Behavior Analysis and Control of Dioxin-like Compounds During Comminution and Compression Process of Wastes

Hidetaka Takigami[1], Shin Takahashi[2], Kozo Ueda[3], Takumi Takasuga[4], Yasuhiro Tomita[5], Shin-ichi Sakai[6]

[1]Nies
[2]Ehime University
[3]Hitachi Zosen Co.
[4]Shimadzu Techno Research Co.
[5]Japan Waste Research Foundation
[6]Kyoto Univ.

Introduction

The fate and behavior of polyhalogenated organic compounds during comminution (crush) and compression processes of wastes have been less known despite the fact that those processes have been conducted in a wide variety of applications for material recycles and waste volume reduction. In this study, small-scale comminution and compression tests were carried out on three different types of waste materials, respectively. The profiles of polychlorinated and polybrominated compounds {i.e., PCDD/Fs, PCBs, PBDD/Fs and brominated flame retardants (BFRs: PBDEs and TBBPA)} in exhaust gas samples (taken at three points along the treatment line for each test) were investigated together with a dioxin-like activity measured by the DR-CALUX®. Then control of the compounds during the currently adopted exhaust gas treatment was evaluated.

Materials and Methods

A sample set of wood wastes (sample 1: 100 mm pieces of crushed furniture), a mixture of wood and plastic wastes {sample 2: sample 1 (50%wt) and crudely crushed food and detergent containers (50%wt)} and a mixture of wood wastes (50 mm pieces of crushed particle board, 50%wt) and BFR-fortified plastic wastes (50 mm pieces of crushed PS, PC, ABS and PVC resins, 50%wt) (sample 3) was used for the experiment.

Figure 1 shows a schematic flow of the pilot-scale comminution and compression plants and gas sampling points. The comminution process was a blade mill type and wastes were treated at the rate of 200 kg/h during experiment. Small refuses after comminuted were collected in the cyclone. The bag filter (BF), high efficiency particle air (HEPA) filter and activated carbon (AC) filter were connected in this order after the outlet of the cyclone to treat a raw comminution gas. The compression process adopted a pellet mill which consisted of die ring which rotates by motor and press rolls. The fed waste materials (finely crushed wastes produced in the above comminution experiment) were pressed to die ring and extruded to outside through die (diameter: 25 mm). The treatment speed was 100 kg/h. During experiment, raw gas (atmosphere surrounding the die) was subjected to filtration treatments through the BF, AC and HEPA filters in this order.

Gas sampling was conducted by a low-volume (LV) air sampler following JIS K0311[1] or a middle-volume (MV) air sampler equipped with glass fiber filter, inpingers with diethylene glycol and polyurethane foam plugs. The collected sample gas volume was approximately 3 m^3 for the LV sampler and 15-20 m^3 for the MV sampler.

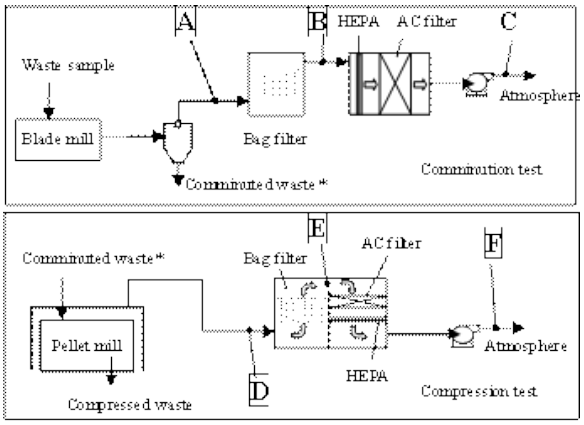

Fig. 1 Pilot-scale comminution and compression plants and gas sampling points. A, D: raw gas, B, E: gas after BF, C, F: gas after HEPA and AC filter.

The target substances were extracted with toluene in a soxhlet extractor (solids) and by liquid-liquid extraction in a separation funnel (liquids). The combined extracts were cleaned up for the determination of PCDD/Fs (4-8 chlorinated), PCBs (dioxin-like PCBs and total PCBs), PBDD/Fs (4-8 brominated), PBDEs (1-10 brominated) and TBBPA by individual adsorption chromatography (multilayer silica column and activated carbon column). For analysis of those compounds an HRGC/HRMS system was used. The presence of dioxin-like compounds was determined using the DR-CALUX® assay (BioDetection Systems B.V., the Netherlands). To obtain the assay fractions, column chromatography was conducted in a similar way as that for chemical analysis (PCDD/Fs, PCBs, PBDD/Fs and PBDEs) without adding internal standards.

Results and Discussion

The comminution and compression experiments for sample 3 (artificial BFR-containing wastes) resulted in remarkably higher concentrations of PBDD/Fs (70-270 ng/m^3N) and BFRs (760-160,000 ng/m^3N) than those for sample 1 and 2 (PBDD/Fs: not detected, BFRs: 2.7-89 ng/m^3N). Releasing concentrations of the polyhalogenated compounds to the gas tended to be higher during compression process compared to comminution (Table 1).

In Fig. 2, air-particle partition ratio values {K_{ap}, K_{ap} = (concentration of the compound in the gas phase, ng/m^3N)/ (concentration in the particle phase, ng/m^3N)} were shown for the raw gas sample after compression of sample 3. Low K_{ap} values (i.e., log K_{ap} < -2) were obtained for PBDD/Fs, PBDEs and TBBPA, which means those compounds are adsorptive to dust, with the exception of low brominated diphenyl ethers. The K_{ap} values for the brominated compounds tended to be lower than those for PCDD/Fs and PCBs on total congener base.

In an exhaust gas treatment process after comminution and compression, the chlorinated/brominated compounds measured could be reduced gradually and significantly. As for the comminution/compression cases of sample 3 (Table 1), the concentration of PBDD/Fs became not detected (ND) after BF and that of TBBPA became ND in the final exhaust gas. PBDE concentration also showed a drastic decrease through each filtering treatment, to a small concentration of < 1 ng/m^3N (ambient air level) in the final gas. A similar tendency was obtained for PCDD/Fs and dioxin-like PCBs.

DR-CALUX 2,3,7,8-TCDD-equivalent (CALUX-TEQ) values were two orders of magnitude higher than WHO-TEQ values in the raw gas samples after both of comminution and compression processes for sample 3. The contribution of the detected PBDD/F and PBDE congeners (1,2,3,6,7,8-HxBDD, 2,3,7,8-TBDF, 1,2,3,7,8-PeBDF, 2,3,4,7,8-PeBDF, 1,2,3,4,7,8-HxBDF, 1,2,3,4,6,7,8-HxBDF and DeBDE) was estimated based on their analytical concentrations and their CALUX-relative potency values[2]. The estimated CALUX-TEQ values obtained for the brominated compounds (•gPBDD/F•h-TEQ and •gPBDE•h-TEQ shown in Table 1) could complement approximately the difference between the experimentally obtained CALUX-TEQ and WHO-TEQ in the raw gas samples. For both of comminution and compression experiments, CALUX-TEQ levels measured in the treated gas samples after BF could be remarkably reduced and finally be lowered to less than detection limits (< 2.0 pg/m^3N) after HEPA and AC filters. Thus, CALUX and analytical results indicate that the measured brominated compounds seem to be responsible for a dioxin-like activity in comminution and compression exhausts for sample 3.

Results obtained suggested that capture of small particles (dust) using filtering devices such as BF, HEPA and AC

filters leads to an effective control of dioxin-like compounds in exhaust gas after comminution and compression of wastes. This would be basic but important information to take a countermeasure to protect human exposure to these compounds through inhalation in the home or working environment.

Acknowledgements

This research was funded by the Japan Waste Research Foundation. The authors wish to thank Prof. Brouwer of the BioDetection Systems B.V.

References

1. JIS (Japan Industrial Standards) K0311 (1999).

2. Behnisch P. A., Hosoe K. and Sakai S. (2003) Environment International, 29: 861-877.

Table 1 Concentrations of the chlorinated/brominated organic compounds and TCDD-equivalent in the exhaust gas samples after comminution and compression experiments for sample 3. ND: not detected.

Experiment		Comminution			Compression		
Sampling point		Raw gas	Gas after BF	Gas after BF and AC	Raw gas	Gas after BF	Gas after BF and AC
		A	B	C	D	E	F
PCDDs + DL-PCBs	Unit	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N
	PCDDs	350	2.1	ND	1100	4.9	0.9
	PCDFs	220	2.6	0.36	640	16	0.84
	DL-PCBs	250	18	3.5	1500	49	3.8
	Σ(PCDD/Fs+DL-PCBs)	820	23	3.9	3200	70	5.5
PBDD/Fs + BFRs	Unit	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N
	PBDDs	170	ND	ND	3300	ND	ND
	PBDFs	70000	ND	ND	270000	ND	ND
	ΣPBDD/Fs	70000	ND	ND	270000	ND	ND
	Unit	ng/m^{3}N	ng/m^{3}N	ng/m^{3}N	ng/m^{3}N	ng/m^{3}N	ng/m^{3}N
	PBDEs	21000	39	0.52	160000	7.5	0.76
	TBBPA	760	3.2	ND (<2.0)	35000	ND (<2.0)	ND (<2.0)
Toxic equivalents	Unit	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N	pg/m^{3}N
	WHO-TEQ	2.9	0.0021	0.00031	5.1	0.11	0.00033
	'PBDD/F'-TEQ	76			270		
	'PBDE'-TEQ	92	0.19	0.0024	650	0.018	0.0032
	CALUX-TEQ	100	ND (<2.0)	ND (<2.0)	900	6.8	ND (<2.0)

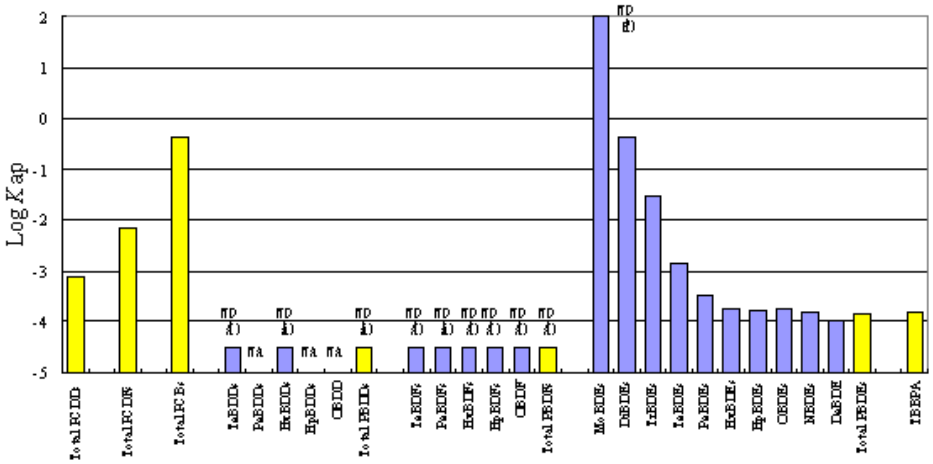

Fig.2 Air-particle partition ratio values (K_{ap}) for the chlorinated/brominated organic compounds in the raw gas after

compression process of sample 3. NA: not detected (quantified) both in the gas and particle phases. ND (A): not detected in the gas phase. ND (P): not detected in the particle phase.