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RELATIVE DEGRADATION OF CHLORINATED DIOXINS AND FURANS IN BOTH A FLOW REACTOR AND A FIXED BED

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Introduction

Most of the experiments, related to polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran (PCDD/F) formation and destruction processes, cited in the literature involved the use of a fixed bed to simulate the fly ash deposited in the different parts of a municipal solid waste (MSW) incinerator. Konduri and Altwicker^{1,2} suggested that an operating MSW incinerator might be thought of as having two reaction regimes for PCDD/F formation: A particle-rich regime, where the fly ash is essentially in a packed configuration with a residence time on the order of minutes to hours; and a particle-lean phase where the particles are suspended in the gaseous flue gas stream with a residence time on the order of seconds. The aim of this study was to provide information on the net degradation of PCDD/F with time scales on the order of 1 second in a flow reactor, and several minutes in a fixed bed using the same type of fly ash. The PCDD/F yields, reported in this study, are the net outputs of the different processes (e.g., decomposition, dechlorination, chlorination, and formation) that may occur concurrently and/or successively.

Materials and Methods

1. Entrained Flow Reactor

Experiments were performed in an entrained-flow reactor, located at U.S. EPA research laboratories in Research Triangle Park, North Carolina. The flow reactor facility consists of a bench-scale experimental setup designed to study the mechanisms of formation of PCDDs/Fs in a controlled environment, while explaining field-observed PCDD/F yields. The flow reactor consists of two concentric quartz tube systems, one horizontal and the other vertical, connected by a quartz cap. The horizontal system consists of an electrically heated, concentric-tube flow reactor (46 x 50 mm outside, 22 x 25 mm inside, and an overall length of 1.44 m) comprising an optional flame source, while the electrically heated vertical system, with an overall length of 3.2 m, serves as the entrained-solids flow reactor. The inside diameter of the inner tube of the vertical-flow reactor is 15 mm, leading to residence times around 1 s, for a total flow of 11-12 L/min. The experiments were performed with a temperature of 1000 °C in the horizontal system and either a quenched temperature profile mode between 650 and 240 °C or an isothermal mode (300 and 500°C) in the vertical reactor. This experimental setup was used to determine the degradation and formation rates of PCDD/F in a non-flame environment. Fly ash particles (<105 µm) collected from a MSW incinerator, designated "EPA AR (As Received)," were fed into the vertical reactor through the connecting cap, using nitrogen (N₂) as a carrier gas.

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2. Fixed-Bed Reactor

The experimental setup consisted of a 1.59 by 30.5 cm quartz tube to hold the sample, placed in a temperature-controlled furnace. One side of the tube was connected to the carrier gas and the other side to a condenser and an XAD trap for released organic compounds. The solid fly ash sample as well as the rinsed glassware and XAD were analyzed separately in order to determine changes in gas- versus solid-phase distribution in the PCDD/F compounds as well as the homologue and isomer distributions from those measured in the nascent fly ash. Fly ash AR was poured into the preheated quartz tube when the set temperature of the tube was reached. Three temperatures (200, 250, and 300°C) and four sampling times (5, 10, 15, and 30 min.) were used during this study to determine the effect of temperature and sampling times on the degradation of the PCDDs/Fs on a fly ash through thermal destruction and dechlorination processes. Release, through evaporation or/and desorption, of the PCDDs/Fs was also investigated in this study by analyzing the back end of the sample train (condenser and XAD trap) of selected runs.

Results and Discussion

1. PCDD/F Degradation in an Entrained Flow Reactor

Since decomposition, dechlorination, chlorination, and formation processes may occur concurrently or/and successively, only net outputs of these processes are reported and their relative contribution assessed for different operating conditions. The results of the flow reactor experiments, presented in Table 1, show that greater than 90% of the total PCDDs nascent to the fly ash are degraded through decomposition/dechlorination processes, in a reducing environment (tests 1, 2, 5, and 6). Only about 70% of the total PCDDs are degraded when air is used instead of N₂ (tests 3 and 4). The net decrease in the degradation of the PCDDs in air is due to a slower degradation process, an increase in the formation process, or both. The destruction of PCDDs is shown to increase with the degree of chlorination in either environment. These data, based only on net outputs, show that the overall degradation process is much greater than the overall formation process. Tests conducted under similar conditions, using a toluene-extracted EPA AR fly ash (EPA EX), were conducted to decouple the overall destruction over the overall formation processes. The results of these tests showed no net production of PCDDs, which supports the hypothesis that degradation of the nascent PCDDs is the dominant process in an N₂ environment. The data do not show the relative importance of dechlorination versus decomposition based solely on the disappearance of the initial mono- to octa-PCDDs since the decomposition products cannot be isolated with this type of experimental setup and analytical technique used. However, tests 5 and 6, performed under isothermal conditions at 500 and 300 °C, respectively, showed a slight increase in the net output of the MCDDs.

An overall net destruction of PCDF compounds is observed in an N₂ environment, while a slight OCDF formation is observed in an air environment. This confirms that a series of competing processes -- destruction (which includes decomposition and dechlorination processes) and formation (through fast *de novo* processes) -- occur simultaneously in an oxidative environment for PCDFs. The results suggest that overall destruction is favored in a reducing environment while formation and destruction processes are of the same order in an oxidative environment. The temperature distribution in the reactor (isothermal at 300 or 500 °C, or quenched from 650 to 240 °C, seems to have a marginal effect on the degradation of the PCDDs/Fs. Nevertheless, formation of MCDFs is observed in the isothermal experiments (tests 5 and 6), which is noticed as well for the MCDDs.

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Table 1 PCDDs/Fs in a Flow Reactor (picomoles/g ash)

Conditions	EPA AR fly ash		In N ₂		In Air		In N ₂	
	Nascent PCDDs/Fs		T (650-240 °C)		T (650-240 °C)		T=500°C	T=300°C
Homologues	Sample 1	Sample 2	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6
MCDD	0	0	3	4	0	2	18	10
DCDD	0	2	1	4	0	5	15	9
TrCDD	8	4	3	3	0	5	8	10
TeCDD	17	14	3	11	0	15	0	0
PeCDD	39	33	10	13	27	27	0	10
HxCDD	123	106	18	23	57	52	14	12
HpCDD	303	303	22	26	91	82	14	12
OCDD	776	918	43	45	215	180	16	14
PCDD Total	1266	1380	103	129	390	368	85	77
MCDF	14	13	21	22	24	28	84	29
DCDF	59	41	32	37	60	62	59	43
TrDCF	106	79	35	49	84	79	54	45
TeCDF	117	83	27	34	88	105	30	12
PeCDF	98	87	19	24	76	83	16	9
HxCDF	70	62	13	13	73	71	8	0
HpCDF	60	58	8	9	83	66	8	3
OCDF	20	21	3	6	76	60	6	10
PCDF Total	544	444	158	194	564	554	265	151

2. PCDD/F Degradation in a Fixed Bed

Ten fixed-bed experiments were performed during this study in which temperature and sampling time were varied. Losses for the nascent PCDDs/Fs on the fly ashes were not detected in the back end of the sampling trains (condenser and XAD trap) for all the experiments conducted irrespective of time and temperature. This was presumably due to the depth of the fly ash bed (25 cm) in which continuous sorption/desorption processes might have occurred within the bed with the sorption process dominant over the desorption process. The "disappearance" of the nascent PCDDs/Fs on the fly ash is presented in Table 2. Disappearance (around 50 % of the initial total PCDD moles, and 20% of the total PCDF moles) occurs at a temperature as low as 200 °C and sampling time within 5 minutes when the fly ash is suddenly exposed to a hot environment. This initial disappearance seems to be independent of the temperature and sampling time ranges of this study, and is probably due to the destruction of the nascent PCDDs/Fs that are less strongly adsorbed onto the surface of the fly ash particle³.

A second process, dechlorination of the PCDDs/Fs, seems to occur at relatively higher temperatures (around or above 250 °C). The dechlorination might be occurring on the nascent PCDDs/Fs that were strongly bonded to the fly ash particle surface. This dechlorination process is shown to be dependent on both the sampling time and temperature. The rate of disappearance of the higher-chlorinated PCDDs/Fs is in the same order as the rate of appearance of the lower chlorinated ones, and supports the dechlorination process scheme.

The overall reaction rates in the flow reactor setup were found to be orders of magnitude higher than comparable experiments in these and other fixed-bed studies⁴. Notwithstanding the large

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differences between the two experimental setups (fixed-bed versus flow reactor), short time scale systems seem to increase the reactivity of the fly ash.

Table 2 PCDDs/Fs in a Fixed Bed (picomoles/g ash)

Conditions	T=200 °C		T=250 °C			T=300 °C			
	5 min	15 min	5 min	10 min	15 min	5 min	10 min	15 min	30 min
MCDD	0	0	0	0	1	46	46	87	92
DCDD	0	0	0	0	3	84	84	138	143
TrCDD	0	0	0	0	8	107	107	130	129
TeCDD	0	0	0	0	27	116	116	133	113
PeCDD	32	26	23	42	66	83	83	74	50
HxCDD	96	91	83	137	184	95	95	74	37
HpCDD	161	142	134	147	170	42	42	32	15
OCDD	346	295	235	119	133	21	21	16	10
PCDD Total	635	554	475	445	592	609	594	684	589
MCDF	18	15	14	14	16	20	37	62	64
DCDF	48	23	45	42	48	59	91	128	121
TrDCF	102	90	94	80	103	119	137	145	128
TeCDF	80	70	78	73	103	81	61	68	55
PeCDF	87	73	72	79	71	68	50	36	18
HxCDF	48	40	40	35	56	22	10	10	0
HpCDF	36	31	28	21	25	12	4	4	2
OCDF	12	10	8	4	7	2	1	0	0
PCDF Total	431	352	379	348	429	383	391	453	388

References

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