

DESTRUCTION BEHAVIOR OF ORGANOPHOSPHORUS FLAME RETARDANTS DURING INCINERATION OF SOLID WASTES

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Introduction

Restrictions and bans on the use of polybrominated diphenyl ethers (PBDEs) have resulted in the increased consumption of chlorinated alkyl phosphates and halogen free aryl phosphates as alternative flame retardants¹. This trend also requires the appropriate management of waste containing such organophosphorus flame retardants (PFRs). Considering that PFRs have been employed in resins, foams, latexes and textiles, the wastes originated from these products are mainly disposed by incineration in Japan. However, the information on the thermal destruction behavior of those PFRs is limited. In addition, chlorine atoms derived from chlorinated alkyl phosphates during incineration processes may contribute to unintentional formation of dioxin-related compounds (DRCs), such as polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (dl-PCBs). Therefore, we carried out thermal treatment experiments using the pilot-scale incinerator and simulated solid wastes containing tris(2-chloroisopropyl) phosphate (TCIPP) or diethylene glycol bis(di(2-chloroisopropyl) phosphate) (DEG-BDCIPP) as chlorinated alkyl phosphates, and triphenyl phosphate (TPHP) or bisphenol A bis(diphenyl phosphate) (BPA-BDPP) as halogen free aryl phosphates (Figure 1) to understand the formation, destruction and emission of PFRs and DRCs.

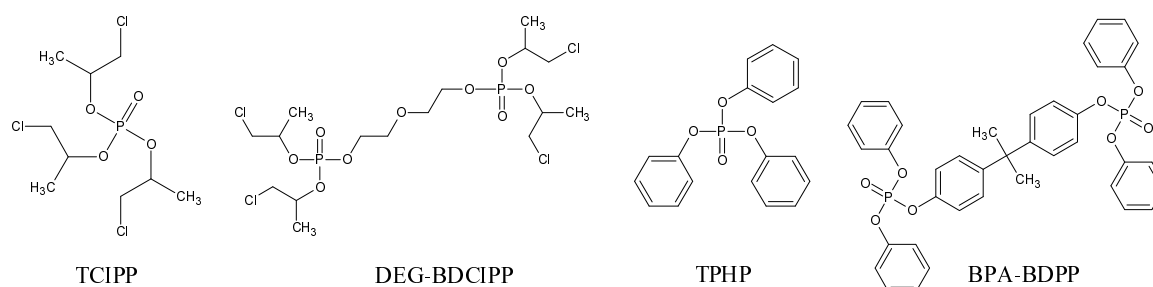


Figure 1. Chemical structures of TCIPP, DEG-BDCIPP, TPHP, and BPA-BDPP

Materials and Methods

The pilot-scale incinerator at the National Institute for Environmental Studies (NIES), Japan, was used in this study (Figure 2). This facility is designed to represent the modern industrial solid waste incinerators in Japan, and consists of a rotary kiln primary combustion chamber, a vertical secondary combustion chamber, a gas cooling zone, a bag filter for particulate control, an activated carbon adsorption tower and a wet scrubber for advanced gas treatment². Five batches of experiments were conducted using simulated solid wastes containing various PFRs as input materials. Input materials in each experiment were as follows; Run #1: refuse derived fuels (RDF) containing approximately 1% (w/w) of technical TCIPP, Run #2: RDF containing approximately 1% (w/w) of technical DEG-BDCIPP, run #3: RDF containing approximately 1% (w/w) of technical TPHP, run #4: RDF containing approximately 1% (w/w) of technical BPA-BDPP and run #5: RDF for control sample. These technical products were obtained from Daihachi Chemical Industry Co., Ltd., Osaka, Japan.

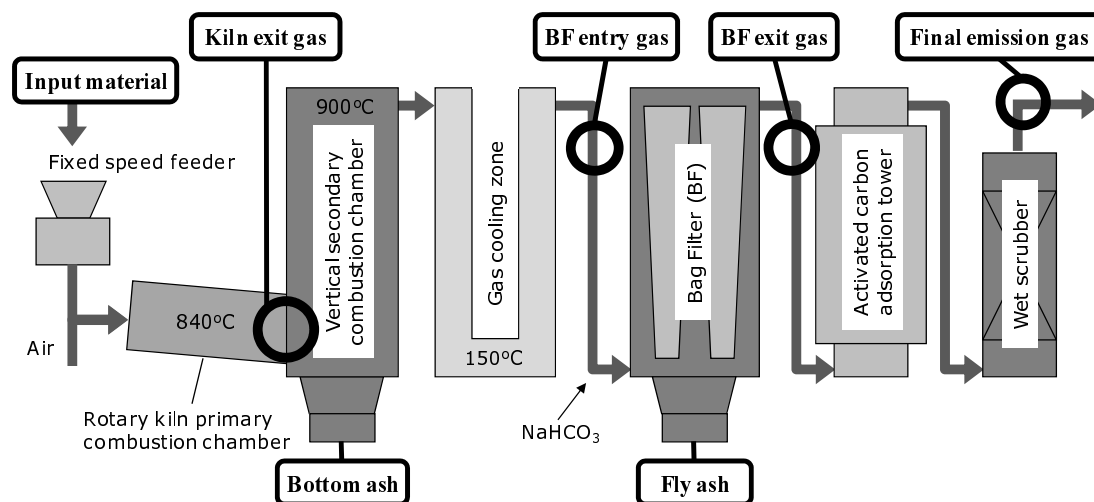


Figure 2. Scheme of the pilot-scale incinerator and the sampling points

The experimental conditions are shown in Table 1. These conditions followed the requirement for waste incinerators of the Japanese government³ and UNEP⁴. Flue gas was taken at four sampling points (kiln exit, bag filter (BF) entry, BF exit and final emission). Bottom ash and fly ash were sampled after the end of each experiment (Figure 2). PFRs and DRCs were analyzed in this study. PFRs in solid samples were extracted with acetone and toluene in Soxhlet apparatuses, and those in liquid samples were extracted with dichloromethane by shaking. These extracts were spiked with isotope-labeled internal standards, and were cleaned up by some column chromatography treatments. TCIPP and TPHP were determined by GC/QMS (Shimadzu GCMS-QP2010 Plus). DEG-BDCIPP and BPA-BDPP were determined by LC/MS/MS (AB SCIEX API3200/ Shimadzu LC-20A Prominence)⁵. DRCs were determined by GC/HRMS (Waters Autospec Ultima/ Agilent Technologies HP-6890) in conformity to the method of JIS K0311⁶.

Results and discussion

Destruction behavior of PFRs

Figure 3 shows the behavior of TCIPP, DEG-BDCIPP, TPHP, and BPA-BDPP during controlled incineration processes using the unit of “flux” on the vertical axis. Most amounts of examined PFRs in input materials were destroyed in primary combustion. The residues in flue gas were further destroyed or removed in secondary combustion and subsequent treatment processes. Overall destruction efficiencies (DEs) of PFRs assuming the BF exit gas or final exit gas as environmental emission gas were calculated to be more than 99.999% (Table 2).

Table 1. Experimental conditions of thermal treatment plant

Experiment	Run #1	Run #2	Run #3	Run #4	Run #5
Input material					
Base	RDF	RDF	RDF	RDF	RDF
PFRs	TCIPP	DEG-BDCIPP	TPHP	BPA-BDPP	-
PFR contents (%) in RDF	0.67	0.76	0.62	0.93	0
Total input amount (kg)	11.0	10.9	10.7	10.7	15.7
Combustion time (h)	5.0	5.0	5.0	5.0	7.5
Feeding rate (kg/h)	2.21	2.18	2.14	2.14	2.09
Temperature (°C)					
Primary combustion	841	841	841	841	842
Secondary combustion	900	900	900	900	900
Bag filter	149	149	149	149	149
Air flow rate (m ³ /h)					
Primary combustion	18.8	18.8	18.7	18.8	18.6
Secondary combustion	0	0	0	0	0
Ash volume (kg)					
Bottom ash	1.004	0.998	0.954	0.988	1.395
Fly ash	0.034	0.032	0.053	0.032	0.041
Acid gas treatment					
	NaHCO ₃	NaHCO ₃	NaHCO ₃	NaHCO ₃	NaHCO ₃
Flue gas at bag filter exit					
O ₂ (%)	9	9	9	10	9
CO (ppm v/v)	1	0	0	1	0
NO _x (ppm v/v)	47	44	40	44	48
HCl (ppm v/v)	0	0	0	0	0

Considering from the action mechanisms of flame retardants⁷, low amounts of PFRs (Figure 3) and relatively high recovery rates of total phosphorus (TP) in bottom ash (Table 3) imply that the phosphorus atoms in PFRs are transformed mainly to inorganic compounds, such as phosphoric acid, polyphosphoric acids and these salts, during primary combustion. These results suggest that environmental emissions of PFRs can be reduced by incineration of solid wastes containing PFRs with the appropriate management.

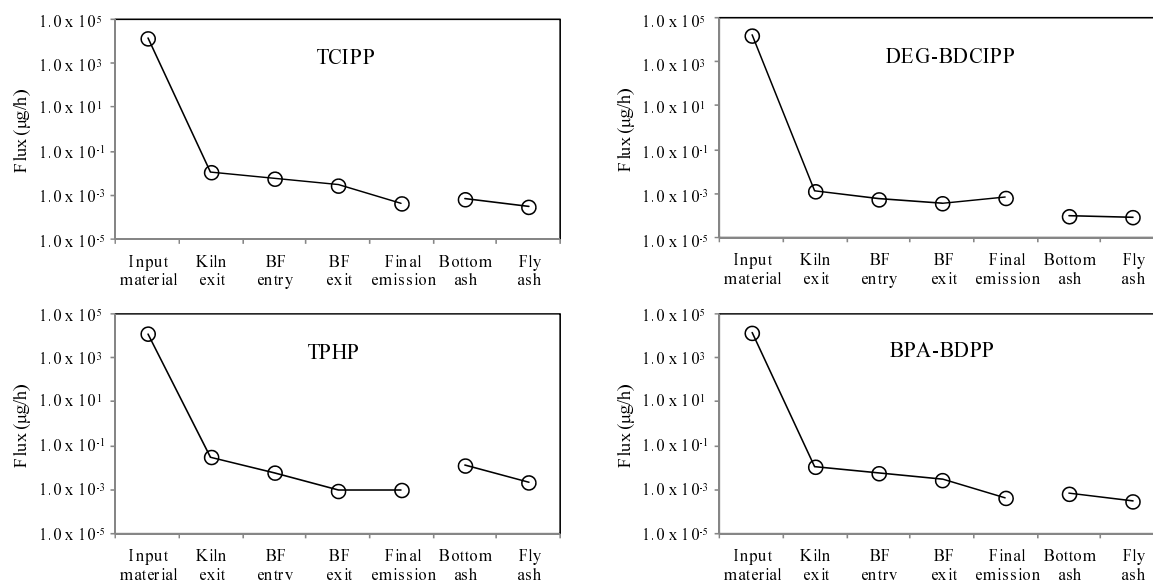


Figure 3. Thermal destruction behavior of PFRs

Table 2. Concentrations and overall DEs of PFRs

Run No.	Chemical name	Input material µg/kg	Flue gas				Ash		DE-1* %	DE-2** %
			Kiln exit µg/m ³ N	BF entry µg/m ³ N	BF exit µg/m ³ N	Final emission µg/m ³ N	Bottom ash µg/kg	Fly ash µg/kg		
1	TCIPP	6,700,000	0.61	0.31	0.15	0.020	0.31	0.14	99.999974	99.999990
2	DEG-BDCIPP	7,600,000	<0.07	<0.03	<0.02	<0.03	0.045	0.041	99.999997	99.999995
3	TPHP	6,200,000	1.7	0.33	0.048	0.046	6.1	1.0	99.999879	99.999878
4	BPA-BDPP	9,300,000	0.14	<0.01	<0.01	<0.01	0.045	0.027	99.999998	99.999998

*DE-1: Overall DE adopting data at BF exit for DE calculation

**DE-2: Overall DE adopting data at final emission for DE calculation

Table 3. Levels and residue rates of total phosphorus (TP) in bottom ash and fly ash

Run No.	Chemical name	Input material	Bottom ash		Fly ash	
		TP amounts µg	TP amounts µg	Residue rate %	TP amounts µg	Residue rate %
1	TCIPP	22,000,000	12,000,000	54.5	3,900,000	17.7
3	TPHP	18,000,000	11,000,000	61.1	3,800,000	21.1

Formation and destruction behavior of DRCs

Figure 4 shows the behavior of DRCs during incineration processes of solid wastes containing chlorinated and halogen free PFRs. DRCs were formed in the primary combustion chamber at all the experiments. Thereby, TEQ amounts of DRCs in the kiln exit gases were two orders of magnitude higher than the input amounts.

DRCs formed in primary combustion were destroyed in the secondary combustion chamber, and were removed by bag filter and the following gas treatment. Consequently, TEQ values in exhaust gas and ash in the all experiments are lower than the most stringent emission standards in Japan⁸ (Table 4). Behaviors and emission levels of DRCs during incineration of wastes containing chlorinated PFRs were almost similar to those containing halogen free PFRs. These results suggested that chlorine contents originated from PFRs do not affect the formation, destruction and emission of DRCs in appropriate managed incineration.

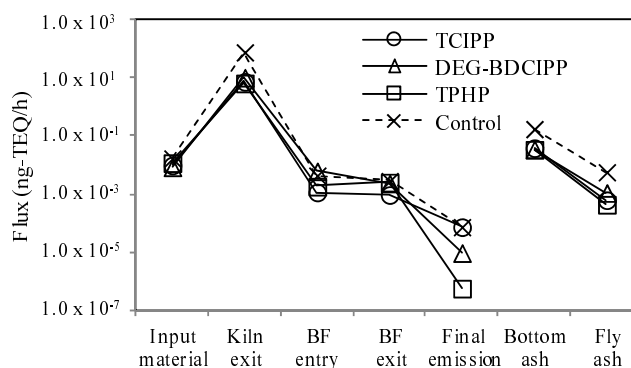


Figure 4. Formation and destruction behavior of DRCs

Table 4. TEQ values of DRCs in exhaust gas and ash

Run No.	Chemical name	Input material ng-TEQ/g	Exhaust gas		Ash	
			BF exit ng-TEQ/m ³ N	Final emission ng-TEQ/m ³ N	Bottom ash ng-TEQ/g	Fly ash ng-TEQ/g
1	TCIPP	0.0016	0.037	0.00022	0.20	0.0051
2	DEG-BDCIPP	0.0032	0.091	0.00023	0.19	0.0096
3	TPHP	0.0044	0.10	0.0000037	0.18	0.0027
Standard value*		(3)	5 (1, 0.1)**	5 (1, 0.1)**	3	3

*Enforcement Regulation of the Law concerning Special Measures against Dioxins

**Incinerators at feeding rate of less than 200 kg/h: 5 ng-TEQ/m³N

Incinerators at feeding rate of 200 to 4000 kg/h: 1 ng-TEQ/m³N

Incinerators at feeding rate of more than 4000 kg/h: 0.1 ng-TEQ/m³N

Conclusion

Thermal treatment experiments using the pilot scale incinerator and simulated solid wastes containing chlorinated alkyl/halogen free aryl phosphates were carried out for understanding the formation, destruction and emission of PFRs and DRCs. PFRs in inputs were destroyed mainly in primary combustion with overall destruction efficiencies of more than 99.999%. Phosphorus compounds (which were considered to be mainly inorganic compounds) degraded from PFRs were accumulated in bottom ashes. Chlorine contents derived from chlorinated alkyl phosphates did not contribute to unintentional formation of DRCs in conventional incineration process of solid wastes containing PFRs.

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