly ashes to catalyse the formation and destruction of chlorinated aromatics (PCDD/PCDF, PCBz, PCB etc.).[3] At 500 °C the PCDD/PCDF destruction outweighed the PCDD/PCDF formation already within 60 seconds in the model fly ash system.

Relevance of short term de novo synthesis for incinerators

Some observed PCDD/PCDF emission behaviour in full scale incinerators are difficult to explain by short term formation rates within seconds:

• memory effects of PCDD/PCDF emission in the high temperature/cooling zones lasting for several hours after disturbed combustion condition[7] in an hazardous waste incinerator.

• the observed time shift in the correlation of CO and PCDD/PCDF emission[8] in a fluidized bed municipal waste incinerator.

In this respect it is interesting to evaluate the significance of short term *de novo* synthesis in full scale incinerators.

Correlation of PCDD/PCDF and PCBz formation during short term de novo synthesis

Several chlorinated aromatic compounds are proposed as indicators for an estimation of PCDD/ PCDF (TEQ) emission from incinerators. PCBz are discussed as one practical surrogate in this respect.[9,10] However, a correlation of indicator compounds and PCDD/PCDF (TEQ) are not well developed with respect to the formation mechanism of chlorinated aromatics.

The formation of PCBz in the present short term *de novo* synthesis proceeded in parallel to the PCDF formation along the whole temperature range (Figure 1 and 3). The total amount of monoCBz to hexaCBz formed were 30 to 60 times higher compared to PCDD/PCDF (Figure 3+4). This ratio is

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[1] "3 second" residence time was the shortest practical residence time from the experimental procedure. However, it is difficult to estimate which temperature the fly ash actually reached within this short time frame. However the actual residence time (temperature) was shorter (lower) than the assigned 3 seconds (500 °C).
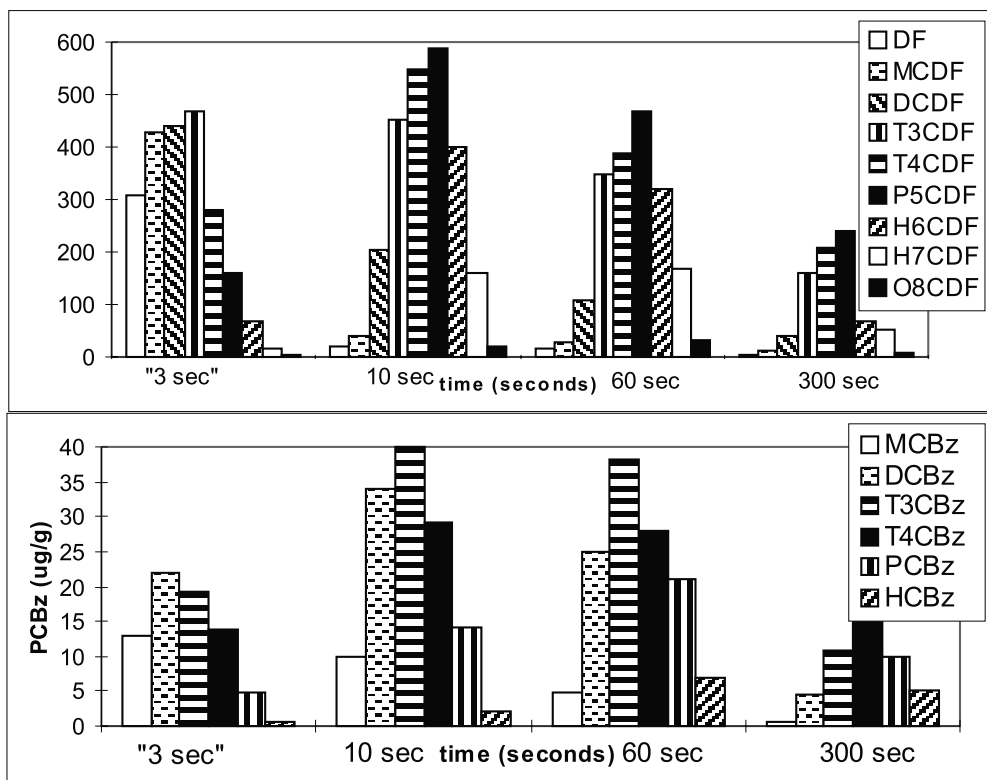
Figure 2. Time dependence of *de novo* formation of PCDF and PCBz at 500°C.

within the range observed in municipal waste incinerators were PCBz are normally detected in one to two orders of magnitude higher concentration compared to PCDD/PCDF.[11] Figure 2 B show the PCBz amount formed during the experiments at 500°C in dependence of time. Similar to PCDF, the PCBz showed a decrease for prolonged residence times. Therefore the final amount of PCBz is determined by formation and destruction similar to PCDF (and PCDD; see below). Furthermore, the homologue shift of PCBz were analogous to the shift observed with PCDF (Figure 2). Therefore the chlorination behaviour in the present *de novo* experiment of PCBz was similar to that of PCDF.

The formation behaviour of PCDD however showed differences compared to PCBz and PCDF. The ratio of PCBz to PCDD depended on the temperature (Figure 3). Above 450 °C only small amounts of PCDD were formed. The PCBz to PCDD ratio increased from 470 (at 350 °C) to 5200 (at 600 °C).

The stable ratio of PCDF (contributing to more than 80 % of TEQ) and PCBz resulted in a stable ratio of PCBz and the total TEQ (Figure 3+4). The slightly higher ratio of PCBz and TEQ at the minimum residence time (3 seconds) (Figure 4) can be explained by the low chlorination degree of PCDF congeners in the early *de novo* phase with a lower impact of TEQ relevant P_5CDF and H_6CDF (Figure 2).

In municipal waste incinerators the PCDF normally contribute to more than 50 % of total TEQ (and to our experience can contribute up to 80 % of TEQ). The results of the present study suggest that a correlation of PCBz and PCDD/PCDF (TEQ) can be understood/developed on the base of formation
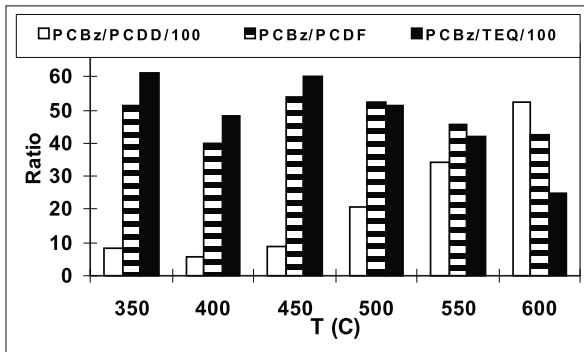
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Figure 3. Temperature dependency of the correlation between PCBz and PCDD, PCDF and TEQ (10 seconds residence time).
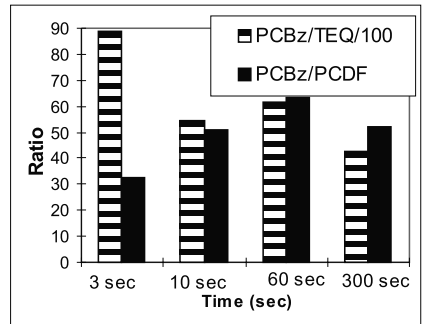
Figure 4. Time dependence of the correlation of PCBz to PCDF and to TEQ (500°C).

mechanism. However more work is necessary to evaluate which parameters effect the correlation of indicator compounds and PCDD/PCDF (TEQ) in large scale incinerators (including mechanistic aspects).

Acknowledgement

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