

PCDD/F Isomer Pattern in Fluidized Bed Incineration and the Correlation to the Isomer Pattern via *De Novo* Synthesis from PAHs

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INTRODUCTION

In 1978 Olie et al. [1] described the occurrence of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in the filter dust of a waste incinerator. By 1984, a number of different incinerators had been analyzed for PCDD and PCDF, both in filter dust and stack gas. In all facilities PCDD/F were detected. It was recognized that in all these instances the isomer distribution patterns of the tetra- to hepta-PCDD/F were very similar [2]. This led to the assumption that the route of formation of PCDD/F in these incinerators must be similar. Later it was proven that these isomer distribution patterns are rather characteristic for the formation of PCDD/F by thermal processes ("thermal pattern").

In a series of measurement at fifteen fluidized bed incinerators (FBI) (39 lines, 2590 tons/day) in Japan, we found however a distinctive different PCDF pattern in 5 of these instances (12 lines) [3,4]. The other ten FBI showed a continuous transition between this extreme FBI pattern and the common "thermal pattern" found in grate fired (stoker) incinerators or other thermal sources [3,4]. PCDD, however, did not show a different congener pattern compared to other thermal sources.

The PCDD/F congener patterns are a fingerprint reflecting the mechanism of the formation and the source of their origin. E.g. the specific PCDD/F patterns in the production of pentachlorophenol (PCP) [5], the herbicide CNP (a trichloronitrodiphenylether) [6] or polychlorobiphenyl (PCB) [7] can be derived from the intermediates present in the respective industrial process.

Therefore the question arises: what is the formation mechanism of PCDF in these incinerators and what are the differences compared to stoker incinerators or other thermal sources?

The most distinctive difference in the extreme FBI pattern compared to the "thermal pattern" is the formation of specific isomers for T₃CDF-P₅CDF and the presence of 1,9-substituted H₆CDF/H₇CDF while the thermal pattern can be characterized by absence of 1,9-substituted P_xCDF [3].

Iino et. al. recently reported [8] of specific PCDF formation from polycyclic aromatic hydrocarbons (PAHs). In these experiments, the 1,9-position in PCDF was also observed. Therefore it seems interesting to investigate the PCDF formation from PAHs in more detail and to compare the resulting PCDF isomer patterns with the actual FBI patterns.

MATERIALS AND METHODS:

Sampling: Sampling for PCDD/F in the fluidized bed incinerators was carried out according to the procedure of the Japanese Waste Research Foundation [9].

Experiments with model fly ashes: The model fly ashes (MFAs) were prepared by dry mixing of silica, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1.7wt%) and the single PAHs (0.1wt%). PAHs tested in this study were anthracene ($\text{C}_{14}\text{H}_{10}$), phenanthrene ($\text{C}_{14}\text{H}_{10}$), pyrene ($\text{C}_{16}\text{H}_{10}$), benzo[b]fluoranthene ($\text{C}_{20}\text{H}_{12}$), perylene ($\text{C}_{20}\text{H}_{12}$), benzo[e]pyrene ($\text{C}_{20}\text{H}_{12}$), coronene ($\text{C}_{24}\text{H}_{12}$), 1,2,8,9-dibenzopentacene ($\text{C}_{30}\text{H}_{18}$), and ovalene ($\text{C}_{32}\text{H}_{14}$). For comparison of formation rates, analogous MFAs were prepared with activated carbon (AC) (0.1wt%) and phenol (0.1wt%) respectively. The MFAs were heated at 300°C for 30min (200ml/min, 10% oxygen).

Clean-up: The clean-up procedures are described elsewhere [8,10].

Analysis: The analysis was carried out on a HP 6890 GC coupled to a HP 5973 MS or a GC/MS Hitachi M-80B. For isomer specific analysis of the mono- to hexaCDD/CDF and detection of the unsubstituted dibenzodioxin and dibenzofuran, a CP-Sil 88 or SP-2331 was used. A DB-5 fused silica column was used for the analysis of the hepta- and octaCDD/CDF, PCB and PCN.

RESULTS AND DISCUSSION**PCDF formation from PAHs**

The yield and the homologue patterns of PCDD/F from 9 examined PAHs, phenol and active carbon (AC) are shown in Figure 1. The CuCl_2 -catalyzed heat treatment of all PAHs resulted in the formation of PCDF and PCDD. The PCDF formation was dominant in every homologue with a ratio of about 10. Of the nine PAHs tested, perylene and benzo[e]pyrene had the greatest potential for the formation of PCDD/F.

With perylene, up to 0.5% of the molecule was transformed into PCDF. Taking into consideration that the PAHs partly evaporated, as could be seen for example for perylene by the condensed yellow matter at the reactor outlet, the transformation rates were even higher.

The PCDF yields from perylene and benzo[e]pyrene were reproducibly higher than those from activated carbon (the carbon source with highest reported PCDF de novo potential in model fly ash systems so far [11]).

Comparison of the PCDF isomer pattern from PAHs and extreme FBI

The average isomer distribution patterns for the T_3CDF , T_4CDF , P_5CDF and H_6CDF found in stoker type incinerators are characterized by a large number of isomers in comparable concentrations. In case of H_7CDF , however, the 1,2,3,4,6,7,8-substituted isomer predominates, amounting to about 70% of the total H_7CDF . In summary this pattern is characterized by absence of 1,9-substituted congeners which is most obvious for the H_6CDF and H_7CDF .

The extreme fluidized bed pattern is almost complementary [3]:

Only a few specific T_3CDF , T_4CDF and P_5CDF isomers are formed. However with H_6CDF and H_7CDF the 1,9- substitution is observed. The substitution patterns of the specific congeners formed are 4- (6-), 3- (7-), 2,4- (6,8-), 3,4- (6,7-) and 2,3,4-fragments. For instance, the sum of the concentrations of 2,4,6,7-, 3,4,6,7-, 2,3,4,6- and 2,3,4,7- T_4CDF isomers amounts to about 70% of the total 38 T_4CDF isomers (Figure 2). The isomers most typical for the usual fly ash pattern are only minor components. With P_5CDF , the two isomers 2,3,4,6,8-, 2,3,4,6,7- represent more than 50% of the 28 isomers.

The characteristic isomers formed from perylene ("perylene pattern") in model fly ash experiments are almost identical. The T_4CDF isomers are shown in figure 2. All characteristic main isomers are in both patterns the same with about the same ratio. With T_3CDF also in both patterns 2,4,6-,

2,4,7-, 3,4,6- and 3,4,7- are predominantly formed. With P₅CDF, the 2,3,4,6,7-P₅CDF is the most abundant isomer. The formation of 2,3,4,6,8-P₅CDF is more emphasized in the extreme FBI pattern where it amounted for up to 30% of total P₅CDF as the 2,3,4,6,7-isomer. In the "perylene pattern", the 2,3,4,6,8-P₅CDF is also the second most abundant isomer for P₅CDF but under our experimental conditions, it was not formed in comparable amounts as 2,3,4,6,7-P₅CDF.

For both patterns we find the same switch in isomer characteristics of H₆CDF and H₇CDF; while for T₃CDF-P₅CDF the 1-substitution is almost neglected (2,4-;3,4-; 2,3,4-), for H₆CDF and H₇CDF the 1,9-substitution (substitution of both upper positions!!) is prominent.

Also e.g. benzo[b]fluoranthene resulted in a similar isomer pattern. The preference of 1,9-substitution we found for all "round" PAHs (coronene, ovalene)

Comparison of PCB and PCN isomer pattern

One more proof for the connection of the extreme FBI pattern with the transformation of PAHs came when we compared the PCB and the PCN patterns of both processes.

The PCB patterns found in the "extreme" FBIs are almost identical compared to those from *de novo* synthesis from perylene. The same specific isomers are formed in both processes, which differ only slightly in the ratios. As for the PCDF, the PCB isomer pattern of the extreme FBI pattern is distinctly different from the PCB pattern found in MWIs [12] and from those known for commercial PCB mixtures [12].

Also the specific isomer pattern of polychlorinated naphthalens (PCNs) found in FBI fly ashes [13] was partially similar to those that resulted from our *de novo* experiments with some PAHs.

Comparison of the PCDD isomer pattern

As mentioned above, PCDD are formed in the oxidative transformation of PAHs only in small amounts (PCDD:PCDF<1:10) and the resulting PCDD show a 2,3-isomere pattern. In all fifteen measured FBI however we found a 2,6-pattern for PCDD [3,4]. Therefore the PCDD in these FBI are not formed directly from PAHs but via the PxCPs as already reported in former papers [3,4] and generally accepted for the 2,6-pattern [14].

On the other hand the transformation path from PAHs may be an explanation of the origin of the 2,3-pattern which can not be correlated with the condensation of the phenols.

PAH values in the FBI and correlation to the laboratory experiments

The 5 facilities with the most extreme FBI pattern are older facilities with unstable combustion (oscillating CO values with temporary peak levels over 1000ppm), high PCDD/F emission values (20-50ng I-TEQ/Nm³) and CaCO₃ spray at 850°C. With the new FBI-generation with good combustion practices and PCDD/F emission values <0.1ng [15,16], we did not find the extreme FBI pattern but a shift towards the thermal pattern with elements of both patterns.

In the older FBI with unstable combustion, we found high PAH values up to 7000ug/Nm³ (Σ16 EPA-PAHs). Therefore the PAHs are present in 3-4 orders of magnitude higher than the PCDF. Wanke et al. found in their facility that the PAHs decreased downstream in the flue gas line (between 700 and 200°C) [17] while PCDD/F are formed during this cooling process. When considering transformation rates of 0.05% of PAHs (this means 10% of the highest transformation rates observed in our laboratory studies), we are within the range to explain the actually formed PCDF amount in these incinerators (total 2-6ug/Nm³ including PCDF in ash). The biggest amount of PAH structures are however embedded in soot and amount to several mg/g ash (about 15g fly ash/Nm³ in FBI).

Also, the time and temperature frame of the investigated incinerator (about 80% of the PCDF are formed in the electrostatic precipitator (EP) with temperatures of 250-275°C and a dwell time of 15-45 minutes of the fly ash in the EP) and the laboratory study (30 minutes at 300°C) are comparable.

The first evidence of the relevance of condensed carbon matter on fly ash for the PCDD/F formation during combustion processes was the observation of Stieglitz et al. [18,18a], and Hagenmaier et al. [19,20], that the carbon in fly ash is capable of PCDD/F formation. However, the structure of the unburned carbon and the main structural elements that contributes to the PCDD/F formation have yet to be clarified. A part of this unburned carbon in the fly ashes results from soot formation. The soot precursors for the carbon nuclei are the PAHs [21-23]. PAHs are therefore not only present in combustion processes orders of magnitude higher than PCDD/F [24-26], but represent also structural elements of the unburned carbon.

Perylene is not a prominent PAH formed during incineration. Therefore in our opinion, perylene (or a single PAH) is not the source of PCDF formation but PAHs and elements in soot with similar structures are the source in the fly ash catalyzed *de novo* synthesis in our fluidized bed incinerators.

One key question, which we could not clarify at this stage of our investigations, is the difference of our incinerators with the extreme FBI pattern and the incinerators with the normal "thermal" PCDF pattern.

CONCLUSION

The correlation of the PCDF, PCB and PCN pattern in the incinerators with the *de novo* formation experiments in our laboratory studies is a strong indicator that PAHs, and PAH structures embedded in the soot/unburnt carbon as macromolecules, are the source for PCDF formation in these fluidized bed incinerators. Moreover, in our opinion they may play a significant role in the sequence of combustion, PAHs/soot formation, decomposition (partial oxidation, oxidative breakdown), chlorination, and PCDD/F, PCB and PCN *de novo* formation*.

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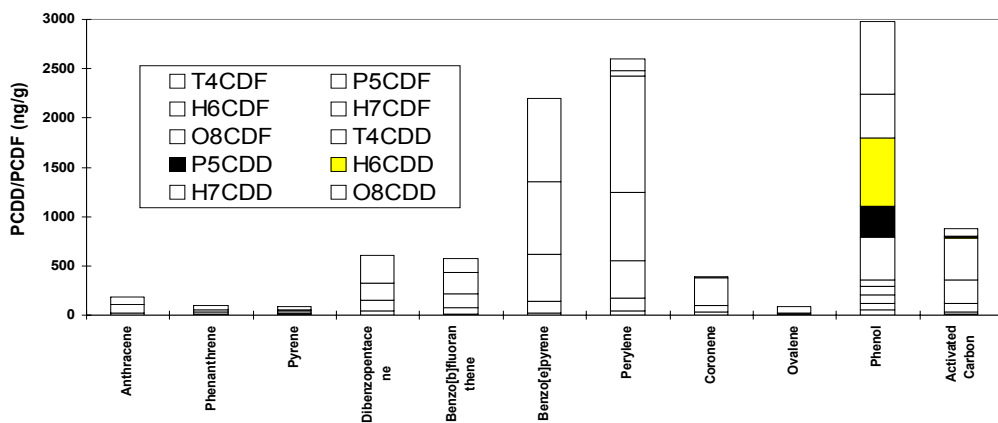


Figure 1: *De novo* formation rates of PCDD/PCDF on model fly ashes (SiO_2 basis, 1.7% $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) from PAHs (0.1wt%) in comparison to phenol (0.1wt%) and activated carbon (0.1wt%) at 300°C (30min).

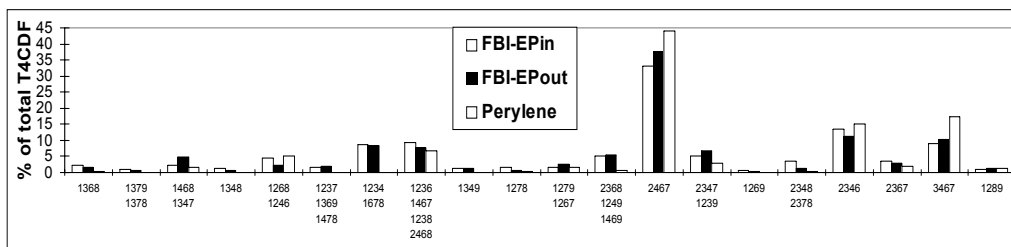


Figure 2: T₄CDF isomer pattern of the extreme fluidized bed pattern (EP-in and EP-out) in comparison to the isomer pattern resulting in the *de novo* synthesis from a model fly ash with perylene.