

THERMAL DEGRADATION OF PCDD/Fs AT MIDDLE TEMPERATURE IN MODEL WASTE INCINERATION

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Introduction

Municipal waste incinerators are an important source of emissions of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs). Though the recent developments of dioxin control technologies on the incinerators have made it possible to reduce their release significantly, such emission is still a problem, and to minimize it, it is indispensable to inhibit the formation itself through the understanding of their formation mechanisms. PCDD/Fs are formed through several pathways such as chlorophenol condensation and de novo synthesis.¹ Since the formation pathway influences the pattern of their congener proportions, it contributes to the understanding of their formation mechanism to examine the congener pattern.² However, it is very difficult to obtain useful information about the formation mechanism from the congener pattern because there is only a small amount of each congener formed and many factors in combustion affect their formation in waste incineration. We have developed the experimental method to obtain the results about the effect of the target factor on PCDD/F formation in model waste incineration with high reliability.² This method makes it possible to compare their congener pattern and discuss the formation mechanism.

The aim of this study is to investigate PCDD/F formation and degradation in thermal-retention section at middle temperature after main combustion section. Sampling is conducted at the inlet, middle, and outlet of the thermal-retention section. The formation and degradation reactions are discussed by comparison with the amounts of PCDD/F congeners formed at the three sampling points.

Materials and Methods

The main combustion section in the experimental setup consisted of primary and secondary combustors (Figure 1). The primary combustor was a laboratory-scale fluidized-bed reactor (60 mm diam., 300 mm tall). The fluidized material was 100–140 μm silica sand, and the static bed height was 100 mm. The secondary combustor was a freeboard section (30 mm diam., 1450 mm tall). All parts of the main combustion section were made of quartz. The thermal-retention section was a straight quartz tube (45 mm diam., 1000 mm length) and was connected to the main combustion section. These sections were kept at constant temperature with external heaters. Fresh sand was used for the fluidized material in each experiment, because even trace amounts of

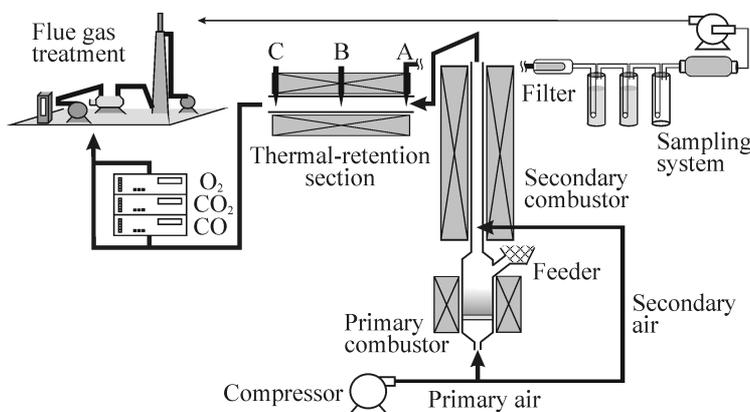


Figure 1. Schematic diagram of experimental setup.

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residues such as chlorine and catalyst in the sand and on the inner surfaces of the reactor strongly affect PCDD/F formation. After each experiment, the inner surfaces of the reactor in contact with flue gas were washed to prevent memory effects. In case washing could not remove the contamination, the quartz parts were replaced with new material. Sampling for PCDD/F analysis was carried out for 4 h at the inlet, middle, and outlet of the thermal-retention section (point A, B, and C) using a water-cooled probe.

Table 1 Experimental conditions.

Temperature	
primary combustor	700 °C
secondary combustor	900 °C
thermal-retention section	600, 650 °C
Flow rate	
primary air	0.46 m ³ _N /h ($\lambda=1.3$)
secondary air	0.26 m ³ _N /h ($\lambda=0.7$)
Fuel feed rate	100 g/h

A model waste was used, so as to have a strictly defined waste composition. The base ingredients of the model waste were 45% unbleached pulp powder, 40% flour, and 15% wood powder. In addition to the base ingredients, poly(vinyl chloride) (PVC) and CuCl₂·2H₂O were mixed as a chlorine source and a formation catalyst. All ingredients were ground separately, mixed mechanically, and then pelletized into particles (1–3 mm diam.). Cl and Cu contents of the model waste were 0.60 wt% and 0.04 wt%. Experimental conditions are listed in Table 1.

Results and Discussion

Figure 2 shows the homologue profile of tetra- through octa-chlorinated dibenzo-*p*-dioxins (T4CDDs through O8CDD) and dibenzofurans (T4CDFs through O8CDF) at the sampling points A, B, and C in the thermal-retention section at 600 °C. All the homologues were reduced at the downstream sampling points. PCDD/Fs were degraded or dechlorinated in this section. The proportion of each homologue to the total amounts of PCDDs and PCDFs was examined at the three sampling points (Figure 3). The homologue profile was shifted toward lower chlorinated species at the downstream points. This could mean that PCDD/Fs were dechlorinated in this section. However, it was confirmed that the homologue profile was shifted toward lower chlorinated species as PCDD/Fs were reduced in the experiments on chlorine content of model wastes and combustion temperature using the same experimental method.³ Only the change of the homologue profile could not lead to the conclusion that dechlorination was a major reaction of PCDD/Fs in the thermal-retention section at 600 °C.

The ratio of the concentration of each congener of PCDDs and PCDFs at the downstream points B and C to that at the inlet point A was calculated to examine the reaction mechanism in the thermal-retention section in detail (Figure 4). When the value of the ordinate is more than 1, the congener is formed at the downstream point B or C more than at the inlet point A. The value less than 1 means the decrease of the amount of the congener formed. The pattern of the ratios of tetra- and penta-chlorinated dibenzo-*p*-dioxin (T4CDD and P5CDD) and dibenzofuran (T4CDF and P5CDF) congeners is given as an example because these congeners have the most characteristic pattern in these experiments.⁴ The ratios of the concentrations of PCDD congeners were dispersed,

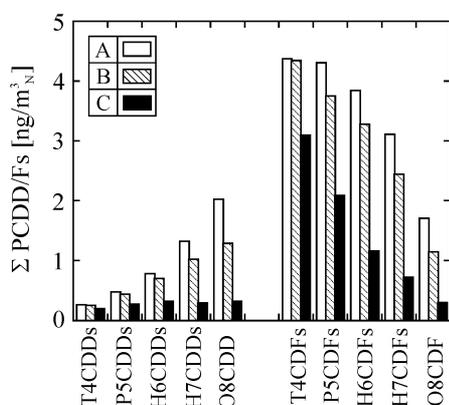


Figure 2. Homologue profiles of PCDD/Fs in thermal-retention section at 600 °C.

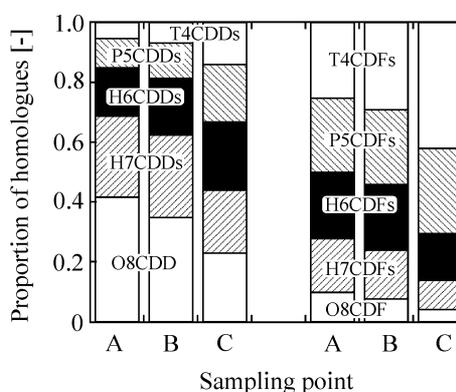


Figure 3. Changes of homologue profiles of PCDD/Fs in thermal-retention section at 600 °C.

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reaction is hardly affected by thermodynamic equilibrium on chlorine-substituted sites, most PCDF congeners were reduced equally. The characteristic one in PCDF congeners is 2,4,6,7-T4CDF. Little change was observed in the amount of the congener formed. This congener is probably formed by pulling one chlorine out of 2,3,4,6,7-P5CDF because it is particularly formed from carbon/polyaromatic hydrocarbons in incineration of model wastes containing copper.⁴ This also shows that PCDFs are dechlorinated as well as PCDDs. However, chlorination has less influence on PCDFs than PCDDs in the thermal-retention section at 600 °C because the dispersion of the pattern of the PCDF congeners is much low.

Most congeners of PCDDs and PCDFs were equally reduced at the sampling points B and C in the thermal-retention section at 650 °C (Figure 5). The remarkable congeners are 1,3,6,8- and 1,3,7,9-T4CDDs. Only these congeners did not decrease at the point B, but these were largely reduced at the point C, which is the difference between 600 and 650 °C. These congeners are formed via condensation of chlorobenzenes and chlorophenols at 650 °C, but, since such single-ring compounds are also degraded in this section, 1,3,6,8- and 1,3,7,9-T4CDDs are reduced at the downstream point C at this temperature.

References

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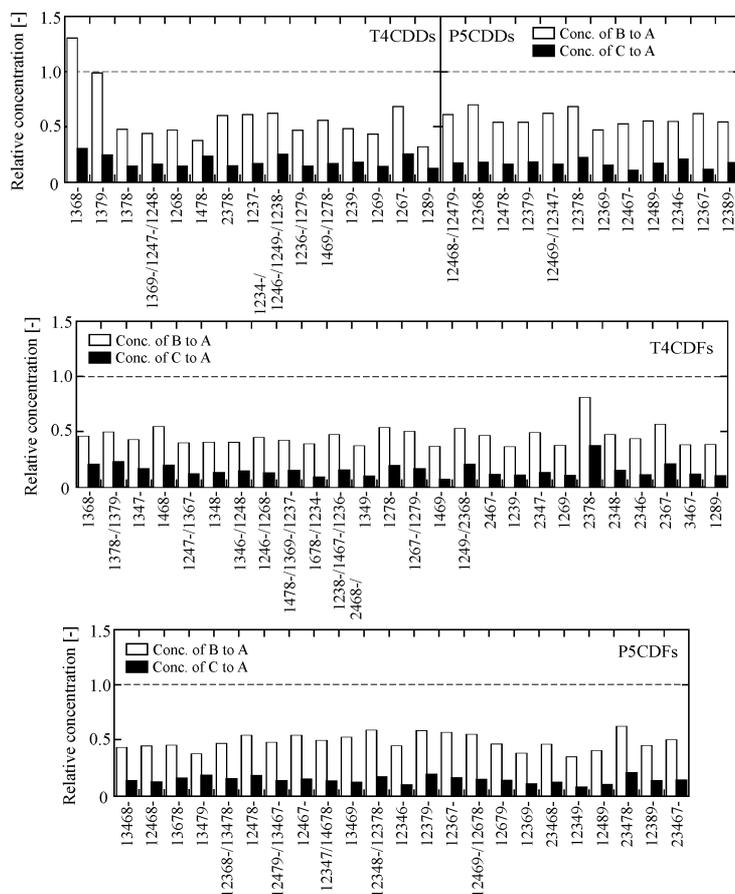


Figure 5. Changes of relative concentrations of PCDD/F congeners in the thermal-retention section at 650 °C.