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BEHAVIOR OF PCDD/Fs FORMED DURING HEAT TREATMENT OF PVC AND COPPER OXIDE MIXTURE

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Introduction

Since Olie et al.¹⁾ reported in 1977 that PCDD/Fs were detected from the fly ash of municipal waste incinerator, large efforts have been made to avoid PCDD/Fs emissions from waste incinerators in the world. A new regulation on the emissions has been enforced and, in such background, a number of new technologies to reduce PCDD/Fs emissions have been developed. This leads to significant decreases in the emissions of PCDD/Fs and relating compounds. Most of these technologies are based on stable and high temperature combustion, and rapid cooling and succeeding filtrating/scrubbing of the waste gas. Although there are many reports on the control/suppression of formation rate and/or the promotion of decomposition of PCDD/Fs, the detailed mechanisms have not been clarified yet. The present paper reports a fundamental study on the formation/decomposition of PCDD/Fs and relating compounds using a sealed quartz ampoule as a reactor. Powder mixture of PVC (Poly-Vinyl-Chloride) and CuO was used as a sample. Wide ranges of reaction temperature, reaction time and cooling rate were applied.

Methods and Materials

A quartz ampoule with about 30ml in inside volume was used as a reactor. The well-mixed powder mixture of CuO and PVC regents was vacuum-sealed into the ampoule. Mass ratio of PVC /CuO was fixed to be 1/6 throughout the series of the experiment, which corresponds to the stoichiometric value that oxygen in CuO completely reacts with carbon in PVC. The ampoule was kept in an oil bath in the case for the reaction temperature 200 °C and in an electric resistance furnace for those 300, 400, 700 and 900 °C.

Experimental conditions are listed in Table 1. The retention time was varied from 2 to 480h at the various reaction temperatures. The reaction during the cooling course from high temperatures was also examined by changing the cooling rate of sample by the following ways after the heat treatment at 700 or 900 °C for 2h: the ampoule was dropped into water or cooled slowly down at a rate of 100 °C/h in the furnace. Then, the sample was carefully washed off from the ampoule by using dichloromethane and then the amount of PCDD/Fs was determined by the procedure of JIS-K 0311.

Table 1 Experimental conditions.

Temperature (°C)	Retention time (h)	Sample mass (mg)		Way of cooling
		PVC	CuO	
200	12, 96, 192, 288, 480	50	300	outside furnace
300	12, 36, 48, 60, 96	40	240	outside furnace
400	2, 6, 12, 24, 36, 72	35	220	outside furnace
700	2	40	240	in water or furnace
900	2	30	200	in water or furnace

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Results and Discussions

Figure 1 shows the relation between the amount of PCDD/Fs formation and retention time at 300 °C. The values are converted to the those corresponding to 1 g of PVC. It is shown that the maximum value is obtained at about 50 h and, at that time, the decomposition rate of PCDD/Fs appears to exceed that of the formation. Although a little variation is found, the ratios of PCDDs/PCDFs obtained are fairly consistent as nearly 1/1.

Figure 2 shows the homologue profiles of PCDD/Fs obtained at 300 °C. The fractions of higher chlorinated homologues such as O8CDD are remarkably large within PCDDs in the case of the reaction time above 48h, while the fraction of H6CDFs is larger than that of O8CDF within PCDFs.

The detected amounts of PCDD/Fs after keeping at 700 and 900 °C are shown in Fig. 3. No clear difference can be seen between the cases of water-quench and in-furnace cooling. Therefore, it can be deduced as that most of detected PCDD/Fs originally existed at such high temperatures, although there is also some possibility that the formation of PCDD/Fs occurs during such extremely short cooling time as the case of the water-quench. These are not well consistent with the widely recognized expression "PCDD/Fs are unstable and therefore decomposed completely at high temperatures". The present result may suggest that there is a certain condition where PCDD/Fs can stably exists at high temperatures. The ratios of PCDDs/PCDFs obtained for 700 and 900 °C are about 3/1. This is larger than the value for 300 °C.

Figure 4 shows the change in the formed amount of PCDD/Fs with retention time obtained for 200 °C. The ratios of PCDDs/PCDFs are about 1/3. As mentioned above, the fraction of PCDDs increases coherently with an increase in temperature. The amounts of PCDD/Fs after reaction for 12 and 96 h are comparable to those of 300 °C. However, extremely large amounts of PCDD/Fs, in the order of several hundred times of those for the shorter retention times, were obtained for 192, 288 and 480 h.

Figure 5 shows the homologue profiles of PCDD/Fs at 200 °C. The fractions of higher chlorinated homologues such as O8CDD are relatively larger comparing to the others, while that of H6CDFs is larger within PCDFs. These are the similar results to those obtained between 200 and 400 °C. Fiedler²⁾ has reported that fractions of O8CDD and P5CDFs are larger in PCDD/Fs emitted from typical municipal waste incinerators. The present result follows such trends. The total amount of PCDD/Fs decreases at 480 h, but the lower chlorinated homologues such as M1CDD/Fs and D2CDD/Fs are still large. It can be deduced from the result that dechlorination of PCDD/Fs proceeds more in the later stage of reaction when their decomposition becomes significant.

The total amount and corresponding toxicity equivalent quantities (TEQ) of formed PCDD/Fs are listed in Table 2. The values in TEQ are also large when the total amounts of formation are large for the samples kept at 200 °C. 2,3,7,8-TCDD was detectable in only four samples kept at 200 °C which showed larger values in TEQ. The ratios of 2,3,7,8-TCDD to total T4CDDs are represented in parenthesis. Both of the amount and ratio of 2,3,7,8-TCDD for 480 h are remarkably large. It has been also reported³⁾ that the formation of 2,3,7,8-TCDD is significant during the dechlorination reaction. It appears that the dechlorination reaction remarkably proceeds after keeping for 288 h at 200 °C in the present condition.

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Table 2 Total amounts and TEQ values of detected PCDD/Fs.

Temperature (°C)	Retention time (h)	PCDD/Fs (ng/g-PVC)	TEQ (ng/g-PVC)	2,3,7,8-TCDD (ng/g-PVC)
200	12	18.6	0.13	N.D.
	96	55.0	0.71	N.D.
	192	30769	566	0.452 (0.01 [*])
	192	19991	369	0.325 (0.007 [*])
	288	17707	323	0.430 (0.01 [*])
	480	5108	6.75	2.743 (0.10 [*])
300	12	27.3	0.06	N.D.
	36	41.1	0.88	N.D.
	48	98.7	1.19	N.D.
	60	47.5	0.88	N.D.
	96	28.8	0.10	N.D.
700	2-(in water)	33.5	0.15	N.D.
	2-(in furnace)	23.6	0.50	N.D.
900	2-(in water)	11.5	0.90	N.D.
	2-(in furnace)	11.4	0.09	N.D.

*2,3,7,8-TCDD/T4CDDs

References

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