FORM

The influence of the oxygen concentration on PCDD/PCDF formation during de novo synthesis on fly ash.

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Introduction
Oxygen is essential for formation of PCDD/F from carbon on fly ash. Oxidative breakdown of the macromolecular carbon structure, which results in formation of PCDD/F, occurs only in the presence of oxygen.[1] It is not clear whether the oxygen used is actually built into the DD/F aromatic ring structure or only serves to release small molecules from carbon which already contain oxygen and subsequently form PCDD/F. In this paper we have investigated PCDD/F formation in a mixture of carbon and Municipal Waste Incinerator fly ash as a function of the O_2 concentration. We look at total amounts of PCDD/F formed, [PCDD] : [PCDF] ratios, congener distribution and isomer composition.

Experimental
Only essential data are given here, experimental details and clean up have been described elswhere.[2] Fly ash (96.4%), carbon (1.5%) and NaCl (2.1%) were mixed by shaking. From the fly ash (MWI Zaanstad, The Netherlands) all organic material had been removed previously. 2.0 g of this mixture was placed in a cylindrical sample basket and coupled with a glass inlet tube for introduction of a gas flow through the fly ash bed. Sample basket and inlet tube were placed in a horizontal pyrex glass reactor, which had been pre-heated in a tube furnace for 30 min. All experiments were performed in duplo for 50 min at 348 °C (accuracy ± 7 °C). Blank controls were made of fly ash, carbon and NaCl. Starting materials contained 2.9 ppb Σ PCDD/F. A gas stream (205 ± 4ml/min N_2 and 0-20 ml/min O_2) was passed through the fly ash bed. Products evaporating from the fly ash surface were collected using a cold trap (80 ml toluene cooled with ice). $^{13}C_{12}$-1,2,3,7,8,9-H6CDD was used as a recovery standard. Average recoveries were (per isomer group): T4CDD 32%, T4CDF 21%,

P5CDD 28%, P5CDF 27%, H6CDD 37%, H6CDF 36%, H7CDD 39%, H7CDF 38%, OCDD 54%.

Results and discussion

In table 1 results are presented of PCDD/F formation when varying the total percentage of O_2 between 0-10 % (defined as [mass flow O_2]/ [mass flow O_2 + mass flow N_2]). In pure nitrogen almost no formation of PCDD/F is observed. In these experiments the total amount of PCDD/F was 1.1 ± 0.3 ng/g fly ash, which is even less than the 2.9 ng/g present in the starting materials (fly ash, carbon, NaCl). Already at 1% O_2 there is a drastic increase of formation with 265 ± 49 ng/g of PCDD/F formed. This is in agreement with the results of H. Vogg et al., who also found an increase in the PCDD/F content of original fly ash (i.e. fly ash which has not been treated after sampling and thus still contains all organic material formed during waste incineration, including PCDD/F) when heating a sample at 300 °C for two hours under a mixture of 1% O_2 in N_2.[3] Note that during our experiments only carbon is present as organic material, whereas original fly ash contains macromolecular carbon but also chlorinated precursors for PCDD/F formation like chlorophenols and chlorobenzenes.

At higher O_2 concentrations the level of PCDD/F formation rises but there is no linear relationship. When setting the total amount of PCDD/F formed at 1% O_2 at 1, relative amounts formed at the other percentages are: 1.6±0.3 at 2%, 2.2±1.1 at 5% and 3.3±1.1 at 10%. Due to the variance between duplo experiments there is an overlap in the relative amounts. One valid conclusion is that more formation takes place at 10% than at 2%. The rise of formation with increasing percentage of O_2 can also be taken seperately. For PCDD at 10% O_2 11.1±5.5 more is formed than at 1% O_2, whereas for PCDF at 10% O_2 formation is 3.0±0.9 times greater than at 1% O_2. Apparently the formation of PCDD, which contains two oxygen atoms, is slightly more sensitive to the O_2 concentration than PCDF containing only one oxygen atom. This results in a somewhat higher [PCDD]:[PCDF] ratio with increasing O_2. This fact has also been observed by Vogg.[3]

The congener distribution of PCDF is presented in figure 1. At percentages of 2 and 5% O_2 there is a small shift in the congener pattern towards higher chlorinated (hexa-octa) congeners. For 10% this tendency is less clear due to the variance between duplo experiments. The presence of more O_2 can stimulate the Deacon reaction according to:

$$2\ HCl + 1/2\ O_2 \text{----}> H_2O + Cl_2$$

This results in the formation of more Cl_2 and could explain the observed shift towards hexa-octa CDF but is not seen with PCDD; that congener distribution remains more

Table 1, yield of PCDD/F in ng/g fly ash at 0-10% O_2. (a)

	0%	1%	2%	5%	10%
Σ PCDD	0.2 ± 0.1	9.0 ± 2.0	19 ± 2	40 ± 21	89 ± 27
Σ PCDF	0.9 ± 0.2	256 ± 47	394 ± 6	489 ± 155	724 ± 91
Σ PCDD + PCDF	1.1 ± 0.3	265 ± 49	413 ± 8	529 ± 176	813 ± 118
[PCDD]: [PCDF]		0.034 ± 0.001	0.047 ± 0.003	0.075 ± 0.015	0.121 ± 0.021

(a): All experiments 96.4% fly ash, 2.1% carbon, 1.5% NaCl, 50 min at 348 ± 7 °C, N_2 205 ± 4 ml/min, O_2 0-20 ml/min, in duplo, mean value ± range.

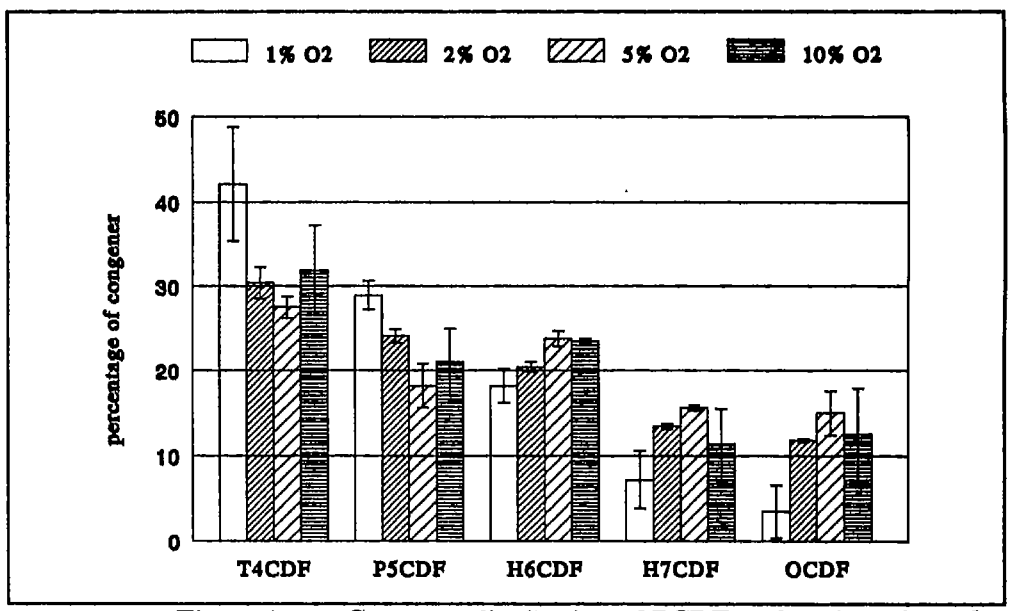

Figure 1 Congener distribution of PCDF as function of the O_2 concentration.

or less equal. If PCDD and PCDF are formed in separate pathways with a different reaction order in [Cl_2], that would explain why PCDF shows a small and PCDD no apparent shift in the congener pattern.

The isomer distribution within isomer groups in our experiments can be compared with our original fly ash. Three 3,4,6,7-substituted PCDF congeners and one 3,4,6,7-substituted PCDD congener are formed in higher concentrations than on the original fly ash. These are 3,4,6,7-T4CDF (varies between 30-70% compared to 12±3% in original fly ash), 2,3,4,6,7-P5CDF (24-56%, original fly ash 22±7%), 1,2,3,4,6,7-H6CDF (16-25%, original fly ash 12±1%) and 1,2,3,4,6,7-H6CDD (15-45%, original fly ash 7±1%). Maximum percentages are found at 2% O_2 for all these four PCDD/F congeners. Thus the carbon/fly ash mixture used in these experiments has a tendency for formation of 3,4,6,7-substituted PCDD/F congeners. This tendency is also dependent on the O_2 concentration.

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