

FORMATION AND DEGRADATION BEHAVIORS OF BROMINATED ORGANIC COMPOUNDS AND PCDD/Fs DURING THERMAL TREATMENT OF WASTE PRINTED CIRCUIT BOARDS

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Abstract

For understanding the formation and decomposition behaviors of brominated organic compounds during thermal treatment of waste printed circuit boards (P-CBs), pilot-scale combustion experiment was conducted. In addition, composition of various flame retardants (FRs) in recent waste P-CBs was examined. polybromodiphenyl ethers (PBDEs) was the highest concentrations in waste P-CBs, followed by decabromodiphenylethane (DBDPE) > polybromophenols (PBPhs) > tri-alkyl/aryl phosphates (PFRs) > tetrabromobisphenol A (TBBPA) > polybromobenzenes (PBBzs) > PBDD/Fs. Hexabromocyclododecanes (HBCDs) were not detected. PBPhs in recent waste P-CBs (using in this study) were higher amounts than those in old ones, while amounts of PBDEs, PBBzs, TBBPA and PBDD/Fs were extraordinarily lower. These results imply that BFRs with high molecular and reactive types might have been applied in recent P-CBs and their mount devices. In primary combustion (incomplete combustion), compounds, which were used as BFRs, were decomposed. In contrast, thermal formation was observed in other brominated organic and dioxin-related compounds. Most amounts of brominated organic compounds and PCDD/Fs, which were remained in flue gas after primary combustion, were decomposed and/or removed during flue gas treatment.

Introduction

Waste printed circuit boards (P-CBs) have been of great concerns as recycling materials, because they consist of high amount of rare metals. On the other hands, appropriate treatment of brominated flame retardants (BFRs) and its byproducts, which were applied in plastic materials up to 10%, is important during recycling and/or waste treatment of waste P-CBs. While several recycling/waste methods have been developed, thermal treatment of waste P-CBs is one of the major methods. Behaviors of brominated organic compounds have been studied during thermal treatments of waste P-CBs^{1,2,3}. However, they focused mainly on PBDD/Fs and PCDD/Fs. There are less consideration regarding on behaviors of BFR selves and low molecular compounds, such as PBBzs and PBPhs. In addition, these studies were done using small heating systems and/or open burning conditions.

As the results of restriction of PBDEs and polybromobiphenyls, usage of alternative BFRs have been increased⁴. However, information regarding on BFRs used in recent P-CBs is not so disclosed.

Based on these backgrounds, the aims of this study are to understand the composition of various FRs in recent waste P-CBs, and the behaviors of brominated organic compounds during thermal treatment of waste P-CBs and flue gas treatment in pilot-scale experiments.

Materials and Methods

Waste P-CBs using in this study were originated mainly from personal computers, which were manufactured mostly in a decade. Approximately 20 kg of waste P-CBs was crushed into small pieces (<5mm) after removing the large metal parts, such as radiators.

Combustion experiment of waste P-CBs was done using the thermal treatment plant equipment at NIES, Japan. This plant consists of a rotary kiln primary combustion chamber, a vertical secondary

Table 1 Experimental condition of thermal treatment plant in this study

Temperature (°C)	Primary combustion	841
	Secondary combustion	901
	Bag filter	149
Air flow rate in primary combustion (m ³ /h)		5.0
Input feeding rate (g/h)		910
Total input (g)		5,460
Volume (g)	Bottom ash	3,565
	Fly ash	150
Acid gas treatment		NaHCO ₃
Flue gas at kiln exit	O ₂ (%)	18.8
	CO (ppm*)	15,000
	HCl (ppm*)	150
Flue gas at bag exit	O ₂ (%)	17.5
	CO (ppm*)	97
	HCl (ppm*)	6

* Concentration normalized on 12% of O₂ concentration.

combustion chamber, a gas cooling zone, a bag filter, an activated carbon adsorption tower and a wet scrubber⁵. The experimental condition was shown in Table 1. High concentrations of carbon monoxide in kiln exit gas indicate that primary combustion was incomplete condition.

Flue gases were collected at four locations (kiln exit, bag filter entry [secondary combustion exit], bag filter exit, and final exit) for 4 hours after steady combustion. Sampling was followed the method of JIS K0311⁶. Bottom ash was collected immediately after the experiment. PBDEs, DBDPE, TBBPA, HBCDs, PBBzs, PBPhs, PBDD/Fs, monobromopolychlorinated dibenzo-*p*-dioxins and dibenzofurans (PXDD/Fs), and PCDD/Fs were analyzed in the samples of flue gases and bottom ash. In addition to these compounds, PFRs were examined in waste P-CBs. Identification and quantification were performed by LC/MS/MS for TBBPA and HBCDs, GC/LRMS for PFRs, and GC/HRMS for other compounds.

Results and Discussion

Figure 1 shows the concentrations of brominated organic compounds, PFRs and PCDD/Fs in waste P-CBs using in this study. The highest concentration was PBDEs. Predominant homologue of PBDEs is decaBDE, followed by nonaBDEs (Fig. 4). These homologues were several orders of magnitude higher than other homologues. Sakai *et al*⁷ reported that tetra- and pentaBDEs were the predominant homologues in waste P-CBs from TVs manufactured on 1987-1995. In addition, PBDE concentrations in recent waste P-CBs (using in this study) were extraordinarily lower than those in old ones (Fig. 2), indicating that difference of PBDE homologues between old and recent waste P-CBs was related to a decrease in consumption of technical pentaBDE/tetraBDE mixtures in last decade. DBDPE, which has been used as an alternate to a technical decaBDE mixture, was detected at approximately half concentrations of PBDEs. PBPhs and PFRs were similar order of magnitude to DBDPE, followed by TBBPA > PBBzs > PBDD/Fs > PCDD/Fs. HBCDs and PXDD/Fs were not detected at levels of 700 µg/kg and 0.02 µg/kg, respectively. The predominant isomers/compounds of PBPhs, PFRs and PBBzs were 2,4,6-triBPh, triphenyl phosphate and hexaBBz, respectively. They are known to be used as flame retardants.

Bromine concentration, which was calculated from brominated organic compounds detected, was 720 mg/kg on waste P-CBs basis. This value is only 2.6% of total bromine content in waste P-CBs (28,000 mg/kg). Compared to waste P-CBs

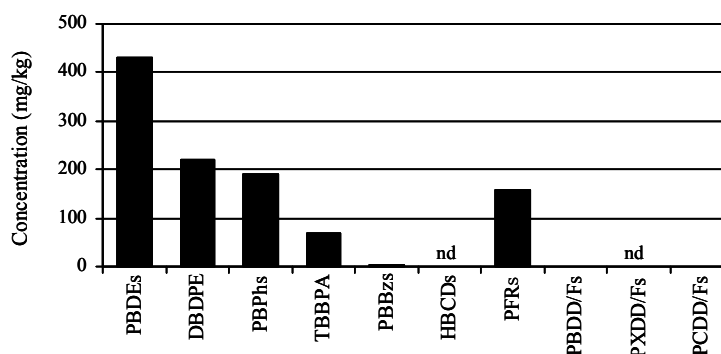


Fig.1 Concentrations of brominated organic compounds, PFRs and PCDD/Fs in waste P-CBs

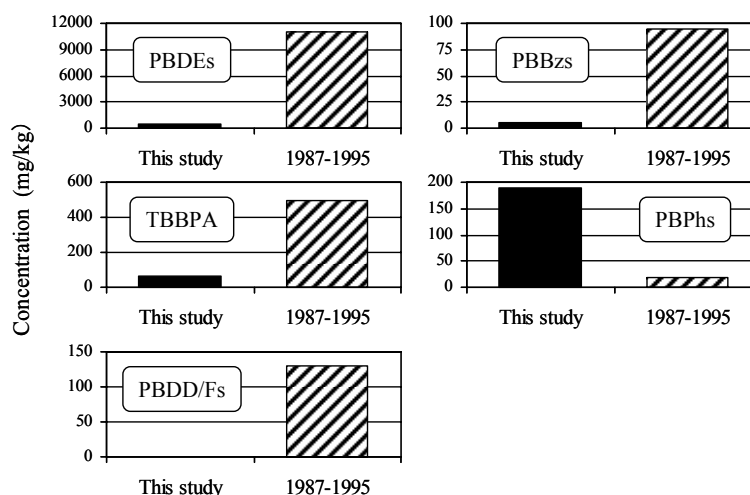


Fig.2 Comparison of concentrations of brominated organic compounds in current waste P-CBs (using in this study) and old ones
Data on 1987-1995 was cited from ref⁷.

from TVs manufactured on 1987 - 1995⁷, recent waste P-CBs (using in this study) retained PBDEs, PBBzs, TBBPA and PBDD/Fs with extraordinary lower concentrations (Fig. 2). However, levels of PBPhs were higher in recent waste P-CBs. 2,4,6-TriBPh, which is predominant isomer of PBPhs in waste P-CBs using in this study, has been used as a raw material and an end-cap for brominated epoxy resins, tribromophenyl aryl ethers and bis(tribromophenoxy)ethane⁸. Actually, 2,4,6-triBPh have been detected at concentrations of 34-520 $\mu\text{g/g}$ from these high molecular BFRs⁹. Considering these and temporal trends of consumptions⁴, BFRs with high molecular and reactive types might have been increased to be applied in recent P-CBs and their mount devices.

DecaBDE, DBDPE, TBBPA, triBPhs and hexaBBz, which were used as BFRs, were decomposed in primary combustion (incomplete combustion). The decomposition rates of these compounds were 30-99.999%. Amounts of tetra- to nonaBDE homologues were also decreased in primary combustion. In contrast, thermal formations were observed in PBDD/Fs, PXDD/Fs, PCDD/Fs, mono- to diBDE homologues, mono- to pentaBBz homologues, mono- to diBPh homologues and tetra- to pentaBPh homologues. Their amounts in primary combustion were several orders of magnitude higher than inputs. As these results, homologue compositions of PBDEs, PBPhs and PBBzs after primary combustion were quite different to those in inputs (Fig. 4).

Extraordinary higher amounts of most compounds were found in kiln exit gas than bottom ash (Fig. 3), indicating that flue gas treatment is important for decreasing the environmental releases of these compounds. However, decabDE and DBDPE were remained in bottom ash at similar amounts to those in kiln exit gas, while more than 99.999% of input amounts were decomposed in primary combustion.

Most amounts of brominated organic compounds and PCDD/Fs were decomposed and/or removed during flue

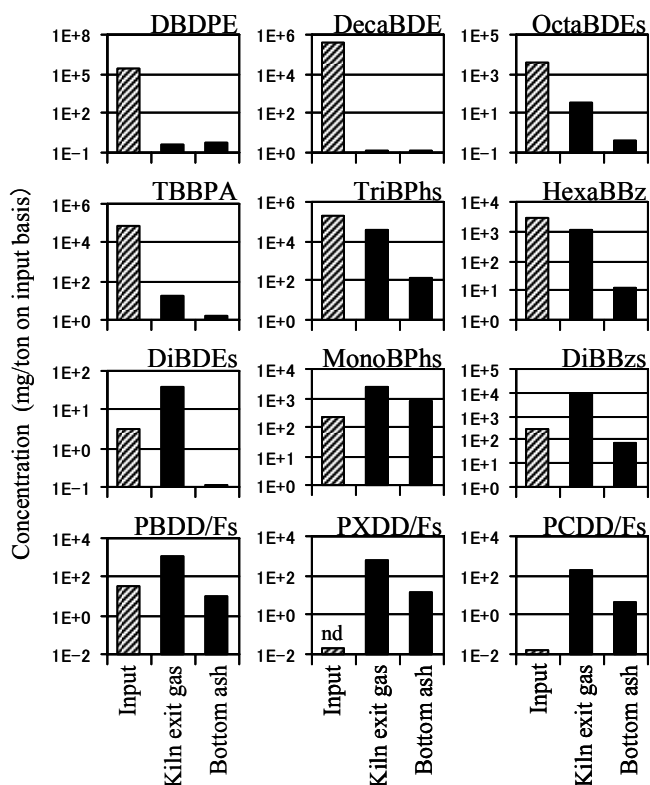


Fig.3 Compound behaviors in incomplete combustion

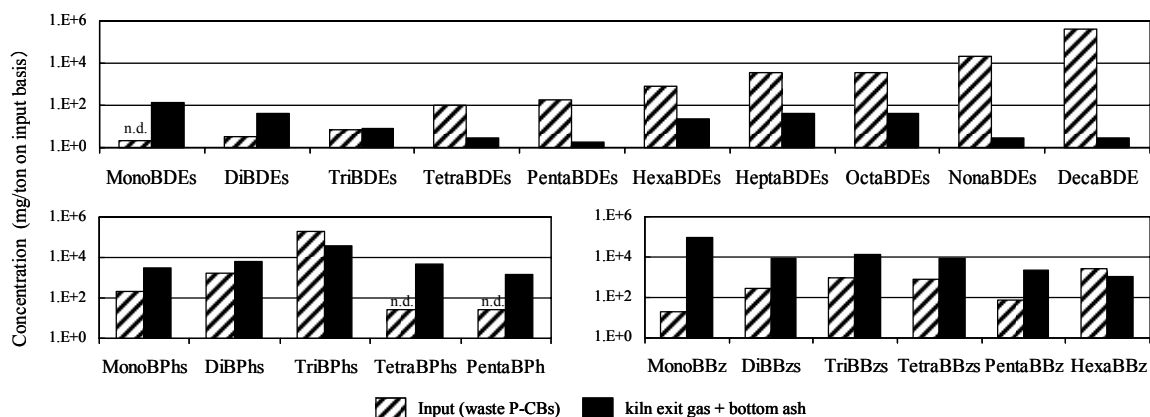


Fig.4 Changes of homologue compositions of PBDEs, PBPhs and PBBzs in incomplete combustion

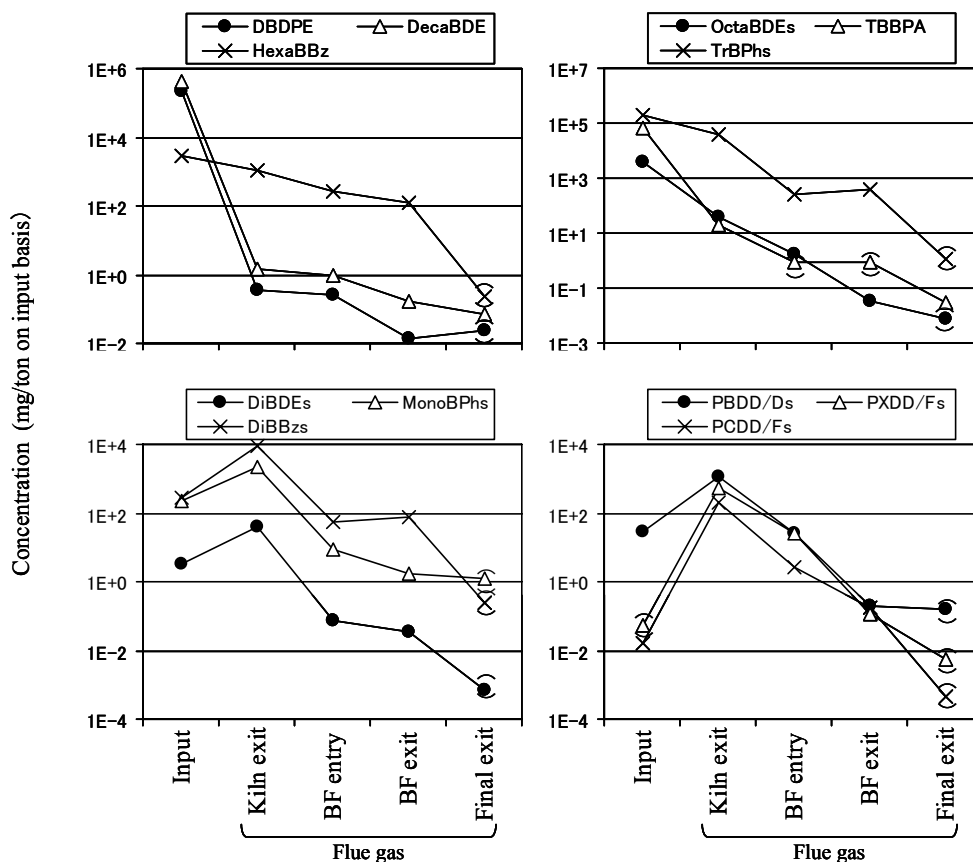


Fig.5 Behaviors of bromiated organic compounds and PCDD/Fs during combustion and flue gas treatments

Mark in parentheses indicate the detection limit.

gas treatment (Fig. 5). Most compounds were not detected in flue gas at final exit. Amounts in final exit gas were up to two orders of magnitude lower than those in kiln exit gas. For compounds decomposed in primary combustion, amounts in final exit gas were up to five orders of magnitude lower than those in input. Amounts of most compounds, which were formed in primary combustion, were decreased their concentrations to more than two orders of magnitude lower than inputs. These results indicate that emission of brominated organic compounds and PCDD/Fs to environment can be decreased by appropriately management of flue gas treatment.

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