Experimental evidence for de novo synthesis of PBDD/PBDF and PXDD/PXDF as well as dioxins in the thermal processes of ash samples

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Introduction

Dioxins can be formed via *de novo* synthesis by the fly ash catalyzed reaction of carbon species. The authors reported that the fly ash in emerging gasification-melting plants as well as that in conventional incineration plants formed dioxins through *de novo* synthesis, even if the ash contained a very low level of carbons[1,2]. Likewise, the same process is naturally expected to be responsible for the formation of brominated and chlorinated-brominated dibenzodioxines and dibenzofurans (PBDD/PBDF and PXDD/PXDF); since ashes usually contain bromine as well as chlorine. Based on this, Weber et al.[3] reported the *de novo* synthesis of mixed brominated-chlorinated PXDD/PXDF from the model ashes prepared by mixing silica, and polyaromatic perylene reagents as a carbon source and chlorine and bromine salts. They recognized the PXDD/PXDF formation and the influence of temperature on the chlorine and bromine molecular substitution profiles. In order to obtain evidence of *de novo* synthesis, thermal experiments using real fly ash were performed using a flow-through reactor in this study. The original objective was to investigate the formation of PBDD/PBDF and PXDD/PXDF using the ash of the gasification-melting plant.

Materials and Methods

Ash samples

Ash samples collected at conventional stoker type incineration and gasification- melting plants were used as shown in Table 1. Ash A was collected in the first bag filter that was part of a two-stage bag filter flue gas cleaning system. Ash C was collected at a fluidized gasification and melting furnace plant. The Cu contents in these samples were in the range of 0.1-0.4 wt% in the form of ash. Ash samples were made into pellets before being packed into the reactor tube with water and a palletizing machine, due to the nature of the fine particles. Tetrabromobisphenol A (TBBP-A) reagent was added to the bottom layer of the bed (representing 0.5 wt% of the total packed amount of ash) using ash B in order to investigate the influence of brominated frame retardants on the formation of bromine substituted dioxins.

Table 1 Ash samples used

Ash	Description	Carbon content [%]	Cl and Br content [mg/kg]	Dioxins [ng/g]
A : Fly ash	Collected using a bag filter in an MSWI[a)]	18	Cl :89000 Br :1400	50
B : Boiler ash	Collected at the bottom of a boiler in an MSWI[b)]	0.44	Cl :14000 Br :120	210
C: Boiler ash	Collected at the bottom of a boiler in a gasification-melting plant	0.15	Cl :62000 Br :320	21
D : Reagent fortified B	Tetrabromobisphenol A was added to the bottom layer of a packed bed	Same as ash B	Same as ash B	–

a) The MSWI has two series of bag filters and the sample was collected using the first filter.
b) This was sampled at the same plant as ash A.

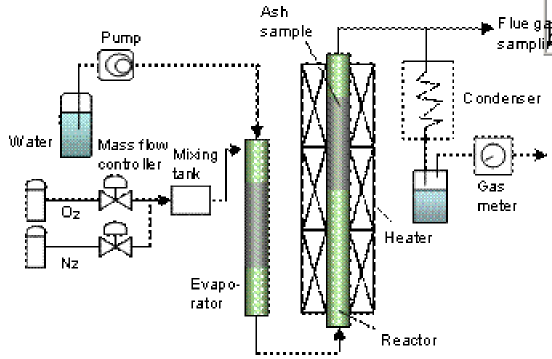

Fig. 1 Experimental apparatus used in thermal treatment for ash samples

Apparatus and experimental conditions

Experiments were conducted using the apparatus as shown in Fig. 1. This consisted of a mixed gas supply system (N_2: 90 vol %, O_2: 10 vol %) tube with an ash sample bed and a sampling system of the outlet gas for the analysis of dioxins, PBDD/PBDF and PXDD/PXDF. Monobromo-polychloro substituted compounds were determined on PXDD/PXDF. The experimental procedure used was mainly the same as that described elsewhere[1]. However, the temperature was set to 300 ºC (also 200 ºC for ash A only), and gaseous HCl and organic vapors were not supplied.

Results and Discussions

Determination of PBDD/PBDF, PXDD/PXDF and dioxins

Table 2 shows the concentrations of dioxins, PBDD/PBDF and PXDD/PXDF. Since the dioxin concentration in the flue gas was very high for ash A at 300 ºC, a very high *de novo* synthesis potential was shown as expected.Thecomparativeresult at 200 ºC for ash A showed that temperature had a significant influence on the formation. The concentration for ash C, with a relatively low carbon content (Table 1), was also moderately high as observed in the early investigation[2]. As for brominated compounds, a considerable concentration of PXDD/PXDF in the flue gas was determined for ash A (300 ºC) although PBDD/PBDF was not detected. It may be natural for bromine to be incorporated into PXDD/PXDF during *de novo* synthesis conditions[3]. Ash C also formed low levels of PXDD/PXDF. On the contrary, however, both PBDD/PBDF and PXDD/PXDF were observed in high concentrations for the flue gas and ash sample after the experiment in the case of the ash D. Obviously, TBBP-A added to ash B must contribute to this formation, comparing to the experiment with ash B. This formation is considered to occur mainly via the precursor compound of TBBP-A in this situation. However, it may also be a result of reactions of various decomposed substances from TBBP-A.

Table 2 Measurement result of dioxins, PBDD/PBDF and PXDD/PXDF

Ash	Flue gas		Ash	
	Dioxins [ng/m^3_N]$^{a)}$	PBDD/PBDF PXDD/PXDF [ng/m^3_N]	Dioxins [ng/g]	PBDD/PBDF PXDD/PXDF [ng/g]
A (200 ºC)	0.37 TEQ: 0.0066	ND (0.004)$^{b)}$	–	–
A (300 ºC)	4000 TEQ: 91	ND 830	54 TEQ: 1.8	0.0025 8.8
B	53 TEQ: 0.94	(0.006) 5.2	210 TEQ: 1.9	(0.011) 7.2
C	180 TEQ: 3.3	ND 25	–	–
D	230 TEQ: 1.9	2900 2700	57 TEQ: 0.75	260 64

a) Concentrations are translated to a condition of 12% O_2.

b) The parentheses indicate that figures exceeding the detection limit and below the quantification limit are included.

The mass balance of pollutants around the experimental system

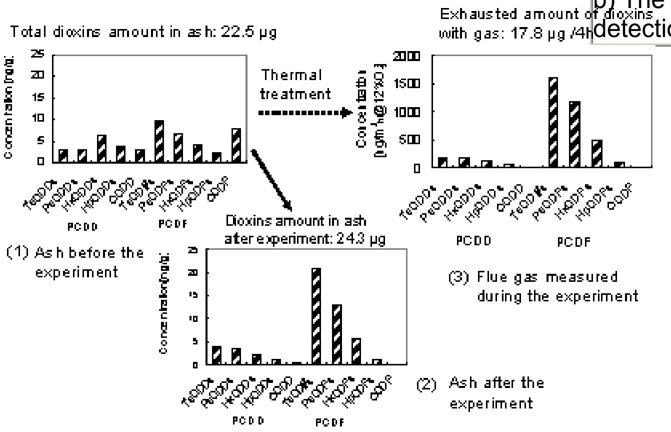

Fig. 2 Mass balance of dioxins and homologue distribution of PCDD/PCDF before and after the thermal treatment of ash A

The mass balance of dioxins was calculated before and after the thermal experiment. The result of ash A is shown in Fig. 2, including the homologue distributions of PCDD/PCDF. Here, two significant points stand out. Firstly, the apparent total amount of dioxins in the ash sample was relatively slow to change before and after the thermal treatment of the sample. However, the exhausted gas from the reactor over a 4 hour period contained 17.8 µg of dioxins, roughly in line with the amount present in all the packed ash. Secondly, the homologue distribution patterns of PCDD/PCDF in both the ash after the experiment and the flue gas were strictly different from the pre-experiment ash. These facts represented strong evidence of the occurrence of *de novo* dioxin synthesis in this experimental system.

Virtually the same result was seen in the mass balance data and homologue distribution of PXDD/PXDF for ash A, as shown in Fig. 3. The thermal heating of ash sample containing 6.3µg PXDD/PXDF produced 3.7µg of that species per 4 hours and the residual ash contained 4.0µg, suggesting *de novo* synthesis of PXDD/PXDF during the thermal treatment. The clear differences in the homologue distribution pattern between the ash samples and those between the ash and gas samples were also evidence of the synthesis. The most abundant homologue was monobromo-triCDFs followed by –tetraCDFs; with a pattern quite similar to that of Fig. 2. This fact suggested the possible substitution of a chlorine molecule by a bromine atom among those in PCDF; probably because of the existence of the Br radical and Br_2.

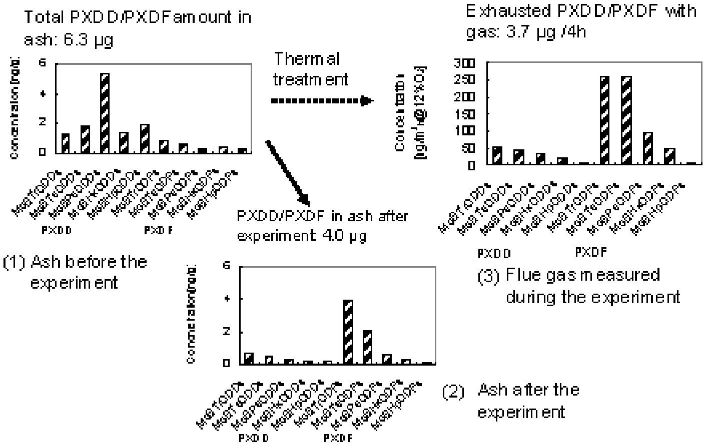

Fig. 3 Mass balance and homologue distribution of PXDD/PXDF before and after the thermal treatment of ash A

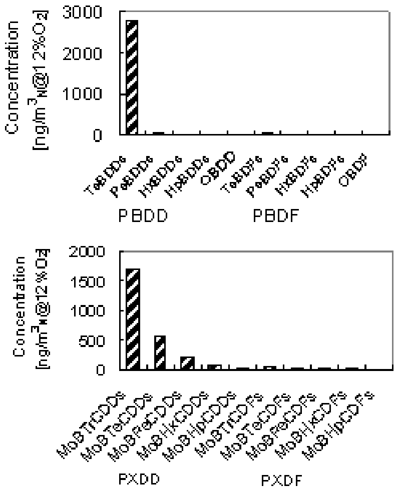

Fig.4 Homologue distributions of PBDD/PBDF and PXDD/PXDF in flue gas of ash D experiment

Ash A contained a relatively large amount of carbon, and much of this was considered to be the powdered variety injected into the duct. This is because the carbon content of ash B was found to be considerably lower when sampled at an earlier stage sampled at the same incineration plant. This signified the importance of carbon materials in the formation of trace organic pollutants.

Formation of PBDD/PBDF and PXDD/PXDF from ash containing TBBP-A

Figure 4 shows the characteristic results in the case of ash D containing TBBP-A. Both homologue patterns were very similar and involved large volumes of lower brominated homologues, potentially a factor of the TBBP-A chemical structure. However, the occurrence of a condensation reaction of TBBP-A molecules or fragment compounds could trigger the dominant formation of tetrabromodibenzodioxins.

References

1. Kawamoto K. and Mabuchi K. (2001) *J. Mater Cycles Waste Manag*, 3: 38-47.

2. Suzuki K., Katagiri M., Kanda N., Itaya M., Kawamoto K. (2002) *Organohalogen Compounds*, 56: 233-236.

3. Weber R., Kuch B., Ohno T. and Sakurai T. (2002) *Organohalogen Compounds*, 56: 181-184.