

# A PRELIMINARY STUDY FOR COMBUSTION OF PLASTICS CONTAINING BROMINATED FLAME RETARDANTS AND BEHAVIORS OF ITS BY-PRODUCTS.

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## Introduction

Polybrominated diphenyl ethers (PBDEs) and Tetra-brominated bisphenol-A (TBBPA) are a group of additive brominated flame retardants (BFRs) that are widely used in electronic equipment, insulation material, and furniture. The major commercial mixtures of PBDEs are composed of deca-BDE in Japan. Approximately 2,000 and 35,000 metric tons of deca-BDE and TBBPA technical products, respectively, were used in Japan in 2004. The rapid increase in the use of BFRs has also raised the level of environmental concern about polybrominated chemicals such as polybrominated dibenzo-p-dioxins/furans (PBDDs/DFs), which are present as low-level impurities in some commercial mixtures of BFRs and are produced upon their combustion<sup>1,2</sup>. PBDDs/DFs are also formed, for example, when plastics that contain BFRs are heated during the welding of mats or the melting of polymers<sup>3</sup>. The thermal formation of PBDDs/DFs from BFRs is considered to be a serious issue<sup>4</sup>.

In the present study, we determined decomposition rates of deca-BDE at a rotary kiln furnace combined with a secondary cylindrical furnace. In addition, the concentrations of extractable organic bromine (EOBr) in flue gas and fly ash were determined using combustion ion chromatography (CIC) and applied in a study to assess by-products from combustion of plastics containing deca-BDE.

## Materials and Methods

**Incineration.** The first combustion chamber is a rotary kiln furnace with a diameter of 150 mm and a length of 1000 mm. The furnace has a stable temperature control (set temperature  $\pm 25^{\circ}\text{C}$ ) and maximum temperature is  $950^{\circ}\text{C}$ . The rotating rate is 30 rpm. The secondary combustion chamber is a cylindrical furnace with a diameter of 68 mm and a length of 900 mm, with a temperature control (Figure 1). Plastic samples containing BFRs such as deca-BDE (1-3 wt% as bromine) were fed into the first furnace (2-3s,  $850^{\circ}\text{C}$ ) and then flue gas from the first furnace was introduced into the secondary furnace (2-3s,  $800$  or  $900^{\circ}\text{C}$ ).

**Thermal gravimetric (TG) and differential thermal analysis (DTA).** TG/DTA was performed in a Delta Series TGA7 made by PerkinElmer. About 10 mg samples of polystyrenes (PS) containing 10% as bromine of deca-BDE and TBBPA were used for the TG/DTA measurement. The samples were placed in a crucible with surrounding of air, and a heating rate was  $10^{\circ}\text{C}/\text{min}$ .

**Sample collection.** Flue gas and fly ash samples were collected from exits of the secondary furnace in order to determine concentrations of BFRs (deca-BDE). Sampling method of the samples was based on a modified standard method for PCDDs, PCDFs, and Co-PCBs<sup>5,6</sup>, which comprised of a cylindrical filter for collecting fly ash, 200 mL of water, and 300 mL of diethylene glycol in 1000 mL bottles that were submerged sufficiently in a cooling box.

**Analytical procedures for deca-BDE.** The determination of deca-BDE was performed according to an established method with some modifications<sup>1,7</sup>. Briefly, samples were extracted using a liquid-liquid extraction method for flue gas or a high-speed solvent extractor (SE-100, Mitsubishi Chemical Corp., Japan)<sup>8</sup> for fly ash. An aliquot of the extracts was spiked with internal standards ( $^{13}\text{C}$ -PBDEs), and then cleaned using 22% and 44%  $\text{H}_2\text{SO}_4$ -silica gel.

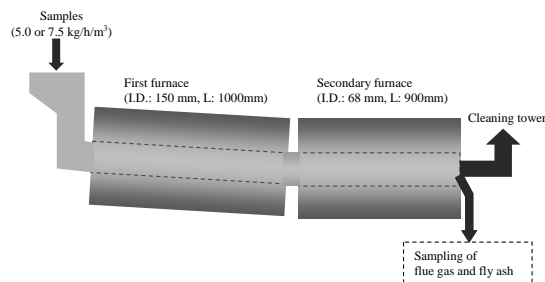


Figure 1. Experimental apparatus.

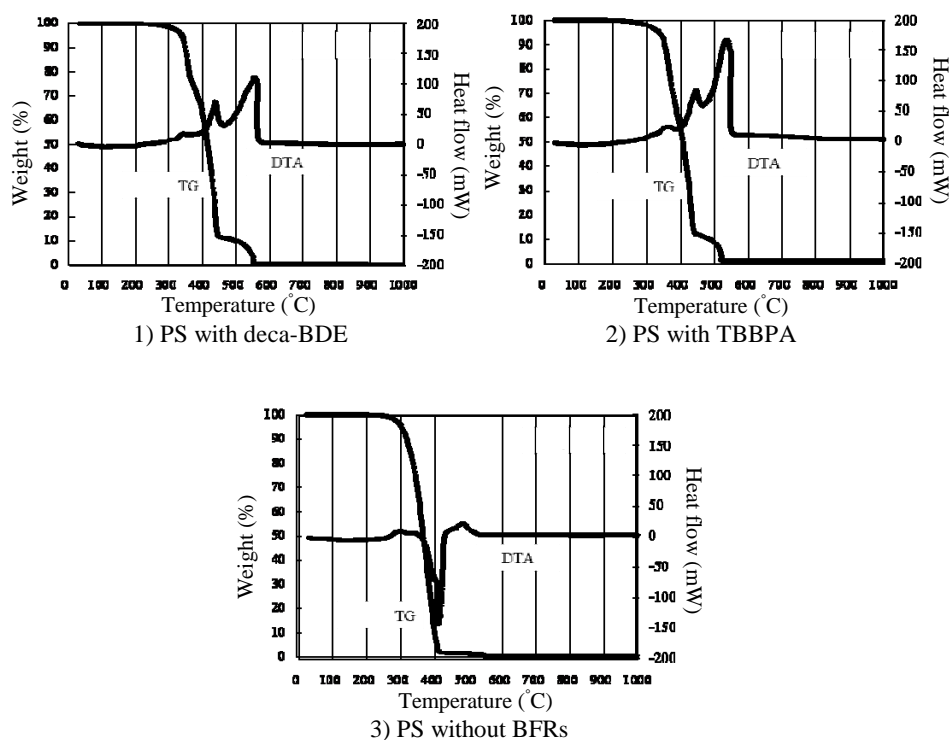
The determination of deca-BDE was performed using high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) with the HP 6890 GC interfaced with a Micromass Autospec-Ultima HRMS. The MS was operated in electron impact mode (38 eV energy and 500 mA ion current) and at a resolution  $R > 10,000$  (10% valley) in the selected ion monitoring (SIM) mode.

**CIC analysis.** Concentrations of EOBr in samples were determined using CIC<sup>9,10,11</sup>. The extract was set on a silica boat and placed into a furnace at 900–1000°C. Combustion of the samples in the furnace converted organobromines into hydrogen bromide (HBr). The HBr was absorbed into sodium hydroxide solution spiking with sodium thiosulfate. The concentration of Br<sup>-</sup> in the solution was analyzed using ion chromatography. The analytical conditions of the ion chromatography have been described in Miyake et al.<sup>9</sup>.

**Quality assurance and quality control (QA/QC).** QA/QC protocols included the analysis of matrix spikes and procedural blanks. Peaks were identified by comparison of the retention times of samples to standards if the signal-to-noise (S/N) ratio was  $>3$ , and were quantified if target/qualifier ion ratios were within 15% of the theoretical values. Any sample with recovery below 40% was discarded and reanalyzed.

## Results and Discussion

**TG/DTA of polystyrene containing BFRs.** TG/DTA was performed using polystyrene with deca-BDE and TBBPA, which were used in large amounts at the past and present, respectively. TG/DTA curves of the polystyrene, polystyrene with deca-BDE, and polystyrene with TBBPA are shown in Figure 2. An endothermic peak appeared at about 400°C on the DTA curve of polystyrene, whereas two exothermic peaks appeared between 400°C to 600°C on the DTA curves of polystyrene containing deca-BDE and TBBPA. Reactions corresponding to the endothermic and two exothermic peaks exhibited different mechanism. In addition, completely similar TG/DTA curves were observed for the polystyrene containing deca-BDE and TBBPA. This may indicate the presence of similar combustion behaviors in these samples.



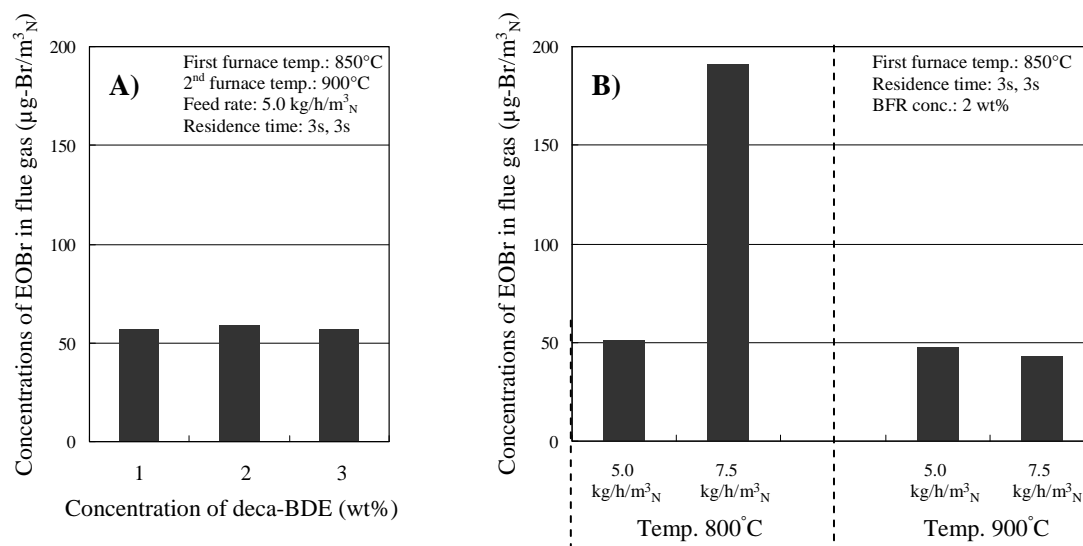
**Figure 2.** TG/DTA curves of 1) polystyrene with deca-BDE, 2) polystyrene with TBBPA, and 3) polystyrene without BFRs.

**Decomposition rate of deca-BDE and by-products from combustion of deca-BDE.** Combustions of polystyrene with BFRs were performed using polystyrene containing deca-BDE, due to the similar combustion behaviors between deca-BDE and TBBPA. Concentrations of deca-PBDE in flue gas and fly ash collected from the exit of secondary furnace were 15 and 8.3 ng/m<sup>3</sup><sub>N</sub>, respectively. The decomposition rate calculated from these results and feed rate of deca-BDE was over 99.9999%.

Concentrations of EOBr in flue gas collected from the exit of secondary furnace were determined in order to analyze generation behaviors of by-products from combustions of deca-BDE (Figure 3). In addition, concentrations of individual bromochemicals such as PBDDs/DFs and PBDEs were also determined, and described elsewhere<sup>12</sup>.

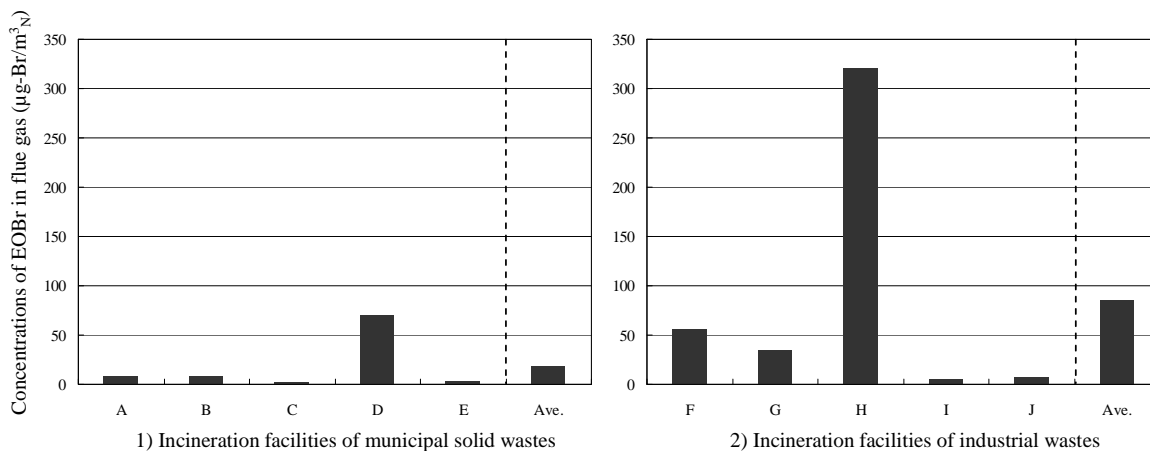
Concentrations of EOBr in cases where deca-BDE contents were 1, 2, and 3 wt% were 57, 59, 57 μg-Br/m<sup>3</sup><sub>N</sub>, respectively. No change was observed with changing the deca-BDE contents as shown in Figure 3 (A). An increase of the concentration of EOBr was observed only in cases where the feed rate was 7.5 kg/h/m<sup>3</sup><sub>N</sub> and temperatures of secondary furnace was 800°C as shown in Figure 3 (B).

Application of the EOBr to evaluation of by-products from the combustion of BFRs will provide valuable information on the contamination by unidentified bromochemicals.



**Figure 3. Concentrations of EOBr in flue gas from combustions of PS containing deca-BDE. (A) With changing deca-BDE contents (1, 2, and 3 wt%); and (B) With changing feed rates (5.0 and 7.5 kg/h/m<sup>3</sup><sub>N</sub>) and temperatures of secondary furnace (800°C and 900°C).**

**EOBr in flue gas from incineration facilities of municipal and industrial solid wastes.** In order to check whether the concentrations of EOBr shown in Figure 3 were acceptable, they were compared with those of flue gas collected from incineration facilities of municipal and industrial solid wastes in Japan. The concentrations of EOBr at the incineration facilities of municipal solid wastes ranged from 2.4 to 70 μg-Br/m<sup>3</sup><sub>N</sub>, and at the incineration facilities of industrial solid wastes they ranged from 5.5 to 320 μg-Br/m<sup>3</sup><sub>N</sub>. The concentrations of EOBr shown in Figure 3 were within the concentration range observed at general incineration facilities.



**Figure 4. Concentrations of EOBr in flue gas from incineration facilities of municipal and industrial solid wastes.**

#### Acknowledgments

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