Rapid Formation of PCDD/F in the Heterogeneous Combustion of 1,2-Dichlorobenzene and the Role of Particles

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INTRODUCTION

Measurements of PCDD/F at the exit of a secondary combustion chamber, at the inlet of an APCD (such as an ESP) and at its exit (stack), often have shown progressively increasing levels of these compounds, suggesting formation as the gases cool. In addition, evidence for phase shifts has been presented. Thus, PCDD/F at the inlet of an ESP tend to be predominantly in the particle phase, whereas at the exit gas phase PCDD/F appear to dominate (based on front half/back half analysis of the MM5-train). As previous calculations have demonstrated[1]), if 95% of all PCDD/F is on particles and 95% of such particles are removed, the PCDD/F concentration between inlet and outlet should decrease by 90%, contrary to the increases that have been reported[2]. Since the PCDD/F particle loadings on inlet particles and collected particles are not drastically different, desorption from collected particles seems unlikely (it is also not favored by temperature). The question then is: can PCDD/F be formed during the gas phase passage time through the APCD, either in the gas phase, on uncollected particles, or both, keeping in mind that typically PCDD/PCDF < 1. As pointed out elsewhere, this requires rates of 10-10^3 µg/g min, which cannot be achieved by the *de novo* reaction, at least not according to published laboratory experiments[2].

Recent laboratory and pilot plant experiments have shown that PCDD/F can form rapidly at relatively low temperatures. Fängmark, et al.[3,4] reported on the combustion of pelletized synthetic RDF in a fluidized bed linked to a cooling section. When this cooling section was held at 340°C large quantities (>1000 ng/m^3) of PCDD/F were formed within 0.8 - 3 s; at higher (400-500°C) and lower (250°C) temperature yields were much lower.

Gullett, et al.[5] injected MSWI-fly ash downstream of a natural gas combustor and sampled 1-3 s later downstream; PCDD/F-quantities increased 2-100 fold over those originally present in the injected fly ash in the 300-370°C range. Exhaustive extraction of this fly ash prior to use to remove any PCDD/F present had virtually no effect on formation rates. Concentrations exceeded 10,000 ng/m^3 in some instances.

We report here on continuation of our combustion studies of 1,2-dichlorobenzene in heptane in a spouted bed combustor in the presence of sand or quartz[6].

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EXPERIMENTAL SYSTEM, SAMPLING, AND ANALYSIS

These aspects have been described earlier[6,7]. Briefly, the experimental system consists of an all-quartz reactor followed by a four-port sampling cross and two separate post combustion regions that can be heated separately (Figure 1). The bed material consists of either sand or quartz (~1 mm). The fuel (10% 1,2-dichlorobenzene in heptane) is preheated and mixed with air and introduced at the bottom of the vertically mounted reactor. At sufficiently high inlet flow rates, these gases penetrate the bed, create a spout and a particle fountain. Spouted particles return to the annulus setting up a counterclockwise motion of particles in the annulus. This mixing leads to very uniform temperatures in the bed, after the fuel has been ignited to create a stable flame.

Samples were taken in the bed at the wall approximately 2 cm below the bed surface, at SC and at the combustor exit (USP), using a cooled mixed solvent/buffer trap followed by a foam plug.

Probe and foam plug were rinsed and combined with the trap contents; ^{13}C-labelled internal standards were added. After separation, the organic layer was reduced in volume and processed for GC/MS-analysis via a silica/alumina cleanup[6,8].

RESULTS AND DISCUSSION

At the reactor inlet the only organic compounds present are 1,2-dichlorobenzene and heptane. The residence time to the sampling point in the bed was estimated from the stream tube model[9] to be about 0.1 s. Under these conditions (annulus T_{bed} = 585 ± 5°C, ϕ = 0.55, 1,2-DCB inlet concentration 6.5 x 10^6 µg/m^3, 20.8% O_2) rapid formation of PCDD/F occurred (Figure 1, bottom box). However, far more PCDD/F was formed in the presence of sand than in the presence of quartz, with T_4CDF and H_7CDF being the most abundant congeners in the presence of sand. Because the gas residence time in the spout is much less than in the annulus, and the annular flow is at most 30% of the total flow, the maximum average concentrations are 22 ng/m^3 (sand) and 5.5 (quartz) for PCDD, and 93 (sand) and 9 (quartz) for PCDF. There is no conversion in the spout below the flame.

Sampling was also conducted at two locations downstream of the flame where there was either a rapid quench of the gas temperature (430 to 125°C, profile q) or a near isothermal condition (430 to 390°C, profile i), depending on the power supplied to the two post combustion regions. Because the temperature at the SC-location (Figure 1) was the same in all experiments (430°C) and the equivalence ratio was constant (0.55), the data support (re)formation of PCDD/F in the cooler region for profile i, but not for profile q (quench); compare middle and upper box, Figure 1. For profile q, sand and quartz gave similar concentrations; under profile i conditions, PCDD/F concentrations rose by about a factor of four when sand was present. Sand and quartz particles in the post combustion region arise from bed attrition; these particles are much (~50% < 5 µm) smaller than the bed particles (~1 mm). Quartz which is nearly pure SiO$_2$ (99.995%) did not appear to promote PCDD/F-formation; the sand used is only 77.6% SiO$_2$ and contains trace metal oxides such as Fe, Ca, Ti, and Mn. Also interesting is the finding that all sampling points and conditions gave PCDD/PCDF ratios < 1 from a single precursor.

The major chlorobenzenes were monochlorobenzene and 1,2,4-trichlorobenzene. There was a large difference in ΣCB between sand and quartz for both profiles, suggesting a catalytic effect of the former, 475 ± 74 µg/m^3 vs. 16.5 (profile q) and 332 ± 12 vs 13.1 ± 2

(profile i), respectively.. On the other hand, total CPs were comparable for sand and quartz, while nevertheless exhibiting differences between the DCP-T4CP isomer distribution, ΣCP 180 ± 23 ($\mu g/m^3$ vs. 184 (profile q) and 140 ± 15 vs. 145 ± 47 (profile i), respectively.

In the bed region the dominant CB was 1,2,4-T3CB (3000 $\mu g/m^3$ for sand; 600 $\mu g/m^3$ for quartz). Both hydroxylation and chlorination must proceed rapidly: the total CP-concentration reached 1.4 x 10^5 $\mu g/m^3$ (corresponding to a 2% conversion of 1,2-DCB) with T_4CP and PCP in greatest abundance, when sand was the bed material. With quartz the total CP-concentration was 34 ± 14 $\mu g/m^3$ with dichlorophenols accounting for nearly 80% of that total.

Preliminary experiments indicate that the PCDD/F-formation may follow specific routes determined by the structure of the starting material: when 1,2-dichlorobenzene was injected into the post flame region of a heptane flame, the principal PCDD/F product was T4CDF.

The apparent reactivity of fine attrited sand particles in the 430-390°C temperature range suggest that model catalysts and fly ash may bring about a higher rate of formation of PCDD/F at a lower temperature than observed here for post combustion zone reformation. This work is in progress. Collectively, these results confirm that formation of PCDD/F may be rapid and that formation can occur in a temperature window that corresponds most closely to the region between a secondary combustion chamber and an APCD in actual incinerators (600-400°C).

Modeling calculations using the Shaub and Tsang gas phase mechanism lead to the conclusion that the gas phase formation of PCDD (only) under the conditions of the post combustion region is negligible[10]. Therefore, surface processes would appear to play a major role in the mechanism of reformation of PCDD and PCDF under post combustion region conditions.

References

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USP

|—5cm—|

65cm

80cm

SCc

8cm — SCw

20cm

25cm — Flame
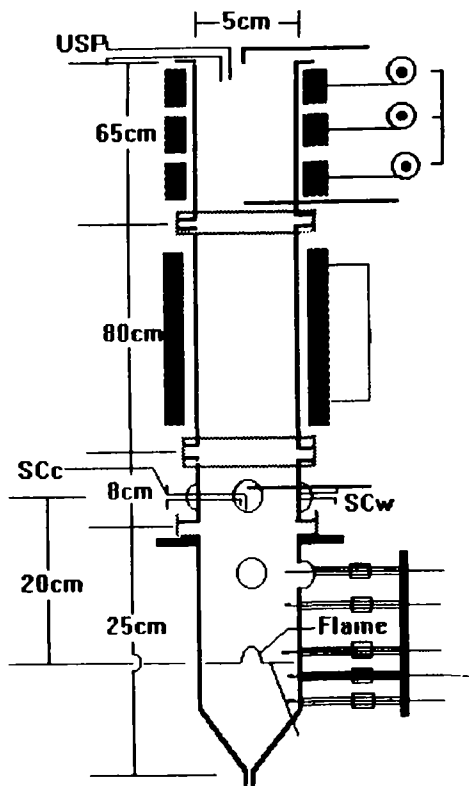
1,2 DCB (10% in heptane)
PCDD + PCDF = 0

	PROFILE q		PROFILE i	
	Sand	Quartz	Sand	Quartz
ΣPCDD	13.0	18.8	48 ± 6	22.3
ΣPCDF	17.9	19.3	74.5 ± 11	29

	PROFILES q & i[1]	
	Sand	Quartz
ΣPCDD	11.5	14.4
ΣPCDF	13.3	15.1

[1]ng/m^3; previously reported range (6): ND-15

BED T, °C	585 ± 5	
	Sand	Quartz
ΣPCDD	67	16.5 ± 3
ΣPCDF	278	27 ± 2

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