QUANTITATIVE ANALYSIS OF TOXIC COMPOUNDS FORMED FROM COMBUSTION OF SOME PLASTIC MATERIALS AND NEWSPAPER

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Introduction

Our earlier investigations demonstrated that formation of hydrocarbons such as polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), polycyclic aromatic hydrocarbons (PAHs), popychlorophenols (PCPhs) and polychlorobenzenes (PCBzs) and their toxic equivalent quantity (TEQ) with dioxin-free flyash and unburnt hydrocarbon with varied temperatures as well as different hydrochloric acid (HCl) concentrations. The results highlighted that minimum concentration of all the chlorinated aromatics with presence of paraffin powder and absence of dioxin-free fly ash. Furthermore depending upon the temperature and HCl concentration, the formation chemistry varied at considerable manner[1,2]. There are several reports documented the formation of toxic substances when burning the plastic materials. However, the studies are scarce about formation of HCl, HCN, PCDD/DFs, co-planar PCBs their TEQ, BTX, parent compounds of dibenzodioxin, dibenzofuran, biphenyl and PAHs from various plastic materials. Besides, so far studies reports only the basic theory of formation chemistry, which lacks the formation of non-chlorine compounds.

In this study we conducted formation of PCDDs, PCDFs, coplanar PCBs, benzene, toluene, xylene (BTX), 16- polycyclic aromatic hydrocarbons (PAHs), HCN, parent compounds of biphenyls, dibenzodioxins and dibenzofurans and carbonmonoxide (CO) from polyethylene (PE), polyethyleneterephthalate (PET), nylon, newspaper, polypropylene (PP), acrylonitrile butadiene styrene (ABS) and polyvinyl chloride (PVC) plastic particles with our incinerator apparatus that was developed in Shimadzu Techno Research Inc., as shown in Figure 1. Based on the formation of PCDD/DFs and co-planar PCBs, we calculated the toxic equivalent quantity (TEQ) using WHO-TEF values in each sample analyzed in present investigation and discussed.

Materials and Methods

Apparatus. As shown in Figure 1, the experimental apparatus were developed with O_2=20.9%/N_2 balance meter that further connected with flow meter and quartz tube. The diameter of quartz tube is 25 mm with 1000-mm length that mainly travels inside the double furnace (600-mm) with the furnace temperature of 900°C. The samples for the formation test were placed in the sample tray located in the quartz tube in furnace 1.

Sampling Unit. For the dioxins and PAHs, the sampling unit can be classified as ice-bath with 3 impinger and XAD. The impinger 1 contains 100-mL toluene with 200 mL H_2O. The impinger 2 and 3 respectively contains 150-mL toluene and 150 mL diethylene glycol. This impinger was

connected with XAD-1 and 2 and the sampling was mainly done in 3 impinger and 2 XADs. For HCN, the ice-batch contains 2 impinger in that both contain 30 mL of 0.1 mol/L NaOH solution. For BTX analysis, it was fixed with 10 L Flek-sampler bag. The impinger and XAD of dioxins and PAHs and HCN impinger unit was finally connected with flow meter with pump and CO, O_2, CO_2 monitoring meter. After the completion of experiment, the back end of quartz tube, impinger of dioxins, PAHs and HCN was rinsed with H_2O, acetone and toluene for analysis.
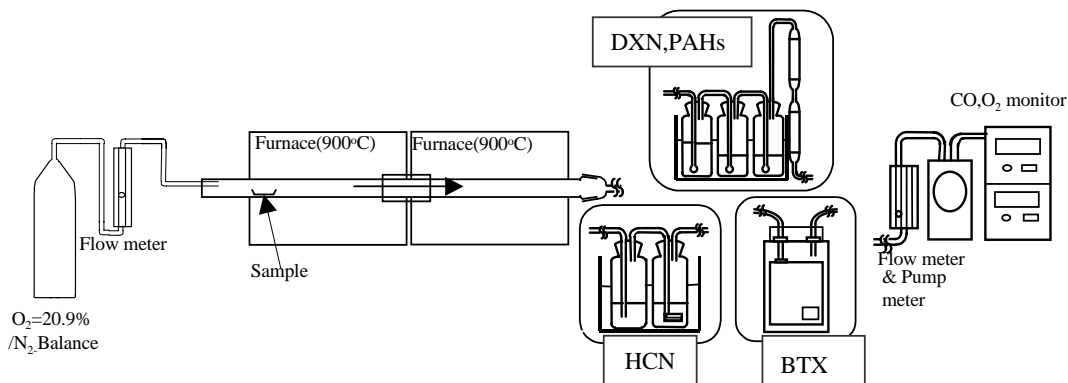

Figure 1. The experimental apparatus employed in this study.

Samples. The PE, PET, nylon, newspaper, PP, ABS and PVC were either cut into tiny pieces or powdered. The sampling speed and gas flow was set as 2.0 L/min trapping time. Each interval 20 μg of sample was burned at 900°C at the double furnace as shown in Figure 1 with regular intervals (until completion of CO, CO_2, O_2 monitor cycles in each and every 20 mg sample burning). For dioxin and PAHs analysis 1 g sample were used with 100 cycles, whereas 200 and 100 μg samples were used for HCN and BTX analysis with 20 and 10 cycles respectively. For each sample matrix, the CO, O_2, CO_2 were monitored and recorded (Figure 2).

Analysis. The identification and quantification of PCDD/DFs, co-planar PCBs, PAHs were performed using Micromass Autospec Ultima high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) at a resolution of $> 10, 000$ along with ^{13}C-internal standards as a reference. For the HCN analysis, the JISK0102 method was adopted. For BTX sampler bag, GC-FID was used and then scanning test confirmation was done with GC-MS quadrapule. The concentrations of BTX, HCN, parent compounds of biphenyl, dibenzofuran, dibenzodioxins, and PAHs were expressed as ng/g-sample basis while TEQ, chlorinated -PCDDs, -PCDFs and -co-planar PCBs represents pg/g-sample basis and CO was expressed on ppm basis.

Results and Discussion
The concentrations of HCl, HCN, Dioxin [PCDFs, PCDDs, co- planar PCBs their TEQ], BTX, parent structure viz., [biphenyl, dibenzodioxins, dibenzofuran] and 16 polycyclic aromatic hydrocarbons (PAHs) were shown in Table 1. In addition to the samples described, the blank run was also conducted and the results were shown in Table 1. In the blank samples, dioxins, furans, co-planar PCBs and few PAH compounds were noticed. This study was conducted without flyash and thus the results were considered to be a theoretical formation of thermo-chemical process.

Table 1. Concentrations of toxic compounds (ng/g-sample) in various sample matrix and blank in the incinerator apparatus.

Sample ⟶	Blank	PE[a]	PET[b]	Nylon	Newspaper	PP[c]	ABS[d]	PVC[e]
HCl								584,000,000
HCN	LRL[g]		LRL[g]	12,000,000		73,000	1,000,000	LRL[g]
CO (ppm)	13	310	20	730	790	400	49	170
% CO_2 (v/v)	<0.2	1.4	1.5	0.9	0.8	1.1	1.0	0.4
% O_2 (v/v)	20.9	18.8	19.4	19.6	20.0	19.1	19.6	20.4
Sum PCDFs	0.021	0.043	0.14	0.014	0.23	0.065	0.005	12
Sum PCDDs	0.031	0.032	0.17	0.06	0.15	0.047	0.058	3.4
Sum Coplanar PCBs	0.074	0.16	0.12	0.077	0.15	0.18	0.08	0.19
Sum PCDD/DFs + PCBs	0.13	0.24	0.43	0.15	0.53	0.29	0.14	16
[h]TEQ[f]	0.58	1.2	4.3	0.072	5.4	0.95	0.59	130
Biphenyl	300	120,000	170	130,000	50,000	370,000	650	450
Dibenzofuran	27	8,400	17	13,000	39,000	14,000	360	28
Dibenzodioxin	LRL[g]	LRL[g]	LRL[g]	LRL[g]	LRL[g]	LRL[g]	LRL[g]	LRL[g]
Benzene	LRL[g]	26,000,000	LRL[g]	12,000,000	2,800,000	730,000	2,300,000	LRL[g]
Toluene	LRL[g]	33,000	LRL[g]	200,000	170,000	38,000	75,000	60,000
Xylene	LRL[g]	LRL[g]	LRL[g]	LRL[g]	LRL[g]	LRL[g]	LRL[g]	LRL[g]
Naphthalene	10,000	1,200,000	7,600	2,200,000	780,000	2,600,000	6,400	4,300
Acenaphthylene	LRL[g]	1,300,000	LRL[g]	1,500,000	270,000	1,400,000	360	26
Acenaphthene	LRL[g]	6,800	LRL[g]	11,000	3,900	13,000	62	100
9H-Fluorene	590	130,000	260	170,000	44,000	220,000	580	1,300
Phenanthrene	500	670,000	410	760,000	250,000	940,000	860	410
Anthrathene	360	140,000	260	190,000	49,000	240,000	280	280
Fluoranthene	60	490,000	61	560,000	180,000	520,000	360	51
Pyrene	130	380,000	120	500,000	160,000	620,000	200	94
Benzo[a]anthrathene	LRL[g]	85,000	LRL[g]	89,000	29,000	120,000	58	37
Crysene*[1]	LRL[g]	95,000	LRL[g]	100,000	38,000	130,000	68	20
Benzo[b]fluoranthene	50	140,000	37	150,000	48,000	180,000	100	40
Benzo[k]fluoranthene*[2]	LRL[g]	45,000	LRL[g]	42,000	14,000	58,000	22	LRL[g]
Benzo[a]pyrene	LRL[g]	140,000	LRL[g]	160,000	38,000	170,000	22	LRL[g]
Indeno[1,2,3-cd]pyrene	LRL[g]	86,000	LRL[g]	110,000	28,000	140,000	18	LRL[g]
Benzo[g,h,i]perylene	LRL[g]	120,000	LRL[g]	140,000	33,000	130,000	11	LRL[g]
Dibenzo[a,h]anthrathene*[3]	LRL[g]	9,300	LRL[g]	9,000	3,700	14,000	LRL[g]	LRL[g]
Total 16 PAHs	12,000	5,000,000	8,700	6,700,000	2,000,000	7,500,000	9,400	6,700

Detection Limit: HCN<3000, PCDD/DF (4-5Cl)<0.001, (6-7Cl,co-PCBs)<0.002, (8Cl)<0.005, BTX<3000, PAHs<10 on ng/g-sample

[a]polyethylene,[b]polyethyleneterephthalate,[c]polypropylene,[d]Acrylonitrile butadiene styrene,[e]polyvinylchloride,

[f]pgTEQ/g-sample basis,[g]Less than reportable limit;[h]Toxic Equivalent Quantity

*[1]Triphenylene, *[2]Benzo[j]fluoranthene, *[3]Dibenzo[a,c]anthracene, respectively. The values rounded to two singificant digits

The HCN formation was explained to be nitrogen containing compounds such as ABS and nylon. The HCN concentration levels were reasonable however, levels in PP likely to be formation from additive hindered amine anti-oxidant (Table 1). The study of Mingjim Piao's pyrolysis experiment[3] showed that PAHs were formed at the incinerator temperature of 900°C due to the aliphatic hydrocarbons was converted as PAHs with benzene ring. These results were compared with our study and results implied that PE, PP, nylon, newspaper formed elevated levels of BTX and PAHs, particularly, benzene, naphthalene, acenaphthalene found to be mg/g levels, the Benzo[a]pyrene with μg/g. The lower levels were found for PET, ABS and PVC with 1/4000-fold

less levels. It is probable that presence of oxygen in PET might impacted the low formation of PAHs. The O_2, CO, CO_2 monitored in PP and PET has been shown in Figure 2. The PAHs were predominantly found in PE, nylon, newspaper and PP. As for an example, in Figure 2, highlights that formation of O_2 reduced burning and reductions of dioxins while PP seemed to form elevated CO due to incomplete burning. This also leads to greater formation of toxic PAHs in PP at 900°C (Figure 2).

In terms of the TEQ and homologues of PCDD/DFs and co-planar PCBs, nylon, ABS levels were similar to blank levels and negligible. The, PE, PP, PET levels were slightly higher but considered to be equal to blank due to the background levels. The elevated levels of TEQ in PVC were considered to the influence of Cl contents which is 57% of parent compound and thus 1 to 100-million of chlorinated aromatics occur to form and nevertheless, these values are several magnitude lesser when compare to the parent Cl contents.
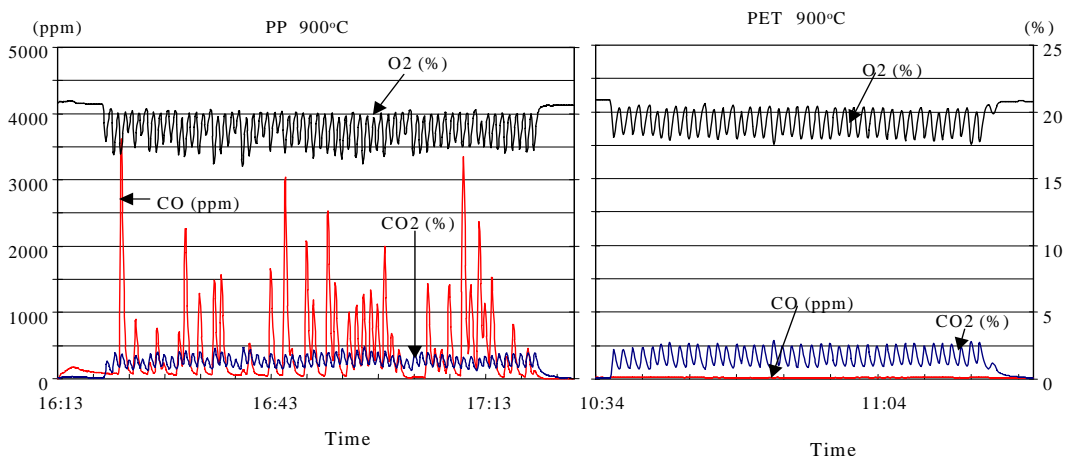

Figure 2. Percentage evolution of CO_2 and O_2 and concentration (ppm) of CO in popypropylene and polyethyleneterephthalate samples.

We also determined the parent compounds of biphenyls, dibenzofurans and dibenzodioxins in order to understand the formation mechanism of above-said compounds. It should be worth indicating that biphenyl and dibenzofuran was detected in all the samples while dibenzodioxin were less than 10 ng/g. It is assumed that chlorinated dioxins might have formed during the reaction of chlorophenol dimerization effect[1,2]. This results indicated that the formation mechanism of PCBs and PCDFs were different from PCDDs that formed with entirely different manner. The formation of PCB and PCDF could be explained as pyrolysis effect and the formation of chlorine from the carbon skeleton might be a suitable explanation.

Literature Cited
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