

Investigation of the Pathways to PCDDs/Fs from an Ethylene Diffusion Flame: Formation from Soot and Aromatics

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Introduction

The formation of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs/Fs) has been shown to occur from the combustion products of fuels as complex as municipal solid waste⁽¹⁻³⁾ and as relatively simple as a methane flame⁽⁴⁻⁶⁾. PCDD/F emissions from flame carbon in the presence of gas-phase chlorine (Cl₂) and municipal solid waste incinerator (MSWI) fly ash have been reported as high as nearly 58,000 pmoles/dscm (12,000 ng/dscm) in a laboratory combustion system⁽⁶⁾. Such formation has been related directly to poor combustion conditions, noted by the emission of soot from the flame, with the source of the carbon directly linked to the fuel. Higher emissions of PCDDs/Fs compared to normal facility operations associated with the start-up (during and for a short period thereafter) of some full-scale combustion facilities, when soot from natural gas or fuel oil is present, have also been reported⁽⁷⁾.

A number of independent studies have shown that aliphatics^(8,9), aromatics (such as benzene and phenol)⁽¹⁰⁻¹²⁾, chloroaromatic compounds (such as chlorophenols and chlorobenzenes)⁽¹³⁻¹⁵⁾ and particulate carbon (such as native carbon in fly ash)⁽¹⁶⁾ can form PCDDs/Fs under a variety of conditions. Some recent studies with respect to the latter have indicated that flame soot can be a persistent carbon source for PCDD/F emissions⁽¹⁷⁾. However, the importance of each of the above mentioned global pathways to PCDDs/Fs during combustion processes has remained elusive for over 25 years. This is in large part due to the complexity of the overall formation process (number of possible pathways to formation and their sensitivity to operating conditions). In addition, most studies have been designed to investigate a particular pathway in isolation and the uncertainty over the representativeness of the simulations adds further complications. Recently, Stanmore⁽¹⁸⁾ has offered a review of the field and suggests the importance of particulate carbon in PCDD/F emissions from incinerators. The purpose of the present study was to assess the importance of flame soot (including adsorbed/condensed aromatics) versus vapor-phase flame products in PCDD/F formation from the products of an ethylene diffusion flame in the presence of Cl₂. Determining the importance of the nature of the flame carbon (soot versus gas-phase precursors) for subsequent PCDD/F formation will aid in understanding the dominant formation pathways within combustion processes. Once identified, such an understanding can lead to comprehensive

predictive models of PCDD/F emissions and better engineering controls to minimize the conditions and reactants necessary for formation.

Materials and Methods

A four-stage, horizontal reactor set-up (Figure 1) was used to investigate the formation of PCDDs/Fs from flame soot and vapor-phase flame products in both catalyzed and uncatalyzed systems. The combustion stage, cooling stage, soot filter and fly ash bed, separated by sampling and injection ports (each independently temperature controlled) allowed for the assessment of PCDD/F formation associated with the available theorized pathways: homogeneous and non-catalyzed formation from vapor-phase flame products (i.e., aromatics) or soot, heterogeneous formation from the non-soot flame products, and distinct formation from the combination of soot and metal catalysts (e.g., fly ash). The first stage consisted of a double-tube quartz reactor ($ID_{inner} = 2.2$ cm, $ID_{outer} = 4.6$ cm, $L = 122$ cm), kept at 1000 °C by electric heating, with an ethylene diffusion flame at the inlet side. The exhaust from this combustion stage entered a cooling stage (Stage 2, $L = 122$ cm) with wall temperatures maintained at 260 - 470 °C to bring the total flow to the soot filter stage temperature (third stage). The soot filter consisted of a quartz microfiber filter held in place against a coarse-grain ground quartz frit with glass wool added upstream for improved soot collection. The combustion gas, minus the soot, was then passed to a similar filter in which a 2 g bed of EPA oxidized fly ash⁽¹⁹⁾ (EPA OX FA) was placed, also held against a coarse-grain ground quartz frit with glass wool (Stage 4). Temperatures of 300 , 400 and 500 °C for stages 3 and 4 were investigated, although the experiments at 400 °C are the focus of the present study, with both stages maintained at the same temperature within a single test. The addition of 50 mL/min of 5% Cl_2 (in Ar) to the combustion gas flow was done either into the flame (Port A), just upstream of Stage 3 (Port B) or just upstream of Stage 4 (Port C). Half of the total flow was sampled after Stage 3 through a sample train consisting of a 25 g XAD-2 resin trap (maintained at ambient temperature) and a 100 mL deionized water impinger. A similar sample train for the remainder of the flow was placed after Stage 4. The XAD-2 resins in each train were analyzed separately for mono-octa PCDDs/Fs according to U.S. EPA Method 0023a⁽²⁰⁾.

The importance of soot/fly ash contact for PCDD/F formation and an understanding of the dual nature of the metal chlorides in such formation were investigated using a three scenario approach: (i) with no addition of fly ash or catalyst to the quartz filter/ glass wool in the soot filter (Stage 3), (ii) the addition of 2 g of EPA OX FA to Stage 3, or (iii) the addition of 2 g of a mixture (MeOX) of copper oxide (CuO , 0.17%), iron oxide (Fe_2O_3 , 1.11%) and silica to Stage 3. Stage 4 always contained 2 g of EPA OX FA. The concentrations of copper and iron in the MeOX mix were chosen to be the same as those measured in the EPA OX FA. The residual levels (below the detection limit) of carbon in the EPA OX FA produced no PCDDs/Fs in blank tests (100 ppm Cl_2 in Air) at 400 °C. The combustion air (1.62 L/min of O_2 , 3.04 L/min N_2) passed through the annulus of the double-tube reactor combustion stage and then co-flowed with the ethylene (0.477 L/min) added through a 2 mm diameter stainless steel nozzle. This flow rate of fuel corresponded to a mass flow rate of 9.12 mg/s; the smoke point of an ethylene diffusion flame in room air has been reported as 3.84 mg/s⁽²¹⁾. The equivalence ratio of the flame in all experiments was 0.88 . The run time for each experiment was 30 minutes.

Results and Discussion

The potential formation of PCDDs/Fs from the flame products without fly ash (measured after Stage 3) and from the vapor-phase flame products (no soot) passed over a fly ash bed (sampled after Stage 4) was investigated according to scenario (i). The combustion gas from the ethylene flame contained both soot (captured at the soot filter in Stage 3) and vapor-phase products (measured after Stage 3). A nominal amount of soot collected was 10 mg or 70 mg/dscm. The estimated concentrations of naphthalene, phenanthrene, fluoranthene and pyrene collected in the XAD-2 resin of the Stage 3 sample train [analyzed via high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS) of the toluene extract] were 14, 7, <1, and <1 $\mu\text{g/dscm}$, respectively. The concentration of benzene, measured online via the method described in Oudejans et al.⁽²²⁾ at this sample location (after the soot filter), was ca. 6 $\mu\text{g/dscm}$. These values are only approximate concentrations, provided to give a general (order of magnitude) idea of the characterization of the flame products. More work regarding the online characterization of organic pollutants from the ethylene flame (diffusion and premixed) is currently ongoing.

Without the addition of fly ash or MeOX to the soot filter, only low concentrations, close to the detection limits, of PCDDs/Fs were measured in the train after Stage 3 at 400 °C; the results were independent of the point of introduction of Cl_2 (Ports A, B, or C). As an example, the PCDD/F concentrations and homologue profiles for when Cl_2 was added at Port B are reported in Figures 2a and 3a (none), respectively. Without catalytic activity, the measured emissions were comprised of isomers of the MoCDF homologue at no more than 3 times the detection limit of 2.5 ng/train (6–12 pmoles/train, depending upon the homologue). This limit is defined as half of the lowest concentration in the HRGC/LRMS calibration curve. Thus, the ethylene flame products (soot and vapor-phase organics) in the temperature range of 400–1000 °C do not produce significant PCDD/F emissions to explain that observed from similar systems in the presence of fly ash⁽⁶⁾; these results are in agreement with those for a methane diffusion flame also in the absence of fly ash⁽⁶⁾.

After the combustion gas (minus the visible soot) passed through the EPA OX FA bed in Stage 4 at 400 °C (Cl_2 added at Port B), the concentrations of PCDDs/Fs increased by only a factor of 3.7 [Figure 2b (none)]. An increase in the concentrations of MoCDFs was accompanied by low levels of DiCDFs, with all isomers of the latter at or below the detection limit. The results from the above studies do confirm the formation of low chlorinated PCDDs/Fs from ethylene diffusion flame products in the absence of metal oxides or chlorides, but in the presence of gas-phase Cl_2 . However, this formation, especially up to and including Stage 3 [in the absence of a catalyst surface (e.g., fly ash)] results in only very minor emissions. Additional chlorination/formation from vapor-phase flame products (including the MoCDF from Stage 3) in the presence of fly ash resulted in only slightly greater emissions (from Stage 4), primarily the low chlorinated congeners.

When EPA OX FA was added to the soot filter (scenario ii) an additional pathway of formation was added to the system, initially recognized by Stieglitz et al.⁽¹⁶⁾. This added formation of PCDDs/Fs by the low temperature partial oxidation of the soot, catalyzed by the fly ash (*de novo* synthesis), resulted in over an order of magnitude increase in concentration (at 400 °C) than that observed from the sum of Stages 3 and 4 in the absence of EPA OX FA in the soot filter [Figure 2a (none vs. EPA OX FA)]. This was due to increases in both PCDDs and PCDFs, although the ratio of PCDDs to PCDFs decreased from 0.64 to 0.25. The homologue profile also changed drastically, as observed in Figure 3a (none vs. EPA OX FA). Formation was no longer characterized by only

MoCDFs, but now Pe-OCDDs and all Mo-OCDFs. When the filtered flame and Stage 3 reaction products were passed to the EPA OX FA in Stage 4, the PCDD/F emissions decreased [Figure 2b (EPA OX FA)], although the homologue profiles remained constant [Figure 3b (EPA OX FA)]; this point will be discussed in more detail below. Thus, the flame soot was the major carbon source for PCDD/F formation and the contact between the soot and fly ash was essential to achieve high emissions such as those observed during sooting combustion.

Fly ash has been reported to contain metal chlorides that can act as both chlorinating agents and carbon (soot) oxidation catalysts; both suggested as key steps in PCDD/F formation from particulate carbon^(23,24). The chlorination of the carbon prevents complete oxidation and results in the formation of chlorinated aromatics (i.e., chlorophenols, chlorobenzenes and PCDDs/Fs)⁽²⁴⁾. Others have proposed that oxidation of particulate carbon results in the release of aliphatics which can then form aromatics as precursors to PCDDs/Fs⁽⁹⁾. A better mechanistic understanding of formation via low temperature partial oxidation of the particulate carbon (soot) was attempted in this work.

To isolate the role of fly ash in low-temperature soot oxidation from that of fly ash as a chlorinating agent of soot, the fly ash in Stage 3 (scenario ii) was replaced by the MeOX mix (scenario iii) and Cl₂ was added after the MeOX bed (Port C). Both copper and iron oxides (present in the MeOX mix) have been shown to lower the oxidation temperature of soot⁽²⁵⁾, a proposed mechanistic step in the formation of PCDDs/Fs from particulate carbon^(26,27). The addition of the MeOX mix resulted in a 5 fold increase in PCDFs and 3-6 fold decrease in PCDDs (exclusively OCDD formed) at the Stage 3 sampling point compared to scenario (i) when there was no addition to the soot filter (not shown in figures). The formation was almost exclusively mono- and diCDFs, also characteristic of the emissions observed in scenario (i). The required chlorine for the observed emissions may have been supplied by a minor amount of diffusion of the added Cl₂ backwards to the sample port (gas-phase chlorination) or to the MeOX bed, a point that will be addressed in future work. Passing the soot oxidation products and vapor-phase flame organics over the fly ash bed in Stage 4 did not result in a clear increase in total emissions (not shown). The degree of chlorination of the PCDFs did increase dramatically with 47% now tri-octaCDFs. This was likely due to chlorination occurring over the fly ash bed, probably via metal chlorides in the fly ash, although chlorination by gas-phase Cl₂ can't be separated here. These results alone, at present, do not indicate whether the formation over the second bed is due to the release of aromatics or unchlorinated/low chlorinated DDs/DFs or from aliphatics that may be products of the low temperature oxidation of the soot. The latter is perhaps not a prominent pathway to formation since others have not seen mixed ring (¹³C_x¹²C_y) PCDDs/Fs under similar formation conditions when mixtures of ¹²C and ¹³C particulate carbons were used^(17,28). Results from the present study with regard to this matter are still pending. The addition of Cl₂ upstream of the MeOX bed (Port B) resulted in 4 and 40 fold increases in PCDF and PCDD, respectively, after Stage 3 at 400 °C (Figure 2a, MeOX vs. none). While the emissions of PCDDs and PCDFs were lower than those at the same conditions with EPA OX FA in the soot filter (Figure 2a, MeOX vs. EPA OX FA), the homologue profiles were almost identical (Figure 3a). The probable formation of metal chlorides in the bed can likely explain the dramatic increase in emissions compared to when Cl₂ was added through Port C. The dual role of the metal chlorides as soot oxidation catalysts and chlorinating agents, resulting in the increase in PCDD/F emissions and a homologue profile similar to that commonly observed from MSWIs, are possibly not distinctly separable.

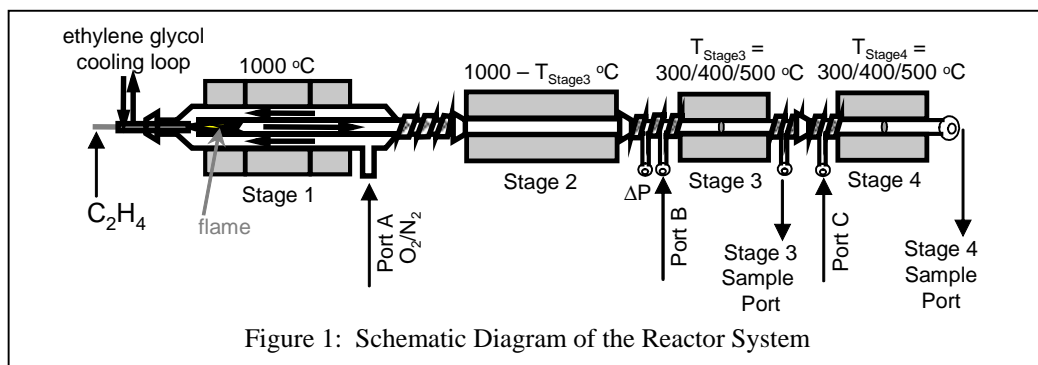
Emissions from Stage 4 were less than Stage 3 (Figure 2b) indicating destruction over the second bed rather than the chlorination/formation that resulted when Cl₂ was added through Port C. These results, together with the similar findings from scenario (ii), might be due to a nearly complete reaction of the Cl₂ in Stage 3; thus, primarily metal oxides remained in the fly ash and catalyzed the destruction of PCDDs/Fs. When Cl₂ was added via Port C, metal chlorides may have been formed that were less prone to promote only the destruction of PCDDs/Fs.

In summary, formation of PCDDs/Fs from the products of a sooting ethylene diffusion flame in the presence of an oxidized fly ash and gas-phase Cl₂ can be attributed mainly to the direct interaction between the metal oxides/metal chlorides in the fly ash and the flame soot (perhaps including adsorbed flame products). More than 85% of the PCDDs and 94% of the PCDFs were formed by this pathway. The remainder of the emissions (mainly, MoCDDs/Fs and DiCDDs/Fs) can be attributed to catalyzed and non-catalyzed formation from the gas-phase (non-soot) flame products; however, this carbon fraction was clearly not the major source of the total PCDD/F emissions. Furthermore, formation from the gas-phase flame products in the absence of fly ash (non-catalyzed formation) accounted for at most 30% of the total PCDD/F emissions attributable to the non-soot carbon flame carbon. These results indicate the importance of PCDDs/Fs formed as products of the partial low-temperature (<500 °C) oxidation of particulate carbon (soot), catalyzed by metal oxides and/or metal chlorides in fly ash.

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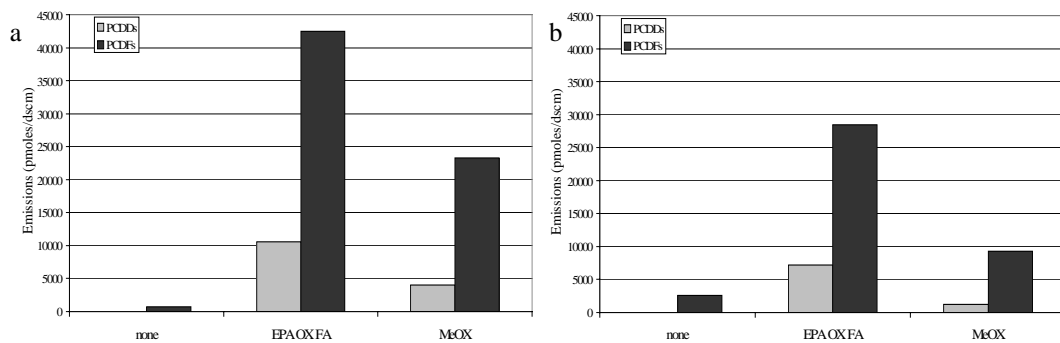


Figure 2: Emissions of PCDDs/Fs from (a) Stage 3 and (b) Stage 4 as a Function of the Additive to the Soot Filter (Stage 3) [400 °C with Cl₂ added via Port B]

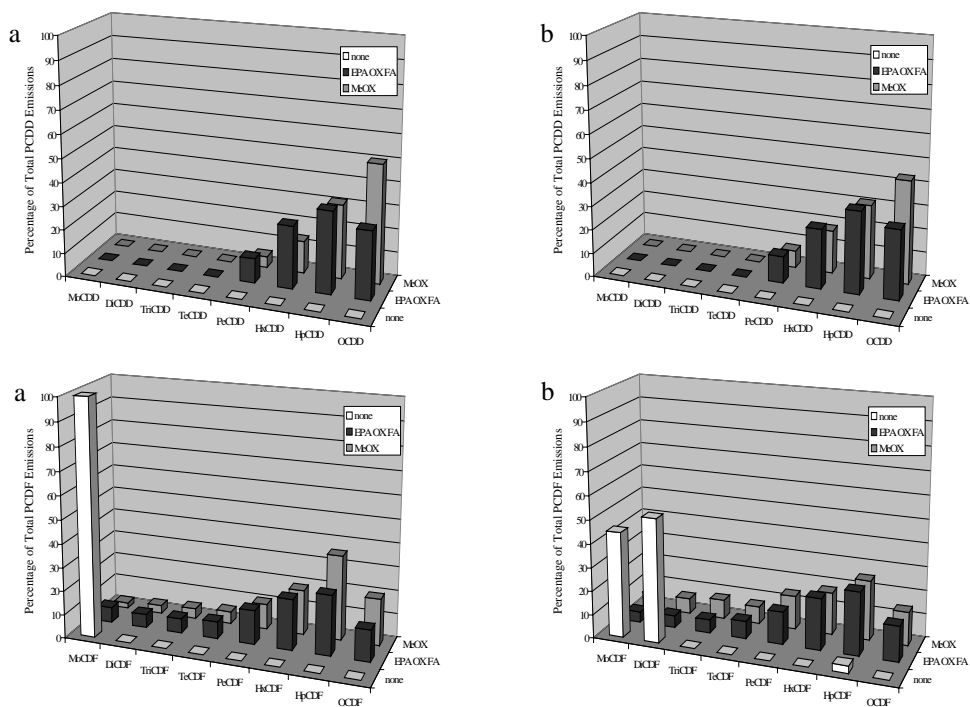


Figure 3: PCDD/F Homologue Profiles (percentage of total PCDD or PCDF) for Emissions after (a) Stage 3 and (b) Stage 4 as a Function of the Additive to the Soot Filter (Stage 3) [400 °C and Cl₂ added via Port B]