SOUR I

Polychlorinated Dibenzo-p-Dioxin/Furan (PCDD/F) Formation Potential of Wood Waste Incinerator Fly Ashes

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ABSTRACT

A number (9) of fly ashes were obtained from the electrostatic precipitator of a waste wood incinerator. The samples were extracted to determine the amounts of PCDD/F present. Experiments were performed to characterize formation potential of some of these ashes in the de novo reaction.

The "as-received" samples are of particular interest in that they exhibited a relatively high ratio of 2,3,7,8-T4CDD/PCDD, 0.004-0.04, with PCDD ranging from 0.3-19 ng. Two of the ashes displayed very high reactivity (PCDD/F >1000 ng/g) under laboratory conditions; this appears to correlate with low pH of the aqueous extracts (6.6-6.9) and wt. % Cl (1.8). The typical peak observed with MSWI-fly ashes at about 300°C was not observed with these samples (yield still increasing at 350°C). However, the 2,3,7,8-T4CDD/PCDD ratio is these samples was much lower than in the "as-received" samples. Very short reaction times (<10 min) gave yield comparable to those originally present.

INTRODUCTION

The combustion of fuels such as wood and wood waste (with and without minor amounts of other fuels, such as coal or rubber tires) results in PCDD/F-amounts in ash that are considerably less than those generally observed in MSWIs. Nevertheless, an unexpected observation was made in a particular plant: here the proportion of 2,3,7,8-TCDD was far greater than typically found. Therefore, laboratory investigations were conducted to attempt to understand the reason(s) for such observations.

Figure 1 is a schematic of the boiler plant from which the samples were taken. At the time the fly ashes were collected, boiler #5 was in operation, combusting a fuel consisting of 70% wood/10% rubber tires/20% pellets. Samples were taken at the mechanical collector (RMC) and at several locations from two parallel electrostatic precipitators (ESP), denoted TS and RS. At the time of sampling the duct work connecting the two ESPs-downstream from the boilers was open.

In this study, the goal is to characterize these ashes in terms of reactivity and composition using de novo conditions for PCDD/F formation and the determination of the relative amounts of 2,3,7,8 -tetramers to the total PCDD/F levels.

EXPERIMENTAL

The experimental setup (an isothermal tubular reactor) has been described previously.[1,2] Fly ash samples were sieved to <210 μm and extracted 24 hrs with toluene. Sample sizes were 1-2g. During an experiment a cold trap downstream from the reactor was used to collect any volatiles. However, usually nothing was found; all results reported below are based on extraction of the fly ash bed. After cleanup, analysis was performed by GC/MS using a DB5-column; samples were then re-analyzed for 2,3,7,8-T4CDD using a Supelco 2331-column.

RESULTS

Table 1 summarizes some parameters for the "as received" samples: ΣPCDD/F, wt % <210 μm, wt % Cl, and pH of the aqueous extract. Total PCDD/F were low, all samples (except one) had a PCDD/PCDF-ratio <1, and the 2,3,7,8-T4CDD/PCDD-ratio was 0.004-0.04. Most of the particles in the ashes were less than 210 μm, and Cl-content and pH of the aqueous fly ash extract varied. Preliminary laboratory experiments indicated (last column of Table 1) that yields of PCDD/F differed little from those originally observed for some samples, while others (especially 4RS and 4TS) were startlingly higher. This prompted us to focus on the 3RS/TS and 4RS/TS samples.

Table 1

Comparison of Σ(PCDD/F), "As received", and Laboratory Results
Together with % <210 μm, wt % Cl, and pH of Aqueous Extract

	ΣPCDD/F[1]	wt % <210 μm	wt % Cl	pH	ΣPCDD/F (lab)[2]
RMC	0.9	80.3	<0.07	12.6	2
2TS	9.2	93.0	0.80	11.7	34
2RS	1.4	87.5	0.21	12.3	3
3TS	15.5	99.99	0.72	11.6	92
3RS	13.6	99.2	0.32	11.0	80
4TS	18.7	98.2	1.80	6.9	1800
4RS	14.8	97.3	1.78	6.5	1320
5TS	6.5	91.7	0.15	12.3	6
5RS	32.0	86.7	0.61	7.3	257

[1]total ng/g; in "as received" ashes
[2]ng/g FA; 300°C/2 HRS/10.3% O_2/80 mlpm

Temperature
At 275°C PCDD/F-yields were very low, comparable to those observed in the "as received" ashes; with increasing temperature (to 350°C) yields increased rapidly; higher temperatures have not been investigated. At 350°C, yields in excess of 10,000 ng/g were obtained (Figure 2). For samples 3RS and 3TS yields were considerably lower; these two samples showed an interesting reversal in the PCDD/PCDF-ratio: from >1 at 275°C to <<1 at 350°C. The observed (at 300°C) 2,3,7,8-T4CDD/PCDD-ratio (~0.0004) for the 4RS-sample (Figure 2) was about a factor of 10 lower than that ratio in the original ash.

Time
For reaction times less than 10 minutes, yields were comparable to those observed in the original samples (Figures 3 and 4). After one hour increases were small. The shape of the ng/g vs. time data was similar to what has been observed with MSWI-fly ash under so-called de novo conditions, i.e., the reaction rate levels off. At 325°C the 2,3,7,8-T4CDD/PCDD-ratio showed little change with time; however, the ratio of 2,3,7,8-T4CDF/PCDF declined sharply (>10x) for reaction times greater than 15 minute.

Oxygen Concentration
The oxygen concentration in the gas phase had a strong effect on PCDD/F-yield. Changing this concentration from 1% to 10% resulted in approximately a 100-fold increase in yield. With a further increase, the yield declined. This is consistent with observations of others and could be interpreted as destruction becoming increasingly important. At the 1% level, the PCDD/PCDF-ratio was much less than one. Both the 2,3,7,8-T4CDD/PCDD and the 2,3,7,8-T4CDF/PCDF ratios were relatively

insensitive to oxygen concentration (0.0004 ± 0.0001 and 0.03 ± 0.01, respectively). These studies were conducted at 300°C with the 4RS sample.

Gas Flow Rate

Gas flow rate over the fly ash bed was varied between 40-120 ml/min to examine the possibility of mass transfer (oxygen) limitations on the rate of PCDD/F-formation. Conditions were 300°C/2 hrs/10.3% O_2 using the 4RS-sample. Though there is some fluctuation in yields between duplicate/triplicate runs, yields of PCDD/F and 2,3,7,8-T4CDD/F varied little with the threefold change in flow rate.

DISCUSSION

From the results it is evident that some of the ash samples have considerable PCDD/F-formation potential under laboratory conditions, whereas other samples give yields comparable to those obtained for the "as received" samples (Table 1). Put another way, some samples require only short reaction times (<10 min) to duplicate the field yields. There does not appear to be a single reason for these observations. One of the parameters that needs to be understood is the level of Cl-content. The RMC-sample (Table) has the lowest Cl-content as well as the lowest PCDD/F levels under both field and laboratory conditions. All other samples - collected further downstream - are much higher in Cl-content, which suggests that the major portion of the chlorine was acquired by vapor condensation between the mechanical collector outlet and the ESP. All of these samples were collected over a relatively short time on the same day. Since the variation in Cl-content was large, yet the field yields of PCDD/F did not vary much, it seems that only the laboratory yields over long times (>15 min) were strongly influenced by the inorganic chlorine in the ash. Together with several MSWI-incinerator ashes, these results also form an apparent correlation between PCDD-yield and pH of the aqueous fly ash extract. This is shown in Figure 6. At a pH >11, there appears to be a distinct change in slope. This figure includes results[3] for three so-called model fly ashes (containing three different aluminas).

Only for short reaction times did the laboratory experiments produce yields comparable to those observed in the field (for some samples). While the trends of PCDD/F vs. time (Figures 3 and 4) are those expected, the absence of a peak in yield at about 300°C is not (Figure 2). Another distinguishing feature for some samples was the change in the PCDD/PCDF-ratio with temperature.

Most importantly, both short time (<15 min) and long time laboratory experiments fail to capture an essential aspect of the "as received" samples: the (relatively) high 2,3,7,8-T4CDD/PCDD-ratio. No quantitative evidence exists at this time to explain that difference.

ACKNOWLEDGMENT

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REFERENCES

1. Milligan, M.S., Altwicker, E.R., Environ. Sci. Technol. 1996, 30, 225-229.
2. Milligan, M.S., Altwicker, E.R., ibid., 1993, 27, 1595-1601.
3. Schoonenboom, M., Ph.D. Thesis, Univ. of Amsterdam, 1995.

Figure 1

Sampling Locations and Codes Between EP Inlet (A) and EP-Outlet (B).

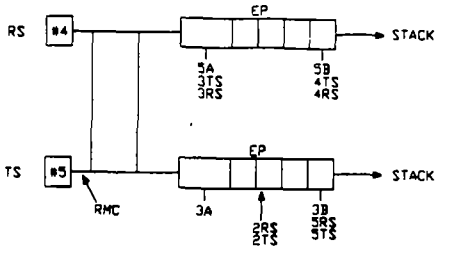

Figure 2

PCDD/F Formation with 4RS vs Temperature

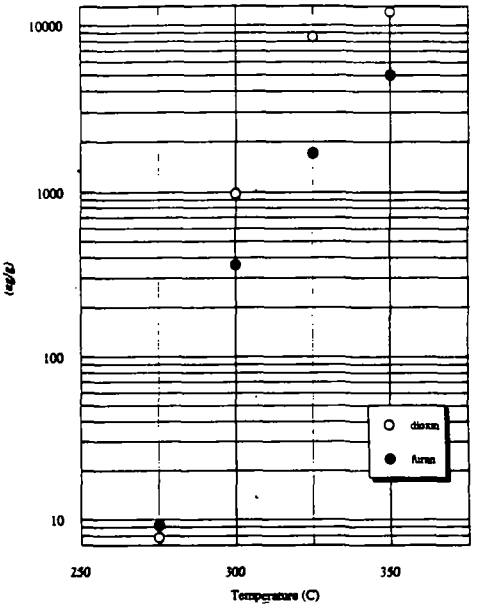

Figure 3

PCDD/F vs Time
(4TS/325C/80ml-min/10.3% O_2)

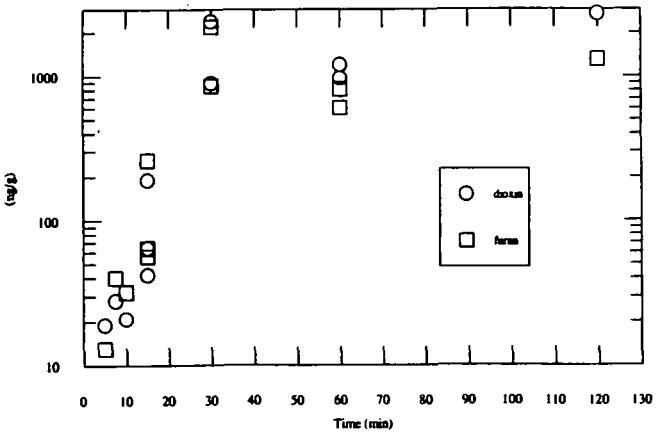

Figure 4

PCDD/F vs Time
(4RS/325C/80ml-min/10.3% O_2)

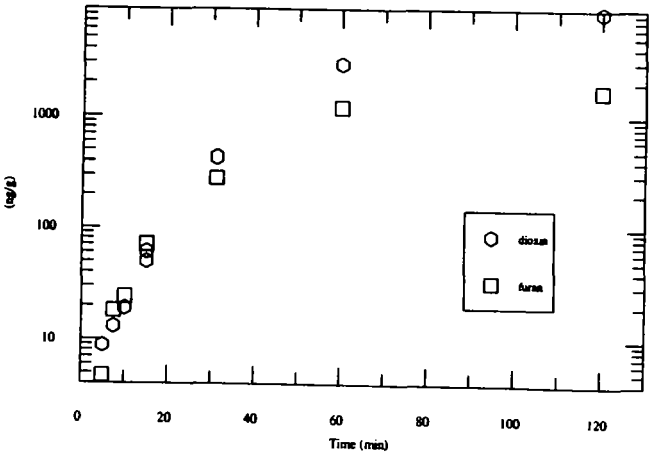

Figure 5

PCDD/F Formation as a Function Oxygen Content
(4RS/2 hr/300C/80ml-min)

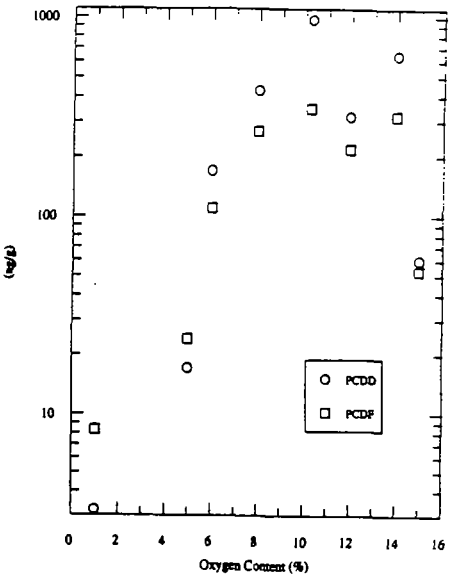

Figure 6

PCDD Formation as a Function of pH