

PCDF Formation from PAH Reactions

Andres Fullana¹, Hannah Nakka¹, Sukh Sidhu¹

¹Environmental Engineering, University of Dayton

Introduction

The de novo mechanism is considered a major pathway for the formation of PCDD/F, however, the exact mechanistic steps are not known. It is still not clear if PCDD/F are formed from the residual carbon present in the fly ash or from the organic compounds that are adsorbed on it.

In an earlier study, Albrecht et al.¹ showed that absorbed compounds play a principal role in dioxin formation. Later studies have also confirmed the importance of absorbed compounds in the de novo mechanism.

Stieglitz et al.² using ¹³C activated carbon with CuCl₂ as catalyst showed that the carbon skeleton in the PCDD structure comes from condensation of monoaromatic structures like phenols, but the carbon for the PCDF structure comes directly from biphenyl structures present in the original carbonaceous material. Results from this work support the theory that PCDD and PCDF are formed by two different pathways. PCDD is formed by condensation of small aromatic compounds like chlorophenol and PCDF is formed from carbonaceous macromolecules.

The PCDF formation pathway suggested by Stieglitz seems to contradict the results of Albrecht et al. (1) because it shows that PCDF are formed directly from the carbon material and not from adsorbed organics on the particle surface. However, a closer examination shows that the Stieglitz PCDF formation mechanism is not contradictory because in the top carbon surface layer significant quantities of non-graphitic organic compounds are attached to the graphitic core. These non-graphitic organic compounds are usually polyaromatic hydrocarbons (PAH) that can form PCDF without losing the original biphenyl structure.

It is clear that PAHs play an important role in PCDF formation²⁻⁵. It does not matter if PCDF are formed from carbonaceous material or from PAH adsorbed on the carbon surface. The role of PAH in the formation of PCDF has been studied by several authors. Probably one of the most complete investigations was conducted by Wilhelm et al.⁴. They investigated PCDF formation from twelve different PAHs with structures similar to the PCDF. The results of this study showed that biphenyl-like structures can be easily converted to PCDFs.

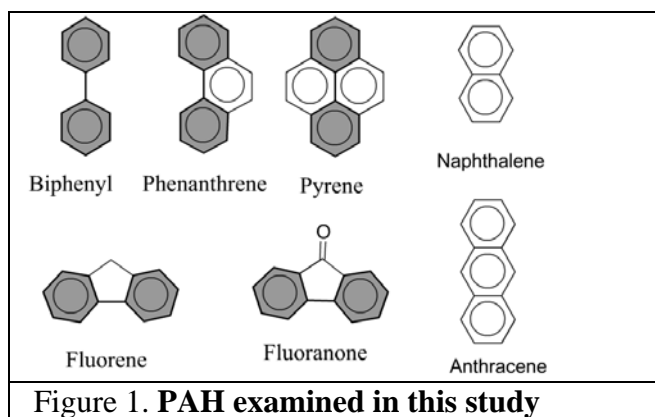
Although the biphenyl-like structures are clearly involved in PCDF formation, there are several aspects of this formation pathway that are not well understood. Iino et al.³ found that higher PCDF yields could be obtained from pyrene than phenanthrene, contradicting biphenyl intermediate formation pathway theory as phenanthrene structure can more easily be converted to biphenyl than pyrene.

All previous PCDD/F formation studies from PAHs were conducted using CuCl_2 as model fly ash. CuCl_2 is highly volatile and probably not present in any significant quantities in the actual fly ash. High temperature oxidative conditions in the high temperature zone are able to oxidize all transition metals to their oxides. Therefore, Cu in actual fly ash is most probably present as CuO or Cu_2O . Also in previous studies, PAH – model fly ash mixtures were prepared at room temperature and then heated to experimental temperatures. This experimental method can lead to some uncertainties because depending on PAH boiling point, various amounts of different PAHs would have evaporated by the time experimental temperatures were achieved.

The main objective of this study is to address all the above issues and develop a better understanding of the role of biphenyl structures in PCDF formation. The salient features of this study are:

- Use of $\text{CuO}+\text{HCl}$ as model fly ash instead of CuCl_2 which was traditionally used in earlier De Novo studies.
- Study major non-PCDD/F compounds formed during PAH oxidation to understand the mechanism of formation.

Methods and Materials



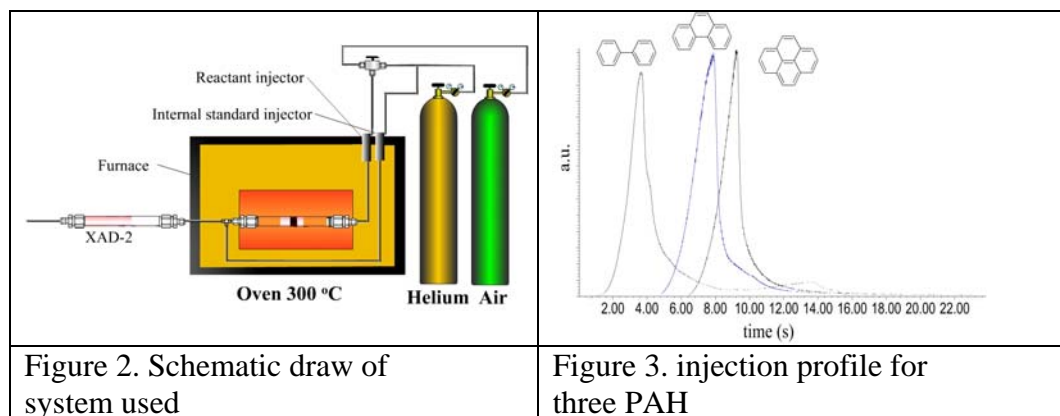
In this study seven PAHs were used as reactants. The biphenyl structure was present in five of these PAHs. Figure 1 shows the structure of these PAHs and the presence of biphenyl structures are shown in grey.

A model fly ash made of florasil and 4% CuO (w/w) was used as a catalyst for all experiments. The model fly ash was prepared by impregnating the florasil with CuNO_3 -water solution and then oxidizing CuNO_3 to CuO by calcinating it in a horizontal furnace for 24 h at 600°C .

Figure 2 shows a schematic representation of the experimental systems used for this study. For each experiment, 0.1 g of catalyst was placed in a tubular glass reactor (100 mm length, 7 mm ID) and heated to 300°C in 50 ml/min gas stream of 10% O₂ in helium. The catalyst bed was approximately 5 mm long with a residence time of ~ 0.5 s. Once the furnace was heated to 300°C, HCl (gas or dilution) was added to chlorinate the surface of catalyst. Experiments were performed using HCl in both gaseous (3 ml of pure HCl gas) and solution (0.1 ml solution of 1.2 M HCl) forms.

After chlorination reaction, the selected PAH was introduced into a glass reactor by increasing the injector temperature to 300°C. Figure 3 shows the efficiency of injection for three PAHs used in this study. This technique ensures that the PAH interacts with the catalyst surface at the target temperature and not during the heating period. After 1 h of reaction, the gas was changed to He and the furnace heated to 500°C to desorb compounds formed during the reaction. In parallel with the reactant, six deuterated standards (dichlorobenzene-D₄, naphthalene-D₈, acenaphthene-D₁₀, Chrysene-D₁₂ and Perylene-D₁₂), were added to the bypass flow (outside of the reactor) for later quantification of reaction products.

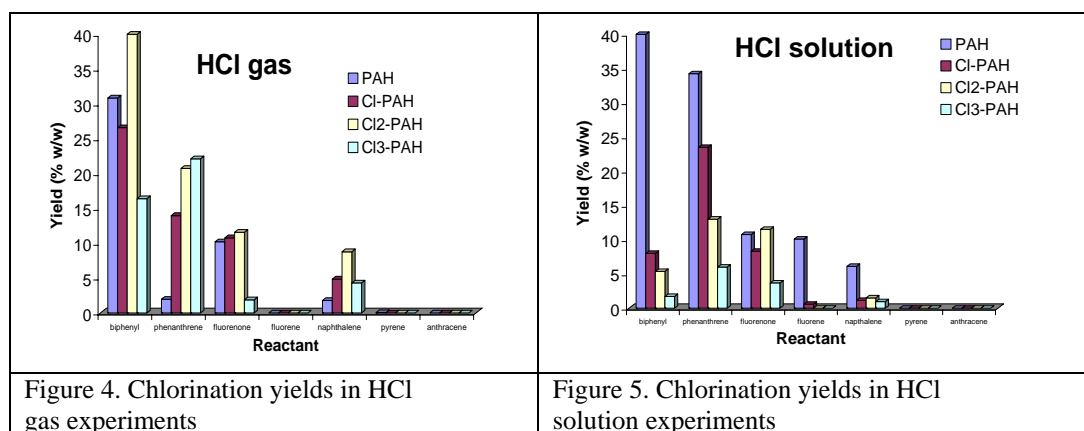
The reaction products were trapped in a resin Amberlite® XAD-2 and extracted with dichloromethane and analyzed by GC/MS. Major products were identified using MS spectral library matches and quantified using a deuterated compounds response. Analysis of PCDD/F was performed using the GC/MS-MS method described by Kemmochi and Tsutsumi⁶.



Results and Discussion

As a consequence of catalytic oxidation in the presence of HCl, part of the PAHs react to produce chlorinated isomer. The results for this chlorination are shown in Figures 4 and 5. Only mono-, di-, and tri-chlorinated PAH were used for comparison in Figures 4 and 5. The yields of the higher chlorinated isomers were too low to be used in this comparison.

Results show a high chlorination for all PAHs considering that no chlorinated metals were present in the original catalyst. The pre-treatment of catalyst with HCl is able to cause sufficient changes to chemical properties of the catalyst to produce chlorinated PAHs. This result supports the hypothesis that the presence of chlorinated transition metals in the fly ash is not necessary to cause chlorination of precursors. The presence of oxides in contact with HCl present in gas is enough to chlorinate some of the PAH studied.



Comparison between Figure 4 and 5 shows that the catalyst pre-treated with HCl gas is able to increase chlorination and oxidation of PAHs. This is probably due to the fact that when HCl is introduced as a solution, the water present competes with PAHs and HCl for available catalytic sites.

It is interesting to note that the PAHs like fluorene, pyrene and anthracene that show low chlorination also show a higher degree of oxidation. Also, fluorene and anthracene give a high yield in fluorenone and anthracenedione, respectively. This high conversion can explain the low chlorination of these compounds. In the case of pyrene, the high aromatization probably leads the formation of soot as no other organic compounds with significant were observed.

Table 1. Yields ($\mu\text{g/g}$) of tetra to octa PCDD/Fs from PAH reactions.

Reactant	HCl gas		HCl solution	
	PCDF	PCDD	PCDF	PCDD
Biphenyl	1229	30	900	14
Phenanthrene	2248	7	1104	32
Fluorenone	199	27	318	26
Fluorene	1824	95	1084	34
Naphthalene	158	16	135	15
Pyrene	83	16	146	31
Anthracene	117	9	25	19

Yields of PCDD/Fs from all experiments are listed in Table 1. In all PAH experiments, PCDF yields are several times higher than those of PCDD. This result is consistent with the hypothesis of Stieglitz et al. (2) that PCDFs are formed directly from PAH structures, whereas PCDD are formed from condensation of chlorophenols which are formed in these experiments at very low concentration.

Examination of Table 1 shows that fluorene, phenanthrene and biphenyl produce the highest yield of PCDFs. This result is expected because these compounds are structurally similar to PCDF. Anthracene and naphthalene, which do not have biphenyl structures in the skeleton, produce a small amount of PCDF. Pyrene is the exception probably because its higher aromatic structure is resistant to oxidation and more likely to form soot via molecular growth reactions. This hypothesis is supported by observation of black film on the surface of the catalyst support after pyrene experiments.

Table 1 also shows that the presence of water caused a slight decrease in PCDF yields. This is probably due to the fact that water competes with HCl and PAHs for available catalytic sites.

Yields of PCDF observed in this study are lower than those observed by Wilhelm et al.⁴ The reason that this catalyst (CuCl_2) was used by Wilhelm is a stronger oxychlorinating agent than the catalyst (CuO with HCl) used in the present study. Another major difference between the two studies is that in the present study, PCDF yields from fluorene and phenanthrene are similar to those observed from biphenyl, whereas in the Wilhelm study, biphenyl generated 25 times more PCDFs than fluorene and 1000 times more than phenanthrene. A possible explanation for these results is that the higher temperature used in the present study (300°C vs 250°C) was sufficient to open a PCDF formation reaction channel for fluorene and phenanthrene and this consequently decreased the differences in PCDF yields between these three compounds. It is important to note that to form PCDF from phenanthrene and fluorene it is necessary break a C-C bond that requires more energy than in the case of biphenyl where this step is not necessary.

The product distribution from biphenyl, phenanthrene and fluorene experiments shows that these compounds are direct precursors to PCDF because the concentration of each one is small when other is the reactant. For example, when phenanthrene was the reactant, very small concentrations of biphenyl and fluorene were found. However, similarity

between structures suggests that a similar intermediate precursor-catalyst complex must be involved in PCDF formation for all three of these PAHs. This intermediate organic-metallic complex could not be identified in this study.

Another interesting result is the low activity of fluorenone in comparison to fluorene despite their structural similarities and the fact that fluorenone is the major oxidation product from fluorene. This observed low activity of fluorenone is probably due to the high stability of carboxyl group that stabilizes this molecule.

The results of this study combined with the results of our previous study⁷ which showed that soluble (or desorbable) organic fraction of soot was responsible for PCDD/F formation, supports the hypothesis that PAHs that are adsorbed on particle surface or that form the non-graphitic layer of soot are an important carbon source for PCDF emissions.

Acknowledgment

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