Thermal Behavior of Brominated Flame Retardants and Brominated Dioxins during Combustion of Automobile Shredder Residue

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Introduction.

In Japan, more than four millions of end-of-life vehicles (ELVs) are annually generated and about 80 % of them as weight are recycled as materials or as parts. The rest parts, about 700,000 tons per year, are emitted as automobile shredder residue (ASR). A large part of ASR is reclaimed in the landfills, but the capacity of the landfills are quite limited in Japan. Thus, in order to reduce the emission of ASR, the law for the recycling of ELVs was enforced in 2005. In this law, the goal of recycling rate of whole ELVs is set as 95% in 2015, so recycling rate of ASR should be raised over 70 %. In many cases, ASR is recycled by thermal processes. Combustible parts of ASR are recovered as heat and incombustible parts are recovered as metals or slag. ASR consists of plastic residues which generally contain brominated flame retardants (BFR). In the thermal processes of ASR, these BFR may be converted to brominated dioxins (brominated dioxins mean polybrominated dioxins/furans (PBDDs/DFs) and polybrominated/chlorinated dioxins/furans (PXDDs/DFs)) (Weber and Kuch, 2003), and released to the environment. It is important to describe thermal behaviors of these BFR and brominated dioxins to prevent the pollution caused by these compounds emitted from the thermal treatment facilities of ASR. Therefore, we conducted the incineration experiments of ASR to examine thermal behavior of BFR and brominated dioxins.

Materials and Methods.

Combustion experiments were performed using a bench-scale incinerator at NIES (Noma et al., 2006). Schematic view of the incinerator is shown in Fig. 1. Experimental conditions are also listed in Table 1. Two kinds of ASR were used in combustion experiments. One was collected before enforcement of the law for the recycling of ELVs, and the other was collected after enforcement the law. Feeding rate of ASR was 2.7 kg/h. Temperature of rotary kiln furnace and secondary combustion chamber was about

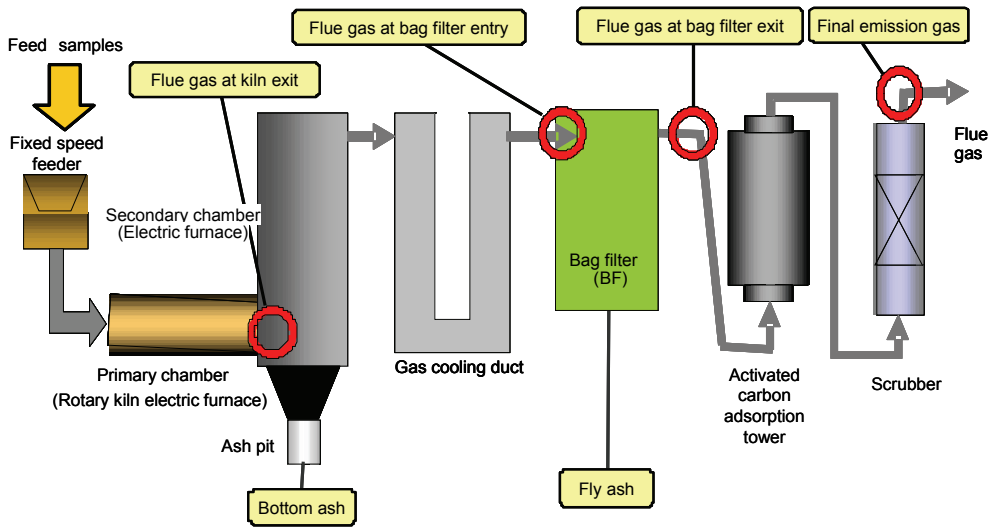

Fig.1. Schematic view of the incinerator used in this study.

Table 1. Experimental conditions.

	Item			Run 1	Run 2
Samples	Content	Combustible	%	72.4	72.9
		C	%	46.3	49
		H	%	8.8	7.8
		N	%	1.4	2.4
		Cl	%	2.28	3.57
		Br	%	0.03	0.04
	Size		mm	<10	<10
Experimental conditions	Sample volume		g	10,800	10,690
	Feeding rate		kg/h	2.7	2.7
	Temperature	Rotary kiln	°C	837	841
		Secondary chamber	°C	900	899
	Gas flow rate	Kiln exit	m^3N/h	18	24
		Bag filter entry	m^3N/h	18	24
		Bag filter exit	m^3N/h	21	26
		Final exit	m^3N/h	30	29
	Flue gas at BF entry	O_2	%	11.1	10.0
		CO	%	13	9.0
		NOx	ppm	-	60
		HCl	mg/m^3N	1,100	790
	Bottom ash		g	3,425	2,857
	Fly ash		g	296	347

840 and 900ºC, respectively. Flue gas was sampled at 4 points, rotary kiln exit, bag filter (BF) entry (=secondary combustion chamber exit), BF exit, and final exit for 4 hours. After incineration experiments, fly ash and bottom ash were also sampled. Four kinds of BFRs, such as polybromodiphenyl ethers (PBDEs), tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD), and tribromophenols (TBPs) were analyzed. PBDDs/DFs, monobrominated-polychlorinated dioxins/furans (monoBr-CDDs/DFs), PCDDs/DFs, dl-PCBs, PCBs, polychlorinated naphthalenes (PCNs) and PAHs were also analyzed. Analytical procedures were described in elsewhere (Sakai et al., 2001).

Results and Discussions.

Concentrations of BFR, brominated dioxins, chlorinated dioxins and other contaminants in the feed samples, flue gas samples, and ash samples are listed in Table 1. Mass balances of BFRs, brominated dioxins, and chlorinated dioxins were also shown in Fig. 2. ASR contained PBDEs at a few hundred ppm levels. ASR also contained HBCD, TBBPA, and TBPs in the range of sub- to a few ppm levels. The levels of BFRs in ASR collected before enforcement of the law for recycling of ELVs seemed to be higher than in ASR collected after enforcement the law. Measured BFRs were almost decomposed by primary combustion as shown in Fig. 2. Overall destruction efficiencies of BFRs were more than 99.99% except TBPs. In previous study using refuse derived fuel (RDF) prepared from municipal solid waste (MSW), we also found PBDEs and TBBPA in RDF samples at a few ppm levels (Asari et al., 2005). These BFRs were also decomposed by primary combustion, and overall destruction efficiencies were more than 99.99%. Sakai et al. reported thermal behaviors of BFRs during high-temperature melting process (Sakai et al., 2004). They used mixture of waste TV casing waste and MSW. Waste TV casing contained PBDEs and TBBPA at 22,000 and 7.2 µg/g, respectively. These BFRs were effectively removed by high-temperature melting process and destruction efficiencies of

Table 2. Concentrations of BFRs, brominated dioxins, chlorinated dioxins, and other contaminants.

	Item	ASR	Flue gas				Fly ash	Bottom ash
			Kiln exit	Bag filter entry	Bag filter exit	Final exit		
		ng/g	ng/m^{3}N	ng/m^{3}N	ng/m^{3}N	ng/m^{3}N	ng/g	ng/g
Run 1	PBDEs	240,000	NA	7.7	30	0.62	2.0	<0.04
	TBBPA	950	18	57	3.5	0.48	0.38	0.022
	HBCD	5,700	<2	<0.5	2.0	0.90	0.41	0.073
	TBP	68	44,000	550	1,800	500	230	26
	PBDDs/DFs	120	<2	2.0	12	<0.8	1.2	<0.1
	monoBr-CDDs/DFs	15	8,000	16	24	<0.2	1.3	2.1
	PCDDs/DFs (TEQ)	0.38	8,400	3.9	5.6	0	0.20	0.65
	dl-PCBs (TEQ)	0.014	310	0.40	0.54	0.000012	0.014	0.017
	PCBs	44	370,000	240	240	0.51	7.5	11
	PCNs	47	620,000	510	380	0.20	68	63
	PAHs	34,000	110,000,000	52,000	2,100	24	13,000	6,200
Run 2	PBDEs	110,000	200	14	43	0.37	0.010	0.020
	TBBPA	220	5.5	3.1	2.3	1.8	0.040	0.29
	HBCD	990	7.4	2.7	1.3	1.2	<0.05	0.070
	TBP	180	44	87	3.6	13	12	1.8
	PBDDs/DFs	10	<2	0.16	2.5	<2	<0.2	<0.2
	monoBr-CDDs/DFs	<0.07	2,700	0.080	0.99	<0.2	<0.02	0.060
	PCDDs/DFs (TEQ)	0.043	5,800	0.77	0.68	0.0021	0.010	0.13
	dl-PCBs (TEQ)	0.015	250	0.037	0.064	0.000012	0.00051	0.0063
	PCBs	230	270,000	50	64	3.7	2.3	1.9
	PCNs	13	2,300,000	21	55	<0.1	0.66	8.4
	PAHs	36,000	63,000,000	2,900	2,900	500	48	77

NA=Not analyzed.

them were more than 99.98%.

The levels of PBDDs and PBDFs in ASR samples were 120 and 10 ng/g, respectively. The levels of monoBr-CDDs and monoBr-CDFs were 15 ng/g and not detectable, respectively, which were lower than those of PBDDs/DFs,. PBDDs/DFs decreased to not detectable by primary combustion. Conversely, monoBr-CDDs and monoBr-CDFs were formed by primary combustion, and their levels increased to 8,000 and 2,700 ng/m^{3}N, respectively. The levels of monoBr-CDDs/DFs decreased by secondary combustion in both test runs. In the flue gas at final exit, both groups of brominated dioxins were not detected. Overall destruction efficiencies of PBDDs/DFs were over 99.97%, whereas those of monoBr-CDDs/DFs were 95% in run 1 (in run 2, destruction efficiency could not be calculated because monoBr-CDDs/DFs were not detected in the fed sample). In previous RDF combustion study, formation and decomposition behaviors of PBDDs/DFs and monoBr-CDDs/DFs were similar to this study. The levels of PBDDs/DFs and monoBr-CDDs/DFs were 4.1 and 0.001 ng/g, respectively. In the flue gas at kiln exit, the level of PBDDs/DFs decreased to not detectable by primary combustion, whereas the level of monoBr-CDDs/DFs increased to 3,400 ng/m^{3}N. Overall destruction efficiency of PBDDs/DFs during combustion of ASR was more than 99.9%. MonoBr-CDDs/DFs were also decomposed by secondary combustion, but total emission amount of monoBr-CDDs/DFs was exceeded the input amount.

The levels of PCDDs and PCDFs in ASR samples were 0.38 and 0.043 ng-TEQ/g (including dl-PCBs, 0.39 and 0.058 ng-TEQ/g), respectively. PCDDs and PCDFs were formed by primary combustion, and their levels increased to 8,400 and 5,800 ng-TEQ/g (including dl-PCBs, 8,700 and 6,000 ng-TEQ/m^{3}N), respectively. Then PCDDs/DFs were removed by secondary combustion. At Final exit, the levels of PCDDs/DFs were not detectable and 0.010 ng-TEQ/m^{3}N (including dl-PCBs, 0.000012

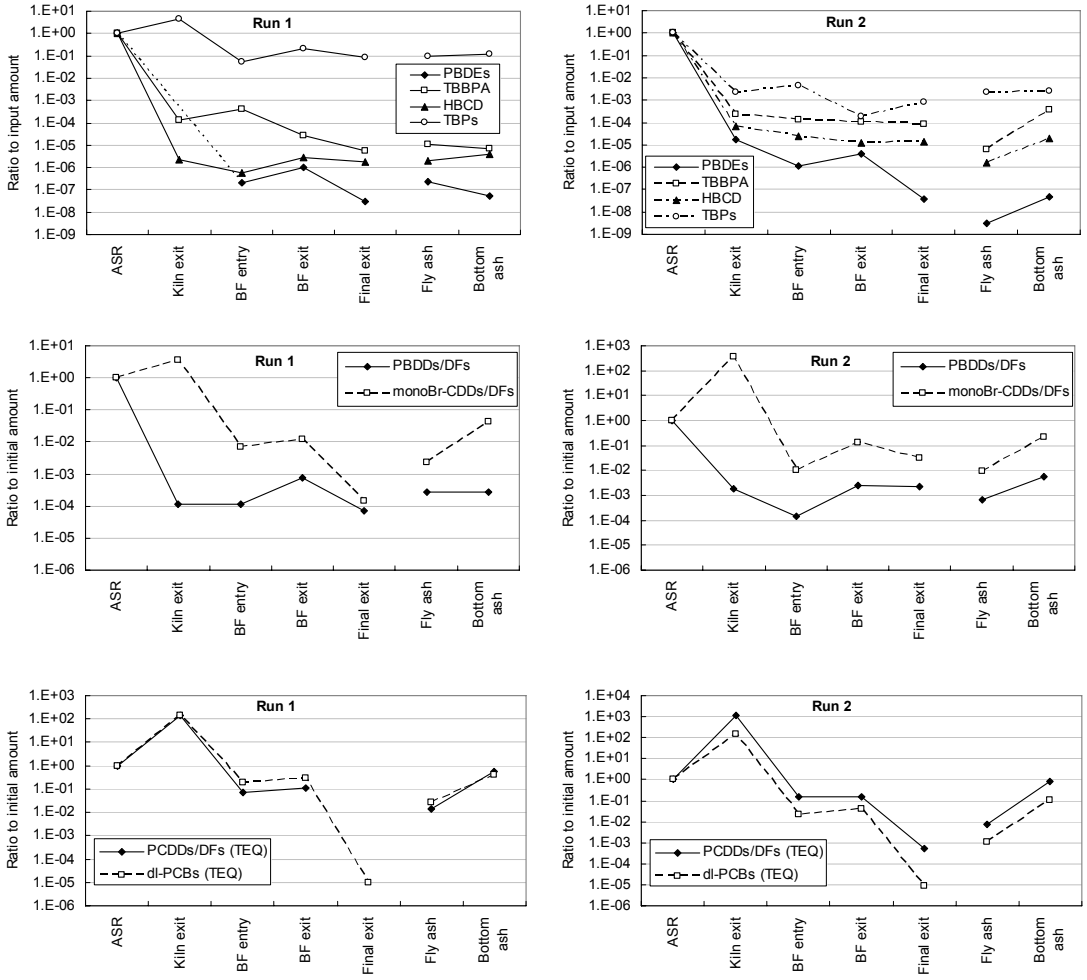

Fig 2. Mass balances of BFRs, brominated dioxins, and chlorinated dioxins during combustion of ASR.

and 0.011 ng-TEQ/m^3N), respectively. These formation and decomposition behavior are similar to the previous studies using RDF.

Reference.

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