

Influence of H₂O and HCl on the formation of polychlorinated dibenzo-p-dioxins/dibenzofurans in a carbon/fly ash mixture.

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Introduction

In earlier studies we have reported on PCDD/F formation from carbon on various surfaces and at increasing reaction times and temperatures.^{1,2,3} In this short paper the influence of H₂O and HCl on PCDD/F formation on MWI fly ash is described. We have studied de-novo synthesis with and without water present. In a series with HCl we have looked at the optimum temperature for formation.

Experimental

From fly ash (MWI Zaanstad) all organic material was removed. The fly ash was mixed subsequently with circa 2% carbon (Aktivkohle Darco G-60, 100-325 mesh). 2.0 g of the 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. The whole system was then placed in an oven. Each experiment (60 min, in duplo) was preceded by 30 min of heating without a gas flow in order for the sample basket, inlet tube and reactor to reach the setpoint temperature (300-400 °C, accuracy ± 6 °C). A gas stream (73 vol.% N₂, 8 vol.% O₂, 19 vol.% H₂O or 85 vol.% N₂, 10 vol.% O₂, 4 vol.% HCl) was then introduced. The gas flow was controlled by Series 840 Side=Trak™ mass flow controllers. The various gases were mixed in a mixing chamber (V=800 ml) containing ceramic pellets. Products evaporating from the fly ash surface were collected using a cold trap (60 ml toluene cooled with ice). After the experiment the fly ash surface was extracted with a 3% HCl solution, dried overnight, spiked with 200 µl [13-C] PCDD/F mix as an internal standard for quantification, and soxhlet extracted with 400 ml of toluene (together with the toluene fraction from the cold trap) for 24 hrs. The extract of toluene was subjected to open column chromatography and preparative HPLC during which the OCDF is separated from the other PCDD/F. The sample was finally analysed by GC/MSD.

Results and discussion

Table I, yields of PCDD/F in ng/g fly ash.

Exp. no.	Temperature	Σ PCDD	Σ PCDF	[PCDD]/ [PCDF]
1 (a)	20-348 °C	20 \pm 10	570 \pm 170	(0.02-0.05)
2 (b)	348 °C	220 \pm 50	1650 \pm 80	(0.10-0.17)
3 (c)	348 °C	160 \pm 5	1390 \pm 250	(0.10-0.14)
4 (d)	20 °C	0.4 \pm 0.1	9 \pm 9	
5 (e)	298 °C	60 \pm 20	260 \pm 20	(0.17-0.35)
6 (e)	323 °C	440 \pm 20	1060 \pm 250	(0.32-0.57)
7 (e)	348 °C	1210 \pm 590	3150 \pm 400	(0.23-0.51)
8 (e)	373 °C	1390 \pm 160	6260 \pm 150	(0.20-0.24)
9 (e)	398 °C	1380 \pm 120	5410 \pm 100	(0.24-0.27)

a: 2.0 g fly ash, 2.0% carbon, no gas flow, sample heated from 20 to 348 °C during 30 min, mean of three experiments.

b: 2.0 g fly ash, 2.0% carbon, gas flow N₂ 103 \pm 1 ml/min, O₂ 12 ml/min and H₂O (vapour) 27 ml/min, reaction time 60 min, mean of two experiments.

c: Same as under b, but no water present.

d: 2.0 g fly ash, 2.0% and 2.2% carbon, gas flow N₂ 103 \pm 1 ml/min, O₂ 12 ml/min and N₂ 99 \pm 1 ml/min, O₂ 12 ml/min, HCl 5 \pm 0.2 ml/min, reaction time 60 min, mean of two blank experiments.

e: 2.0 g fly ash, 2.2% carbon, gas flow N₂ 99 \pm 1 ml/min, O₂ 12 ml/min, HCl 5 \pm 0.2 ml/min, reaction time 60 min, mean of two experiments.

Table I gives an overview of the experiments. Experiment 1 shows that PCDD/F formation can take place in a carbon/fly ash mixture without oxygen. No gas flow was present during this experiment. Note that the temperature increased during the experiment from 20 to 348 °C. Oxygen for PCDD/F formation could come from the carbon used (e.g. functional groups) or the inorganic fly ash matrix. It could also be adsorbed on the fly ash surface, and thus be available for reactions. The [PCDD]/[PCDF] ratio is lower than when a gas flow is present (cf. exp. 1 vs. 2-9). Apparently PCDF formation is favoured under these conditions.

The presence of water does not exert an influence on the total amount of PCDD/F formed (cf. exp. 2 and 3), which is in contrast with results found by Stieglitz et al.⁴ They found more PCDD/F with carbon/fly ash at 300 °C in the presence of water. There is a difference in the distribution over the various congeners of PCDD (figure 1,

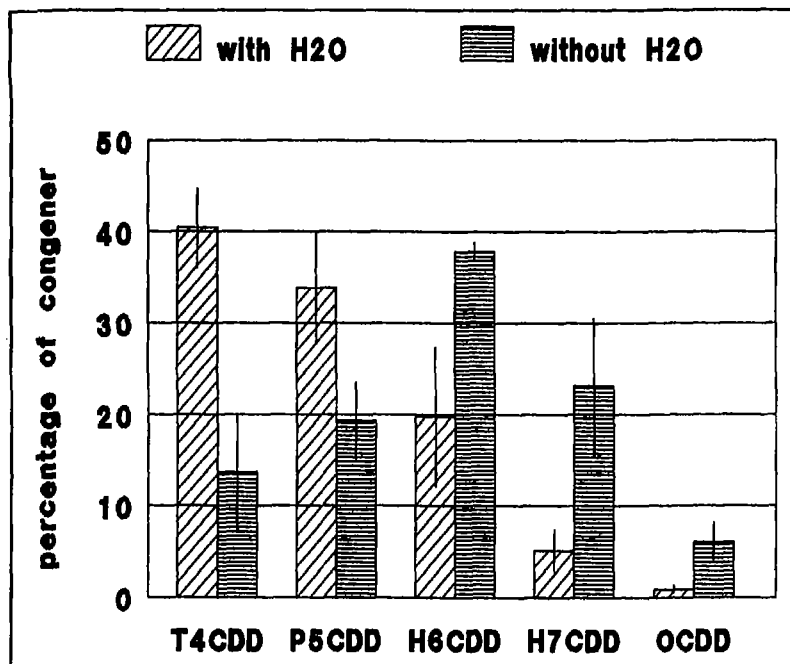


Figure 1 Congener distribution of PCDD with and without water.

(Σ PCDD=100%). More lower chlorinated species are formed with water. For PCDF the congener distribution showed too great a variance between duplo experiments to draw conclusions from. Water has no effect on the isomer distribution of the PCDD/F formed, as is illustrated in figure 2 (Σ H6CDF=100%). This is also seen with the other isomer groups. Thus the typical fly ash pattern, which contains all tetra-octa isomers possible, is preserved and the formation remains non-selective.

When using HCl as a chlorinating agent the optimum temperature for PCDD/F formation lies around 373 °C. Schwarz et al have reported two optimum temperatures for formation- 300 °C and 470 °C - using extracted fly ash (thus only containing residual carbon) heated in synthetic air/water vapour.⁵ These differences indicate that the optimum temperature depends on the reaction conditions employed and the fly ash used.

Formation of hepta-octa congeners is strongly favoured in HCl. The Σ H7CDD-OCDD increases from 58 ± 10 % (relative to Σ PCDD=100%) at 298 °C to 98 ± 0 % at 398 °C. For the PCDF congeners Σ H7CDF-OCDF (Σ PCDF=100%) is 30 ± 17 % at 298 °C and 86 ± 0 % at 398 °C.

Within isomer groups the distribution does not change when increasing the reaction temperature. Differences found are small. The increase in formation of 1,2,3,4,6,7,8-H7CDF (61 ± 2 % at 298 °C to 81 ± 0 % at 398 °C, Σ H7CDF=100%) is an exception.

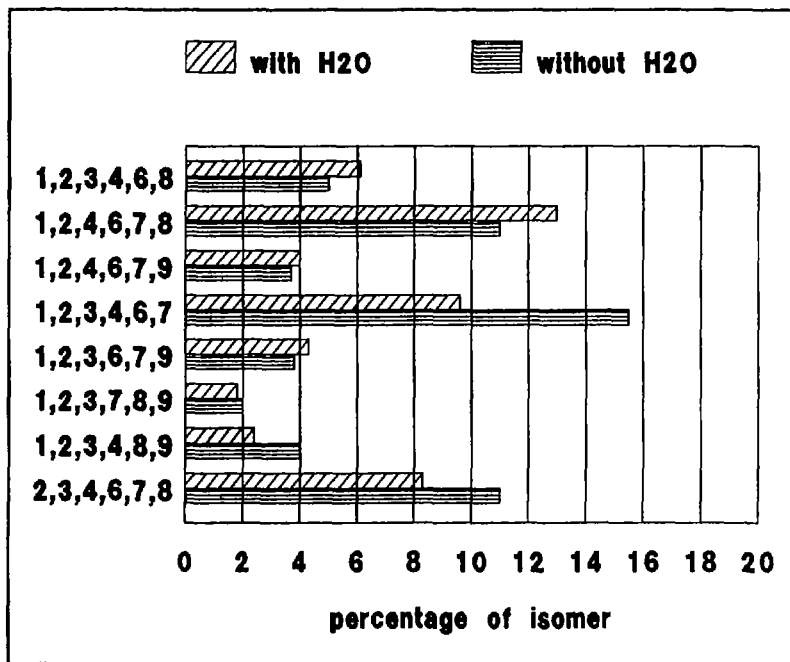


Figure 2 Isomer distribution of H₆CDF with and without water.

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