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PCDD/F formation from oxy-PAH precursors in waste incinerator flyash

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ABSTRACT

The yield of PCDD/F in relation to the presence of oxygenated PAH in model waste incinerator flyash has been investigated in a fixed bed laboratory scale reactor. Experiments were undertaken by thermal treatment of the model flyash at 250 and 350 °C under a simulated flue gas stream for 2 h. After reaction, the PCDD/F content of the reacted flyash and the PCDD/F released into the exhaust gas, and subsequently trapped by XAD-II resin in a down-stream condensation system were analyzed. The PAHs investigated were, dibenzofuran and benzo[b]naphtho[2,3-d]furan and were spiked onto the model flyash as reactant precursors for PCDD/F formation. The results showed significant formation of furans from both of the PAH investigated, however except from some highly chlorinated dioxin congeners, the formation of dioxins was not so common. Benzonaphthofuran was significantly more reactive than dibenzofuran in PCDD/F formation, in spite of the fact that dibenzofuran is structurally more similar to that of PCDD/F. Thus, there was no clear attribution between the chemical structure of PAH used and the formation of PCDD/F. There were considerable differences between the yields of PCDD/F congeners in the gaseous species and those in the reacted flyash under the same operational conditions. The concentration of PCDD/Fs was reduced at the higher reaction temperature of 350 °C; however, the higher temperature resulted in the majority of the PCDD/F formed on the flyash being released into the gas phase.

1. Introduction

A variety of non-polar organic compounds such as polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated didenzofurans (PCDFs), and moderately polar organic compounds such as oxygenated PAH have been reported in municipal solid waste incinerator flyash. For example, in the quantitative analysis of oxy-PAH in municipal solid waste incinerator flyash using GC/MS, about 97 oxy-PAH having 2–6 rings were detected and there were some low chlorinated compounds (Akimoto et al., 1997). The 16 US-EPA priority PAH content of flyash from different scale of hospital waste incinerators were analyzed and a mean PAH level of between 4.16 and 199 mg kg^{-1} flyash was reported (Zhao et al., 2008). Emission of 16 PAH from various combustion sources, including municipal solid waste incinerators has been reported at around 6043 ton year^{-1} and 1638 ton year^{-1} respectively (Dyke, 2000).

The formation mechanism of PCDD/F has been the subject of much research (Dickson and Karasek, 1987; Addink et al., 1995; McKay, 2002; Stanmore, 2004; Jansson et al., 2009). One of the main formation pathways for PCDD/F is from organic precursors in the flyash, and PAH in flyash is most likely involved in PCDD/F formation as an intermediate reactant (Addink et al., 1996). Generally, three main reaction steps including degradation, oxygen insertion and chlorination are involved in the transformation of PAH to PCDD/F (Webber et al., 2001; Fullana et al., 2004). Research has been carried out to understand the PCDD/F formation mechanism in particular to elucidate the role of different PAH based precursors (Iino et al., 1999b; Webber et al., 2001; Wilhelm et al., 2001; Cieplik et al., 2006).

Developing a better understanding of the role of PAH with biphenyl-like structures in PCDF formation, Fullana et al. (2004) examined the PCDF formation potential of seven types of PAH as intermediate reactants on pre-chlorinated model flyash at 300 °C. Fluorene, phenanthrene and biphenyl produced the highest level of PCDF, whereas, anthracene and naphthalene, not having biphenyl structure in the skeleton, produced a small amount of PCDF. The yield of PCDD was very low and negligible compared to the PCDF (Fullana et al., 2004). The results support the idea that PAHs either adsorbed on particulate surfaces or formed via the non-graphitic layer of soot are an important carbon source for PCDF formation.

In a similar study by Wilhelm et al. (2001) model flyashes made from Florisil (activated magnesium silicate), $CuCl_2{\cdot}2H_2O$ and spiked with low concentrations of 12 individual PAH with structures similar to dibenzo-p-dioxin and dibenzofuran were heated at 250 °C for 1 h in a gas stream of 5% O_2 in helium. The results showed that biphenyl-like structures could be easily converted to PCDF. The authors postulated that the substitution of α-hydrogen

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atoms of biphenyl-like compounds by an ether group was the most efficient reaction for PCDF formation. However several aspects of this formation pathway are still not clearly understood (Wilhelm et al., 2001).

The potential formation of PCDD/F from PAH on model flyash at 300 °C was investigated and their relative formation rates with those formed from activated carbon and phenol were compared (Iino et al., 1999b). Within the group of tested compounds, perylene with biphenyl-like structure showed a higher potential for PCDF formation. Furthermore, apart from some highly chlorinated PCDD the lower chlorinated PCDD were hardly produced from PAH. In contrast, the PCDD were significantly formed from phenol. Iino and co-workers concluded that PAH and soot act as carbon source for furans, while phenols act as precursors for dioxins formation.

The results of similar research conducted by Webber et al. (2001) showed that significant amounts of PCDF, polychlorinated biphenyls, polychlorinated naphthalenes and polychlorinated benzenes were formed during the de novo synthesis from PAH on a model flyash. However PCDD and polychlorinated phenols were formed in lower concentrations via 'de novo' indicating additional formation pathway for these compounds. Homologue distribution of PCDF formed by all tested PAH showed that OCDF had the highest concentration when $CuCl_2$ was used as chlorine source. It was reported that during the degradation of PAH the position of C–C cleavage played a major role in chlorination reactions (Webber et al., 2001).

In another study, PCDF formation via chlorination of dibenzofuran on flyash was assessed (Addink et al., 1996). All organic materials were removed from a municipal waste incinerator flyash and then spiked with dibenzofuran solution in hexane and the solvent evaporated. The sample was heated at 348 °C in a $N_2/O_2/HCl$ atmosphere for 50 min. Chlorination of dibenzofuran on flyash produced all possible PCDF congeners, but the yield of 2378-PCDF was substantial. These authors suggested that the chlorination reaction followed an electrophilic aromatic substitution mechanism. By conducting a series of experiments with 123478-HxCDD at the same experimental conditions they found that chlorination and dechlorination were not simultaneous but separate processes.

Post-combustion formation of PCDD/F, polychlorinated benzenes (PCBz) and polychlorinated phenols (PCPh) during combustion of an artificial municipal solid waste was studied in a laboratory-scale fluidized-bed reactor (Jansson et al., 2009). The PCDF, PCBz and PCPh were significantly formed at the temperature of 450 °C with a dominance of lower chlorinated homologues, whereas the PCDD formation was dominant at 300 °C. The ortho/para directionality of formed PCPh congeners confirmed the electrophilic aromatic substitution reactions. Injection of dibenzo-p-dioxin at 650 °C led to increased formation of Tri-HxCDD and a decrease in the dibenzofuran levels, however, the total PCDF level was not very pronounced suggesting that the affected PCDD/F congeners were the products of chlorophenols condensation rather than chlorine substitution products.

Consideration of the PCDD/F formation pathway shows that the specific mechanism of their formation is still a subject of debate, particularly for the heterogeneous formation on flyash and air pollutant control residues. Furthermore, there is still a lack of data describing the tendencies of oxygenated precursors in the formation of PCDD/F on flyash. Based on the two well known heterogeneous formation routes, this study has focused on evaluating the yield of PCDD/F in relation to a number of parameters including the presence of oxygenated PAH, the influence of their chemical structures and the reaction temperature. In this study, dibenzofuran and benzo[b]-naphtho[2,3-d]furan have been used as oxygenated PAHs. Results would suggest the potential of these compounds as precursors or intermediates for PCDD/Fs formation in the presence of typical and important sources of chlorine atoms in flyash.

2. Materials and methods

2.1. Sample preparation

A model flyash composed of 1.0% w/w $CuCl_2 \cdot 2H_2O$ and 1.0% w/w KCl in silica gel were prepared by precipitation, and calcined at 250 °C in a vacuum oven overnight. All organic material was removed from the silica by heating it at 450 °C in a muffle furnace for 4 h prior to mixing it with other compounds. $CuCl_2$ and KCl have been applied as sources of chlorine atoms to test the potential formation of PCDD/F from oxy-PAHs in this work. In real flyash, the sources of chlorine could include a large variety of metal salts and their proportions also differ from one flyash sample and another (Zhu et al., 2008). Copper metal is known to catalyze de novo synthesis of PCDD/F in flyash (Cunliffe and Williams, 2009; Jasson et al., 2011). Moreover, KCl is a common chloride salt that can be found along with NaCl in MSW. Recently, Lu et al. (2007), showed that the trend in PCDD/F formation in the presence of some common mineral chlorides was $NaCl < MgCl_2 < KCl < AlCl_3 < CaCl_2$. The median position of KCl in their study indicated that it could have an appreciable effect of dioxin formation on flyash.

In the literature, chlorine contents of flyash ash have been reported to range from 0.5% to 1.7% (Chang and Huang, 2002; Lu et al., 2007; Aurell and Marklund, 2009; Jansson et al., 2009; Themelis, 2010). In addition, we analyzed the chlorine content of a real MSW incinerator flyash sample using SEM-EDX and found it to be 1.6% of flyash dry mass. For a 10 g model flyash sample used in our experiments, the chlorine content was about 1.1%, which was within the range found in literature.

Two kinds of oxygenated PAH which have been examined in this study were dibenzofuran (DBF) and benzo[b]-naphtho[2,3-d]furan (denoted here as benzonaphthofuran or BNF). These two compounds have been selected because of their structural similarities to PCDD/Fs, particularly PCDFs. With their dibenzofuran skeletons, it was important to test their potential for chlorination and thus PCDD/Fs formation in flyash under the conditions studied. In addition, their chlorinated homologues have been reported as products of secondary reactions of chlorophenols for the formation of PCDD/Fs in flyash (Mulholland et al., 2001). These compounds were purchased from Sigma–Aldrich Ltd., UK. The oxy-PAHs (40 mg) were each dissolved in 100 mL HPLC grade cyclohexane (0.4 mg mL^{-1}). In each experiment 5 mL of the solution containing 2 mg (0.02% w/w) of the test compounds were spiked onto 10 g of the model flyash and left to dry at 80 °C in a vacuum oven for 1 h then left to cool at room temperature.

2.2. Experimental apparatus

Experiments were undertaken by thermal treatment of the model flyash at temperatures of 250 and 350 °C using a laboratory scale static-bed reactor equipped with furnace and temperature controller (Fig. 1). It has been reported that substantial amounts of PCDD/F formation from PAH on municipal waste incinerator flyash occurs at the temperature ranges between 250 and 450 °C (Stanmore, 2004; Fullana et al., 2004; Cunliffe and Williams, 2009; Jansson et al., 2009). The model flyash was placed into a quartz liner supported by a glass frit and mounted inside the stainless still reactor tube. A simulated flue gas stream composed of 12 vol% CO_2 and 6 vol% O_2 in nitrogen was then introduced and the exhaust gas was directed into the condensation and trapping systems. Literature shows that for PCDD/F formation, the optimum