DIOXINS FORMATION ON FLY ASH OF PYROLYSIS-MELTING PROCESS FOR MSW (I) - FORMATION BEHAVIOR IN A FLY ASH MODEL SYSTEM -

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Introduction

Formation of dioxins (PCDDs and PCDFs) and coplanar PCBs in a pyrolysis-melting process for municipal solid waste (MSW) is low enough because of their high combustion temperature, compared with a conventional Municipal solid waste Incinerator (MSWI). But it is still important to inhibit the formation in the downstream of a combustor, in order to further decrease dioxins emissions. In this work, their formation behavior on fly ash of the process was investigated in a dioxins formation enhanced model reaction system using a labo-scale test equipment with a packed fly ash bed reactor. A comparison with fly ash of conventional MSWI and influences of precursor species and some reaction conditions are discussed in this paper. Another discussion based on characterization of congener and isomer patterns of these experiments is reported in the following paper(1).

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Table 1 Compositions of fly ash used

	ash-A	ash-B
Si (%)	14.2	13.1
Al (%)	6.97	10.7
Ca (%)	12.5	13.5
Mg (%)	2.14	2.1
Na (%)	3.77	4.8
K (%)	3.15	1.8
Cu (%)	0.1	0.052
Fe (%)	1.73	3.8
C (%)	<0.01	3.4
T-S (%)	2.9	1.5
T-Cl (%)	5.52	1.5
PCDD/F (ng/g)	0.67	7.4
PCDD/F(ng-TEQ/g)	0.0072	0.12

Table 2 Settings of experimental runs

Run	Fly ash	precursor	Temp/°C
1	ash-A	CP	350
2	ash-A	none	350
3	ash-A	n-octane	350
4*	ash-A+$CuCl_2$	CP	350
5	ash-B	CP	350
6*	Synthetic ash	CP	350
7	ash-A	CP	200
8	ash-A	CP	275
9	ash-A	CP	420
10	ash-A	CP	550
11	ash-A	CBz	350
12	ash-A	Bz	350
13	ash-A	CP(1/10)	350

* Run 4 and 6 are for referenced paper (1)

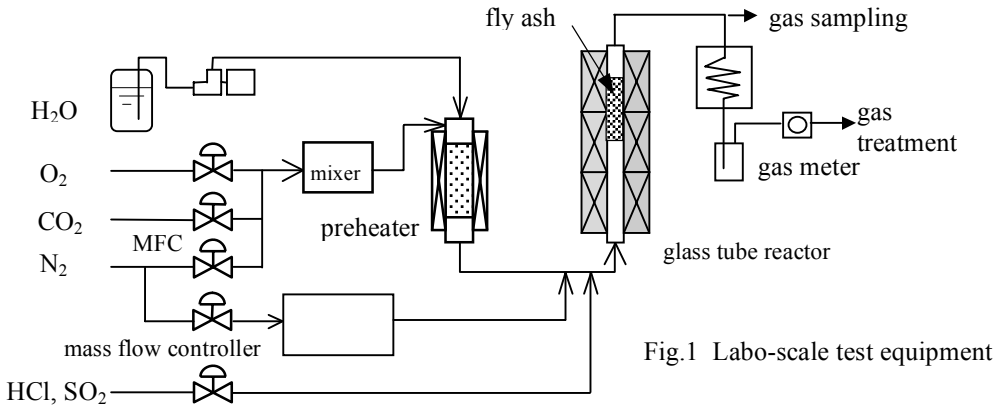

Fig.1 Labo-scale test equipment

Materials and Methods

An enhanced model reaction experiments for formation of PCDD/Fs and coplanar PCBs on fly ash were carried out using a test equipment shown in Fig.1. Fly ashes and water were kneaded and dried to form pellets before use. Compositions of fly ashes used are shown in Table 1. The compositions of fly ash and its pellets were almost same. Fly ash-A of Table 1 was derived from a demonstration plant of pyrolysis-melting process for MSW, and fly ash-B was derived from a conventional stoker type MSWI under operation. A model gas with or without precursor vapor was fed at a flow rate of 20 l_N/min to a glass tube reactor packed with fly ash pellets of 450g. Experimental runs listed in Table 2 were carried out in temperature range of 200 - 550 °C, using various precursors, namely o-chlorophenol (CP), chlorobenzene (CBz), benzene (Bz) and n-octane, in feed rate of 0 - 200 μg/m^3_N. The reactor was heated to a designated temperature and kept for 4hrs to achieve stable sampling of flue gas for quantitative analysis of PCDDs and PCDFs (and coplanar PCBs, CPs and CBzs in some cases). A high resolution GC-MS (Shimadzu/Kratos Concept32 Type 1-S or Micromass Autospec Ultima) was used in the standard methods (SIM mode) . Fly ash after the reaction were also sampled and analyzed in the same way.

Table 3 Concentrations of PCDD/F and Co-PCB in flue gas and fly ash after reaction

	flue gas(ng/m^3_N @12%O_2)				ash after reaction (ng/g)			
	PCDD	PCDF	PCDD/F	Co-PCB	PCDD	PCDF	PCDD/F	Co-PCB
Run 1	120	320	440	8.7	0.77	1.1	1.9	0.23
Run 5	79	370	449	18.0	74.00	100.0	174.0	3.10

Results and discussion

Comparison of dioxins formation behaviors on the two types of fly ashes

Concentrations of PCDD/Fs and coplanar PCBs in fly ash-A after the reaction of Run 1 were quite low as shown in Table 3. They were about 1/90 and 1/13 of those in ash-B of Run 5 respectively, whereas concentrations in flue gas were similar. It must be noted here that the absolute concentration values themselves have no significant meaning because high contact efficiencies between gas and ash very much accelerated dioxins formation in the experiments.

Fig.2 shows total amounts of PCDD/Fs formed during stable reaction periods (4hrs) calculated by integrating data of flue gas and ash. These results of Table 3 and Fig.2 suggest that the formation of PCDD/Fs and coplanar PCBs on fly ash-A of the pyrolysis-melting process for MSW (Run 1) is much lower than that on fly ash-B of the conventional MSWI (Run 5). On the other hand, volatilization of dioxins may occur easier in ash-A than in ash-B, resulting in similar concentrations in flue gas in both runs shown in Table 3 and Fig.2. In other words, dioxin adsorption ability of ash-A may be lower than that of ash-B, which has been also reported in the case of fly ash of ash melting process (2).

Influences of the reaction temperature

Concentrations of PCDD/Fs in flue gas peaked at 350 °C and extremely decreased at temperatures below 275 °C and over 420 °C as shown in Fig.3, whereas concentrations of PCDD/Fs in ash were higher at lower temperature in range of 200 – 550 °C as shown in Fig.4. Total amounts of PCDD/Fs formed during stable 4hrs calculated by integrating both data of flue gas and ash were in a narrow range of 2300 ~ 3000ng at temperatures of 200 - 350 °C , and were about 600ng and 100ng at 420 °C and 550 °C respectively. These results suggest that dioxins formation on fly ash-A unchanged in a temperature range of 200 – 350 °C, while volatilization behavior changed drastically between 275 °C and 350 °C, because fly ash-A had only adsorption ability as described previously. In addition, it is suggested that dioxins formation on fly ash-A hardly occurred and/or decomposition took place at temperature over 420 °C.

Influences of precursors and consideration of de-novo synthesis

Influence of precursor feed rates on the formation behaviors of PCDD/Fs on fly ash-A (Run 1, 2 and 13) is shown in Fig.5. Reduction of precursor feed rates, even no precursor feed, produced little difference in concentrations of PCDD/Fs in flue gas and ash after reaction. In addition, changing precursors of o-chlorophenol to chlorobenzene, benzene, n-octane, or none did not produce significant changes in dioxins concentration in flue gas and ash after reaction as shown in Figs. 6 and 7, though small variations in concentrations were observed. Congener distribution pattern of dioxins also remained unchanged in Run 1, 2 and 3 as described in the following paper (1). These results indicate that dioxin formation is independent of precursors and suggest that the dioxins formation on fly ash of a pyrolysis-melting process for MSW is due to the reaction of precursors, but due to the de-novo synthesis resulting from carbonaceous matters in fly ash it self, though it is low as below 0.01 wt. % in fly ash-A. This may be supported by the comparison of dioxins formation on ash-A and ash-B in which carbon content was 3.4 wt. %.

The results in this paper are due to data on the enhanced dioxins formation in the labo-scale model reaction system so that data in the practical plant operation also must be obtained. Further works are necessary in order to elucidate the dioxin formation mechanism in detail and influences of other parameters.

Acknowledgements

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References

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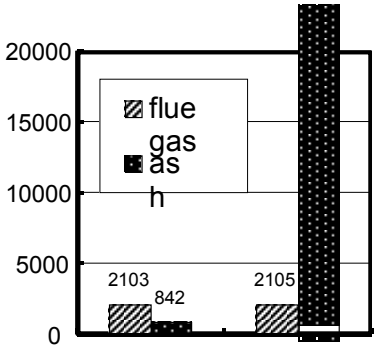

Fig.2 Total amounts on PCDD/F on fly ash during stable periods (4hrs)

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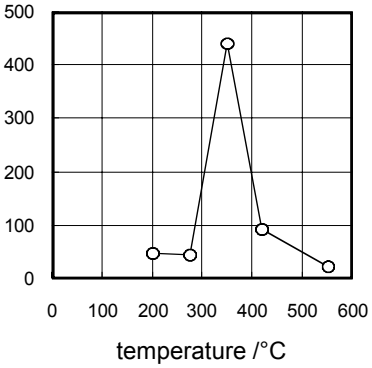

Fig.3 Temperature dependence of PCDD/F concentrations in flue gas

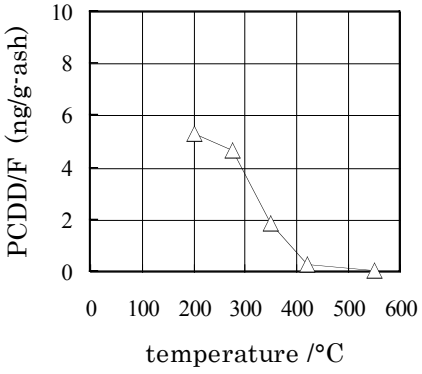

Fig.4 Temperature dependence of PCDD/F concentration in fly ash after reaction

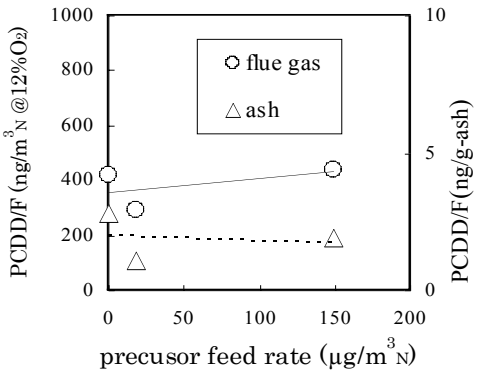

Fig.5 Relationship of PCDD/F formation

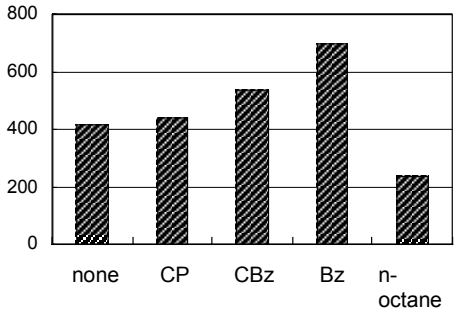

Fig.6 PCDD/F concentration of flue gas in the case of various precursors

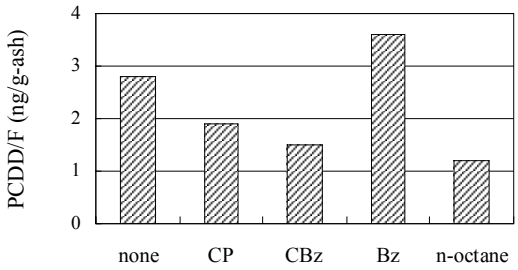

Fig.7 PCDD/F concentration of fly-ash after reaction of various precursor fed