

Mechanism of Formation of PCDD/PCDF in MSWI: Investigation of Role of HCl, Particulate Carbon and Precursors

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1. Abstract:

The thermal formation of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans on the fly ash treated by HCl compared to non-treated fly ash provides better understanding of role of HCl in the mechanism of formation of PCDD/PCDF. A carbon-less fly ash residue was obtained by heating MSWI fly ash at 800-900 °C for 2 h in a ceramic crucible. The thermal formation of PCDD/PCDF on HCl treated carbon-less fly ash residue and activated carbon compared to non-treated fly ash residue with activated carbon confirmed the prominent role of HCl in the formation of PCDD/PCDF. The thermal formation of PCDD/PCDF on HCl treated carbon-less fly ash residue with activated carbon at various temperatures and the reaction time has provided better understanding of possible mechanism of formation of PCDD/PCDF in MSWI processes.

2. Introduction:

In general the formation of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in combustion processes is a well established phenomenon. It is considered that the generation of PCDD/PCDF occurs as a consequence of reaction of precursors in the flue gases and fly ash in the cooler zones (250-450 °C). The thermal formation of various chlorinated compounds including PCDD/PCDF from particulate carbon and artificial fly ash has been reported¹. It has also been reported that the formation of PCDD occurs by catalytic activity of the fly ash and various precursors^{2,3}. Several other investigations with variation of parameters and conditions provides different pathways for the formation of PCDD/PCDF. However, still no clear evidence has been provided showing which mechanism is dominating and which parameters and constituents are important.

In the current investigation the role of HCl, the role of particulate carbon and the metallic residue of the fly ash, the effect of variation in reaction time and temperature has been studied to understand the mechanism of formation of PCDD/PCDF in municipal solid waste incineration (MSWI) processes.

3. Experimental:

Municipal solid waste incinerator fly ash (<180 μm) was precleaned by Soxhlet extraction for 96 h using toluene. Soxhlet extract was concentrated and analyzed to determine the amount of PCDD/PCDF produced in the MSWI process (Expt. 1). The precleaned fly ash was spiked by ^{13}C -pentachlorophenol (^{13}C -PCP) at 100 $\mu\text{g/g}$ and catalytic activity test was conducted at 300 $^{\circ}\text{C}$ (Expt. 2). The other portion of the precleaned fly ash was acid digested using 10% concentrated HCl for one hour. The fly ash was washed three times by deionised water and then air dried. The air dried fly ash was spiked by ^{13}C -PCP at 100 $\mu\text{g/g}$ and catalytic activity was conducted at 300 $^{\circ}\text{C}$ (Expt.3).

In the another set of experiments, a carbon-less fly ash residue (CFAR) was obtained by heating precleaned MSWI fly ash at 800-900 $^{\circ}\text{C}$ for 2 h in a ceramic crucible. The CFAR thus obtained was Soxhlet extracted to remove any organic compounds that may have formed during the heat treatment. The Soxhlet extract was concentrated and analyzed for PCDD/PCDF (Expt.4). The dry CFAR was spiked with ^{13}C -PCP and 2% activated carbon was added, and catalytic activity test was conducted at 300 $^{\circ}\text{C}$ (Expt.5). The dry CFAR was digested using 10% concentrated HCl for one hour. The acid digested CFAR was washed three times by deionised water and then air dried. The air dried CFAR was spiked by ^{13}C -PCP at 100 $\mu\text{g/g}$ and mixed with activated carbon at 2% to the CFAR. Then catalytic activity tests were conducted on ^{13}C -PCP spiked and activated carbon added CFAR at 300 $^{\circ}\text{C}$, 350 $^{\circ}\text{C}$, 400 $^{\circ}\text{C}$ and 450 $^{\circ}\text{C}$ (Corresponding Expt.6, 7, 8 and 9 respectively). Also, catalytic activity tests were conducted for 30 minutes and three hours durations (corresponding Expt. 10 and 11 respectively). In one test sodium chloride was used with ^{13}C -PCP and activated charcoal instead of fly ash or CFAR (Expt.12).

General Procedure for Catalytic activity test:

A 3.5 g portion of fly ash sample of particles <180 μm size was suspended in 10 ml methanol. The mixture was stirred using magnetic stirrer. ^{13}C -PCP (calculated 100 $\mu\text{g/g}$ to the fly ash sample) in 2 ml methanol was added to the mixture in portions over a period of 30 minutes. The methanol was then removed by heating the mixture at 70 $^{\circ}\text{C}$ while stirring. The ^{13}C -PCP spiked fly ash sample was then packed in a glass column (50 X 2.5 cm I.D.) using glass wool plugs on the both sides of the fly ash. The glass tubing was connected to carrier gas (air). The carrier gas flow was adjusted to 10 mL/min. and the column was inserted in a tube oven so that the portion of the column with fly ash was in the heated zone. The exit of the column was connected to an ice cold impinger containing toluene. The fly ash was heated at the desired temperature for specific time. After the specific time reaction the heating was stopped, carrier flow was halted and the column was cooled to room temperature. The column was then disconnected from the impinger and the fly ash sample was transferred to a glass extraction thimble. The impinger toluene and the column rinses were used for Soxhlet extraction of the tested fly ash for 48 hours. The toluene extract was concentrated to 1 - 2 mL by rotary evaporation, and then transferred to a reactive vial and then concentrated to a final volume of 50 to 200 μl under slow stream of high purity nitrogen. The concentrated extracts were analyzed using GC-ECD and GC-MS.

4. Results and Discussion:

The amount of PCDD, PCDF and ^{13}C -PCDD detected in all extracts of the experiments 1-12 are shown in Table 1.

Table 1. Amount of N-PCDD/N-PCDF (ng/g fly ash) for all experiments.
Amount of ¹³C-PCDD (ng/g fly ash/100 ug ¹³C-PCP)

| | | | | | | |
|----------------------|---------|---------|---------|----------|----------|----------|
| Compound | Expt. 1 | Expt. 2 | Expt. 3 | Expt. 4 | Expt. 5 | Expt. 6 |
| N-PCDD | 1049 | 1078 | 1919 | nd | 2697 | 20596 |
| N-PCDF | 690 | 583 | 1243 | nd | 650 | 934 |
| ¹³ C-PCDD | - | 997 | 3628 | - | 902 | 1521 |
| Compound | Expt. 7 | Expt. 8 | Expt. 9 | Expt. 10 | Expt. 11 | Expt. 12 |
| N-PCDD | 21166 | 9009 | 509 | 14209 | 24949 | nd |
| N-PCDF | 2460 | 4774 | 1143 | nd | 1803 | nd |
| ¹³ C-PCDD | 1186 | 721 | nd | 1717 | 1751 | nd |

nd = not detected, N-PCDD = Native PCDD, N-PCDF = Native PCDF, Expt. = Experiment.
(For experiments 5-12, 2% activated carbon was added to carbonless fly ash residue)

Expt. #1 shows the amount of N-PCDD/N-PCDF detected on the fly ash sample, which were produced in the incineration process. Expt.#2 shows the amount of N-PCDD/N-PCDF produced from the particulate carbon present on the fly ash which was produced in the MSWI processes. The ¹³C-PCDD produced were from ¹³C-PCP spiked prior to the experiment. Under the identical conditions acid digested fly ash produced an approximately double amount of N-PCDD/N-PCDF and about a four times higher amount of ¹³C-PCDD. Heating the fly ash at 800-900°C results in complete removal of all chlorinated organic, which was evident from GC-ECD chromatogram and GC-MS analysis of Expt. # 4 sample. However, heating the fly ash at 800-900°C did not deactivated the fly ash, which when mixed with precleaned activated carbon (2%) has produced about the same amount of N-PCDF and ¹³C-PCDD, and more than double amount of N-PCDD (Expt. #5) under identical conditions as Expt. #2. Comparison of amounts of PCDD/PCDF produced in Expt. #5 and 6 shows that acid digestion has profound effect on activity of fly ash, where significantly high levels of PCDD/PCDF are produced on acid digested fly ash. No PCDD/PCDF were formed from activated charcoal when fly ash was replaced by sodium chloride (Expt. #12). The amounts of N-PCDD/N-PCDF and ¹³C-PCDD formed from activated carbon and ¹³C-PCP respectively, under identical conditions except reaction time are shown in Figure 1. Significantly high amounts of N-PCDD/N-PCDF were formed by catalytic reactions of fly ash with activated carbon, the levels increases with increase in reaction time. Surprisingly, the amount of ¹³C-PCDD formed was unaffected by the increase in the reaction time.

5. Conclusions:

1. Hydrochloric acid treatment of fly ash prior to heating at 300°C results in production of significantly high amounts of N-PCDD/N-PCDF compared to untreated fly ash.
2. Catalytic activity of the fly ash remains unaffected even if the fly ash was heated at 800 °C.
3. Significantly high amount of N-PCDD/N-PCDF were produced from catalytic activity of fly ash treated with HCl and mixed with activated charcoal.

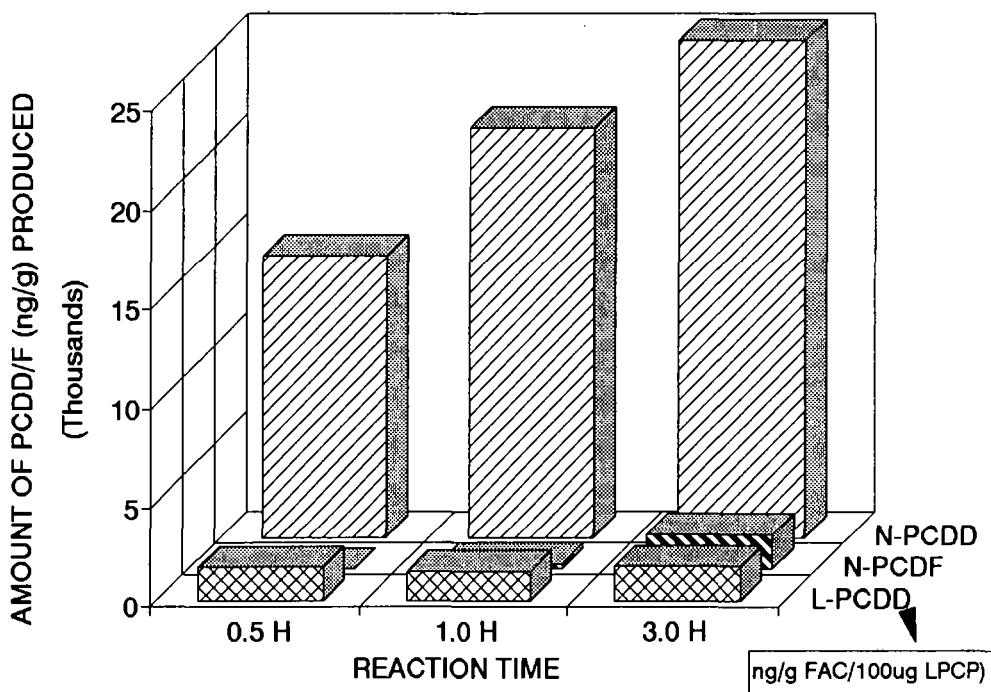


Figure 1. Amount of PCDD/PCDF (ng/g) Produced at 300°C on Carbon-less Fly Ash Spiked With ^{13}C -PCP and Mixed With 2% Activated Carbon (N-PCDD= Native PCDD, N-PCDF= Native PCDF, L-PCDD= ^{13}C -PCDD)

6. References:

- 1) Stieglitz L., Zwick G., Beck J., Roth W. and Vogg H. (1989): On *de-novo* Synthesis of PCDD/PCDF on Fly ash of Municipal Waste Incinerators. *Chemosphere*, **18**, 1219.
- 2) Naikwadi K. P., Albrecht I. and Karasek F. W. (1993): Mechanism of formation of PCDD/PCDF in industrial waste incineration and a method of prevention of their formation, *Chemosphere*, **27**, 335-342.
- 3) Altwicker E. R., Konduri Ravi Kumar N.V. and Milligan M.S.,(1990): The role of precursors in formation of PCDD and PCDF during heterogenous combustion, *Chemosphere*,**20**, 1935.