

## EMISSION CHARACTERISTICS OF HAZARDOUS AIR POLLUTANTS FROM CO-COMBUSTION OF VARIOUS PLASTICS

Kim Kyung-Seop, Kang Won-Kuk, Ko Young-Hwan, Hong Kil-Hwan, Lee Jung-Hun, Cha Jae-Doo  
Korea Testing Laboratory, 222-13 Guro-3Dong Guro-Gu, Seoul, Korea

### Abstract

To investigate the emission characteristics of hazardous organic pollutants from co-combustion of plastic waste, PVC and other plastic materials such as LDPE, HDPE, PP, PS, and ABS were combusted in a tubular furnace with airflow. Organic pollutants emitted from co-combustion experiments such as PCDD/Fs, PCBs and PAHs were investigated. These pollutants from plastic combination combustion were evaluated at a temperature of 900 °C, which was normal operation temperature of practical municipal waste incinerator.

With co-combustion of PVC and other plastics, formation of PAHs increased apparently while no significant increase from the total of PCDD/Fs, PCBs was found in this study. All combustion experiments yield predominantly PCDFs over PCDDs. Emissions of PCBs were dominated by tetra-, penta- and hexa-chlorinated homologues, but highly chlorinated homologues were minor components. Co-combustion stimulated the total emission of PAHs, including carcinogenic Benzo(a)pyrene (BaP). The PAHs concentration generated from PVC was approximately one order of magnitude lower than that from other pure plastics such as PP, PS and LDPE.

### Introduction

Due to heavy use of plastic products, a great many plastic wastes have been discharged in the world. Plastics such as low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), acrylonitrile butadiene styrene (ABS) and polyvinylchloride (PVC) are major types used through worldwide. To dispose such non-biodegradable and voluminous wastes, the incineration is regarded as a most valuable method, since it has significant advantages over other methods of waste disposal: mass, volume reduction by 90-95% and useful energy recovery.

However, the hazardous air pollutants such as polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and polynuclear aromatic hydrocarbons (PAHs) could be released from the incineration process of these plastic wastes.<sup>1</sup>

The types and quantities of pollutants from the incineration of plastic waste are greatly influenced by the constituents of plastics and conditions of combustion. So, this study aimed to investigate the emission characteristics of hazardous air pollutants by co-combustion of major plastics at the combustion conditions similar to actual incineration plant experimentally. We found that the influence of plastic types and combination of these upon the amount of PCDD/Fs, PCBs and PAHs in the emission from plastics co-combustion at 900°C, which is a practical operation temperature of MWIs. In addition, PCDD/Fs and the other pollutants in the emission gas were also analyzed to investigate the relationship.

### Materials and Methods

Batch type one-stage combustion experiments were conducted in an electric muffle furnace fitted with a tubular quartz tube, 4 cm diameter and 50 cm height (Fig. 1). The combustion apparatus was downstream vertical type for simplicity of sample insertion and induction of turbulence. The combustion air passed through a side-connected ramp. The temperature of the furnace was kept at 900 °C during experiments lasting 15 minutes. Upon reaching the temperature of 900 °C, a platinum sample vessel loaded with a pool of 0.5 g of pure plastics or 1 g of co-combustion sample (0.5 g of PVC + 0.5 g of each PS, PP, LDPE, HDPE or ABS) was inserted from the top entrance and it was positioned in the middle of the quartz tube. The combustion experiments were conducted at atmospheric pressure with purified air (>99.999%) and the air flow rate in the furnace was set 2 l/min. LDPE, HDPE, PP, PS, ABS and PVC as powder type applied were free of additives and purchased from Aldrich except for ABS, LG Chem. Ltd. (Korea). Thermal decomposition of plastic samples occurred immediately after insertion and the flue gas was passed through sampling device. The concentrations of oxygen, carbon monoxide and carbon dioxides were measured simultaneously. The sampling device consisted of

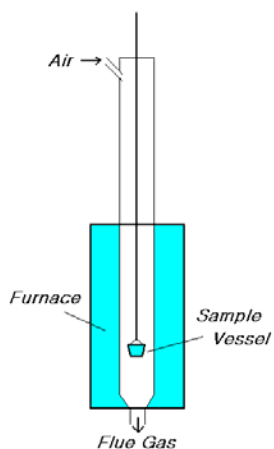


Fig.1. Combustion apparatus

a silica glass microfiber filter followed by XAD- II resin, backup solvent (toluene 50 ml).

Sample extraction and clean-up were carried out in a manner similar to U.S. EPA method 1613/1668A. After cooling the furnace to room temperature, glass fiber filter and XAD- II resin were collected altogether and soxhlet extracted with toluene for 24 hours. The extracts, backup solvents and washes were concentrated and replaced by n-hexane and combined to a volume 100 ml.

For PCDD/Fs and PCBs analysis, the sample was firstly treated with concentrated  $H_2SO_4$  and purified by multi-layered silica gel and it was divided into two parts for PCDD/Fs and PCBs fraction, which samples was purified by alumina column separately. The fraction containing PCDD/Fs and PCBs was concentrated for HRGC/HRMS analysis. For PAHs analysis from plastics combustion, Phenanthrene- $d_{10}$  was added to the 10 ml of raw extract, which was purified with activated aluminum and silica gel in sequence. The concentrations for the following 16 priority PAHs were determined: Naphthalene(Nap), Acenaphthylene (AcPy), Acenaphthene (Acp), Fluorene (Flu), Phenanthrene (PA), Anthracene (Ant), Fluoranthene (Fl), Pyrene (Pyr), Benz(a)anthracene (BaA), Chrysene (CHR), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno(1,2,3-cd)pyrene (IND), Dibenz(a,h)anthracene (DBA), Benzo(ghi)perylene (BghiP).

The PCDD/Fs and PCBs analysis were carried out using a HRGC(HP6890, Hewlett-Packard) / HRMS(JMS-700 Mstation, JEOL) system in the selected ion monitoring mode. A Shimadzu QP5050A gas chromatograph/mass spectrometer was used to analysis for PAHs.

### Results and Discussion

Fig. 2 represents the effect of combination difference of load materials on the formation of PCDD/Fs. All combustion experiments showed predominantly PCDF with PCDD concentration and major species were 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,6,7,8-HpCDD, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, and OCDD at all experiments. While the pure plastics (PP, PS, ABS, LDPE and HDPE) were combusted, no PCDD/Fs was naturally found due to no chlorine source. ABS and PS have aromatic ring structure, so that the co-combustion of PVC+ABS and PVC+PS has different profile with respect to the other co-combustions. It was showed that hepta- and hexa-CDD/Fs were dominant for PVC+ABS and PVC+PS, but penta-CDD/Fs were more generated for the other co-combustion.

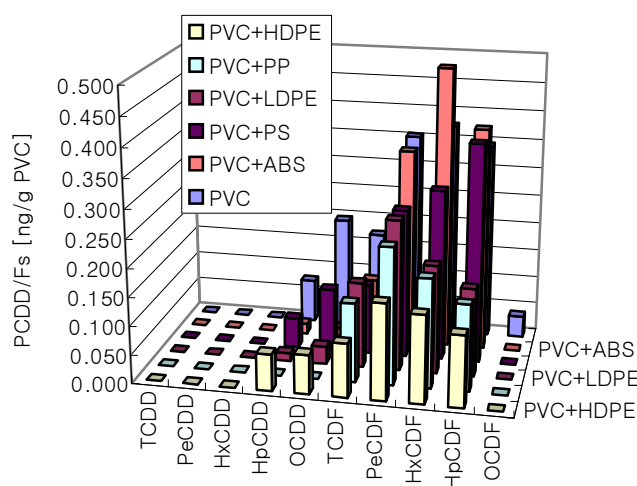


Fig. 2. Formation of total PCDD/Fs

Table 1 shows the weight % of PCDD/Fs congeners at various kinds of experiments. It has observed that PCDFs except for OCDF were dominated overall PCDD/Fs emissions. The degree of chlorination remains nearly constant within the PCDF-group, with penta-, hexa- and hepta-CDF congeners were dominant. The ratio of PCDFs to PCDDs always exceeds 1, with the lowest values 4.0 obtained from the PVC+HDPE co-combustion. Because of the similarity in congener distribution from all combustion experiments in this study, especially the PCDF/PCDD ratio >1, it is very likely that the combustion mechanism of dioxin formation are similar in all co-combustion of plastics. These result were coincided with other result about PVC combustion.<sup>2</sup>

Table 1. Weight % of PCDD/Fs congeners

Experimental Conditions	wt % of Congeners										PCDF/D ratio
	TCDD	PeCDD	HxCDD	HpCDD	OCDD	TCDF	PeCDF	HxCDF	HpCDF	OCDF	
PVC	< 0.0	< 0.0	< 0.0	2.5	7.7	13.2	28.4	27.8	20.5	< 0.0	8.8
PVC+LDPE	< 0.0	< 0.0	< 0.0	1.7	3.9	18.7	32.9	23.7	19.2	< 0.0	17.0
PVC+HDPE	< 0.0	< 0.0	< 0.0	9.6	10.3	13.9	25.0	22.8	18.5	< 0.0	4.0
PVC+PP	< 0.0	< 0.0	< 0.0	< 0.0	< 0.0	19.2	33.3	26.6	21.0	< 0.0	∞
PVC+PS	< 0.0	< 0.0	< 0.0	4.2	9.0	10.0	21.2	24.4	31.2	< 0.0	6.6
PVC+ABS	< 0.0	< 0.0	< 0.0	1.3	1.1	8.0	25.2	35.9	28.5	< 0.0	41.0

Fig. 3 shows the 12 toxic coplanar PCBs profile at co-combustion of various plastics. From the analyzed isomer of PVC, the contribution of the selected PCBs to the TEQ (Toxic equivalents) is IUPAC congener #118>81>77>126 that is the main components of the non-ortho and mono-ortho substituted PCBs. Emissions were dominated by tetra- and penta- chlorinated homologues, but highly (hepta-, octa-, nona- and deca-) chlorinated homologues are minor components (data not shown). PCB #126, contributing the highest TEQ (0.1), was not minor component in this study. The distinctive point of this result is that the total PCBs emission of pure PVC is greater than that of co-combustion (PVC 0.5 g + other plastic 0.5 g), which co-combustion of PVC + ABS was the lowest emission in all isomers of PCBs. No PCBs was found in the combustion of the individual plastics such as PP, PS, ABS, LDPE and HDPE due to no chlorine in their chemical structures.

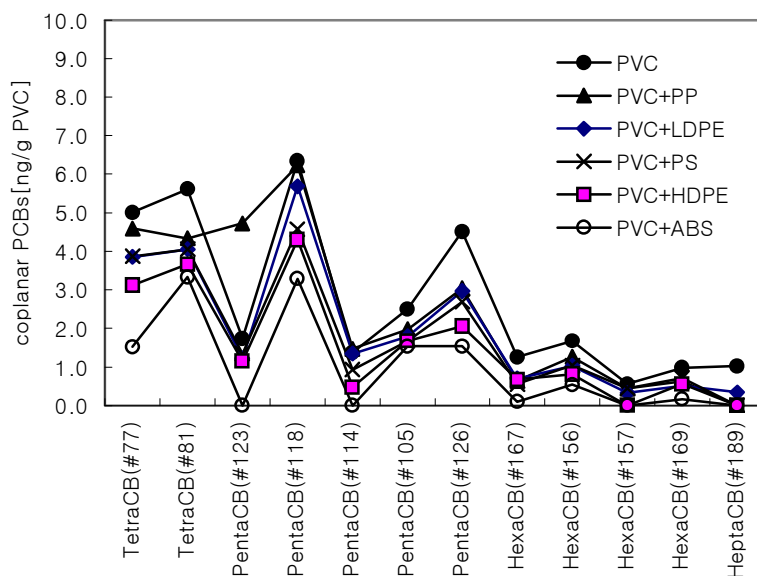


Fig. 3. Congener profile of toxic PCBs

The concentrations of PAHs emitted from the plastic co-combustion were presented in Table 2. The table lists the 16-priority pollutant PAHs formed from the combustion under various combinations. Pure polystyrene formed more PAHs than the other pure plastics when combusted, presumably because of the presence of aromatic rings. However, it has been shown that the total PAHs formation from the combustion experiments of PVC plastic was far less than that from the other plastics. The PAHs concentration generated from PVC was approximately one order of magnitude lower than that from other pure plastics such as PP, PS and LDPE.

Table 2. PAHs formation from each polymer (0.5 g) and PVC (0.5 g) + each polymer (0.5 g) co-combustion [ $\mu\text{g}$ ]

Compounds	# of Rings	PVC	PS	PP	LDPE	HDPE	ABS	PVC + PS	PVC + PP	PVC + LDPE	PVC + HDPE	PVC + ABS
Nap	2	554	2532	4063	5697	1911	1967	4829	4004	2894	4185	4480
Acpy	3	68	527	1030	1236	516	762	1255	1922	1594	2534	1390
Acp	3	5	16	33	67	34	318	15	29	26	37	16
Flu	3	40	40	238	301	179	170	321	383	293	435	304
PA	3	679	8808	3022	2603	1755	3285	7981	5610	4774	5886	5023
Ant	3	110	1156	788	800	560	565	1344	1494	1252	1595	1238
Fl	4	377	2963	1870	1615	997	1631	4030	3431	3162	3628	3019
Pyr	4	163	1189	2257	2242	1429	783	1093	3094	2870	3390	2105
BaA	4	71	522	307	360	211	319	630	774	603	647	625
CHR	4	246	1206	571	543	332	636	1690	1305	1044	1312	1358
BbF	5	69	599	296	247	156	264	641	646	598	770	599
BkF	5	116	78	393	352	210	500	1143	934	734	879	818
BaP	5	27	290	545	476	290	233	405	955	754	856	706
DBA	5	4	196	29	18	9	33	134	59	42	52	81
IND	6	67	450	467	330	194	270	592	929	841	806	670
BghiP	6	51	168	519	408	250	130	186	610	581	627	415
Total		2,645	21,755	16,419	17,292	9,030	11,863	26,285	26,174	22,060	27,634	22,844

The PVC+HDPE was found to have the highest PAHs concentration (27,634  $\mu\text{g/g}$  PVC+HDPE), while the PVC had the lowest PAHs concentration (5,290  $\mu\text{g/g}$  PVC). Furthermore, this could not be applied no arithmetic summation for total PAHs formation under various sample combinations. For instance, 27,634  $\mu\text{g}$  of total PAHs was generated from PVC (0.5 g) + HDPE (0.5 g), while 9,030  $\mu\text{g}$  of total PAHs for HDPE (0.5 g) and 2,645  $\mu\text{g}$  of total PAHs for PVC (0.5 g). It could be assumed that conjugated reaction between PVC and other plastics could occur and the combustion also underwent at the same time with more complicated deplasticization and favor the formation of ring compounds in our experimental condition. PAHs generated from the plastic combustion were primarily dominant in the lower molecular weight PAHs such as Nap, PA, Fl, Pyr except for Acp. These dominant contents of combustion of plastics were in agreement with those of municipal waste incinerator in spite of the difference of operating conditions and the systems.<sup>3</sup> The fraction of PAH-homologue mass (F%) was counted for the total-PAH mass. The mean fraction of PAH-homologue mass was 18.4%, 35.3% and 32.0% for the 2-ring, 3-ring and 4-ring PAHs, respectively. The summation of F% of 2-ring, 3-ring and 4-ring PAHs was higher than 84%. The concentration of Acp was still low during the combustion of all kinds of plastics in this study. There is no much difference between the PAH-homologue patterns corresponding to individual combustion and co-combustion of plastics, however, co-combustion stimulate the total emission of PAHs and carcinogenic Benzo(a)pyrene (BaP).

## References

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