

FORMATION OF PCDDs AND PCDFs FROM METHANE-FLAME, GAS-PHASE BY-PRODUCTS; SOOT DEPOSITS; AND FLY ASH

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Introduction

Simple methane or propane flame combustion at sooty conditions with hydrogen chloride (HCl) present, as well as numerous experiments conducted with only fly ash present as the source of carbon and chlorine (*de novo* synthesis) have shown significant formation of chlorinated compounds, such as polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)^{1,2}. In a full-scale incinerator, both fly ash and flame products are present simultaneously, and the relative importance of the two carbon sources for the formation of PCDDs/Fs is still undetermined. An important question to be answered is whether PCDDs/Fs are formed through a series of reactions of gas-phase flame by-products formed at various concentrations depending on the equivalence ratio and/or from the carbon matrix present in flame soot and fly ash. Additionally, how important are catalytic reactions by metals present in the fly ash for the formation of PCDDs/Fs? Experiments conducted in a laboratory scale reactor using a methane flame doped with chlorine and addition of fly ash in the flue gas provided answers to many of the important questions regarding the PCDDs/Fs formation mechanism during high-temperature processes.

Methods and Materials

Experiments were conducted in an entrained-flow reactor (EFR), consisting of a horizontal and a vertical, concentric tube quartz reactors connected in series. The horizontal reactor was equipped with a bluff body diffusion type burner. A flow of 1.0 L/min of methane (CH₄) was added through the burner, while oxygen (O₂) and other gases such as chlorine (Cl₂) and nitrogen (N₂) were added into the opposite end of the outer annulus of the horizontal reactor. An additional flow of 1.0 L/min of O₂ was added as an oxidant into the outer annulus of the vertical reactor. A fluidized particle feeder (particles <105 μm) was connected to the top of the vertical reactor. Two derivatives from a fly ash collected at the electrostatic precipitator of a grate-fired municipal solid waste incinerator were employed in these experiments, *viz.* an extracted (EX) fly ash and an oxidized (OX) "carbon-free" fly ash. Chemical and physical properties of the EX and OX ash, such as chlorine (5.7 and 5.9 %, respectively) and metal content, were very similar, except that the total amount of carbon in the as-received fly ash was reduced from 1.23 to 1.00 % and to 0.04 % in the EX and OX ash, respectively. The initial content of PCDDs/Fs was non-detectable in the two fly ash derivatives used. The experiments in this study were planned using an experimental design (MODDE 5.0)³ to extract the maximum amount of information from the data set. A full factor design in two levels was used to screen the experimental domain for linear main and interactive effects from each studied parameter. Individual response functions for the PCDD/F data were fit using multiple linear regression techniques. The quality of the model was exemplified by the squared correlation coefficient (R²), its predictive measure (Q²). To elucidate the role of the ash and the

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flame products for the formation of PCDDs/Fs, the equivalence ratio of the horizontal reactor (*ErHR*), the amount of gas-phase chlorine (Cl_2), and the presence or absence of EX ash (*Ash*) was studied thoroughly in a two-level full-factor design. The high and low set points for the three independent parameters are listed in Table 1. The design contained eight (2^3 , from two levels, three parameters) experimental conditions, each tested with two or more repeats (except at two conditions). Supplemental experiments were conducted to further investigate the function of different solid phases added (silica, EX, or OX ash) and the role of soot deposits for the formation of PCDDs/Fs. To more closely evaluate the importance of gas- and particle-phase carbon, additional experiments with labeled methane ($^{13}CH_4$) were performed. In total, 40 experiments were included in the study. The sampling and analyses of the mono- to octa-PCDDs/Fs in the flue gas were conducted according to a slightly modified version of U.S. EPA Method 0023a⁴.

Results and Discussion

The results from the model calculation (Table 2) indicated that the most important parameters for both PCDD and PCDF formation were the equivalence ratio in the horizontal reactor (*ErHR*) and the presence of ash (*Ash*) (to be a significant parameter, its coefficients, b_i , must exceed the 95% confidence interval criteria; the magnitude of the coefficient reflects its relative importance). However, gas-phase Cl_2 was shown to be insignificant for the formation of PCDFs and only a weak, but significant effect, was shown for the PCDDs. The high R^2 and Q^2 values show that this model incorporates the variations in PCDD/F formation caused by the three parameters studied in this experimental set-up.

The model suggests that the presence of ash is an important parameter for PCDD/F formation, but it is not clear whether the fly ash is acting as a chlorine source, carbon source, catalyst, or all of these.

Formation of PCDDs/Fs was observed from a sooty methane flame (*ErHR* = 0.86, 200 ppm Cl_2) without the addition of fly ash (Figure 1). The importance of increasing surface area for the formation of PCDDs/Fs was studied in additional experiments with silica (surface area of 500 m²/g) added into the flue gas. The addition of silica did not cause the PCDD/F concentrations to increase, suggesting that an increase in surface area did not have an influence on formation from the sooty flame even though the silica surface area was significantly higher than that of the two fly ashes (1-4 m²/g). However, with fly ash (EX and OX) added to the flue gas, greater than 3- fold increases in concentrations were observed. The two fly ashes showed very similar results; *i.e.*, the differences in carbon content (1.00 vs. 0.04% for EX and OX, respectively) between the two ashes did not affect the PCDD/F yields. This implies that the increase in formation when ash was present was not caused by formation from the carbon present in the EX ash or only by increased surface area from the solid phase (silica); the ashes contribute to the formation with other properties, such as being a catalyst and/or an additional chlorine source.

Although the combustion conditions (*ErHR*) were found to be the most important parameter for PCDD/F formation, one question still remains which carbon source (the gas-phase flame by-products or the flame soot) was the most important source? Soot contains two kinds of carbon: *viz.*, chemically adsorbed, condensed, gas-phase carbon compounds (organic carbon, OC) and the larger condensed carbon matter (elemental carbon, EC). The PCDD/F levels at three different conditions are shown in Figure 2: a fuel-rich flame (*ErHR*=1.03), a fuel-lean flame (*ErHR*=0.67) with soot deposits on the reactor walls from the fuel-rich experiment, and a fuel-lean flame (*ErHR*=0.67) in a clean reactor. Considerable amounts of PCDDs/Fs were formed during fuel-rich combustion, a condition at which both high concentrations of soot (observed) and gas-phase flame by-products are also formed. At fuel-lean conditions in the clean reactor, PCDD/F formation was much lower in comparison. Thus, the formation of soot and/or gas-phase flame by-products is very important for the formation of PCDDs/

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Fs. However, what is the relationship between these other flame products and PCDD/F formation? To help determine whether PCDD/F formation originates from gas-phase flame by-products and/or from soot deposits, a lean flame (ErHR=0.67) was run in a reactor containing soot from a fuel-rich experiment, (Figure 2, ErHR=0.67 w/soot). The lower concentrations formed, compared to the fuel-rich experiment, demonstrate that PCDD/F formation is likely related to formation from gas-phase fuel-rich flame by-products since previous fuel lean experiments have shown low formation. As a note, no decrease in formation was observed from soot deposits in consecutive experiments (not shown), indicating that aging of the deposits was probably not the cause of the decreased yields in the present experiments. A comparison of concentrations between the two experiments (ErHR = 1.03 vs. ErHR = 0.67 w/ soot) suggests that the gas-phase flame by-product reactions occurring at fuel-rich conditions account for more than 80% of the PCDD/F formation and that the carbon sources present in the soot play a minor role. An additional test with a sooty ^{13}C flame (ErHR=1.04) to pre coat the reactor surfaces with ^{13}C -soot deposits followed by a fuel-lean (ErHR=0.67) ^{12}C flame was conducted to further investigate the role of the soot deposits compared to the gas-phase flame by-products during fuel-lean conditions. The data indicate that the major carbon source for the PCDDs/Fs was found to be the soot, either from the elemental or the organic carbon; not from flame by-products supplied by the fuel-lean flame. These results seem to suggest that formation of PCDDs/Fs from gas-phase flame products at fuel-rich conditions is faster than formation from soot deposits. However, formation from soot deposits is significantly greater than formation from gas-phase flame by-products of fuel-lean flames.

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Table 1. The experimental domain tested, each parameters high respectively low level. (*ErHR equals to Equivalence ratio in Horizontal reactor*)

Parameter	Low	High
ErHR	0.67	0.86
Ash (g/h)	0	1
Cl ₂ (ppm)	0	200

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Table 2. The calculated coefficients (b_i) for each main parameter and their interactions and the model validation (R^2 and Q^2). The significant parameters for each response are typed in **bold** and non-significant in *italics*.

Coefficient	PCDDs	PCDFs
Constant (b_0)	123.5	1005
ErHR (b_3)	117.0	876
Ash (b_1)	74.0	630
Ash*ErHR (b_5)	74.5	593
Cl_2 (b_2)	44.0	252
Cl_2 *ErHR (b_6)	44.0	208
Ash* Cl_2 (b_4)	-2.5	-14.5
95% Conf. interval	± 31.76	± 304.95
R^2 value	0.99	0.99
Q^2 value	0.98	0.98

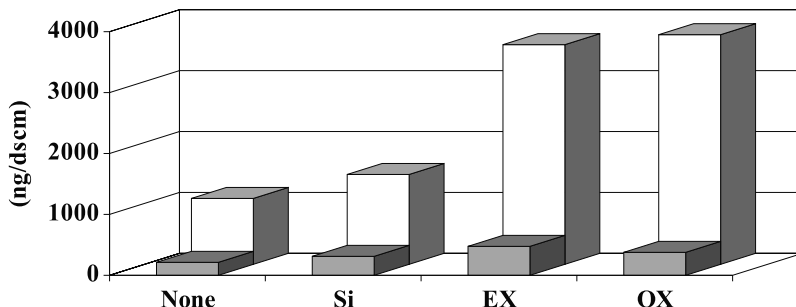


Figure 1. Average PCDDs (grey bars) and PCDFs (white bars) formation (ng/dscm) from experiments conducted with different solid phases present (experimental condition ErHR=0.86, 200 ppm Cl_2).

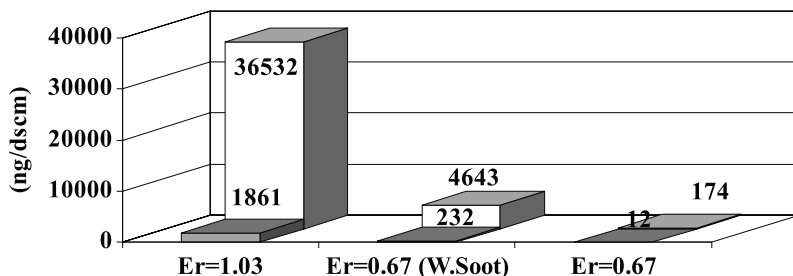


Figure 2. PCDDs (grey bars) and PCDFs (white bars) formation (ng/dscm) at different burning (ErHR) and soot conditions all performed with 200 ppm of Cl_2 and no ash added (numbers above the bars represent the actual values).