BEHAVIOR OF 2-(3,5-DI-*TERT*-BUTYL-2-HYDROXYPHENYL)BENZOTRIAZOLE (DBHPBT) AND UNINTENTIONALLY PRODUCED POPS DURING INCINERATION OF SOLID WASTE CONTAINING DBHPBT

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Abstract

2-(3,5-Di-*tert*-butyl-2-hydroxyphenyl) benzotriazole (DBHPBT), one of the UV stabilizer for plastics, waxes, *etc*., is classified as a "Class I Specified Chemical Substance" by the Chemical Substance Control Law, Japan, meaning that DBHPBT has a comparable nature and toxicity to well-known Persistent Organic Pollutants (POPs). Considering that DBHPBT has been used in long-life articles, the products containing DBHPBT still have to undergo waste management. Therefore, an appropriate treatment for waste containing DBHPBT is strongly required. In this study, using the Best Available Technology approach, we performed a combustion experiment of solid waste containing DBHPBT using a pilot-scale incinerator to determine the destruction behavior of DBHPBT and its influence on behaviors of unintentionally produced POPs release, such as PCDD/Fs, dioxin-like PCBs and HCB. DBHPBT was destroyed mainly in the primary combustion zone. Overall destruction efficiency of DBHPBT was > 99.9999%. The input of DBHPBT did not affect the formation and destruction behavior of PCDD/Fs, dioxin-like PCBs and HCB. These results indicate that appropriate management of combustion conditions and flue gas treatment can minimize the emission of DBHPBT and unintentionally produced POPs into the environment.

Introduction

2-(3,5-Di-*tert*-butyl-2-hydroxyphenyl) benzotriazole (DBHPBT, CAS no. 3846-71-7, Figure 1) was classified as a "Class I Specified Chemical Substance" by Chemical Substance Control Law (CSCL), Japan in 2007, which meant that DBHPBT was comparable in nature and toxicity to well-known Persistent Organic Pollutants (POPs). This class includes PCBs, DDT, hexachlorobenzene (HCB), chlordanes, mirex, toxaphenes, heptachlors, *etc.*

DBHPBT has been used as an UV stabilizer applied to various products, such as plastics, waxes, dressing boards, paints, sensitizers, adhesive agents, sealing agents and aromatics. Approximately 70% of DBHPBT usage in Japan has been in plastics, especially those used for construction materials and car parts[1].

According to the hazard assessment by CSCL[2], it is understood that DBHPBT has a persistent nature in the environment and the high bioaccumulative nature. While DBHPBT has no acute toxicity, the adverse effects to liver was observed in a chronic exposure test of DBHPBT in rats. NOEL was considered to be 0.1 mg/kg/day for male and 2.5 mg/kg/day for female rats.

Considering that DBHPBT has been used in long-life articles, the products containing DBHPBT still have to undergo waste management. Therefore, an appropriate treatment for waste containing DBHPBT is strongly

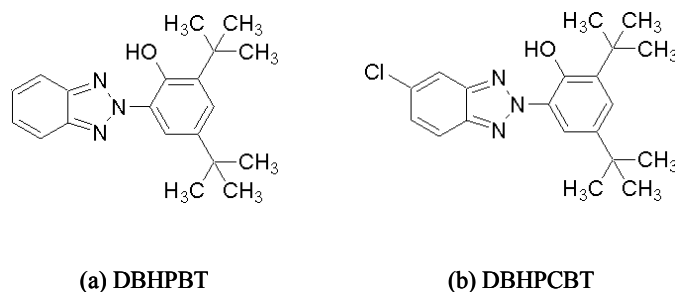(a) DBHPBT   (b) DBHPCBT

Fig.1   Chemical structures of DBHPBT (a) and DBHPCBT (b)

required. However, to our knowledge, there is no information regarding the waste treatment of DBHPBT-containing materials. Because DBHPBT is used mainly in plastics, it is expected that incineration may be the predominant method of treatment for wastes containing DBHPBT.

Based on this background, we performed thermal treatment experiments using the pilot-scale equipment and the waste injected with DBHPBT as an input material to determine the destruction behavior of DBHPBT and its influence on the behavior of unintentionally produced POPs, such as PCDD/Fs, dioxin-like PCBs and HCB.

Materials and Methods

Combustion experiments were done using the thermal treatment plant equipment at NIES, Japan (Figure 2).

Two experiments using refuse derived fuels (RDF) as input materials were carried out with and without DBHPBT injection. RDF was obtained from municipal solid waste after removing the incombustible materials. DBHPBT solution was injected into a grain of RDF, resulting that the final concentration of DBHPBT in RDF was 5,000 mg/kg (0.5%). This concentration was selected due to the following assumptions: DBHPBT was contained in waste plastics at a concentration of 1.0%. Weight percentages of waste plastics in the input materials of incinerators were 50%. All the waste plastics in the input materials of incinerators contained DBHPBT. According to these assumptions, the final concentration of DBHPBT in the input materials of incinerators was calculated to be 0.5%. The experimental conditions are shown in Table 1. These operating conditions followed the requirement for waste incinerators of the Japanese government[3] and UNEP[4].

At stable combustion conditions, the flue gases were collected for 4 hours at 4 sampling points (Figure 2). Sampling was performed according to the method of the Japanese Industrial Standard (JIS) K0311[5] with the modification that the filter and the XAD cartridge were set after the liquid gas samplers. Bottom and fly ashes were collected at the end of each experiment and analyzed.

In this study, DBHPBT, 2-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-5-chlorobenzotriazole (DBHPCBT, Figure 1), which has been used as an UV stabilizer and is similar in chemical structure to DBHPBT, dioxin-related compounds (DRCs: tetra- to octa-chlorinated dibenzo-*p*-dioxins and dibenzofurans, and dioxin-like PCBs) and HCB were analyzed. The extraction of DBHPBT and DBHPCBT in the flue gas was performed by the methods
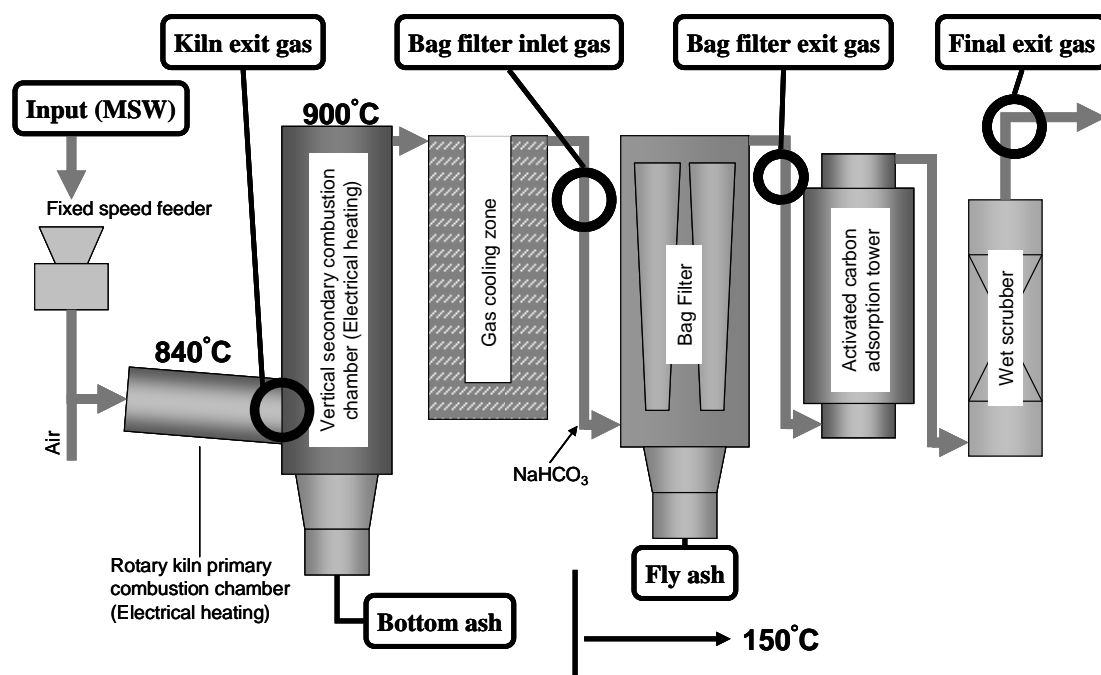

Fig.2 Scheme of thermal treatment plant equipment used in this study and the sampling location positions.

Table 1 Experimental conditions of thermal treatment plant in this study

Experiment		Blank exp.	DBHPBT addtive exp.
DBHPBT addtive weight % to RDF		0%	0.50%
Temperature (°C)	Primary combustion	839	839
	Secondary combustion	900	900
	Bag filter	149	149
Air flow rate into primary combustion (m^3/h)		19.5	17.0
MSW feeding rate (kg/h)		2.6	2.3
Total MSW input (kg)		10.3	9.3
Volume (g)	Bottom ash	805.1	709.3
	Fly ash	89.5	80.2
Acid gas treatment		$NaHCO_3$	$NaHCO_3$
Flue gas at bag filter exit O_2 (%)		9.4	9.8
	CO (ppm*)	1	1
	NOx (ppm*)	29	27

* Concentration normalized on 12% of O_2 concentration.

of JIS K0311[5]. 10 g of solid samples were refluxed with 1 mol/L KOH-ethanol solution. DBHPBT and DBHPCBT in the ethanol extract were transferred to hexane. An aliquot of the flue gas extract and the hexane extracts of solid samples were cleaned up by Sep-Pak plus NH_2. Solution eluted was concentrated and resolved into methanol with diethylhexyl phthalate-d_4 as an internal standard. Identification and quantification of DBHPBT and DBHPCBT were performed using a LC/MS/MS (Micromass Quattro Ultima). Ionization mode was positive electrospray ionization (ESI[+]) at a capillary voltage of 3,000 V.

The extraction of DRCs and HCB in the flue gas and those in the input materials (RDF) and ash samples was performed using the methods of JIS K0311[5] and Noma et al[6]. The clean-up procedure and quantification of DRCs was performed according to the methods of JIS K0311[5]. For analysis of HCB, an aliquot of the extract was concentrated and spiked with $^{13}C_6$-labeled HCB as an internal standard. Identification and quantification of HCB were performed using a GC/HRMS at a resolution of > 10,000 with a DB-5ms fused silica capillary column.

Results and Discussion
Figure 3 shows the amounts of DBHPBT, DBHPCBT, PCDD/Fs, TEQs and HCB in the input materials, flue gases and ashes of RDF combustion (blank experiment) and combustion of RDF injected with DBHPBT (DBHPBT additive experiment). The amounts of chemicals at each sampling points were recalculated as follows: the concentrations of the chemicals were multiplied by the flue gas volumes or amounts of ash formation during the sampling times (4 hours).

Levels in RDF (Input Materials)
Because the RDF used in this study was obtained from municipal solid waste, the concentrations reflected the levels of DBHPBT, DBHPCBT and unintentionally produced POPs in actual municipal solid waste in Japan. Concentrations of DBHPBT and DBHPCBT in RDF without DBHPBT injection were 7.1 μg/kg and 20 μg/kg, respectively (Figure 3). Those in RDF with DBHPBT injection were 5,000,000 μg/kg (5,000 mg/kg) and 20 μg/kg, respectively. No increase in the concentration of DBHPCBT occurred with DBHPBT injection. Similarly, HCB concentrations in RDF with and without DBHPBT injection were 41 μg/kg and 40 μg/kg. The concentrations of DRCs were 0.021 ng-TEQ/kg and 0.021 ng-TEQ/kg, respectively, meaning that the DBHPBT standard injected into RDF did not contain significant levels of HCB and DRCs.

Formation and Destruction Behavior in the Primary Combustion Zone
During the sampling time (4 hours), 0.0728 mg and 46,700 mg of DBHPBT were input, when RDF without and
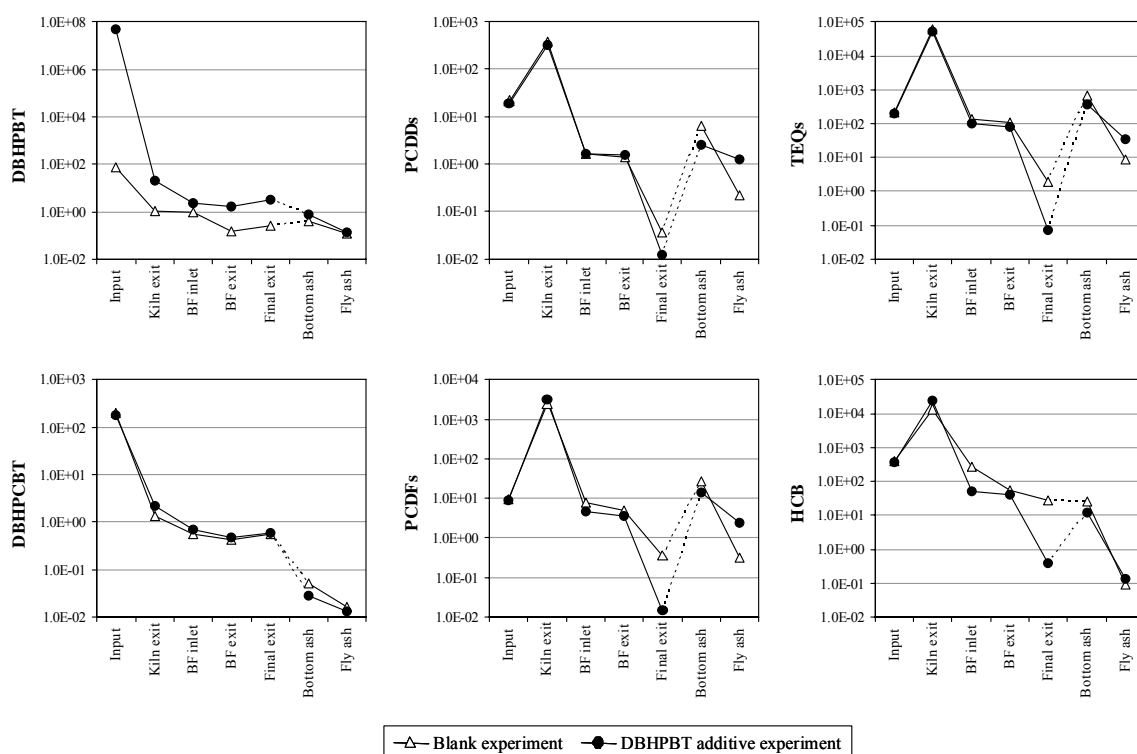
Fig.3   Behavior of DBHPBT, DBHPCBT, DRCs and HCB during combustion and flue gas treatment in blank and DBHPBT additive experiments. The vertical line indicate the chemical amount in each sampling point (ng for TEQ, μg for others)

with DBHPPBT injection were combusted, respectively (Figure 3). After primary combustion in the DBHPBT additive experiment, the amounts of DBHPBT in the kiln exit gas and bottom ash were 20.2 μg and 0.780 μg, respectively. These results suggested that DBHPBT was destroyed in the primary combustion zone with a destruction efficiency of more than 99.9999%. Similarly, after primary combustion in the blank experiment, DBHPBT in RDF was destroyed to 1.12 μg and 0.419 μg in the flue gas of the kiln exit and bottom ash, respectively. These values were 1-2 orders of magnitude lower than the input amount of DBHPBT.

After primary combustion, DBHPCBT was thermally destroyed to about 2 orders of magnitude lower than the input amounts (Figure 3). There was less of a difference in the concentrations and amounts of DBHPCBT in the kiln exit gas and bottom ash between the two combustion experiments. These results indicate that no chlorination of DBHPBT occurred during primary combustion.

In contrast to DBHPBT and DBHPCBT, DRCs were formed in the primary combustion zone in both experiments (Figure 3). TEQ amounts of DRCs in the kiln exit gases were two orders of magnitude higher than the input amounts. The TEQ amount of DRCs in the bottom ashes was 362 – 660 ng. These values were several times higher than those in the input materials. The concentrations of total TEQs of DRCs in the bottom ashes, however, were 0.82 ng-TEQ/g and 0.51 ng-TEQ /g for the blank and DBHPBT additive experiment, respectively. These values were below the Japanese standards (3 ng-TEQ /g). The amounts and homologue patterns of DRCs in the kiln exit gas and bottom ash in the DBHPBT additive experiment were comparable to those in the blank experiment, indicating that the input level of DBHPBT did not affect DRC formation in the primary combustion zone (Figure 3 &4).

HCB levels in the kiln exit gases were 13,400 μg and 22,400 μg in the blank and DBHPBT additive experiments,
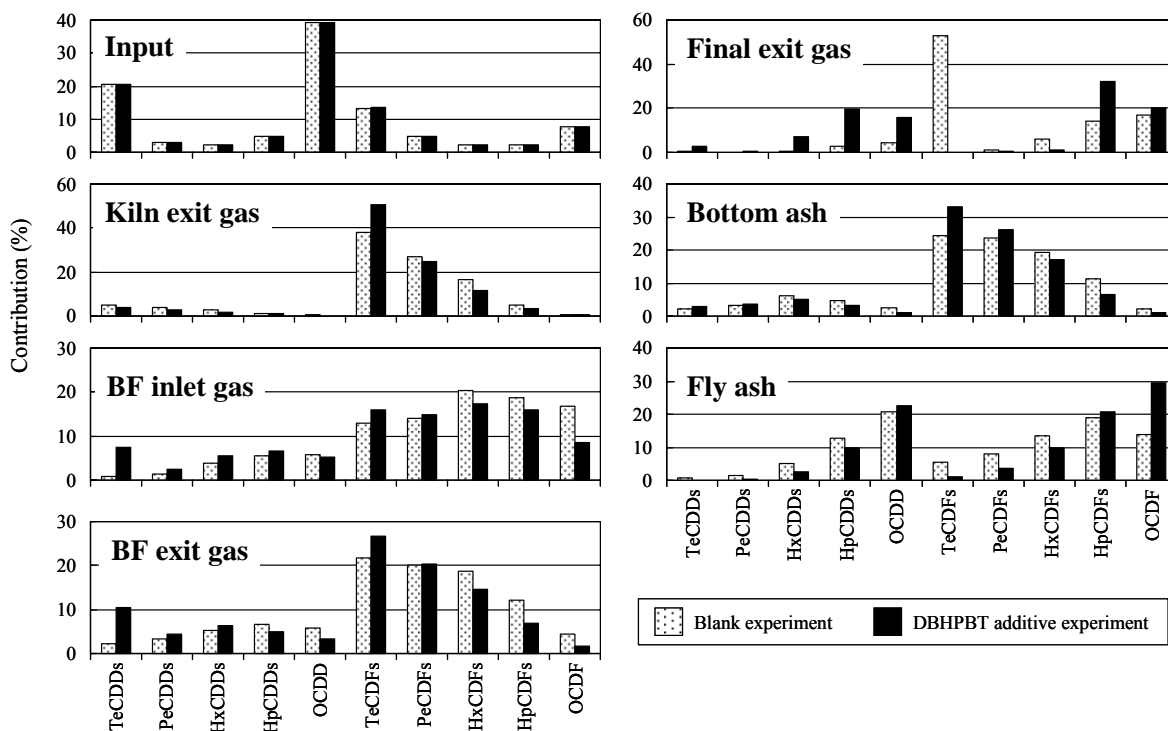
Fig.4　Homologue profiles of PCDD/Fs in the flue gases and ashes

respectively, suggesting that HCB was also formed in the primary combustion zone to amounts two orders of magnitude higher than the input amounts. HCB amounts in the bottom ashes were 11.3 – 25.0 μg. There was less of a difference in HCB concentrations and amounts in the kiln exit gases and bottom ashes between the blank and DBHPBT additive experiments, indicating that the input amount of DBHPBT did not affect HCB formation in the primary combustion zone.

All the compounds including DBHPBT were present in the kiln exit gas at amounts several orders of magnitude higher than the bottom ashes (Figure 3). In addition, amounts of DBHPBT, DBHPCBT and HCB in bottom ashes were lower than those in input materials. TEQ levels in the bottom ashes were below the Japanese standard and the relatively high international standards specified for POPs by the Basel Convention. These results indicate that flue gas treatments, such as secondary combustion and air pollution control devices, are important for the reduced emission of DBHPBT and unintentionally produced POPs.

Destruction and Removal Behavior in the Secondary Combustion Zone
The concentrations of DBHPBT in the flue gas after secondary combustion (at the bag filter inlet) in the DBHPBT additive experiment were about one order of magnitude lower than those in the flue gases after primary combustion. Similarly, concentrations of DBHPCBT were several times lower than those in the flue gases after primary combustion. It may be concluded, therefore, that DBHPBT and DBHPCBT were continuously destroyed in the secondary combustion chamber.

In both experiments, the concentrations of DRCs and HCB in the flue gases after secondary combustion were more than two orders of magnitude lower than those in the flue gases after primary combustion (Figure 3). It may be concluded, therefore, that the DRCs and HCB were destroyed with efficiencies of more than 98% in the secondary combustion chamber. This demonstrates that a secondary combustion zone is the key to controlling emission of DRCs and HCB in solid waste incineration in this experimental condition.

The amounts of DRCs and HCB in the flue gas after secondary combustion in the DBHPBT additive experiment

were almost similar to those in the blank experiment (Figure 3). Homologue profiles of PCDD/Fs in the flue gas after secondary combustion showed almost similar patterns between the blank and DBHPBT additive experiments (Figure 4). These results indicate that the input amount of DBHPBT did not increase the amounts of unintentionally produced POPs in the flue gases after destruction at the secondary combustion zone.

Behavior in the Post Combustion Zone and Air Pollution Control Devices
The amounts of DBHPBT, DBHPCBT and unintentionally produced POPs in the fly ashes, which were collected at the bag filter, were found to be lower than or comparable to those in the gas phase at the bag filter exit (Figure 3). Therefore, in the experimental set-up used in this study, with adequate secondary combustion and extremely low dust concentrations in the raw gases (0.23-0.45 mg/m^3), the removal efficiency at the bag filter was low for those compounds and accordingly, the amounts of DBHPBT, DBHPCBT and unintentionally produced POPs in the flue gases at the bag filter exit were comparable to those at the bag filter inlet.
The removal efficiencies of DBHPBT and DBHPCBT were less in the final flue gas treatment (a carbon adsorption tower and a wet scrubber), while 98% of DRCs present in the bag filter exit gases were reduced to a TEQ amount between 0.0713 – 1.85 ng (Table 2). Similar to DRCs, HCB was reduced to 0.396 – 24.6 μg, which was between several times to one order of magnitude lower than that in the flue gas of the bag filter exit.

Final Exit
The amounts of DBHPBT in the final exit gases and ashes of DBHPBT additive experiment were several orders of magnitude lower than those in the input materials (Figure 3). Overall destruction efficiency of DBHPBT in the DBHPBT additive experiment was more than 99.9999%. This efficiency level is sufficient to conclude that incineration of waste containing DBHPBT is one of the Best Available Technologies.
DBHPBT in the final exit gases and ashes in the blank experiment, and DBHPCBT in the final exit gases and ashes in both experiments were several orders of magnitude lower than those in the input materials. Almost amounts of HCB and DRCs, which were formed in primary combustion, were destroyed mainly in secondary combustion, and these amounts remained in flue gases after secondary combustion were further removed by air pollution control devices. Consequently, final emission amounts (sum amounts in the final exit gas and ashes) of HCB were one order of magnitude lower than amounts in input materials. The TEQ concentrations of DRCs in the final exit gas (0.00054 – 0.014 ng-TEQ/m^3) and solid residues - bottom ashes (0.51-0.82 ng-TEQ/g) and fly ashes (0.026-0.11 ng-TEQ/g) - in both experiments were below the Japanese standards (0.1 ng-TEQ/m^3 and 3 ng-TEQ/g), and international BAT standards (0.1 ng-TEQ/m^3). In addition, final emission amounts of DBHPCBT, DRCs and HCB in the DBHPBT additive experiment were comparable or lower than those in the blank experiment. These results suggest that regulations for the waste incinerator introduced to minimize emissions of DRCs (e.g. regulations in Japan[3]; combustion temperature: > 800˚C, residence time: > 2 sec., excess air conditions) also lead to reductions in DBHPBT emissions. Currently, waste incinerators are addressed globally under the framework of the Stockholm Convention for the reduction of PCDD/Fs and other unintentionally produced POPs release[4], which specifies that BAT is applied to the different types of waste incineration[4]. The current combustion tests reported here indicate that complying with these specifications will also lead to a significant reduction in the emissions of DBHPBT and therefore to a reduction in the emissions of POPs-like contaminants from these sources into the environment.

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