

DIOXINS FORMATION ON FLY ASH OF PYROLYSIS-MELTING PROCESS  
FOR MSW (II)  
-CHARACTERIZATION BASED ON CONGENER AND ISOMER PATTERN-

Katsuya Kawamoto\*, Nobuyasu Kanda\*\*, Katsuhiko Kobayashi\*\*\*, Tomohiro Wada\*\*\*\*, Shigehiro Shibakawa\*\*\*\*\* and Yasuaki Harada\*\*

\* Department of Architectural Environmental Engineering, Kanto Gakuin University, 4834 Mutsuuracho, Kanazawa-ku, Yokohama, 236-8501 Japan

\*\* Mitsui Engineering & Shipbuilding Co., Ltd., Tokyo, 104-8439 Japan

\*\*\* Mitsubishi Heavy Industries, Ltd., Yokohama, 236-8515 Japan

\*\*\*\* Hitachi, Ltd., Hitachi, 317-0073 Japan

\*\*\*\*\* Takuma Co., Ltd., Amagasaki, 660-0806 Japan

### Introduction

As described in another paper [1] PCDDs, PCDFs and coplanar PCBs formation on ashes discharged from pyrolysis-melting process of municipal solid waste (MSW) was strongly influenced by the kind and composition of ash applied in experiments when temperatures and reaction time were kept constant. This observation of a *de novo* synthesis suggests that the composition of dioxins changes considerably depending on the property of ash in an actual plant. In order to elucidate dioxin formation mechanisms congener and isomer patterns of dioxins were analyzed. In this paper distinctive characteristic patterns of dioxins are demonstrated. This work is conducted and sponsored by the R & D committee of the next generation incinerator in Japan Waste Research Foundation.

### Materials and Methods

#### *Experimental settings*

Fine ash particles were pelletized to large particles and were filled in a glass tube reactor. Experimental settings on the apparatus, operation procedure and materials used were detailed in another paper. Experimental runs especially related to this paper are shown in Table 1. Organic precursors were fed in concentrations of 150 - 200  $\mu\text{g}/\text{m}^3$ . Hydrogen chloride of 1000 ppm was fed as an inorganic chlorine source. Temperatures were controlled at 350 °C in all runs described here. Reaction time or apparent retention time in the reactor was 1.5 second at normal state. Synthetic ash in Run 6 composed of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and small amounts of  $\text{MgO}$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ .

Table 1 Set of experimental runs

Run No.	Ash	Precursor used
1	Fly ash of pyrolysis-melting process	<i>o</i> -chlorophenol
2	Fly ash of pyrolysis-melting process	None
3	Fly ash of pyrolysis-melting process	n-Octane
4	Cu-impregnated ash of melting process	<i>o</i> -chlorophenol
5	Fly ash of comprehensive incinerator	<i>o</i> -chlorophenol
6	Synthetic ash composed of $\text{SiO}_2$ , $\text{Al}_2\text{O}_3$ , etc.	<i>o</i> -chlorophenol

**Analytical methods**

Sampling of dioxins in flue gas was conducted at the reactor outlet by the method described in another paper [1]. Analysis was done by using a high resolution GC-MS system. Toxic PCDD and PCDF isomers were determined individually, then congener patterns based on chlorine numbers and isomer patterns were analyzed.

**Results and discussion**

**Congener and isomer patterns in the case of using ash formed in pyrolysis-melting process**

Ash formed in pyrolysis-melting process hardly had any carbon contents. The content was only below 0.01 % compared to 3 % of incineration fly ash. Hence, we considered that the reaction between organic precursor molecules and chlorine atoms resulted in the formation of dioxins. Figure 1 shows a congener pattern of dioxins in flue gas of Run 1. This is a typical pattern for dioxins formed on fly ash of a pyrolysis-melting process, which consists of slight increase in PCDDs concentrations with increase in chlorine substitution numbers and symmetric distributions of PCDFs in that hexa-CDFs or hepta-CDFs is a dominant peak.

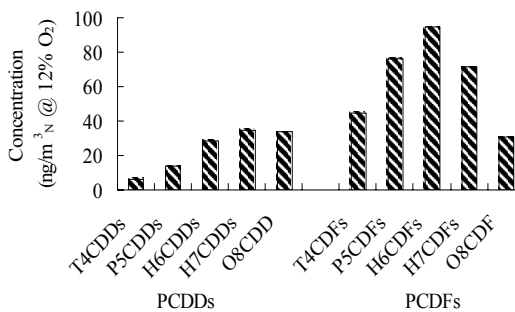


Fig. 1 Congener distribution pattern of dioxins in Run 1 flue gas

A very similar distribution pattern could be seen in other runs that used the same fly ash even if the experimental conditions regarding to temperatures, reaction time and precursors fed were different. Figure 2 shows a very similar pattern to that of Run 1, though no *o*-chlorophenol was fed in Run 2. Concentrations of dioxins in Runs 1 and 2 were almost the same, 440 and 420 ng/m³ N, respectively. Congener patterns for three other kinds of organic vapor, chlorobenzene, benzene and even aliphatic n-Octane, were almost the same as those in Runs 1 and 2. An example is shown in Fig. 3. The facts suggest that some common material existing on fly ash matrix cause

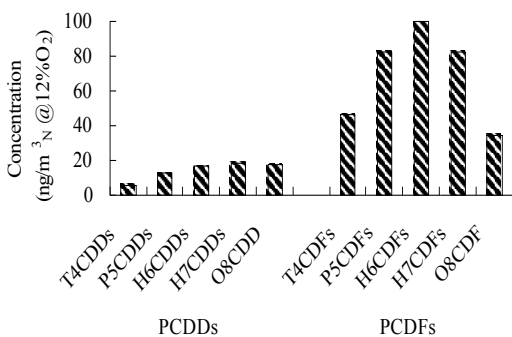


Fig. 2 Congener distribution pattern of dioxins in Run 2 flue gas

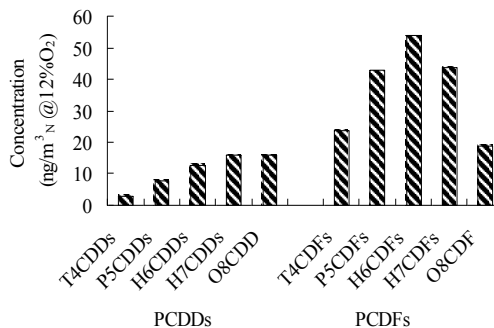


Fig. 3 Congener distribution pattern of dioxins in Run 3 flue gas

formation of dioxins. Based on many other experimental results, we assumed that carbon macromolecules existed in fly ash in very small quantities functioned as an important carbon source for dioxins formation. On the other hand, dioxin formation in Run 6 was very low ( $12 \text{ ng/m}^3_{\text{N}}$ ). The major difference in experimental settings between Run 6 and the other Runs was that Run 6 used synthetic ash that did not include macromolecular carbon.

It was observed in all runs that the ratios of PCDFs/PCDDs were different in flue gas and ash. The value in flue gas was 4.4 in average whereas the value in ash was 1.2 in average. Ash samples had larger PCDDs amounts. The results may reflect rather high volatility of PCDFs.

#### ***Influences of ash compositions***

Figure 4 shows a congener distribution pattern for pyrolysis-melting fly ash impregnated with  $\text{CuCl}_2$ . The copper content was 1.5 % as Cu compared to 0.1 % of usual melting fly ash samples. Formation of octa-, hepta- and hexa-CDFs dramatically increased and total concentration in gas reached  $2500 \text{ ng/m}^3_{\text{N}}$ , about five times of Run 1. PCDFs concentrations in ash, however, did not increase in contrast with flue gas. The facts suggest that catalyst copper on fly ash highly promote formation of dioxins from precursors when catalyst is rich. Metal compounds such as copper and iron are well known catalyst [2,3] in formation of dioxins on incineration fly ash. Catalyst metals play an important role also in the pyrolysis-melting ash system.

Figure 5 shows a congener distribution pattern for incineration fly ash. The distribution pattern is obviously quite different from Figs. 1, 2 and 3. Tetra-CDFs was the most abundant congener and the concentrations decreased with increase in substitution numbers of chlorine atoms in both PCDDs and PCDFs. Although the total concentration in flue gas was  $450 \text{ ng/m}^3_{\text{N}}$ , nearly equal to that in Run 1, the total concentration in ash was extremely higher than that in Run 1. The amount was  $170 \text{ ng/g}$  compared to  $1.8 \text{ ng/g}$  in Run 1. Incineration fly ash rich in unburned carbon strongly accelerate the *de novo* synthesis on the matrix. The results suggest that different formation mechanisms exist on two types of ash though the same *de novo* synthesis may proceed on them. Distinctive patterns

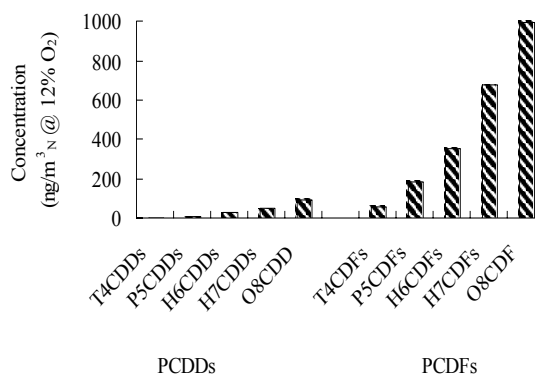


Fig. 4 Congener distribution pattern of dioxins in Run 4 flue gas

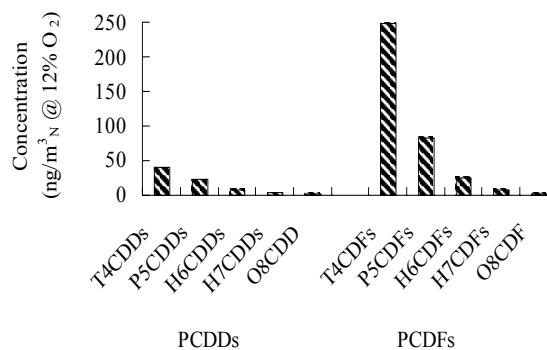


Fig. 5 Congener distribution pattern of dioxins in Run 5 flue gas

can be seen in isomer distributions shown in Fig. 6. Fly ash of the pyrolysis-melting system and Cu impregnated ash resulted in formation of 2,3,4,7,8-P5CDF, 2,3,4,6,7,8-H6CDF and 1,2,3,7,8-P5CDD and so on, while fly ash of incineration resulted in formation of 2,3,7,8-T4CDD and 2,3,7,8-T4CDF and so on, as distinctive isomers. The ash sample impregnated with Cu (b) exhibited a very interesting feature. The isomer pattern resembled that of fly ash with less Cu, though the congener patterns were quite different as shown in Figs. 1 and 4.

**Patterns of coplanar PCBs**

Isomer distribution profiles of coplanar PCBs are shown in Fig. 7. Three kinds of ash formed different compositions of coplanar PCBs. 3,3',4,4'-T4CB was the most abundant isomer in Run 4 and 2,3,3',4,4',5,5'-H7CB in Run 5, whereas no component existed over 15 % in Run 1. This difference might be caused by different reactions in ashes just like dioxins.

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

**Acknowledgments**

The authors wish to thank Japan Waste Research Foundation for permitting to publish the results of this work.

**References**

1. Kanda N et al.; *Organohalogen compounds*. 1999, 37 (submitted)

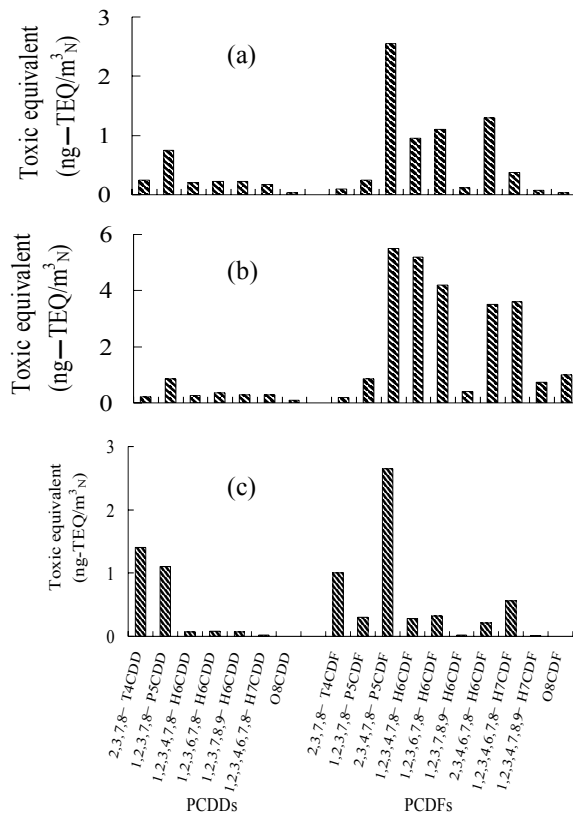


Fig. 6 Isomer distribution patterns of dioxins in flue gases (a) Run 1 (b) Run 4 (c) Run 5

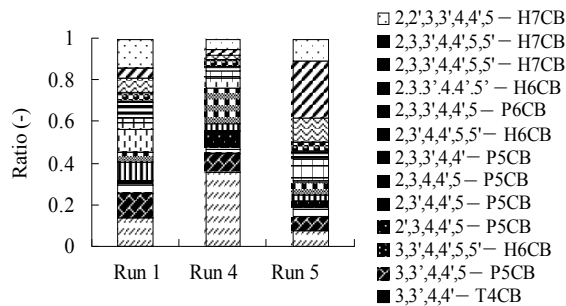


Fig. 7 Distribution ratio of isomers of coplanar PCBs

## Formation and Sources P129

2. Gullet B K, Bruce K R, Beach L O and Drago A M; *Chemosphere*. **1992**, 25, 1387
3. Tuppurainen K., Halonen I, Ruokojärvi P, Tarhanen J and Ruuskanen J; *ibid.* **1998**, 36, 1493