# High-Temperature Melting of Waste Brominated Flame Retardants and Behaviors of Organic Brominated Compounds

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## Introduction

Polybrominated diphenyl ethers (PBDEs) have been widely used as brominated flame retardants (BFRs) and enhance the flame retardation quality of consumer products through the addition to or reaction with plastics and synthetic fiber. Waste consumer products will be recycled and/or in the process of waste management[1-4)]. In this study, high-temperature melting system has become a major focus as a destruction technology for bromine containing materials. Some organic halogenated compounds including polybrominated dioxins and dibenzofurans (PBDDs/DFs) in the process of melting were investigated at a full-scale testing plant.

## Materials and Methods

Melting treatment was performed at more than approx.1500 C with coke-bed gasification furnace (capacity 20 tons/day, Figure 1). In this system, the addition of small amounts of coke and limestone flux to the melting furnace makes it possible to directly melt waste, including incombustibles, at high temperatures, allowing all slag and metal byproducts to be effectively utilized as resources. The gas generated from thermal decomposition in the melting furnace is completely combusted in a downstream combustion chamber and, after that, a heat recovery system effectively utilizes the energy. The waste gas is then discharged from a stack after rapid cooling by a gas cooler, dedusting by a low-temperature bag filter, and waste gas decomposition in a catalytic reactor.

Target material was waste TV casing which were supplied into the melting with normal municipal solid waste (MSW). Feeding ration of waste TV casing was 5.4 % of MSW. We had also reference measurements for only MSW melting. In this experiment, samples were taken from the input materials, melting slag and flue gas (at the exits of the combustion chamber, the bag filter and the catalytic reactor). The following substances were analyzed in flue gas samples: moisture, gas volume, HCl, HBr. The PBDEs homologue distribution and tetrabromobisphenol A (TBBP-A) were analyzed. And polybrominated, polychlorinated and mixed brominated/chlorinated dioxins (PBDD/DFs, PCDD/DFs, PXDD/DFs) were also the target compounds. In addition, total chlorine and bromine contents were analyzed in solid samples. Analytical methods were reported in the previous study[3)].

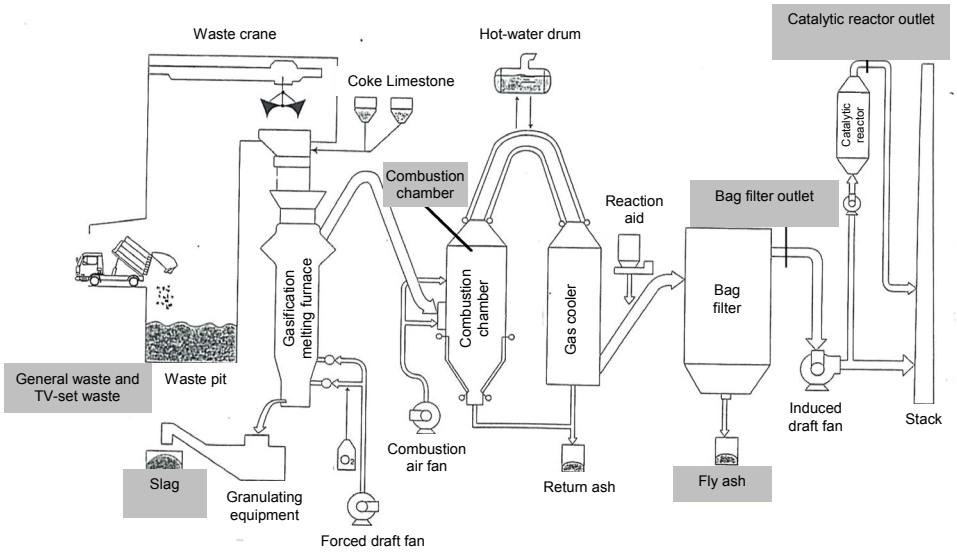


Figure 1 Pilot plant flow of coke-bed gasification melting system (20 tons/day)

## Results and Discussion

High-temperature melting testing was promoted on the condition that approximately 5% waste TV casings were added to MSW. During approx. 24 hours' operations, MSW of 21.3 tons and waste TV casings of 1.14 tons were able to be supplied. In terms of melting slag, 84 kg/MSW ton were obtained. Compared to mixed melting testing of waste TV casings, solo melting operation of MSW was conducted for about 20 hours and comparative data was obtained. Analytical results on BFRs and PCDDs/DFs that are contained in MSW and waste TV casings are shown in Table 1. Waste TV casings included PBDEs of 22,000 ug/g and TBBP-A of 7.2 ug/g respectively. Since waste TVs that discharged at present were produced approx. 10 years ago, it seems to imply that major BFRs may be PBDEs. Principal homologues of PBDEs in waste TV were dominated by DeBDE of 15,000 ug/g, followed by NoBDEs, OBDEs and TeBDEs of 0.68ug/g.

Table 1 BFRs and organic halogenated compounds in MSW and waste TV casing

| | General Waste | Waste TV-set (Plastic) |
|---|---|---|
| PCDDs/DFs[ng/g]*1 | 1.2<br>(0.0019) | 2.4<br>(0.0080) |
| Co-PCBs[ng/g] | 2.0<br>(0.00020) | 12<br>(0.0010) |
| PCDDs/DFs+Co-PCBs [ngTEQ-'97/g] | (0.0021) | (0.0090) |
| PBDDs/Ds[ng/g]*2 | 1.4 | 19,000 |
| MoBPXDDs/DDs[ng/g]*3 | N.D. | N.D. |
| Brominated diphenyl ethers [ng/g] *4 | 7,000 | 22,000,000 |
| Tetrabromobisphenol-A[ng/g] | 560 | 7,200 |
| Total chlorine (%-dry) | 0.73 | 0.10 |
| Total bromine (%-dry) | <0.051 | 2.2 |

The values within ( ) are converted to TEQ-'97 concentration levels.
*1:4~8 chloride *2:4~8 bromide *3:3~7 chloride *4:1~10 bromide

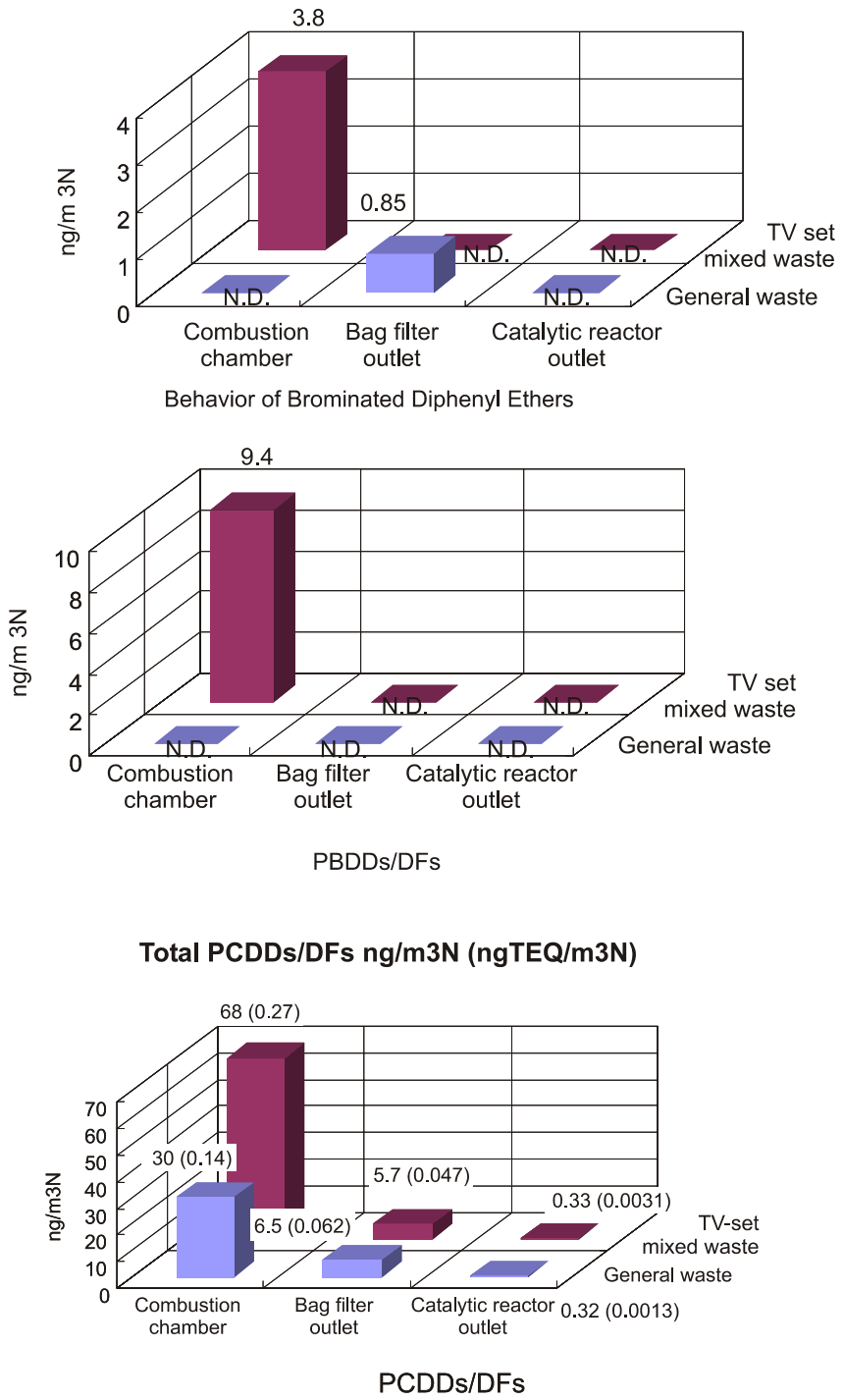


Figure 2 PBDEs, PBDD/DFs and PCDD/DFs in melting gas and purified emission gas

PBDD/DFs in TV casings were 19ug/g, of which were mostly furans. It was within the range of 3-66ug/g[3] the previous paper reported, whereas it was higher than 4.1ug/g[5] that was the highest value reported by another paper.
With regard to behaviors of emission gas at melting experiment, transitions of PBDEs, PBDD/DFs and PCDD/DFs were showed in Figure 2. They showed respective concentrations at the combustion chamber outlet after melting, subsequent bag filter outlet and catalytic reactor outlet. While PBDEs of 3.8ng/m3N were detected at combustion chamber outlet, the emission gas was not detected at the next phases. Even at the combustion chamber outlet, this is less than $10^{-7}$ of PBDEs amounts that were brought into the chamber with waste TV and there are very small amount of PBDEs existed in emission gas in high-temperature melting system. Figure 2 demonstrated behaviors of PBDD/DFs were the same trend of those of PBDEs. It showed that PCDD/DFs were decreased in concentrations by one digit from exit of furnace through bag filter, and were decreased by further one digit by means of passing through catalytic reactor. It can be said that respective waste gas treatments worked effectively. At the time of mixed melting of waste TV, PCDDs/DFs were 68ng/m3N (0.27ngTEQ/m3N) at exit of furnace, which are high compared to 30ng/m3N (0.14ngTEQ/m3N) at the time of MSW solo melting. As Lemieux et.al. pointed out that chlorinated PIC (products of incomplete combustion) were increased when bromines were added, the similar trend was indicated at this experiment, too[6] . However, it is necessary to consider the ratio of chlorine/bromine amounts, in addition to temperature and combustion conditions[7] .
Moreover, in the light of BFRs and PBDDs/DFs that were contained in solid emissions such as melting slag and fly ash, mass balance of the whole system was considered. 99.9999% and more of PBDEs and 99.98% and more of TBBP-A were destructed in the system. The destruction ratio of PBDD/DFs at the time of mixed melting of waste TV was 99.99% and more. While a large amount of PBDDs/DFs were existed in waste TV, 99.99% and more were combusted and destructed by gasification melting and synthesizing was not seen again. Regarding MoBPXDDs/DFs, they were the same behavior of PCDDs/DFs in terms of possibilities of synthesis in the processes of combustion decomposition and cooling stage, and abilities of adsorption removal and catalytic destruction by activated carbon.

**Conclusions**

This study aims at obtaining fundamental knowledge concerning behavior of dioxin-related compounds in the process of gasification melting treatment of wastes including brominated flame retardants, and its effects of emission control. The behaviors of dioxin-related compounds were surveyed at the times of treatment of MSW waste and TV mixed waste. Although input amounts were high due to the addition of waste BFR plastics, PBDEs, TBBP-A and PBDDs/DFs were decomposed to more than 99.9% in the melting system. Melting destruction is one of the more effective measures for emission control of chemicals such as organic bromine compounds.

**References**

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