Comparison of 2,4,6-Trichlorophenol Conversion to PCDD/PCDF on a MSWI - Fly Ash and a Model Fly Ash

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1. Introduction

PCDD/F and other chlorinated aromatic substances are mainly formed in thermal processes in MSWI by heterogeneous reactions. These reactions can be divided into two classes:
i) oxidative degradation of carbon, the so called de-novo-synthesis [1,2,3]
ii) reactions of precursors e.g. chlorophenols, chlorobenzenes, chlorobiphenyls etc. on fly ash [4,5,6,7,8,9] while these precursors can be formed themselves de-novo from carbon.
Among the variety of precursors, chlorinated phenols seem to be the most reactive substances with respect to the formation of dioxins. Thermal experiments with ^{13}C-pentachlorophenol, 2,4,5- and 2,3,4-Cl_3Ph on Ontario fly ash demonstrated that chlorophenols are capable of forming dioxins on fly ash and that the isomer pattern of the PCDD is dependent on the chlorophenol used [4,5].
A series of experiments with chlorophenols and different fly ashes showed that 2,3,4,6-Cl_4Ph has the highest capability to form dioxins for a specific set of conditions [7], but gave very low furan yields.
This contribution describes the results of a detailed investigation of the formation of PCDD/F on a municipal solid waste incinerator (MSWI) fly ash obtained from the USEPA (United States Environmental Protection Agency; termed EPA fly ash) and a model fly ash as a function of the concentration of 2,4,6-Cl_3Ph. The precursor was administered in two different ways:
a) vaporization from a reservoir into the gas stream entering the fly ash bed
b) mixed as a solid substance with the fly ash.
We have chosen 2,4,6-Cl_3Ph as precursor for our investigations because some measurements of volatile organic compounds in emissions of a MSWI showed that this compound has the highest concentration (ca. 10 $\mu g/m^3$ = 0.01 ng/mL) among the chlorophenols [10].
In addition, we observed in previous studies with model fly ashes doped with ^{12}C- and ^{13}C-carbon only the 2,4,6-Cl_3Ph isomer among the trichlorinated phenols produced [11]. This compound formed via de-novo from carbon is the likely intermediate molecule in the formation of PCDD. Most probably two of the main tetrachlorinated dioxins: 1,3,6,8- and 1,3,7,9-T4CDD are formed (at least partly) through condensation of 2,4,6-Cl_3Ph.

2. Experimental Methods

The experiments were performed with an apparatus similar to that described earlier [7]. The EPA fly ash (sieve fraction with diameter < 200 μm) was pre-extracted with toluene for 24 hours to remove native precursors as well as PCDD/F. A much higher precursor concentration than typically found in incinerators (ca.10^4 higher) was chosen. This ensured that the amounts of

PCDD/F formed from residual carbon were negligible compared to the PCDD/F due to condensation reactions of added chlorophenol.

For the preparation of the model fly ash following substances were mixed: 842.3 mg florisil (mesh 60-100) as matrix, 147 mg KCl as chlorine source and 10.7 mg $CuCl_2*2\ H_20$ as catalyst. Florisil itself consists of SiO_2 (85 %) and MgO (15 %).

The fly ashes (EPA and model fly ash) were mixed with glass beads (diameter < 200 µm) in order to enhance the potential for operating the reactor in the differential mode e.g. only small conversion of the added precursor. The glass beads were analyzed earlier and their inactivity in PCDD/F formation proven [7]. For the thermal experiments we used 2 g samples which contained 0.2 g fly ash and 1.8 g glass beads.

Heating a reservoir containing the precursor to different temperatures produced different concentrations of the precursor in the gas stream. As gas phase we used 10 % oxygen in nitrogen. The concentration of gaseous 2,4,6-Cl_3Ph ranged between 2 and 470 ng 2,4,6-Cl_3Ph/mL gas phase. With a gas flow of 80 mL/min and a reaction time of 30 min the lowest concentration of 2,4,6-Cl_3Ph in the gas phase led to a total input of 4.8 µg 2,4,6-Cl_3Ph, while the highest concentration of 2,4,6-Cl_3Ph in the gas phase led to a total input of 1200 µg 2,4,6-Cl_3Ph. When solid chlorophenol was mixed with the fly ash a range of concentrations, 200 - 1000 µg/0.2 g fly ash, was used.

The volatile compounds were collected in an ice cooled impinger filled with dichloromethane. After spiking the solution of the impinger and the fly ashes with 2,6-dichloro-4-fluorophenol and ^{13}C-dioxin internal standards, the fly ashes were extracted with toluene for 24 hrs. The solutions of the impinger and the soxhlet extracts were cleaned up separately and analyzed by HRGC-LRMS for PCPh and PCDD/F.

3. Results and Discussion

3.1. Formation of PCDD/F on EPA Fly Ash as a Function of the Concentration of 2,4,6-Trichlorophenol in the Gas phase

A series of experiments using 0.2 g of EPA fly ash mixed with 1.8 g of inactive glass beads were run at 300 °C with 2,4,6-Cl_3Ph concentrations ranging from 0 to 470 ng/mL in 10 % O_2 / 90 % N_2 for 30 min.

The concentrations of PCDD (left y-axis) and PCDF (right y-axis) in ng/g EPA fly ash versus concentration of 2,4,6-Cl_3Ph in the gas stream are depicted in Figure 1. (Note that the scaling factors between the left and right y-axes differ by a factor of 100). Without added precursor EPA fly ash yielded 1800 ng PCDD and 1225 ng PCDF/g EPA fly ash and negligible amounts of 2,4,6-trichlorophenol compared with the bulk amounts used as precursor. These products stemmed from the de-novo-synthesis from residual carbon.

At a chlorophenol concentration of 18 ng/mL 75 % of the PCDD produced stemmed from the precursor and 96 % at a chlorophenol concentration of 186 ng/mL.

The PCDD/PCDF ratio without added precursor was 1.5. For the range of chlorophenol concentrations used the PCDD/PCDF ratio increased from 5.4 at 18 ng 2,4,6-Cl_3Ph/mL gas phase to 74 at 467 ng/mL and 85 at 400 ng/mL. In the whole concentration range (0- 467 ng Cl_3Ph/mL gas phase) the concentrations of PCDF were about 100 times lower than the concentrations of PCDD.

It is interesting to note that the shape of both curves are very similar. This suggests that the intermediate(s) in the formation of PCDF are the same as for the PCDD assuming that formation of the intermediate(s) is the rate limiting reaction. As the PCDF concentrations are very low a distinction between the isomers formed from residual carbon and from the precursor was not possible. The concentration of PCDD is highest for chlorophenol concentrations ranging between 200 and 400 ng/mL. The nominal reaction order in Cl_3Ph appears to be about 1.75.

At high chlorophenol concentrations the curve seems to flatten out, from that can be concluded that the fly ash has a limited potential for dioxin formation or that other side reactions predominate.

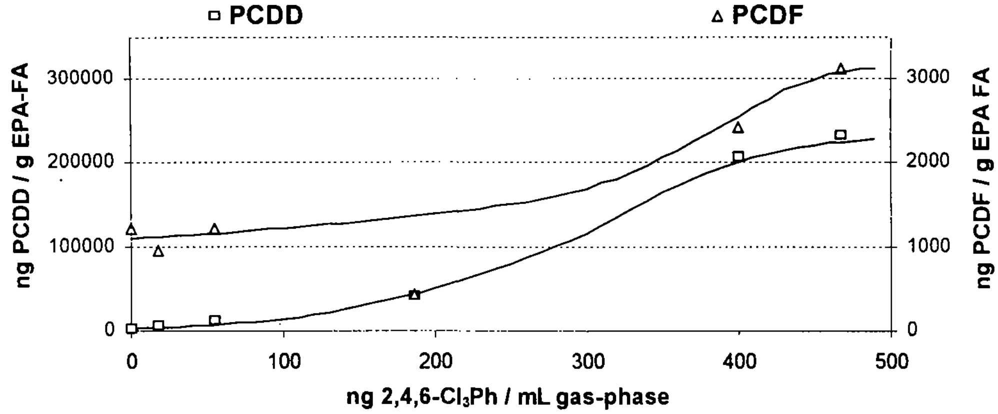

Figure 1. *PCDD and PCDF yields on EPA fly ash as a function of the concentration of 2,4,6-*Cl_3Ph *in the gas stream. 10 % EPA fly ash, 90 % glass beads, 10 %* O_2, *90 %* N_2, *flow rate = 80 mL/min, reaction time = 30 min, reaction temperature – 300 °C.*

The amount of PCDD in the gas phase increased with the chlorophenol concentration while the concentration of PCDD in the solid phase remained nearly constant. As expected from the number of chlorines attached to the phenol the concentrations of dioxins decreased from T4CDD to O8CDD. With increasing concentration of 2,4,6-Cl_3Ph the chlorination degree shifted towards T4CDD. This might be explained by assuming a competition between 2,4,6-Cl_3Ph and chlorinated dioxins for catalytic sites: the higher the chlorophenol concentration the higher the tendency for adsorbed chlorinated dioxins to be displaced against more strongly adsorbing chlorophenols or polymerization products. Desorption of a low chlorinated dioxin would interrupt the chlorination sequence thus lowering the relative amounts of P5CDD to O8CDD compared with those of T4CDD.

In the experiment with EPA fly ash without added chlorophenol a typical de-novo isomer pattern was observed while from chlorophenol a precursor pattern was obtained, i.e. 1,3,6,8-, and 1,3,7,9-T4CDD, 1,2,4,6,8-/1,2,4,7,9-, 1,2,3,6,8- and 1,2,3,7,9-P5CDD and 1,2,3,4,6,8-H6CDD. With exception of the experiment with the lowest chlorophenol concentration (18 ng/mL gas phase) the fraction of the two T4CDD isomers added up to more than 92 % of the total amount of tetradioxins. Similar results were observed for the four pentadioxins: 1,2,4,6,8-, 1,2,4,7,9-, 1,2,3,6,8- and 1,2,3,7,9-P5CDD, while each of these isomers was formed in nearly the same amount. The two pentadioxins: 1,2,4,6,8- and 1,2,4,7,9-P5CDD, were not separated on the DB-5 column. Among the hexadioxins 1,2,3,4,6,8-H6CDD dominated with a concentration of about 65 % of the total amount of hexadioxins.

The formation of the main tetradioxins can be easily explained by condensation of two 2,4,6-Cl_3Ph molecules either directly or via a Smiles rearrangement while 2 molecules HCl are eliminated. The formation of the higher chlorinated main dioxin isomers can proceed via two pathways: condensation of higher chlorinated chlorophenols (which would result from chlorination of 2,4,6-Cl_3Ph) or further chlorination of the produced T4CDD – H7CDD. With the data received a distinction between the two mechanism was not possible.

3.2. Formation of PCDD/F on Model Fly Ash as a Function of the Concentration of 2,4,6-Trichlorophenol in the Gas phase

The thermal experiments with model fly ash were conducted using conditions identical to those for EPA fly ash. As already noted for the EPA fly ash, PCDF concentrations were at least two orders of magnitude smaller than those of PCDD; only with high gas phase concentrations of 2,4,6-Cl_3Ph were small amounts of PCDF obtained.

Again it seems that the reaction rate for PCDD is maximal for chlorophenol concentrations between 150 and 350 ng/mL. The main PCDD isomers were identical with those formed on the EPA fly ash. The two main tetrachlorinated isomers and the four pentachlorinated isomers added up to more than 98 % of the total amount of tetradioxins and pentadioxins. The 1,2,3,4,6,8-H6CDD constituted more than 75 % of the total amounts of the hexadioxins.

Among the PCDF mainly following isomers were formed: 2,3,6,7-; 2,4,6,8-; 2,4,6,7-; and 1,3,6,8-T4CDF; 2,3,4,6,7-; 1,3,4,6,8-; 1,2,4,6,8-;1,2,6,7,8-; and 1,2,3,7,9-P5CDF; 1,2,3,4,6,8- and 2,3,4,6,7,8-H6CDF; 1,2,3,4,6,7,8- and 1,2,3,4,6,7,9-H7CDF.

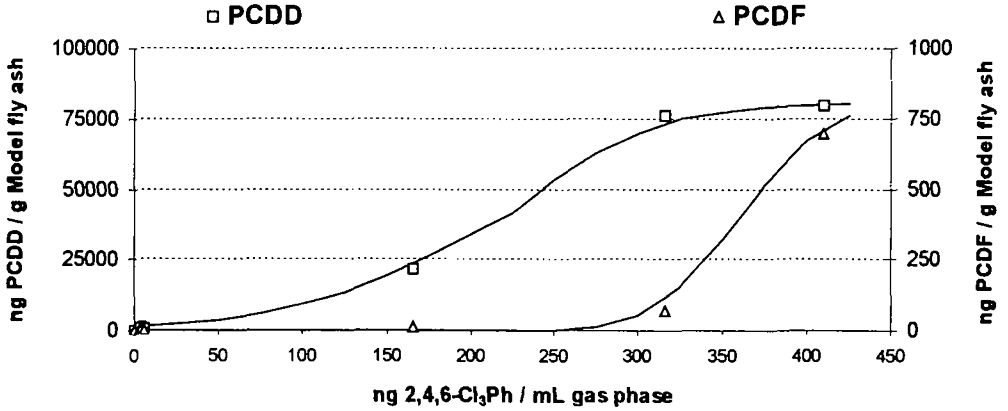

Figure 2. PCDD and PCDF yields on model fly ash as a function of the concentration of 2,4,6-Cl_3Ph in the gas stream. 10 % model fly ash, 90 % glass beads, 10 % O_2, 90 % N_2, flow rate = 80 mL/min, reaction time = 30 min, reaction temperature = 300 °C.

3.3. Comparison of the Two Different Techniques of Spiking Fly Ashes with 2,4,6-Trichlorophenol as Precursor

A series of runs was performed with EPA fly ash and model fly ash doped with solid 2,4,6-Cl_3Ph prior to the experiments. The amounts of the precursor were selected in such a manner that they corresponded to the total amounts of 2,4,6-Cl_3Ph which were used in the experiments described in 3.1 and 3.2. (e.g. a concentration of 400 ng 2,4,6-Cl_3Ph/mL during a reaction time of 30 min. and with a gas flow of 80 mL/min. led to a total input of 960 µg/0.2 g, or 4800 µg/g). The other experimental conditions remained unchanged. The two techniques differ in the method of adding the precursor to the fly ash:

a) the precursor was flushed continuously at a constant flow and concentration through the fly ash or
b) the precursor was mixed prior to the experiment with the fly ash.

EPA fly ash and model fly ash (see Figure 3.) show similar features: in both cases the yield of dioxins of 2,4,6-Cl_3Ph was higher when the precursor entered the fly ash bed with the gas stream compared to mixing it as a solid compound with the fly ash. For EPA fly ash the yield of dioxins when using gaseous 2,4,6-Cl_3Ph in higher concentrations was about six times greater versus spiking the ash with solid precursor before the thermal treatment. For the model fly ash this increase was higher by a factor of three.

When the 2,4,6-Cl_3Ph was mixed as a solid with the fly ash, reactions like polymerization or oxidation to CO_2 and CO may be more pronounced than when the gaseous precursor was passed through the fly ash bed. This might be due to the prolonged reaction time of the precursor on fly ash. The average yield of PCDD on EPA fly ash amounted to (6.2 ± 3) % [(for model fly ash: 2.2 ± 1 %)] when the chlorophenol was evaporated into the inlet gas stream and to (0.9 ± 0.5) % [(for model fly ash: 0.7 ± 0.1 %)] when the precursor was mixed as a solid substance with the fly ash before the experiment.

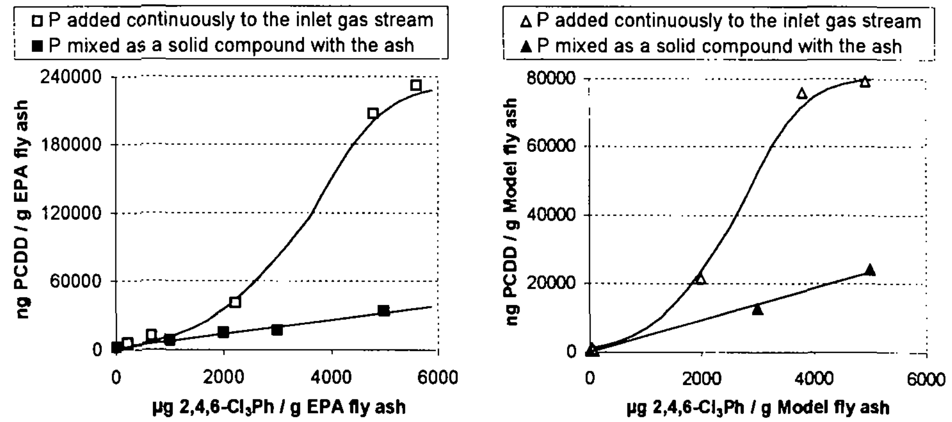

Figure 3. PCDD yields on EPA fly ash and model fly ash as a function of the total input of 2,4,6-Cl_3CPh. 10 % model fly ash, 90 % glass beads, 10 % O_2, 90 % N_2, flow rate = 80 mL/min, reaction time = 30 min, reaction temperature = 300 °C.

4. Conclusions

- In this study we showed that 2,4,6-Cl_3Ph (concentration range between 0 and 5000 µg 2,4,6-Cl_3Ph/g EPA or model fly ash) is a very reactive precursor in PCDD formation, whereas it plays only a minor role in the formation of PCDF. The concentrations of PCDF were about two orders of magnitude smaller than those of PCDD.
- Although the EPA fly ash was diluted tenfold with inert glass beads in order to promote differential reactor conditions (i.e. small conversion of the precursor) they were in fact not obtained. The conversion of the phenol ranged between 35 and 90 % on EPA fly ash as well as on model fly ash so that the true reaction order in chlorophenol could not be ascertained. Lower precursor concentrations and greater dilution of the fly ashes with glass beads appear to be necessary to achieve lower conversions.
- In the experiments in which the phenol was evaporated from a reservoir into the gas phase the PCDD concentrations are comparable to those found on Ontario fly ash with 2,3,4,6-Cl_4Ph as precursor, the other reaction conditions being the same. On Ontario fly ash 2,4,6-Cl_3Ph was about six times less reactive than 2,3,4,6-Cl_4Ph. This result suggests that EPA fly ash is more reactive than Ontario fly ash.
- EPA fly ash was about three times more reactive in the formation of PCDD from 2,4,6-Cl_3Ph than our composed model fly ash. Altogether both matrices showed similar behavior in PCDD/F formation from 2,4,6-Cl_3Ph. On EPA fly ash as well as on model fly ash the PCDD/PCDF ratio was >> 1. Thermal experiments with a $CuCl_2$-doped alumina and gaseous trichlorophenol led to a PCDD/PCDF ratio of about 0.7. From that it can be concluded that the nature of the surface influences the PCDD/PCDF ratio.

Acknowledgements

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