IMPACT OF SOOT CONCENTRATION ON PCDD /F EMISSIONS

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Introduction

Results from recent laboratory and field dioxin formation and control studies have shown a direct correlation between soot formation in the flame zone and pollutant formation in the post-combustion cool zone. Based on the results of their pilot plant study, Zimmermann and coworkers suggested that carbonaceous layers, deposited on the inner walls of the high temperature zone of the plant, are responsible for increased emissions of PAH and drastic changes in the profiles of PCDD/F homologues [1]. Wikström et al. have also shown that under fuel lean conditions, soot deposits in the post-combustion zone are the main carbon source for the observed PCDD/F emissions [2]. Identification of soot as a carbon source is at odds with consensus pollutant formation theories, which have usually considered fly ash carbon and organics present in the effluent stream as the only carbon source for post-combustion zone pollutant formation reactions [3, 4]. Even though the Zimmermann and Wikström studies were able identify soot as a significant carbon source for pollutant formation reactions, the exact nature of the relationship between soot and pollutant formation is still not known [1, 2].

In this study, we conducted soot and fly ash carbon oxidation experiments under post-combustion cool zone conditions to better understand the relationship between soot and PCDD/F emissions. Soot (or carbon) oxidation has been studied extensively by both the particulate control and air emissions research community [5-7]. Soot oxidation studies conducted in the particulate control community are focused on the conversion of soot to CO_2 (or CO) [5, 6], whereas the majority of studies conducted in the air emissions (e.g., PCDD/F) community are focused on the conversion of soot/carbon to aromatics or PCDD/Fs [7]. However, to better understand the relationship between soot and pollutant emissions, all carbon-containing products formed during soot (carbon) oxidation need to be identified and quantified. There is also a need to determine the relative importance of soot and fly ash as carbon sources in the post-combustion pollutant formation reactions. This study was designed to fulfill these research needs.

Methods and Materials

In soot oxidation experiments, Printex-U (a flame soot supplied by Degussa AG) was used as a carbon source and EPA-OX fly ash was used as a catalyst. There is extensive data available in the literature for both Printex-U and EPA-OX fly ash [7, 8]. All experiments were conducted in a fixed bed flow reactor system that has been described in detail elsewhere [9]. A schematic of the reactor system used in the present study is shown in Figure 1. The system was built around the fixed bed flow reactor. The experiments were conducted at reactor temperatures of 300, 400, 500, and 600°C. For all experiments, the fixed bed reactor was made of 0.1 g soot and the total reaction time was 60 minutes. A part of the effluent (1/25 of total flow) from the reactor chamber was trapped at –60°C on the head of a DB-5 column. The rest of the effluent was trapped by a U-tube carbon trap at held at –20°C. It has been shown that active carbon held at –15°C can successfully trap the volatile compounds methane and ethylene. The reactor flow was kept constant at 20 ml/min (dry air) and an extra flow of 5 ml/min (helium) was added after the reactor stage to

introduce an internal standard (IS). Internal standards with low volatility (six deutered aromatic compounds dichlorobenzene-D4, naphthalene-D8, acenaphthene-D10, phenanthrene-D10, crysene-D12 and perylene-D12) were introduced using a pyroprobe. The portion of effluent trapped in a DB-5 capillary column (30 m; ID 0.25 mm film thickness 0.25 μm) at –60°C was used to analyze semivolatile compounds (high boiling point). Quantification of these semivolatile products was based on the response of six deuterated semivolatile to internal standards.
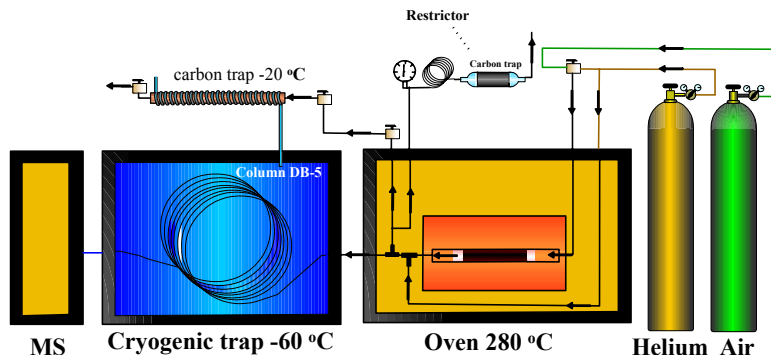

Figure 1. Schematic drawing of the flow reactor system.

  The effluent trapped in the U-tube carbon trap was transferred to a gas chromatograph (GC) by heating the trap. The products were trapped cryogenically at –60°C at the head of the PORAPAKQ GC column (100/120 mesh, 2 mm x 2 m). The products were detected using a Flame Ionizer Detector (FID). Quantification for aliphatic products was accomplished using standard calibration curves and response of the internal standard (hexafluoropentane), which was added during transference from the U-tube to GC.

Results and Discussion
  As-received Printex-U (soot) contained a significant quantity (around 0.6%) of aromatic and polyaromatic hydrocarbons (PAHs) adsorbed on it. These PAHs were adsorbed during the soot collection process after they were generated by flame reactor. Before every experiment, soot was heated at 500°C in helium for one hour to desorb all these PAHs. This PAH desorption procedure has been carefully tested to ensure that all adsorbed organics were removed from the soot before soot oxidation experiments were conducted.
  It is known that at post-combustion temperatures (250 to 400°C) fly ash carbon can form a considerable amount of chlorinated aromatic compounds (chlorobenzenes, chloronapthalenes, PCDD/F) via the de novo mechanism. In the de novo mechanism, aromatic structures are postulated to directly come from structures present in the carbonaceous material [10]. This study was designed to investigate if soot present on the walls of post-combustion zone can form chlorinated pollutant with very little or no fly ash. This is why desorption of soot at the start of experiments is very important; otherwise, organics previously adsorbed on soot can act as precursors for chlorinated pollutants and thus produce misleading results. In the present work, soot oxidation was investigated with and without the presence of fly ash. The fly ash used in this study was oxidized previously at 500°C during a 24 hour period to oxidize all fly ash carbon, thus preventing any interference from organic carbon present in the original fly ash.

Soot oxidation without fly ash did not yield any semivolatile compounds - only a small signal of ion 78 corresponding to benzene was observed. The detection limit for these analyses was estimated to be less than 0.1 mg/kg of soot. This result shows that soot combustion without any catalyst does not generate significant quantities of aromatic or polyaromatic structures. For this set of experiments, the yield of aliphatic compounds was between 4 mg/kg and 10 mg/kg. Major aliphatic compounds identified were methane, ethane, ethylene, propane, and butane. To study the impact of fly ash on soot oxidation, 5% (wt) fly ash (EPA-OX) was added to soot. Soot and fly ash were mixed by milling.
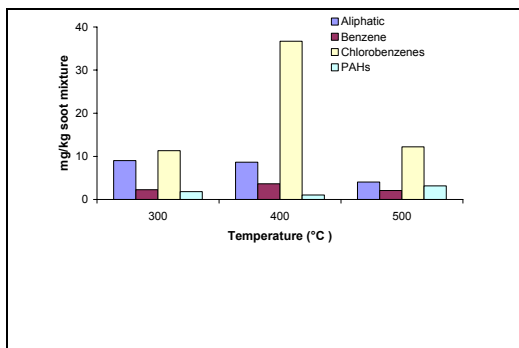

Figure 2 Yield of products identified in combustion of soot with fly ash

The product distribution was completely changed with the addition of fly ash. Soot-fly ash experiments yielded significant quantities of chlorobenzenes (3-16 mg/kg) and some PAH (1-3 mg/kg) along with benzene and volatile aliphatics (see Figure 2). The highest yield of chlorobenzenes was observed at 400°C. Total yield of aliphatic products obtained in this set of experiments was similar to that obtained in earlier uncatalyzed (without fly ash) soot oxidation experiments.

In order to study the impact of fly ash concentration on yields of chlorobenzenes, combustion experiments with ox-fly ash concentrations of 25% and 50% were conducted at 400°C. Figure 3 shows yields of benzene and chlorobenzene as a function of ox-fly ash concentration. These results suggest that if the yield of chlorobenzene is normalized with the amount of soot burned, then the concentration of ox-fly ash has no significant impact on overall chlorobenzene yields. The 95% ox-fly ash data is in fact obtained using as-received fly ash that is known to contain about 5% carbon.

Although chlorobenzene yields from as-received fly ash are similar to those obtained for soot + Ox-Fly mixtures, they are lower than chlorobenzene yields observed in other fly ash denovo studies. Milligan and Altwicker [10] observed ten times bigger chlorobenzene yields than those observed in present study. After a comparison between the Milligan-Altwicker experiments and ours the only important difference was the thermal desorption of fly ash. In order to study the influence of thermal desorption on chlorobenzene yield, two experiments were conducted where fly ash was desorbed at 300 and 400°C. Yields of chlorobenzene (Figure 4) increases close to chlorobenzene yields of Milligan and Altwicker when the soot is desorbed at 300°C. This result suggests that compounds adsorbed on the fly ash are the major source of chlorobenzenes during Milligan and Altwicker (classic de novo) experiments.
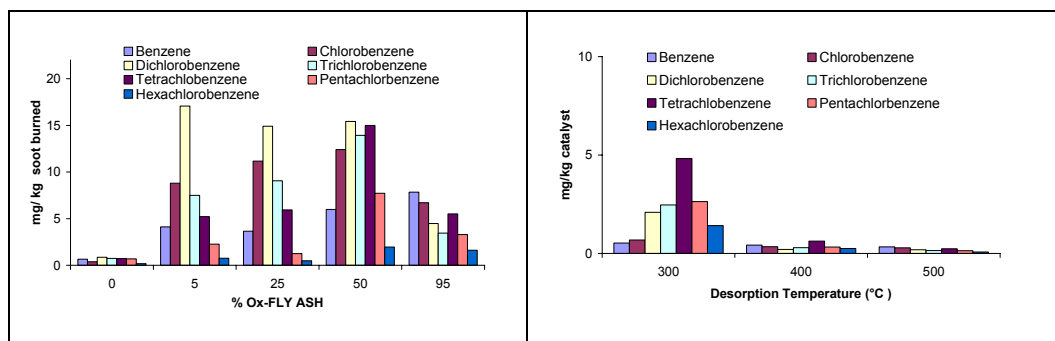
Figure 3. Effect of catalyst concentration on chlorobenzene yields.

Figure 4. Effect of desorption temperature on chlorobenzene yields.

The concentration of soot in the incinerator is around 100 mg/Nm^3 (before particle removal systems) based on a soot yield of 0.2-0.6 % of fuel feed. Based on the results of this study, 100 mg/Nm^3 of soot in the presence of a small quantity of fly ash (5%) will produce 1300 ng/Nm^3 chlorobenzenes. This estimated chlorobenzene concentration is very similar to the concentration of chlorobenzenes (1600 ng/Nm^3) that was observed by Zimmermann et al. [1] during normal pilot incinerator plant operations. Using the correlation of Zimmermann et al. between monochlorobenzene/dichlorobenzene and total PCDD/F I-TEQ, the chlorobenzene concentration of 1300 ng/Nm^3 from soot combustion translates into 0.1 ng/Nm^3 of PCDD/F I-TEQ. This shows that products of soot oxidation can be an important contributor to overall hazardous air pollutant emissions from a variety of combustion sources.

Conclusions

Aliphatics are the only organic compounds detected during combustion of soot that are desorbed at 500ºC. Small quantities of Ox-fly ash, present in the soot, catalyzes formation of chlorobenzenes. About 90% of the chlorobenzenes from the fly ash are from absorbed compounds and only 10 % are from combustion of carbonaceous material.

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