Effect of oxygen concentration in primary and secondary furnaces on the formation of PCDDs and PCDFs 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, together: PCDD/Fs). 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. Many complicatedfactors in combustion phenomena largely influence PCDD/F formation in incineration.One of the major factors is combustion condition. Disturbed combustion conditions cause high amounts of PCDD/Fs formed.[1,2] Some of the key controlled variables that determine combustion conditionsare furnace temperature and oxygen (O_2) concentration in a furnace. We showed in the combustion of model wastes in a laboratory-scale fluidized-bed reactor that PCDD/F formation is reduced with lower temperature of the primary combustor and higher temperature of the secondary combustor.[3] This means that the furnace temperature exerts a different influence on their formation between the primary and secondary combustors. O_2 concentration in a furnace is the important factor that affects PCDD/F formation in incineration because products of incomplete combustion (PICs) are closely related to their formation.[1] High O_2 concentration in flue gas is expected to promote combustion, resulting in the reduction of PCDD/F formation. However, Lenoir et al. reported in a fluidized bed incinerator that high O_2 values increased PCDD/F levels under normal operating conditions.[4] The O_2 concentration in the incinerator could intricately affect their formation because it is related to other factors such as furnace temperature and the amount of air supplied. In addition, oxygen is involved in their formation reactions.[5] It exerts direct and indirect influences on their formation.

The aim of this study is to investigate the effects of O_2 concentration in primary and secondary furnaces on PCDD/F formation in model waste incineration. Combustion experiments of model wastes were performed supplying air with the different O_2concentration to the primary and secondary furnaces. Since the experimental setup used in this paper makes it possible to set the O_2concentration to a specific value without changing other operating conditions, the effects of O_2concentration in each furnace are separately examined in detail.

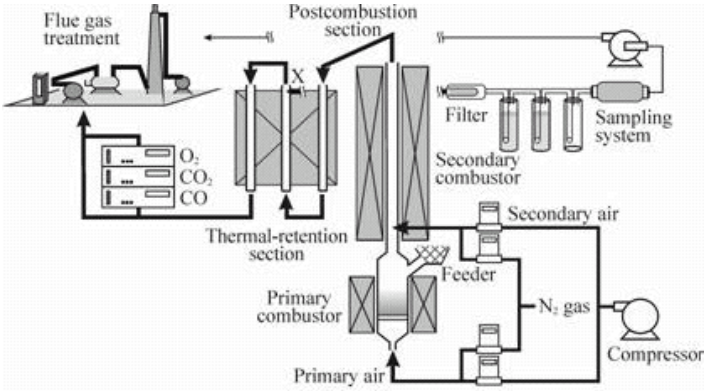

Figure 1: Schematic diagram of experimental setup.

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 mm 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 coming in contact with flue gas were made of quartz. The postcombustion section connected the main combustion section with the thermal-retention section. The thermal-retention section consisted of 3 glass tubes (30 mm diam., 300 mm tall).Fresh sand was used for the fluidized material in each experiment, because even trace amounts of 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. Model wastes were 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 $CuCl_2 \times 2H_2O$were mixed as a chlorine source and a catalyst. All ingredients were ground separately, mixed mechanically, and then pelletized into particles (1–3 mm diam.).Sampling for PCDD/F analysis was carried out for 4 hafter the thermal-retention section (point X).

Experimental conditions are listed in Table 1. The O_2concentration of air supplied to the combustor was adjusted by mixing air from a compressor with nitrogen (N_2) gas. The amount of the mixed air supplied was constant for all experiments and determined so that the excess air ratio was set to 1.3 in the primary combustor and 0.7 in the secondary combustor in run 1. Cl and Cu contents of model waste A used in run 1 were different from those in other experiments owing to the shortage of waste B. Cl and Cu contents were 1.24 wt% and 0.07 wt% in waste A, and 1.11 wt% and 0.04 wt% in waste B. Model wastes were supplied to the fluidized-bed reactor at 100 g/h.The temperature was kept at 700 °C in the primary combustor, 900 °C in the secondary combustor, and 350 °C in the thermal-retention section with electric heaters.

Table 1: Experimental conditions.

Run No.	1	2	3	4
O_2 conc. of primary air [%]	21	21	21	15
O_2 conc. of secondary air [%]	21	15	10	21
Model waste	A	B	B	B

Results and Discussion

Figure 2 shows the relation between the total concentrations of tetra- through octa-chlorinated dibenzo-*p*-dioxins (T4CDDs through O8CDD)and dibenzofurans (T4CDFs through O8CDF) and the average O_2 concentration in flue gas. The amounts of PCDDs and PCDFs formed straightly increased as the O_2 concentration of the secondary air became low. Lower O_2 concentration in the secondary combustor causes incomplete combustion, resulting in the increase of their formation. This indicates that oxygen in the furnace exerted a stronger influence on combustion than on their formation reactions in these experiments.

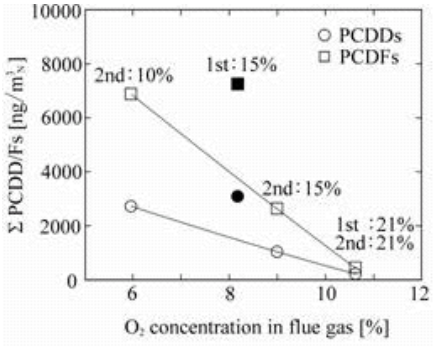

Figure 2: Effect of oxygen concentration in primary and secondary airs on PCDD/F concentrations.

Lower O_2 concentration of the primary air also promoted PCDD/F formation similarly to that of the secondary air.

This influence is apparently greater than that of the secondary air. The amount of PCDD/Fs formed is more than twice as much as that obtained when the O_2 concentration in flue gas is set to the same value by changing the O_2 concentration of the secondary air. The average CO concentration in flue gas was 40 ppm in run 1, 110 ppm in run 2, and 64 ppm in run 3, which was examined as the representative parameter of combustion conditions. The CO concentration reflects the O_2 concentration in flue gas, but the PCDD/F concentration does not directly reflect these parameters though it is positively correlated with the CO concentration in flue gas under the same experimental conditions other than the target factor in the previous studies.[3,6] This probably shows that the effects of O_2 concentration on PCDD/F formation are different between the primary and secondary combustors. When the O_2 concentration of the primary air becomes low, the waste is combusted in oxygen deficient conditions and a large amount of PICs could be formed. Though PICs formed in the primary combustor are burned in the secondary combustor with the additional oxygen supplied, these compounds could not be sufficiently decomposed in the residence time, which results in high amounts of PCDD/Fs formed for O_2 concentration in flue gas. These results show the importance of combustion in the primary furnace for the reduction of PCDD/F emission.

Highly chlorinated homologues were less formed as the O_2 concentration of the primary and secondary air decreased (Figure 3). The same trend were observed in a fluidized bed incinerator.[4] We showed in the previous studies that more PCDD/F formation causes a shift to higher chlorinated species.[7] However, the results in this study show the opposite trend. Some factors that suppress chlorination might exert a greater influence on their formation than those that promote it when O_2 concentration in the furnace decreased in these experimental conditions. The mechanisms of the shift to lower chlorinated homologues cannot be proposed from these results. However, the previous and present results show that there are some mechanisms that promote and suppress chlorination in combustion reactions that are involved in PCDD/F formation.

References

1.Zimmermann R., Blumenstock M., Heger H.J., Schramm K.-W. and Kettrup A. (2001) *Environ. Sci. Technol.*35: 1019-1030.

2.Hunsinger H., Jay K. and Vehlow J. (2002) *Chemosphere* 46: 1263-1272.

3.Hatanaka T., Imagawa T., Kitajima A. and Takeuchi M. (2001) *Environ. Sci. Technol.*35: 4936–4940.

4.LenoirD., KauneA., HutzingerO., Mutzenich G. and HorchK. (1991) *Chemosphere* 23: 1491-1500.

5.Wikstrom E., Ryan S., Touati A. and Gullett B.K. (2003) *Environ. Sci. Technol.*37: 1962-1970.

6.Hatanaka T., Imagawa T. and Takeuchi M. (2000) *Environ. Sci. Technol.*34: 3920–3924.

7.Hatanaka T., Kitajima A. and Takeuchi M. (2003) *Organohalogen Compd.*63: 90-93.

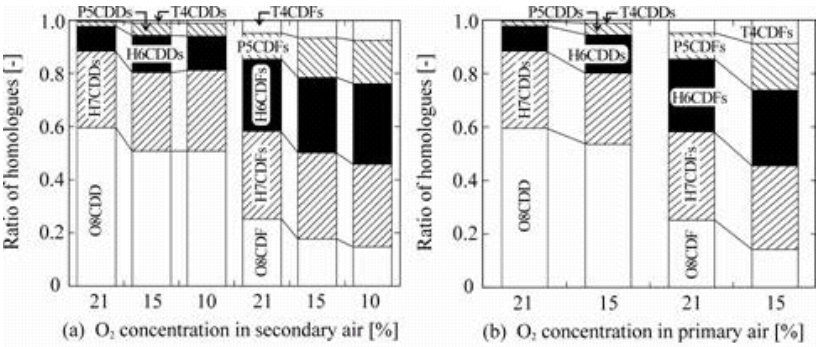

Figure 3: Changes of relative homologue profiles of PCDD/Fs in different oxygen concentration of primary and secondary airs.