

Time dependence of the *de novo* Synthesis of PCDD/PCDF and potential precursors on a model fly ash

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1. Abstract

Formation of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) as well as their potential precursors PCB, chlorobenzenes and chlorophenols are investigated on an aluminium silicate based model fly ash in the time range of 1 to 30 min. Amounts of compounds formed from active carbon are presented showing that *de novo* synthesis occurs in short times comparable to the residue times in municipal waste incinerators. Isomer patterns do not show any change with time, homologue distributions vary slightly.

2. Introduction

Polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) among other chlorinated compounds are formed during incineration on fly ash at low temperatures. In recent years researchers showed that PCDD/PCDF can be formed from residual carbon, inorganic chlorides and copper [1, 2]. Copper seems to be involved in two ways. First it catalyzes the production of chlorine from chloride via the Deacon process, secondly it catalyzes the formation of dual ring structures [3, 4].

An alternative hypothesis considers polychlorophenols as precursors for the formation of PCDD/PCDF. Karasek et al. showed that the condensation of PCP to OCDD proceeds at short times (5 min) with good yields. whereas *de novo* synthesis experiments were typically designed for 30 min to two hours [1, 2, 5]. To overcome this disadvantage, short time *de novo* synthesis experiments with a model fly ash were carried out. Additionally to the PCDD/PCDF, PCB, chlorophenols, and chlorobenzenes were detected.

3. Experimental

Aluminium silicate (Fluka), activated carbon (Merck), copper chloride (Fluka), and potassium chloride (Merck) were extracted in a Soxhlet-apparatus with toluene for 12 h and dried in vacuo.

Model fly ash was prepared by mixing aluminium silicate with activated carbon, copper chloride, and potassium chloride to contain 1.8 % carbon, 0.04 % copper and 6.6 % chloride. Water was added and the slurry thoroughly mixed. Finally, the mixture was dry frozen.

1 g of model fly ash was placed into a glass tube (0.7 cm diameter) and heated in an oven at 300 °C. The tube was connected to a gas bottle and a controlled gas flow, which passed through a water filled bubbler, was applied. Downstream the gas flow passed through an absorption flask filled with 100 ml ice cooled toluene to absorb gaseous products. The model fly ash was heated 10 min in a stream of nitrogen for temperature equilibration first. Afterwards an air stream (120 ml/min) was applied for 1 min, 2.5 min, 5 min, and 30 min. A blank experiment was performed too.

To stop the reaction the tube was cooled rapidly with ice. The model fly ash was transferred to a 500 ml round bottom flask, the tube rinsed several times with toluene and the content of the absorption flask added. After adding 200 ml toluene, 30 ml ethoxyethanol 5 ml concentrated hydrochloric acid and ¹³C-labeled standard mixtures for PCDD/PCDF, PCBs, chlorobenzenes and chlorophenols the mixture was heated under reflux for 12 h.

Clean-up was carried out according to standard laboratory procedures. PCDD/PCDF, PCBs, chlorobenzenes and chlorophenols were determined by HRGC/LRMS. Quantification was carried out by isotope dilution mass spectrometry.

4. Results and Discussion

Figure 1 shows that already after one minute significant amounts of PCDD/PCDF are formed. The amount of PCDD/PCDF formed increases rapidly with time, with PCDF being formed faster than PCDD. As a result the PCDD/PCDF ratio increases from 0.5 to 3 for a reaction time of 1 min to 30 min.

The distribution of the PCDF homologues remain constant over the examined time span. For the PCDD a shift towards higher chlorinated homologues is observed. The isomer pattern remain relatively constant. In Figure 2 a homologue profile, in Figure 3 isomer patterns for the T₄CDD, P₅CDD and H₆CDD, and in Figure 4 isomer patterns for T₄CDF, P₅CDF and H₆CDF are shown. This indicates that the underlying mechanisms are completed after one minute, and that the formation is a relatively fast process. Only the yield rises with time.

The resulting isomer patterns can be classified as "phenol" patterns. If phenol is heated on carbon free model fly ash the same patterns are being formed [7]. These patterns differ significantly from the normal "thermal" patterns, e.g. the 1,3,6,8- and 1,3,7,9-substituted isomers dominate the T₄CDD, and the 1,2,3,6/8-substituted isomers dominate the T₄CDF. Both T₄CDD isomers can be formed via condensation of 2,4,6-trichlorophenol, the most abundant isomer found when phenol is chlorinated on model fly ash. This indicates that chlorinated phenols play a key role as intermediates in the oxychlorination/degradation of carbon.

Besides PCDD/PCDF, PCBs, chlorobenzenes and chlorophenols are formed.

The amount of PCBs formed stays constant over time, so it can be excluded as direct precursor for the formation of PCDD/PCDF (Figure 5). Chlorobenzenes are formed rapidly, after 2.5 min the amounts reach a plateau (Figure 6). There is an increase of chlorophenols with time which is not so clear at short times (Figure 7). Chlorophenols may condense rapidly to PCDD and PCDF.

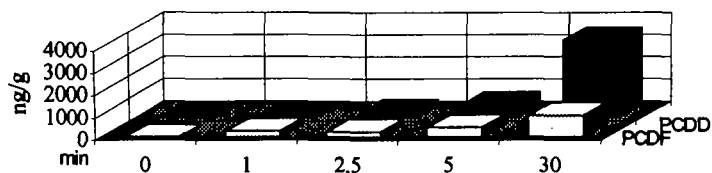


Figure 1 PCDD/PCDF formation with time



Figure 2 Homologue profile obtained after one minute reaction time

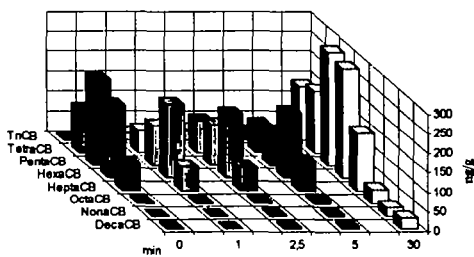


Figure 5 PCB formation with time

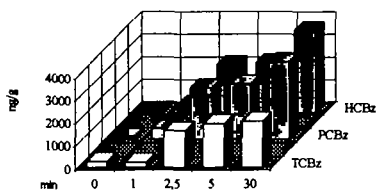


Figure 6: Chlorobenzene formation with time

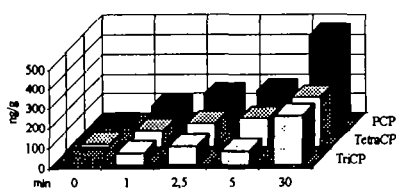


Figure 7: Chlorophenol formation with time

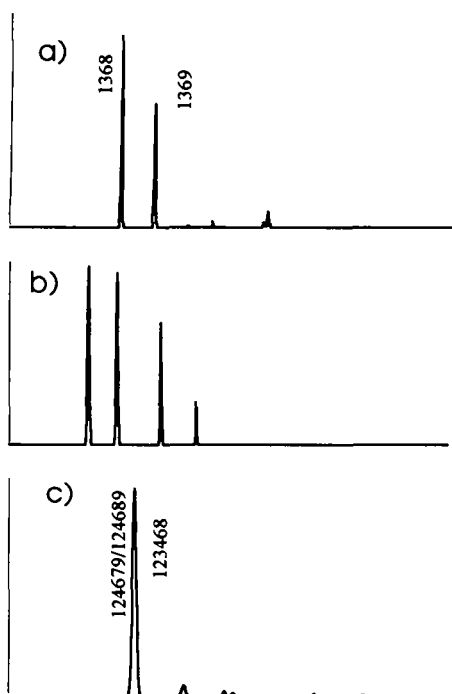


Figure 3 Isomer patterns of a) T₄CDD, b) P₅CDD, c) H₆CDD obtained after heating model fly ash for one minute (reconstructed mass fragmentograms)

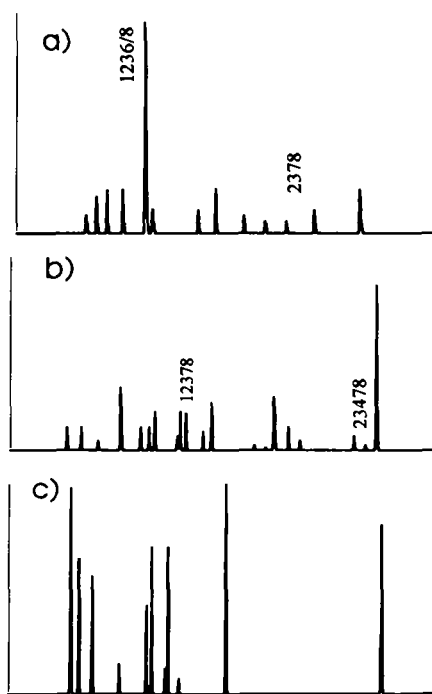


Figure 4 Isomer patterns of a) T₄CDF, b) P₅CDF, c) H₆CDF obtained after heating model fly ash for one minute (reconstructed mass fragmentograms)

5. References

- 1) Stieglitz L., Zwick G., Beck J., Bautz H., Roth W; *Chemosphere* **19** (1989) 283-2902
- 2) Stieglitz L., Zwick G., Beck J., Roth W., Vogg H.; *Chemosphere* **18** (1989) 1219-1226
- 3) Lippert T., Wokaun A., Lenoir D.; *Environ. Sci. Technol.* **25** (1991) 1485-1489
- 4) Griffith R.D.; *Chemosphere* **15** (1986) 1987-1996
- 5) Hagenmaier H., Kraft M., Brunner H., Haag R.; *Environ. Sci. Technol.* **21** (1987) 1080-10846
- 6) Ross B.J., Naikwadi K.P., Karasek F.W.; *Organohalogen Compounds* **3** (1990) 147-150
- 7) Blaha J.; doctoral thesis, Tübingen, 1995