

SUPPRESSION OF PCDD/Fs FORMATIONS ON THE COMBUSTION PROCESS BECAUSE OF THE PRESENCE OF GASEOUS HYDROCARBONS

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Introduction

In the method of waste disposal, combustion process is one of the most useful techniques because it is sanitary and it can reduce the volume of garbage. However, the environmental contaminants generated during combustion process, especially dioxins become a serious problem. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are one of the most concerned contaminants because of their extreme toxicity and persistency in the environments. PCDD/Fs are mainly formed unintentionally during combustion process, with municipal solid waste incinerators (MSWIs) as one of the major sources¹⁾. In the MSWIs, PCDD/Fs formation was observed mainly in the combustion chamber and the electrostatic precipitator²⁾. It has been suggested that chlorinated aromatic compounds generated during combustion process, such as phenols and benzenes, contribute greatly to the formation of PCDD/Fs as precursors³⁾. Therefore, a lot of model combustion studies of which these precursors used as starting material had been accomplished^{4, 5)}.

In the past, a number of model combustion studies used chlorinated phenols as a PCDD/Fs precursor about formation mechanism of PCDD/Fs had been examined. It was suggested that chlorinated phenols were greatly contributed to the formation of PCDD/Fs. In these model combustion study, chlorinated phenols combusted alone. However, there are a variety of other compounds in the actual incinerator. So it is important to study the influence of these co-existent compounds for the PCDD/Fs formation reactions. In the previous study, we had carried out the combustion experiments of chlorinated phenols to elucidate the formation mechanisms of PCDD/Fs in the combustion chamber⁶⁾. As the result, it was suggested that the yields of PCDD/Fs during combustion of chlorinated phenols decreased in the case of co-combustion with particular organic compounds⁷⁾. Moreover, it was suggested that the suppression effect of PCDD/Fs formation was based on the hydrocarbon chain and the short-chain hydrocarbons which were easier to decompose indicated relatively high suppression ability. From these results, the cause of this suppression effect might be the pyrolytic products of hydrocarbons, such as hydrogen or gaseous low-molecular hydrocarbons.

In this study, we investigated the suppression effect of PCDD/Fs formation by addition of gaseous hydrocarbons. Combustion experiments that used chlorinated phenols as a PCDD/Fs precursor were accomplished. Congener distribution of PCDD/Fs and these related compounds formed during combustion of chlorinated phenols in the presence or absence of gaseous hydrocarbons were analyzed.

Materials and Methods

Materials

Combustion experiments were performed using 2,4,6-trichlorophenol (2,4,6-TCP), 2,4-dichlorophenol (2,4-DCP), 4-chlorophenol (4-MCP), and phenol obtained from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan); their purities were over 98%, respectively. Dioxin compounds were not present in the starting materials as impurities before thermal treatment. Dry air and gaseous hydrocarbon (methane gas balanced with nitrogen gas) were obtained from Nippon Megacare Co., Ltd. (Tokyo, Japan). All solvents used in this study were for pesticide residue and polychlorinated biphenyl analysis grade and were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). The commercial standard substances of PCDD/Fs were obtained from AccuStandard Inc. (New Heaven, USA).

Combustion

The combustion experiments of chlorinated phenols were performed as previously reported with minor modifications⁷. Fig. 1 illustrates a schematic diagram of the experimental apparatus. Experiments were performed using an electric furnace and a quartz reaction tube (400 mm in length and 20 mm in diameter). Five hundred microliter of starting material (50 mmol l^{-1}) dissolved in diethyl ether was placed in a quartz sample boat and dried at room temperature. Then, starting material was thermally treated in a dry air stream by placing the quartz sample boat at the center of a preheated quartz reaction tube and heating it for 3 min. During the heating process, the airflow was regulated to maintain a constant residence time for approximately 10 s. The gaseous products formed during the thermal reaction were cooled and quenched in water and salted out with 15 g of NaCl; then, it was extracted twice with 40 ml of diethyl ether. After cooling to room temperature, the residual compounds in the reaction tube and quartz sample boat were rinsed with Acetone/n-hexane (1:1, v/v). After dehydrated with anhydrous sodium sulfate, the combined solvent was concentrated to approximately 1 ml by using a rotary evaporator and then to 0.1 ml under a gentle stream of dry nitrogen gas. Phenanthrene- d_{10} was added to the concentrate as internal standard substances and the solvent was adjusted to 1 ml of toluene. Fifty microliter of analyte was derivatized with 50 μl of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) for GC/MS analysis. All experimental data in this study were expressed as an average of triplicate experiments, and the reproducibility of the experiments was within 10%.

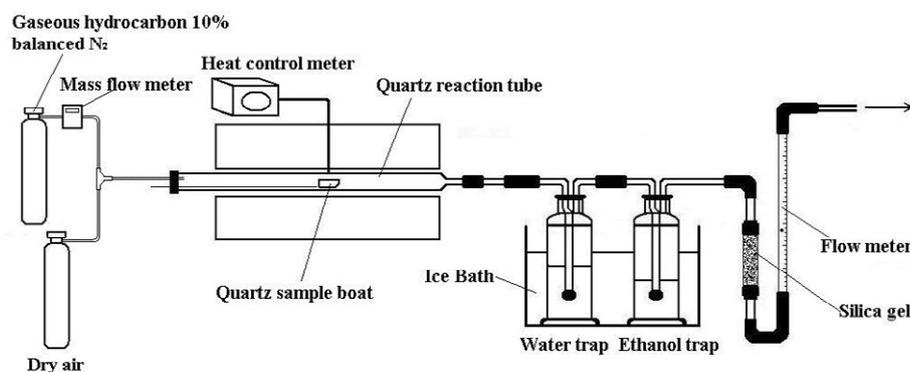


Fig. 1. Schematic diagram of experimental apparatus used for combustion of samples.

Analysis

Qualification of the combustion products was performed using a Varian CP-3800 gas chromatograph equipped with a fused silica capillary column (VF-5ms, $30 \text{ m} \times 0.25 \text{ mm i.d.}$, $0.25 \mu\text{m}$ film thickness) coupled to a Saturn 2200 ion-trap mass spectrometer (Varian, Walnut Creek, CA, USA). The column oven temperature was programmed as follows: $40 \text{ }^\circ\text{C}$ for 3 min (initially), $40\text{-}160 \text{ }^\circ\text{C}$ at a rate of $25 \text{ }^\circ\text{C min}^{-1}$, $160\text{-}300 \text{ }^\circ\text{C}$ at a rate of $10 \text{ }^\circ\text{C min}^{-1}$ (held at $300 \text{ }^\circ\text{C}$ for 5 min). Helium was used as carrier gas at a constant flow-rate of 1 ml min^{-1} . The injector temperature was kept at $280 \text{ }^\circ\text{C}$, and $1 \mu\text{l}$ of each sample was injected in the splitless injection mode (0.75 min). Quantification of the combustion products was carried out in the tandem mode (MS-MS). Calibration curves for the quantification of combustion products were determined by injecting solutions of commercial standard substances. In the case of PCDD/Fs, quantification was determined for a specific isomer and then applied to all the isomers having the same number of chlorine atoms.

Results and Discussion

When gaseous hydrocarbon was combusted alone, aromatic compounds were not observed in our experimental conditions. Therefore, the combustion products originated from gaseous hydrocarbon could be discounted in this study.

2,4,6-TCP was combusted in the dry air stream with or without methane gas at temperature ranging from 450 to 850°C. Fig. 2 shows the total yields of PCDD/Fs and residual ratio of starting material during combustion of 2,4,6-TCP, as a function of combustion temperature. When 2,4,6-TCP combusted in the dry air stream without methane, PCDD/Fs were formed at the temperature between 500 to 800°C. The maximum molar yields of PCDD/Fs was 30.1 mmol mol⁻¹ observed during the combustion at 650°C. The major products of PCDD/Fs were 1,3,6,8-/1,3,7,9-TCDD, and the minor products were tri to penta chlorinated PCDD/Fs.

When 2,4,6-TCP combusted in the condition of methane mixed to dry air, the yields of PCDD/Fs decreased remarkably as compared to the combustion in a dry air stream. The 1% (v/v %) of methane added to a dry air stream reduced the PCDD/Fs yields by approximately 67% on the combustion of 2,4,6-TCP at 650°C. In contrast, the residual ratio of starting material was relatively higher on the combustion of 2,4,6-TCP in a dry air stream with methane. Fig. 3 shows the congener distribution of combustion products formed during the combustion of 2,4,6-TCP in the dry air stream with or without methane at 650°C.

The yields of high-chlorinated compounds and dimmers, such as tri to penta chlorinated PCDD/Fs were decreased with an increase the mixing ratio of methane. In contrast, low-chlorinated phenols and benzenes were increased. These results suggested that methane suppressed the dimerization of 2,4,6-TCP and stimulated the dechlorination of 2,4,6-TCP. DCDF was not observed on the combustion of 2,4,6-TCP in the absence of methane, it was only detected on the combustion with methane. The formation pathway of DCDF would be the dimerization of low-chlorinated phenol, such as 4-MCP. This tendency was similar to co-combustion of 2,4,6-TCP and phthalate esters. Therefore, the cause of suppression effect of PCDD/Fs formation by co-existing organic compound was gaseous hydrocarbons which formed during organic compounds.

Same combustion experiments were accomplished using 2,4-DCP, 4-MCP and phenol as a starting materials. The combustion temperature was set to 650°C,

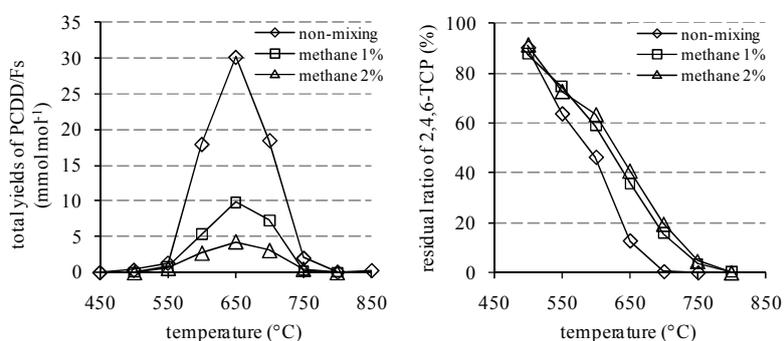


Fig. 2. Total yields of T₄CDDs (A) and residual ratio of 2,4,6-TCP (B) during combustion of 2,4,6-TCP on a dry air stream with or without methane, as a function of temperature.

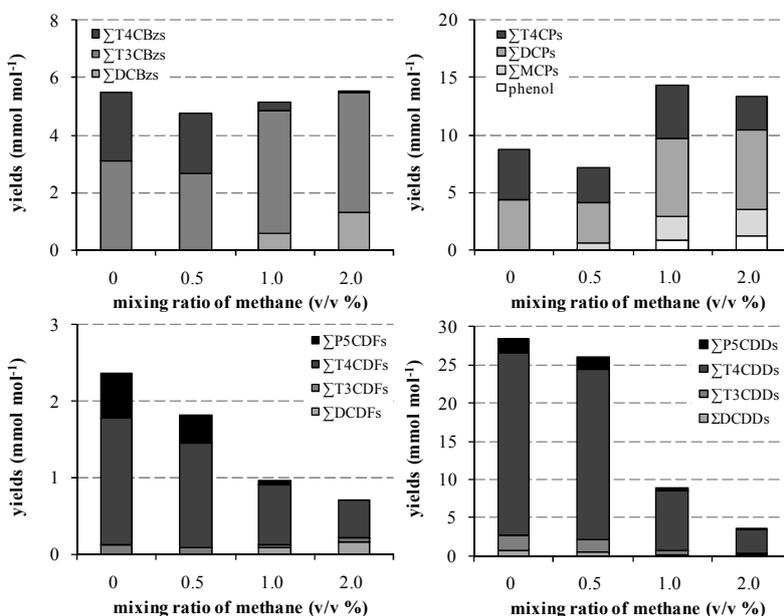


Fig. 3. Congener distribution of combustion products, PCBzs (A), PCPs (B), PCDFs (C) and PCDDs (D) during combustion of 2,4,6-TCP on a dry air stream with or without methane at 650°C.

which was the maximum yields of PCDD/Fs was observed in the experiment of 2,4,6-TCP. The major products of PCDD/Fs on the combustion of 2,4-DCP was 2,4,6,8-TCDF and 2,7-/2,8-DCDD, and the minor products were tri chlorinated DD/Fs. The total yields of PCDD/Fs during combustion of 2,4-DCP on a dry air stream without methane at 650°C was 5.33 mmol mol⁻¹. The major products of PCDD/Fs on the combustion of 4-MCP was 2,8-DCDF, and the minor products was 2-MCDF. The total yields of PCDD/Fs during combustion of 4-MCP on a dry air stream without methane at 650°C was 26.4 mmol mol⁻¹. DF was only detected on the combustion of phenol and the yield was 3.26 mmol mol⁻¹. The PCDD/Fs isomer patterns of the combustion products were similar to the previous studies.

Combustion experiments of low-chlorinated phenols were accomplished in the condition of slightly mixing the methane with dry air stream. The total yields of PCDD/Fs and suppressing ratio of PCDD/Fs were summarized in Table 1. Remarkable suppressing effect on the formation of PCDD/Fs was observed when the methane was mixed to dry air by 1% or more. On the combustion of 2,4-DCP or 4-MCP with methane, the yields of dechlorination by-products and the related compounds were increased with an increase the mixing ratio of methane. Relatively high suppressing effect by methane was observed on the combustion of high-chlorinated phenols. We proposed the two prospective pathways: (1) suppression of phenoxy radical formation and prevent the condensation of chlorinated phenols, (2) stimulation of dechlorination. In case of combustion of 2,4,6-TCP, it was thought that the dechlorination made a large contribution to suppression of PCDD/Fs formations.

Table 1. Total yields of PCDD/Fs during combustion of chlorinated phenols and inhibition ratio of PCDD/Fs formations by addition of the methane. (mmol mol⁻¹)

starting material	mixing ratio of methane (v/v %)			
	0	0.5	1.0	2.0
2,4,6-TCP	30.1	28.4 (94.2%)	9.78 (32.5%)	4.10 (13.6%)
2,4-DCP	5.33	5.53 (103.7%)	2.99 (56.1%)	1.17 (21.9%)
4-MCP	26.3	23.5 (89.1%)	16.8 (63.8%)	7.26 (27.6%)
phenol	3.26	3.16 (96.9%)	2.15 (66.0%)	0.91 (27.9%)

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