CHLORINATION EFFECTS ON PCBzs, PCPhs, PCDD/DFs AND PAHs BY DIOXIN-FREE FLYASH AND UNBURNT HYDROCARBON: 1. EFFECT OF TEMPERATURE

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Introduction

Formation of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in municipal waste incinerators (MWIs) and industrial solid waste incinerators (ISWIs) involved with complex chemistry. It needs insight view of exact mechanism that needs sophisticated instrumentation and skill. Earlier we developed an instrument to overcome and understand the exact mechanism and we proposed the following conclusions;

1. The materials without chlorine and with flyash as a catalyst leads to form PCDD/DFs.
2. Inorganic and organic materials in furnace played as a major chlorine source (HCl) to form PCDD/DFs.
3. These observations alone provided that PCDD/DFs also formed with the presence of inorganic chlorine (NaCl) buring with dioxin-free fly apart from PVC burning.
4. It is quiet apparent, chlorinated chemicals such as chlorobenzenes (PCBzs) and chlorophenols (PCPhs) are major chemicals evolved during heating of dioxin-free flyash catalytic reaction rather than PCDD/DFs.

In this study we conducted temperature dependent formation of PCDDs, PCDFs, PCBzs and PCPhs during burning of paraffin powder and heating of dioxin-free flyash (catalyst) with the presence of hydrogen chloride (HCl) at incinerator concentrations.

Materials and Methods

Dioxin-free fly ash

Fly ash was obtained from the electrostatic precipitator of municipal solid waste incinerator and subjected into thermal heat of 500 °C for 2 hours with the presence of nitrogen stream that removed 99.99 % of dioxin. Although, unburnt carbon remains at 2.0-2.2 %.

Experiment

The experiment was conducted using experimental apparatus shown in Figure 1. Briefly, the paraffin powder (1 g) was sprayed 100 times with 10 micro gram for the duration of 2 hour. The hydrogen chloride concentration was maintained as 100 ppm, which is a general incinerator concentration at solid burning conditions. The temperature was adjusted for 100, 200, 300, 400, and 500 °C in dioxin-free flyash zone. CO, CO_2, O_2 were also monitored simultaneously during the entire period of experiment. The experiment also conducted without paraffin powder with the absence of fly ash and with the presence but the absence of fly ash to see the background concentrations.

HRGC/HRMS analysis

The identification and quantification of PCDD/DFs were performed using Micromass Autospec Ultima Additionally chlorobenzenes, (PCBzs) and chlorophenols (PCPhs) were analyzed in HRGC-

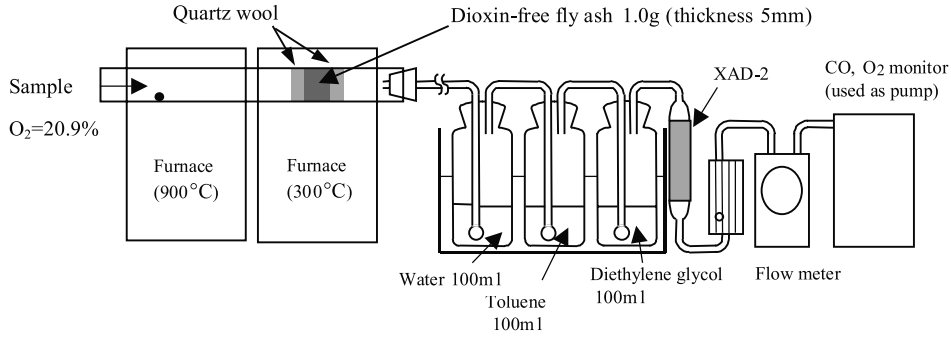

Figure 1. Experimental apparatus.

Table 1. Thermal formation of PCBzs, PCPhs, PCDD/DFs and TEQ (ng/g) with HCl paraffin powder.

	A	B	C	D	E	F	G
Sample	None	Paraffin	Paraffin	Paraffin	Paraffin	Paraffin	Paraffin
HCl [1] concentration stream	100 ppm	100 ppm	100 ppm	100 ppm	100 ppm	100 ppm	100 ppm
Fly ash	Absence	Absence	Presence	Presence	Presence	Presence	Presence
Temperature °C	300	300	100	200	300	400	500
Chlorobenzene (Cl%/MW)			*	*			
MoCBZ (0.316/112.5)	10	10	200	190	290	1200	9300
DiCBZ (0.483/147)	**230** [a]	**450** [a]	**320** [a]	210	4300	37000	10000
TrCBZ (0.587/181.5)	22	10	150	120	10000	65000	9000
TeCBZ (0.657/216)	10	20	13	50	15000	41000	4400
PeCBZ (0.705/250.5)	10	10	10	120	14000	23000	1600
HxCBZ (0.747/285)	59	130	41	310	6200	5800	380
PCBzs [nmol.]	310	600	730 [5]	1000 [5.5]	50000 [230]	170000 [920]	35000 [230]
Cl%			48	58	65	60	50
Chlorophenols (Cl%/MW)							
MoPCPhs (0.276/128.5)	100	150	390	550	6700	25000	15000
DiPCPhs (0.436/163)	200	250	230	170	3500	26000	6000
TrPCPhs (0.539/197.5)	100	100	230	260	11000	45000	1000
TePCPhs (0.612/232)	130	100	190	110	16000	46000	70
PeCPCPhs (0.666/266.5)	120	100	33	11	5500	5800	50
PCPhs [nmol.]	450	400	1100 [6.5]	1100 [7.1]	43000 [220]	150000 [800]	22000 [160]
Cl%			44	40	53	50	33
PCDDs (Cl%/MW)							
TeCDDs (0.441/322)	0.006	0.0099	0.2	0.2	100	540	75
PeCDDs (0.498/356.5)	0.006	0.009	0.08	0.4	240	760	42
HxCDDs (0.545/391)	0.0097	0.016	0.1	1.6	470	610	19
HpCDDs (0.584/425.5)	0.0095	0.017	0.08	3.2	600	260	6.6
OCDD (0.617/460)	0.014	0.017	0.11	6.1	640	62	1.1
PCDDs [nmol.]	0.046	0.069	0.57 [0.002]	11 [0.027]	2100 [5]	2200 [6.1]	140 [0.42]
Cl%			52	59	57	51	48
PCDFs (Cl%/MW)							
TeCDFs (0.464/306)	0.016	0.03	4.9	3.1	1400	7300	1000
PeCDFs (0.521/340.5)	0.016	0.025	0.68	1.9	1300	5400	600
HxCDFs (0.568/375)	0.014	0.021	0.17	2.2	1100	2700	250
HpCDFs (0.607/409.5)	0.01	0.012	0.15	3.3	850	970	66
OCDF (0.640/444)	0.01	0.01	0.88	5.1	420	170	6
PCDFs [pmol.]	0.056	0.088	6.7 [0.02]	16 [0.04]	5100 [14]	17000 [50]	1900 [5.9]
Cl%			50	57	54	51	50
Sum PCDD/DFs	0.102	0.16	7.3	27	7200	19000	2000
TEQ			0.1	0.2	95	300	32

[1] hydrochloric acid; * indicates the values derived from column B; [a] indicates in black background concentrations.

HRMS at a resolution of > 10, 000 using ^{13}C-internal standards. The concentrations of PCBzs, PCPhs and PCDD/DFs were reported as ng/g sample.

Results and Discussion

The results of our study showed that minimum concentration of all the chlorinated aromatics presence and absence of paraffin powder and absence of dioxin-free fly ash (Table 1). In lower temperature (100-200 °C) conditions, formation of chlorinated aromatics found to minimal. When temperature exceeds more than 200 °C, concentrations increased exponentially until 400 °C and then sharp decrease were noted from 400 to 500 °C. It is considered to a maximum chlorine formation at the temperature of 300 and 400 °C. With temperature conditions in between 300 and 400 °C, 100-1000 fold exponential formation of all chlorinated aromatics has been observed when compare to 100 °C (Figure 2).

It should be worth indicating despite pronounced increase of concentrations (Figure 2), the chlorine percentage of analyzed chemicals showed less pronounce ($\pm$ 10 %) (Figure 3). Besides, the homologue pattern of PCBzs and PCPhs showed contrast results of increasing lower chlorinated homologues at the temperature of 500°C (Figure 4). Furthermore, isomer profiles of chlorinated compounds was found similar at all temperature conditions (Figure 5).

The results of this study in general indicated that HCl and unburnt hydrocarbon with the dioxin-free fly ash formed PCBzs, PCPhs and PCDD/DFs. Especially, formation of PCDD/DF even at 100°C and suggested the dioxin-free flyash played catalytic reaction and therefore formation (Table 1).

Based on our results we can enumerate that the Deacon type of reaction can explain increased formation of most of chemicals viz;

$$2R\text{-}H + 2[CuCl_2 \text{ or } FeCl_3] + (O) \rightarrow 2R\text{-}Cl + 2[CuCl \text{ or } FeCl_2] + H_2O \quad (I)$$

$$2[CuCl \text{ or } FeCl_2] + 2HCl + (O) \rightarrow 2[CuCl_2 \text{ or } FeCl_3] + H_2O \quad (II)$$

in which the continuous back reaction of both $CuCl_2$ and $FeCl_3$ play a chlorine source with combine to dioxin-free flyash. The results also prevailed that fly ash catalyzed dioxin formation is apparent although there was a limit to dioxin formation when active chlorine site in dioxin-free fly ash was the only chlorine source. During the thermal effect, the chlorination reaction may be fast which is contrast to the chlorinated hydrocarbons, which is slow reaction and consequently higher chlorinated PCPhs has been formed. Eventually when continuous chlorination occurs, the less adsorption of activesite fly ash may lead to the less surface radical reaction. During these stage, dispersion of HCl probably greater. Therefore, greater molecular weights of chlorinated hydrocarbons may supress the reaction of HCl.

Another possible explanation of decreased chlorine percentage and increased homologues at lower chlorine configurations probably due to the less adsorption zone in the fly ash for the activated reaction. For instance, with fast reaction conditions, the adsorption of chlorinated chemicals seems too lesser rather than hydrocarbons. Thus, the chlorinated chemicals may be deposited without absorbed by fly ash. Furthermore fluctuation of chlorine active zone in the fly ash at 100 °C, catalytic reaction could be formed. In addition, in gas phase, only the fly ash gets activated and dioxin formation is likely. Particularly, benzene, phenol type of reaction may increase chlorinated chemicals and consequently formation of PCBzs, PCPh and PCDD/DFs expected to decrease.

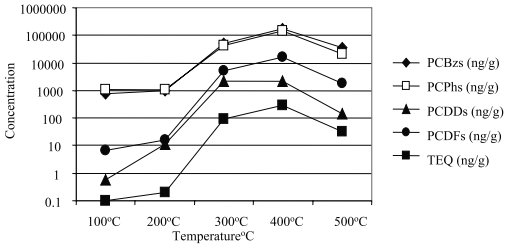

Figure 2. Concentration of PCBzs, PCPhs, PCDD/DFs and TEQ at varied temperature conditions.

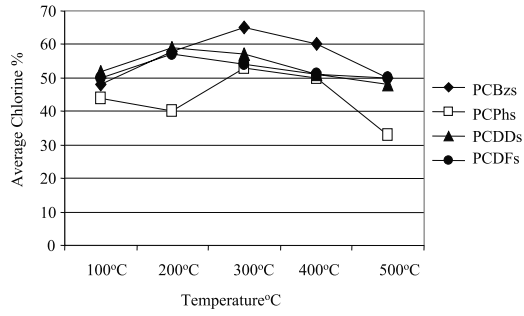

Figure 3. Chlorine percentage of PCBzs, PCPhs and PCDD/DFs at varied temperature conditions.

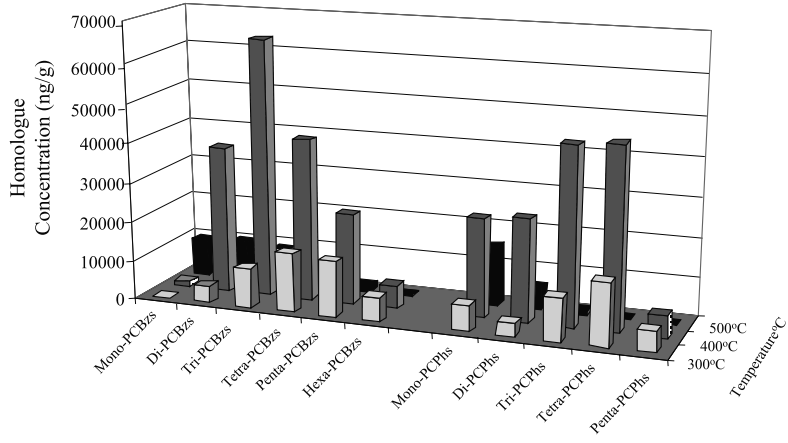

Figure 4. Homologue distribution of PCBzs and PCPhs, in fly ash at varied temperature conditions.

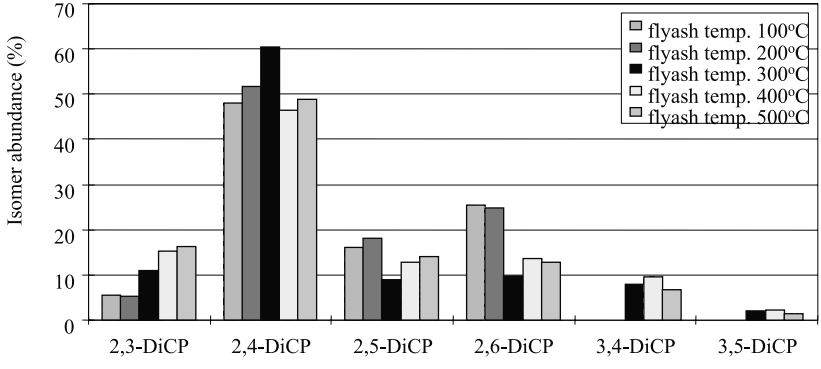

Figure 5. Isomer abundance (%) of dichlorophenols in fly ash at varied temperature conditions.