

# Suppression of PCDD/Fs formation by mixing of phthalate plasticizers during gas phase reaction of 2,4,6-trichlorophenol

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## Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are unintentionally by-products, and the main emission source is combustion process, with municipal solid waste incinerators (MSWIs) as one of the major sources<sup>1)</sup>. Chlorine content plastics, such as polyvinyl chloride, are considered to be greatly contributed to the formation of PCDD/Fs<sup>2)</sup> and it is concerned about formation of PCDD/Fs by the combustion of such materials and environmental pollution by these emissions.

During recent years, a number of studies about formation mechanism of PCDD/Fs in laboratory scale<sup>3)</sup> and in full scale<sup>4, 5)</sup> incinerator were published. We had investigated the formation of PCDD/Fs by the combustion of various materials which have aromatic ring, such as phenols<sup>6, 7)</sup>, phenyl phenols<sup>8, 9)</sup>, and phenoxy phenols<sup>10, 11)</sup>. It was suggested that the generation of chlorinated aromatic hydrocarbons during combustion process were greatly contributed to the formation of PCDD/Fs as precursors<sup>12)</sup>.

However, there are not only precursors but also various kinds of compounds in the actual incinerators. It had been discussed whether inorganic materials, such as metals, sulfur compounds, and nitrogeous compounds had effected on the formation of PCDD/Fs or not. For example, Stieglitz et al.<sup>13)</sup> noted that copper chloride in the incinerator and electrostatic precipitator acted as a catalyst of formation of PCDD/Fs. Raghunathan and Gullet<sup>14)</sup> demonstrated that sulfur dioxide reduced the concentration of PCDD/Fs during combustion of natural gas or coal in pilot-scale tests. Ammonia<sup>15)</sup> and urea<sup>16, 17)</sup> were also shown to reduce the concentration of PCDD/Fs in the exhaust gas. On the other hand, there are few notices for co-existent organic materials despite the fact that there are much more organic compounds in the incinerator than inorganic compounds. Therefore, it is important to study about influence of co-existent organic compounds for the formation of PCDD/Fs.

In the previous study, we had studied the various factors, such as temperature, resident time, and co-existent organic compounds on the formation of PCDD/Fs during combustion of chlorinated phenols<sup>7)</sup>. It became clear after this investigation that mixing of phthalate plasticizers with 2,4,6-trichlorophenol (2,4,6-T<sub>3</sub>CP) reduced the concentration of T<sub>4</sub>CDD remarkably. However, most of its suppression mechanism has still remained unknown. Therefore, more detailed data will be needed to elucidate the suppression mechanism for the formation of T<sub>4</sub>CDD. In this study, we reported analytical results on the chlorinated aromatic hydrocarbons of the high-temperature, homogeneous gas-phase reactions of mixture of 2,4,6-T<sub>3</sub>CP and phthalate plasticizer. The various factors, such as temperature, mixing ratio, and kinds of phthalate esters for the formation of T<sub>4</sub>CDD during combustion of 2,4,6-T<sub>3</sub>CP were also studied.

## Materials and Methods

### Materials

Experiments were performed using 2,4,6-T<sub>3</sub>CP, phthalic acid anhydride, and phthalate plasticizer. Abbreviation of co-existent organic compounds used in this study was summarized in Table 1. These samples were obtained from Tokyo chemical industry co., Ltd. and their purities were over 98%, respectively. No dioxin compounds as impurities were detected in the starting materials before thermal treatments. All the solvents were for pesticide residue and polychlorinated biphenyl analysis grade and obtained from Wako pure chemical industries, Ltd.

Table 1. Abbreviation of co-existent organic compounds used in this study

Straight-chain esters	
DMP	Dimethyl phthalate
DEP	Diethyl phthalate
DProP	Di-n-propyl phthalate
DBP	Di-n-butyl phthalate
DHxP	Di-n-hexyl phthalate
DOP	Di-n-octyl phthalate
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Branched-chain esters	
DIBP	Diisobutyl phthalate
DEHP	Di(2-ethylhexyl) phthalate
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Anhydride	
PAA	Phthalic acid anhydride

### Combustion

A laminar flow, isothermal quartz reaction tube (100 mm in length and 20 mm in diameter) was used to study formation of dioxin related compounds from each material. Five hundred  $\mu\text{l}$  of each material dissolved in acetone (2,4,6- $\text{T}_3\text{CP}$ ; 50  $\text{mmol l}^{-1}$ , co-existent organic compounds; 0.05 – 5  $\text{mmol l}^{-1}$ ) were placed on a quartz sample boat and dried at room temperature. Then, quartz sample boat was loaded into the preheated quartz reaction tube and heated 3 minutes in an air stream. Through the heating, the air flow was regulated to hold the resident time constant. The resident time of the exhaust gas was approximately 20 seconds. The evolved gaseous products were introduced to the water and ethanol traps in an ice bath and quenched. Water trap acidified to pH 2 with HCl and salted out with 15 g of NaCl was extracted twice with diethylether 40 ml. After cooling to room temperature, the reaction tube was rinsed with diethylether and it was mixed with diethylether extract from the water trap. The combined solvent was concentrated to approximately 1 ml by a rotary evaporator and then concentrated to 0.1 ml under dry nitrogen gas stream. *p*-Chlorophenol- $\text{d}_4$  and phenanthrene- $\text{d}_{10}$  were added to the concentrate as internal standard substances and the solvent was adjusted to 1 ml with n-hexane.

### Analysis

Qualitify and quantify of combustion products was accomplished with Varian CP-3800 gas chromatograph equipped with fused silica capillary column (VF-5ms, 30  $\text{m} \times 0.25$  mm i.d., 0.25  $\mu\text{m}$  film thickness) with Saturn 2200 mass spectrometer. The column oven temperature was programmed as follows: initially held at 60°C for 5 min, 60-200°C at a rate of 10°C/min, 200-280°C at a rate of 4°C/min, and finally held at 280°C for 5 min.

## **Results and Discussion**

### Suppression of $\text{T}_4\text{CDD}$ formation by mixing DEHP to 2,4,6- $\text{T}_3\text{CP}$

Three kinds of starting materials; Non-mixing 2,4,6- $\text{T}_3\text{CP}$ , solutions which consists of 100:1 (1%) or 10:1 (10%) mixture of 2,4,6- $\text{T}_3\text{CP}$  with DEHP in the molar ratio, were combusted. Various kinds of compounds, such as PCBzs, PCPs PCDFs, and PCDDs on the combustion of 2,4,6- $\text{T}_3\text{CP}$ . Although 2,4,6- $\text{T}_3\text{CP}$  remained at the temperature below 750°C, DEHP decomposed completely at all the temperature in this study. Fig. 1 shows the influence of mixing DEHP for the combustion of 2,4,6- $\text{T}_3\text{CP}$ , which presented the yield of  $\text{T}_4\text{CDD}/2,4,6\text{-T}_3\text{CP}$  during combustion of starting materials versus temperature. In the case of combustion of 2,4,6- $\text{T}_3\text{CP}$  without DEHP, formation of  $\text{T}_4\text{CDD}$  was detected over the temperature range of 550°C to 750°C. The maximum molar yield of  $\text{T}_4\text{CDD}$  was 38.1  $\text{mmol/mol}$ , which observed combustion of 2,4,6- $\text{T}_3\text{CP}$  without DEHP at 650°C. When the DEHP 1% mixture combusted, there was no difference in the yield of  $\text{T}_4\text{CDD}$ , as compared with combustion of 2,4,6- $\text{T}_3\text{CP}$  without DEHP at the temperature above 700°C. However, remarkable decreasing of yield of  $\text{T}_4\text{CDD}$  was appeared at the temperature below 650°C. The yield of  $\text{T}_4\text{CDD}$  during combustion of DEHP 1% mixture at 650°C was 4.86  $\text{mmol/mol}$ , and reduced by approximately 87%, as compared with combustion of 2,4,6- $\text{T}_3\text{CP}$  without DEHP at 650°C. Furthermore, the yield of  $\text{T}_4\text{CDD}$  decreased at all the temperatures we experimented when the amount of DEHP in the mixture was increased to 10%. Fig. 2 indicates the influence of DEHP ratio in the mixture of 2,4,6- $\text{T}_3\text{CP}$  and DEHP for the formation of  $\text{T}_4\text{CDD}$ . Up to 1% of DEHP mixing ratio, the suppression effects increased sharply with increasing the DEHP mixing ratio. Only 0.1% of DEHP mixed with 2,4,6- $\text{T}_3\text{CP}$  reduced the formation of  $\text{T}_4\text{CDD}$  by 52.2%. On the other hand, the residual ratio of 2,4,6- $\text{T}_3\text{CP}$  during combustion of DEHP mixture was higher than that of non-mixing 2,4,6- $\text{T}_3\text{CP}$ . The residual ratio of 2,4,6- $\text{T}_3\text{CP}$  during combustion of DEHP 1% mixture was 46.3%, and that of non-mixing 2,4,6- $\text{T}_3\text{CP}$  was 12.8%. This tendency was remarkably observed at high temperature. Although almost all the starting materials were decomposed at 700°C on the combustion of 2,4,6- $\text{T}_3\text{CP}$  without DEHP, 2,4,6- $\text{T}_3\text{CP}$  remained even 750°C when DEHP was mixed with 2,4,6- $\text{T}_3\text{CP}$ . This result suggested that co-existence of DEHP with 2,4,6- $\text{T}_3\text{CP}$  suppressed the dimerization of 2,4,6- $\text{T}_3\text{CP}$ . In addition, all of the yields of dimers, such as PCDDs or PCDFs, except for DCDF decreased by almost 65-75% or not detected. DCDF was only detected in the case of combustion of DEHP mixture. In contrast, yields of PCPs, especially DCP, increased remarkably. Kim et al.<sup>18)</sup> reported that DCDF generated during combustion of DCP. Therefore DEHP would stimulate the dechlorination of  $\text{T}_3\text{CP}$ , and DCDF would generate from DCP combustion. Suppression mechanism of dimerization might be due to dechlorination of 2,4,6- $\text{T}_3\text{CP}$ .

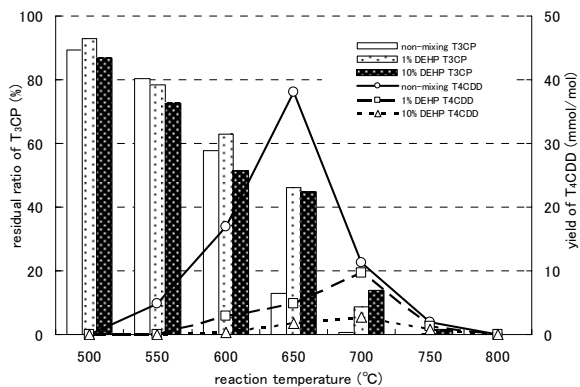


Fig. 1. Residual ratio of 2,4,6-T<sub>3</sub>CP and yield of T<sub>4</sub>CDD during combustion of 2,4,6-T<sub>3</sub>CP as a function of reaction temperature.

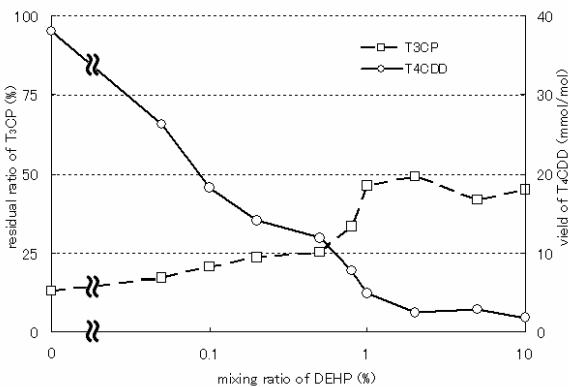


Fig. 2. Residual ratio of 2,4,6-T<sub>3</sub>CP and yield of T<sub>4</sub>CDD during combustion of mixture of 2,4,6-T<sub>3</sub>CP and DEHP at 650°C as a function of mixing ratio of DEHP.

### Influence of ester chain length of phthalate plasticizers for the suppression of T<sub>4</sub>CDD formation

Various kinds of phthalate plasticizers were combusted with 2,4,6-T<sub>3</sub>CP to clarify the influence of ester chain length on the suppression of T<sub>4</sub>CDD formation during combustion of 2,4,6-T<sub>3</sub>CP. Six kinds of straight-chain esters, two kinds of branched-chain esters and phthalic acid anhydride were tested as co-existent organic compounds in this study. Each co-existent organic compound was mixed with 2,4,6-T<sub>3</sub>CP in the combination ratio of 50:1 in the molar ratio. Fig. 3 shows the yield of T<sub>4</sub>CDD during combustion of each mixture at 650°C. There were few differences in the yield of T<sub>4</sub>CDD during combustion of PAA mixture, compared with combustion of 2,4,6-T<sub>3</sub>CP without co-existent organic compounds. This result suggested that every material didn't have suppression effects for the formation of PCDDs and phthalate structure hardly had suppression effects. In contrast, when straight-chain esters mixed to 2,4,6-T<sub>3</sub>CP, the suppression effects of formation of T<sub>4</sub>CDD was observed. The yield of T<sub>4</sub>CDD decreased with increasing of the carbon numbers of phthalate chain. There were few differences between suppression effect of DIBP and that of DBP, which had carbons of the same number. Moreover, the suppression effect of DOP and DEHP was almost the same. This result suggested that the suppression effects of formation of T<sub>4</sub>CDD by mixing of phthalate esters might depend on these ester chains and the carbon numbers of ester chain would affect on the suppression effects of PCDD/Fs formation.

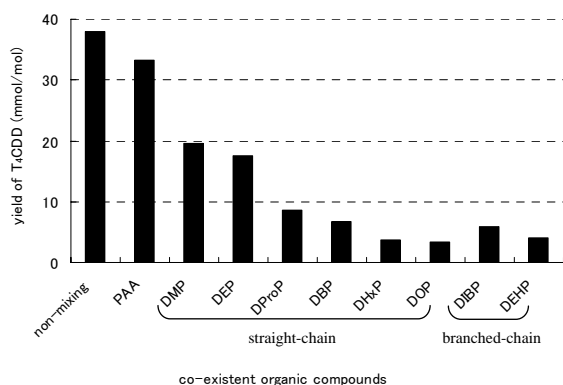


Fig. 3. Yield of T<sub>4</sub>CDD during combustion of 2,4,6-T<sub>3</sub>CP or mixture of 2,4,6-T<sub>3</sub>CP and co-existent organic compounds.

## Conclusion

The thermal reactions of 2,4,6-T<sub>3</sub>CP and mixture of 2,4,6-T<sub>3</sub>CP and phthalate plasticizer in an air stream was investigated using a silica flow reactor at resident time of 20 seconds and temperature from 500°C to 800°C. T<sub>4</sub>CDD was the most abundant products during combustion of 2,4,6-T<sub>3</sub>CP without co-existent organic compounds and observed at the temperature range of 550°C to 750°C, with maximum yields of T<sub>4</sub>CDD/2,4,6-T<sub>3</sub>CP of 38.1 mmol/mol at 650°C. While, mixing DEHP to 2,4,6-T<sub>3</sub>CP showed remarkable decreasing of yield of T<sub>4</sub>CDD at all the temperatures. The suppression effects were strongly dependent on the mixing ratio of phthalate plasticizer in the mixture. There is a positive relationship between carbon numbers of ester chain and suppression effects.

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