

# Evaluation of gas-particle partition of dioxins in flue gas I: Evaluation of gasification behavior of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in fly ash by thermal treatment

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## Abstract

The gasification behavior of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in fly ash by thermal treatment has been investigated to estimate gas-particle partition in flue gas. The results obtained in thermal experiments under various conditions showed that gasification of PCDD/Fs depends on air flow rate and treatment weight of fly ash as well as treatment temperature. On the other hand, the results obtained in the thermal experiments using dioxin-free fly ash revealed that during thermal treatment, the de novo synthesis, gasification, and decomposition of PCDFs proceeded at different rates. This difference in the reaction rates indicates that thermal treatment time is also a factor in determining the gas-particle partition of PCDD/Fs in fly ash. Therefore, reasonable thermal treatment conditions were established and applied to three ash samples. For all samples, PCDD/Fs started to gasify at 350 °C treatment, whereas 53–98% of PCDD/F homologs gasified at 400 °C treatment, implying that gaseous PCDD/Fs are dominant in flue gas at temperatures in the range 350–400 °C regardless of particle concentration. © 2007 Elsevier B.V. All rights reserved.

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## 1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), major components of the so-called dioxins, are considered as highly toxic persistent organic pollutants. In Japan, the Ministry of the Environment revealed the contamination levels of PCDD/Fs in various environmental matrices around the country in an urgent monitoring campaign conducted in fiscal year 1998 [1]. In addition, the law concerning special measures against dioxins, introduced in January 2000, have been enforcing continuous environmental monitoring of PCDD/Fs on all prefectural and city governments;

therefore, the in-depth details of the current contamination levels became apparent. At present, development of emission control techniques [2–4], decomposition techniques [5], and statistical analysis of abundant data on their levels in environmental matrices [6,7] are in progress for PCDD/Fs.

In advanced countries, waste incineration activities were the most significant PCDD/F sources. However, since the past decade, high-performance PCDD/F emission abatement techniques have been developed. High-temperature combustion (900–1200 °C) is a primary method for PCDD/F abatement. Catalytic decomposition is also a potent abatement technique. Everaert et al. have reported the utility of catalytic decomposition of chlorinated hydrocarbons and PCDD/Fs using catalyst-coated sintered metal fleece, which allows low-cost operation and prevention of PCDD/F formation under low temperatures (250–350 °C) [8,9]. Prior to stack emission, PCDD/F

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residues in flue gas are almost entirely eliminated by entrained-phase (e.g., active carbon powder or lignite coke powder) adsorption and filtration with a fabric filter (bag filter) [10–12]. Installation of the above-mentioned PCDD/F abatement techniques has dramatically decreased PCDD/F emissions from municipal waste incinerators. On the other hand, other kinds of waste incinerators such as hazardous waste incinerators or hospital waste incinerators are considered as possible significant PCDD/Fs emission sources [13]. In addition, the “European Dioxin Air Emission Inventory Project” concluded that, in Europe, metallurgical processes such as iron ore sintering plants or electric arc furnaces for steel production are the most likely emission sources [14]. Therefore, the contribution of thermal processes to PCDD/F emission is still significant.

There are two major PCDD/F formation mechanisms in thermal processes that have been investigated by numerous researchers—a “de novo” mechanism from particulate carbon [15,16] and a precursor mechanism, which is the result of the polycondensation of precursors such as polychlorophenols, polychlorobenzene, or polychlorinated biphenyls [17–19]. A detailed comparison of these two mechanisms has been conducted by Everaert and Baeyens [20]. They have indicated that the de novo synthesis is several orders of magnitude faster than the precursor reaction, and that de novo synthesis is the dominant mechanism in actual thermal processes where conditions that favor precursor formation are not experienced. In all cases, the two reactions occur simultaneously and/or independently in a combustion process; therefore, it is important to improve combustion conditions for inhibition of the reactions.

Development of flue gas treatment technologies is also important to reduce PCDD/F emissions. PCDD/Fs in flue gas can exist in either the gaseous form or the particle-bound form; therefore, useable treatment technologies should effectively remove PCDD/Fs in both forms. In order to develop such technologies, gas-particle partition of PCDD/Fs in flue gas should be precisely understood. Further, information on the physical states of PCDD/Fs in flue gas helps us to accurately determine their concentration in that medium.

Behavior of PCDD/Fs produced in fly ash, such as gasification or decomposition, depends on various properties of the ash (e.g., elemental composition or carbon content). With respect to gasification, flue gas temperature is the most significant factor because gasification is mainly dominated by the vapor pressures of the PCDD/Fs [21]. Therefore, information on the correlation between gas temperature and behavior of PCDD/Fs in fly ash will help us to determine their physical states in flue gases at various temperatures. Some researchers have estimated the gasification behavior of PCDD/Fs in fly ash by thermal experiments; however, the reported results are inconsistent. For example, Altwicker et al. reported that, with 350 °C treatment of Ontario fly ash, 94% of PCDD/Fs were in the gaseous phase [22], whereas Addink et al. reported that only 28% were detected in their gaseous form even with 398 °C treatment [23]. Such a difference in results would be understandable when the difference in thermal experimental conditions is considered and the differences in the properties of the ash samples are examined. Therefore, reasonable experimental parameters should be estab-

lished in thermal experiments on fly ash. To our knowledge, no detailed evaluation of the influence of experimental parameters on gasification of PCDD/Fs in fly ash has been performed.

In this study, we evaluated the gasification behavior of PCDD/Fs in fly ash by thermal treatment. First, we evaluated the influence of some experimental parameters (amount of ash sample treated, air flow rate, and thermal treatment time) on gas-particle partition of PCDD/Fs in fly ash. Next, we evaluated gas-particle partition of PCDD/Fs by thermal experiments, in which each parameter was set according to the results of the above-mentioned experiments.

## 2. Experimental

### 2.1. Apparatus

Thermal treatment of fly ash samples was performed using a GC-12A gas chromatograph (Shimadzu Corp., Kyoto) column oven. During the thermal treatment, the gas flow rate was regulated with an FC-224 mass flow controller (GL Sciences, Tokyo). PCDD/Fs were analyzed by high-resolution gas chromatography/mass spectrometry (HRGC-HRMS) with an HP-6890 Plus (Agilent, Palo Alto, CA) gas chromatograph coupled to a JMS-700D mass spectrometer (JEOL, Tokyo), where the analytes were separated with a BPX-DXN (SGE, Austin, TX) capillary column. The levels of carbon (total carbon and inorganic carbon) and metal elements in fly ash were determined with an SSM-5000A + TOC-V<sub>CPN</sub> total organic carbon analyzer (Shimadzu) and a JSX-3202M (JEOL) X-ray fluorescence spectrometer, respectively.

### 2.2. Materials and reagents

For thermal treatment of fly ash, samples were packed into a VOST-trap glass tube (Supelco, 16 mm o.d., 14 mm i.d., 127 mm length). The analytes gasified from the heated fly ash were trapped in a deactivated stainless steel tube (Silcosteel<sup>®</sup>, GL Sciences, 1.6 mm o.d., 1.02 mm i.d., 1 m length) connected downstream from a VOST-trap. A GF-75 glass fiber filter (Toyo Roshi, Tokyo, 110 mm diameter, 0.3 μm particle retention) was used for filtration of HCl-treated fly ash.

All dioxin-analytical-grade solvents and adsorbents were purchased from either Wako Pure Chemical Industries (Osaka, Japan) or Kanto Chemicals (Tokyo, Japan). Sodium chloride for polychlorinated biphenyls (PCBs) analysis and analytical-grade sodium sulfate were purchased from Kanto. Sodium sulfate was heat treated at 600 °C prior to use in order to remove organic impurities.

PCDD/F standards, including <sup>13</sup>C-labeled congeners, were purchased from Wellington Laboratories (Ontario, Canada) or Cambridge Isotope Laboratories Inc. (Andover, MD). The abbreviations for the number of chlorine atoms are as follows: tetra (Te), penta (Pe), hexa (Hx), hepta (Hp), and octa (O). A surrogate solution (SuS) was prepared in toluene. This solution contained 17 <sup>13</sup>C-labeled 2,3,7,8-substituted PCDD/F congeners (2,3,7,8-TeCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-

Table 1  
Characteristics of the three ashes

	ESP-1	ESP-2	CT	N-CT
Facility Type	Stoker ESP <sup>a</sup> ash	Stoker ESP ash	Fluidized bed CT <sup>b</sup> ash	
Total carbon (% of dry substance)	2.8	3.2	0.70	– <sup>c</sup>
Inorganic carbon (% of dry substance)	0.48	0.21	0.65	–
Na <sub>2</sub> O (% of dry substance)	9.5	5.5	3.9	–
MgO (% of dry substance)	2.9	2.2	4.3	–
Al <sub>2</sub> O <sub>3</sub> (% of dry substance)	8.6	5.7	20	–
SiO <sub>2</sub> (% of dry substance)	12	8.0	28	–
Cl (% of dry substance)	19	17	2.0	–
K <sub>2</sub> O (% of dry substance)	7.2	5.0	2.5	–
CaO (% of dry substance)	24	43	26	–
Fe <sub>2</sub> O <sub>3</sub> (% of dry substance)	1.4	1.3	3.1	–
CuO (% of dry substance)	0.15	0.05	0.08	–
ZnO (% of dry substance)	1.4	1.1	0.28	–
PCDDs (ng g dry <sup>-1</sup> )	1400	150	8.1	<0.05
PCDFs (ng g dry <sup>-1</sup> )	1400	69	2.9	<0.05

<sup>a</sup> Electrostatic precipitator.

<sup>b</sup> Cooling tower.

<sup>c</sup> Not analyzed.

HpCDD, OCDD, 2,3,7,8-TeCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF, and OCDF), each at a concentration of 20 µg L<sup>-1</sup>, with the exception of <sup>13</sup>C-OCDD/F at 40 µg L<sup>-1</sup>. A recovery standards solution (RS) in nonane was prepared, which contained <sup>13</sup>C-labeled 1,2,7,8-TeCDF, 1,2,3,4,7-PeCDD, 1,2,3,4,6,9-HxCDF and 1,2,3,4,6,8,9-HpCDF, each at a concentration of 10 µg L<sup>-1</sup>.

Fly ash samples used in this study were as follows: (1) a fly ash sample for the intercalibration exercise organized by the Japanese Ministry of the Environment in FY 2001 (ESP-1), (2) a fly ash reference material JSAC0501, distributed by the Japan Society for Analytical Chemistry (ESP-2), and (3) a fly ash sample collected from a gas cooling tower in a municipal waste incinerator in Saitama, Japan (CT). In addition, CT thermally treated at 400 °C for 2 h under nitrogen stream in order to remove residual PCDD/Fs (N-CT) was also examined. The properties of each sample are shown in Table 1. Prior to use, the samples were dried in a desiccator with silica gel granules.

### 2.3. Thermal treatment of fly ash and PCDD/Fs analysis

A fly ash sample (0.1 or 0.5 g) dispersed in Na<sub>2</sub>SO<sub>4</sub> granules was packed into a VOST-trap tube. The VOST tube was connected to a mass flow controller using a stainless steel tube, and a Silcosteel<sup>®</sup> tube was connected downstream of the VOST tube. In a preliminary recovery experiment, it was confirmed that all amounts of gasified <sup>13</sup>C-PCDD/Fs were recovered from the Silcosteel<sup>®</sup> tube. Therefore, in this study, an impinger (20 mm i.d., 150 mm height) with 30 mL of toluene, cooled in an ice bath, was placed downstream of the Silcosteel<sup>®</sup> tube as a backup. A fly ash sample was heated under a stream of

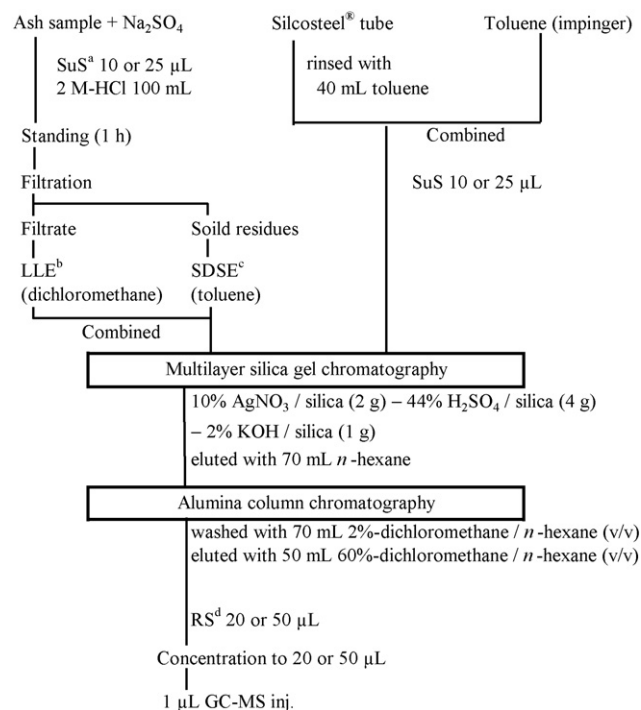


Fig. 1. Quantitative procedure for determination of PCDD/Fs in the particle-bound form (in fly ash) and in the gaseous form (from the Silcosteel<sup>®</sup> tube or the impinger) after thermal treatment of fly ash. <sup>a</sup>Surrogate solution. <sup>b</sup>Liquid–liquid extraction. <sup>c</sup>Soxhlet/Dean–Stark extraction. <sup>d</sup>Recovery standards solution.

ultra pure air or nitrogen (>99.99995% purity). The flow rate was adjusted to 160 or 800 mL min<sup>-1</sup> at the heating temperature.

A flow chart for the sample treatment procedure after thermal treatment (i.e., extraction of PCDD/Fs from the treated ash, a Silcosteel<sup>®</sup> tube and an impinger, and clean-up) is shown in Fig. 1. PCDD/Fs in the particle-bound form (i.e., analytes detected from the fly ash) and in the gaseous form (i.e., analytes detected from the Silcosteel<sup>®</sup> tube and the impinger) were individually determined. Briefly, fly ash was spiked with SuS, HCl-treated, and Soxhlet extracted with toluene. Analytes adsorbed on the inside wall of the Silcosteel<sup>®</sup> tube were recovered with toluene, and mixed with toluene in an impinger followed by the addition of SuS. Each extract was redissolved in *n*-hexane and cleaned using chromatography on a multilayer silica gel column and an alumina column according to the procedure outlined in Fig. 1. Each eluate was spiked with RS, concentrated and dissolved in 20 or 50 µL *n*-nonane.

### 2.4. HRGC-HRMS analysis

An aliquot (1 µL) of the resulting solution was injected into the GC, which was equipped with a BPX-DXN column. The detailed conditions for GC–MS analysis and the quantification procedure have been described elsewhere [24]. Recovery of the surrogates was calculated using the ratio between their peak areas against that of the corresponding recovery standard and by using the corresponding relative response factor.

## 2.5. Accuracy control

The glassware used in this study was rinsed with acetone and *n*-hexane prior to use. A glass fiber filter was heated at 450 °C for 4 h to remove analyte residues.

Variations in the HRGC-HRMS analysis were estimated by multiple determinations of an identical resulting solution of a fly ash sample. The relative standard deviations of every PCDD/F homolog were confirmed to be less than 5%.

An instrumental blank was measured prior to the GC-MS analysis by injecting clean *n*-nonane, and it was confirmed that no analyte was detectable. Analysis of a method blank was performed for each sample batch to confirm that the background was sufficiently low. Throughout this study, the quantities of all of the method blanks were maintained low at 0.01 ng g<sup>-1</sup> for all PCDD/F homologs. The method blank values were subtracted from all quantitative values of each sample.

All of the sub-samples were spiked with SuS (including the blank tests), and the recoveries of the standards were confirmed before data processing. The recoveries from all of the samples fell within the range of 70–110%, proving the validity of the analytical method.

Prior to this study, the assay accuracy was estimated by determining the fly ash intercalibration sample, and the results are described elsewhere [24]. Briefly, for all of the 2,3,7,8-chlorinated PCDD/F congeners and homologs, the absolute values of the *z*-score were below 2, proving the high accuracy of the determinations.

## 3. Results and discussion

### 3.1. Effects of various parameters of the thermal experiments on gasification of PCDD/Fs in fly ash

#### 3.1.1. Treated amount of ash and air flow rate

In most of the previous reports on evaluation of gasification behavior of PCDD/Fs in fly ash by thermal treatment, an ash sample was placed on a heating boat [25,26] or was packed in a heating tube [22,23]. As fly ash has low thermal conductivity, an excess of sample amount may result in insufficient thermal action into the sample irrespective of the method employed. On the other hand, fly ash particles in flue gas are considered to be exposed to a strong thermal action because the particle density in flue gas is quite low. Therefore, a thermal experiment performed to elucidate the physical state of PCDD/Fs in flue gas should establish reasonable experimental conditions to ensure that thermal conditions act on the fly ash sample. In this study, we employed a thermal experiment in which ash particles were dispersed in Na<sub>2</sub>SO<sub>4</sub> granules in a heating tube to increase the thermal activity on the fly ash particles. In addition, we employed air as the flow gas because PCDD/Fs decomposed when nitrogen was used as the flow gas.

Fig. 2 shows the gasification ratios of PCDD/Fs by thermal treatment of CT ash with identical temperatures (400 °C) and various sample amounts and air flow rates. For the three kinds of experiments conducted, the gaseous form ratios decreased with increasing number of substituted chlorines, which would

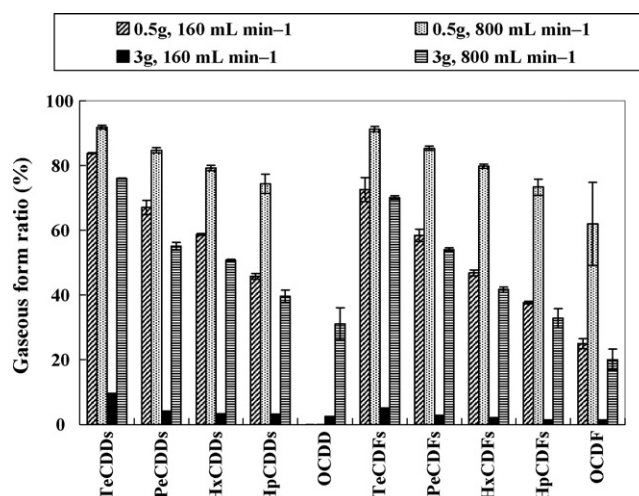


Fig. 2. Ratios of gaseous PCDD/F homologs (to the total amounts) by various charged amounts of ash (g) and air flow (mL min<sup>-1</sup>) in thermal treatment experiments using CT. Temperature and heating period were 400 °C and 2 h, respectively. The confidence interval at the top of each bar chart indicates mean  $\pm$  standard deviation of duplicate determinations. The missing data on OCDD are attributable to unsatisfactory sensitivity (severe degradation of the analyte).

be attributable to the lower vapor pressure of higher-chlorinated PCDD/Fs. In experiments in which sample amount and air flow were 0.5 g and 800 mL min<sup>-1</sup>, respectively, gasification ratios were high (62–92%), whereas the ratios of higher-chlorinated PCDD/Fs (i.e., HpCDD/Fs and OCDD/F) were reduced to 20–46% when only the sample amount was changed to 3 g or only the air flow rate was changed to 160 mL min<sup>-1</sup>. In addition, when both the sample amount and the air flow rate were changed to 3 g and 160 mL min<sup>-1</sup>, respectively, gasification ratios were apparently reduced (1.1–10%) for all PCDD/F homologs. The results indicate that both the amount of ash packed in a tube and the gas flow rate influence the gasification of PCDD/Fs in fly ash. Altwicker et al. have also reported that no shift of particle-bound PCDD/Fs to gaseous form occurs at a low gas flow rate [22]. A gas flow rate to sample weight (B/W rate) above a certain level would be required for gasification. Fig. 3 shows the gasification ratios of PCDD/Fs by thermal treatment of ESP-1 with identical sample amounts (0.1 g), various heating temperatures, and air flow rates. When the temperature and air flow were set at 400 °C and 160 mL min<sup>-1</sup>, respectively (1.6 L min<sup>-1</sup> g<sup>-1</sup> as B/W rate), gasification ratios were high (82–98%) for all homologs. However, when the temperature and air flow were changed to 350 °C and 800 mL min<sup>-1</sup>, respectively, the ratios were lowered to below 30% despite a much higher B/W rate (8 L min<sup>-1</sup> g<sup>-1</sup>). The results in Fig. 3 indicate that temperature is more influential than sample weight and air flow rate (it will probably be the most influential parameter).

#### 3.1.2. Heating period

In the thermal experiments reported by Altwicker et al. [22] and Addink et al. [23], the total PCDD/F amounts in the gaseous form and particle-bound form after thermal treatment were apparently different from the amounts in the original fly ash.

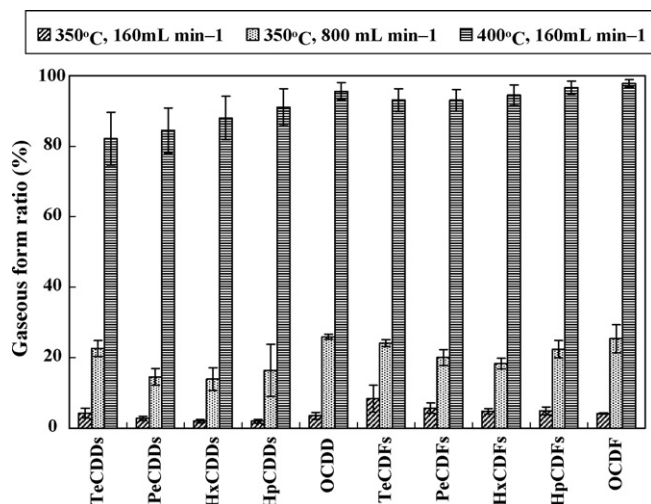


Fig. 3. Ratios of gaseous PCDD/F homologs (to total amounts) at various temperatures and air flows ( $\text{mL min}^{-1}$ ) in thermal treatment experiments using ESP-1. The charged amount of ash was 0.1 g. The confidence interval at the top of each bar chart indicates mean  $\pm$  standard deviation of duplicate determinations.

These results indicate that, in addition to gasification, formation and/or decomposition of PCDD/Fs occurred during thermal treatment of fly ash.

Possible origins of PCDD/Fs in fly ash are as follows: (i) de novo formation in fly ash, (ii) condensation of some precursors that have existed in the fly ash or as the gaseous form, (iii) adsorption of gaseous PCDD/Fs onto fly ash particles. PCDD/Fs of different origins may exist in different physical states and therefore may exhibit different gasification behaviors. In such cases, it may be difficult to interpret a complex gasification behavior in the three physical states. Therefore, we first prepared PCDD/F-free fly ash (N-CT) by thermal treatment of CT ash with nitrogen flow, and evaluated the behavior of PCDD/Fs newly produced by

thermal treatment of the N-CT under air flow. In the preliminary experiments, we confirmed that a large amount of PCDFs and a small amount of PCDDs were produced by thermal treatment of N-CT under air flow. The PCDFs would only be produced by de novo formation and not from precursors for the following reasons: (i) it has been reported that the PCDFs/PCDDs ratio is  $>1$  for de novo synthesis whereas the ratio is  $<1$  for the precursor mechanism [20], supporting the absence of the precursor mechanism during the thermal treatment, (ii) N-CT was obtained by heating CT at  $400^\circ\text{C}$  under a nitrogen flow, and precursors such as chlorobenzenes or chlorophenols definitely vanish from the ash under these conditions by decomposition or gasification.

Using this procedure, the gasification behavior of PCDFs derived from a single origin can be evaluated. Therefore, the procedure would not only make it possible to easily interpret the obtained results but also give reliable evaluation of gasification behavior.

Fig. 4 shows the relationship between heating periods and detected amounts (gaseous, particle-bound and total) and the gas-particle partition of PCDFs produced (temperature:  $400^\circ\text{C}$ , sample amount: 0.5 g, air flow:  $800\text{ mL min}^{-1}$ ). As shown in Fig. 4a, a significant decrease in particle-bound PCDF amounts was observed during 15–30 min of heating. The decrease was gradual after 30 min of heating, and the amounts were below their quantification limits after 2 h of heating. On the other hand, with respect to the gaseous PCDFs amounts, a significant increase was observed during 15–30 min of heating, whereas no increase was observed thereafter (Fig. 4b). Table 2 shows the decrease in the amounts of the particle-bound form (P), the increase in the amounts of the gaseous form (G), and G/P% for each PCDF homolog during the 15–30 min and 30–60 min heating periods. For all homologs, a remarkable difference in G/P% was observed between the two heating periods. The loss of the particle-bound form by gasification accounted for 28–103% of

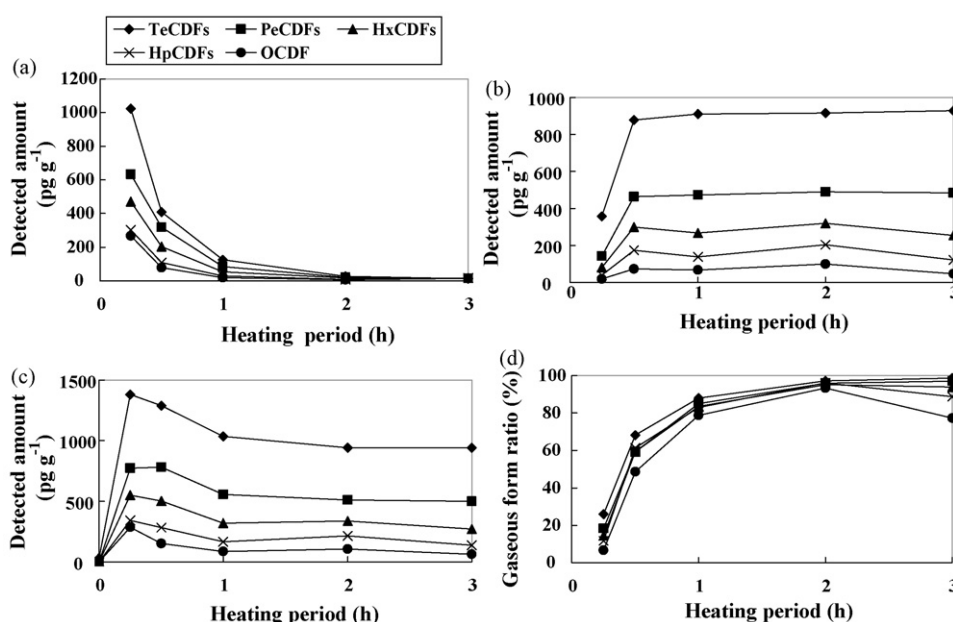


Fig. 4. Transition of the detected amounts and gas-particle partitions of the PCDFs produced by thermal treatment of N-CT (0.5 g) at  $400^\circ\text{C}$ : (a) particle-bound form, (b) gaseous form, (c) total amounts, (d) ratios of gaseous form.

Table 2  
Decrease and increase in amounts of the produced PCDFs in the particle-bound and gaseous forms by thermal treatment of N-CT (0.5 g) at 400 °C

	15–30 min of heating period			30–60 min of heating period		
	Decrease in PM-bound form (pg) (P)	Increase in gaseous form (pg) (G)	G/P%	Decrease in PM-bound form (pg) (P)	Increase in gaseous form (pg) (G)	G/P%
TeCDFs	610	520	85	290	31	11
PeCDFs	310	320	103	230	9	4.0
HxCDFs	270	220	81	150	~0	~0
HpCDFs	190	130	68	81	~0	~0
OCDF	190	54	28	59	~0	~0

the total loss during the 15–30 min period. The higher G/P% for lower-chlorinated PCDFs can be attributed to their ease of gasification, that is, their higher vapor pressures. In addition, the higher G/P% of PeCDFs (103%) than that of TeCDFs (85%) can be attributed to conversion of a portion of gasified TeCDFs to PeCDFs by chlorination during thermal treatment. On the other hand, most of the loss of the particle-bound form was attributed to decomposition on the ash during the 30–60 min period. These results indicate that the PCDFs produced would take two forms, that is, a readily gasified form and a hard-to-gasify form, where the latter form would be subject to decomposition. Such a difference in forms on the fly ash can be attributed to the difference in some of the properties of the formation sites on the ash particle. Altwicker has proposed two kinds of active sites in fly ash for the formation, gasification, and decomposition of PCDD/Fs, that is, active sites and superactive sites. The former are associated with long-time scale kinetics (minutes) and the latter with short-time scale kinetics (seconds) [27]. Such a difference in activities can be attributed to the presence of elements such as carbon or metals in fly ash [28–30], and such properties of the active sites of PCDFs on ash, as well as their vapor pressures, may be responsible for the degree of gasification and degradation of the PCDFs produced. In any event, it was considered that the PCDFs produced in the readily gasified form would be rapidly gasified within 15 min of heating, and those in the hard-to-gasify form would be slowly decomposed on the ash particles.

The total amounts of each PCDF homologs were maximal at 15 min of heating, and showed a gradual decrease during 15–60 min of heating (Fig. 4c). The results obtained by changing the temperature and air flow to 350 °C and 160 mL min<sup>-1</sup>, respectively (under these conditions, all PCDFs were detected as the particle-bound form), are shown in Fig. 5 as a reference. The amount of total PCDFs produced reached a ceiling at 2 h heating possibly due to the depletion of raw materials, and the ceiling amount was almost equivalent to the amount produced that is described in Fig. 4c. These results indicate that the amount of PCDFs produced at 15 min heating (Fig. 4c) would be equivalent to the maximal producible amount of PCDFs from 0.5 g N-CT. Therefore, we considered that de novo formation of PCDFs would be completed within 15 min of heating (Fig. 4c).

The results in Fig. 4 indicate that three reactions with different rates, that is, rapid de novo formation, moderate gasification of easily gasified form, and slow decomposition of hard-to-gasify form simultaneously occur during thermal treatment of the ash. The increase in the ratios of the gaseous form of PCDF

homologs during the 30–60 min heating period (see Fig. 4d) can be attributed to decomposition of PCDFs which were still adsorbed on the fly ash, because no increase in the amount of gaseous PCDFs was observed during the period. Therefore, it was concluded that, by heating over a certain period, apparent gas-particle partition of PCDD/Fs can vary even after the partition achieved equilibrium.

### 3.2. Evaluation of gasification of PCDD/Fs in fly ash by thermal treatment

The results shown in Section 3.1 indicate that gasification ratios of PCDD/Fs in fly ash in thermal experiments are influenced by experimental conditions such as sample amount, gas flow rate or heating period, and heating temperature. Therefore, when performing a thermal experiment using fly ash, it is necessary to set experimental conditions in which each parameter is reasonably established according to the aim of the experiment. This study aims at evaluation of gasification behavior of PCDD/Fs in fly ash to determine their gas-particle partition in flue gas. In this case, experimental conditions should simulate the conditions encountered in flue gas pathways. However, establishment of such conditions is extremely difficult because gasification behavior in real flue gas depends on the various parameters of the gas.

In a combustion process equipped with a high-temperature combustion chamber (over 800 °C), PCDD/Fs formation exclusively occurs in a post-combustion zone. It has been reported that

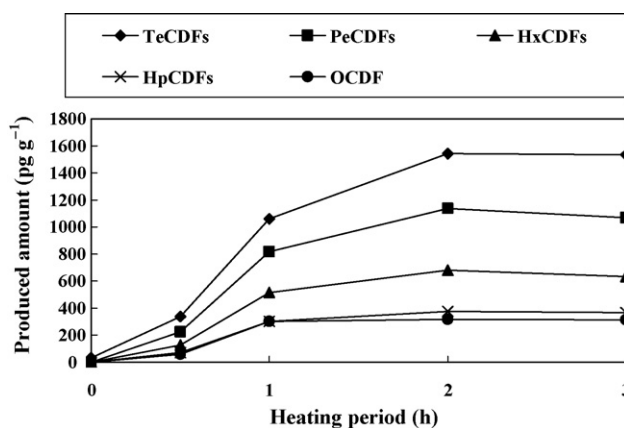


Fig. 5. Transition of the amounts of PCDFs produced by thermal treatment of N-CT (0.5 g) at 350 °C.

Table 3  
Gas-particle partitioning of PCDD/F homologs on three fly ash samples by thermal treatment

	Original ash (ng g <sup>-1</sup> )	300 °C			350 °C-1			350 °C-2			400 °C-1			400 °C-2		
		G <sup>a</sup>	P <sup>b</sup>	G/Sum% <sup>c</sup>	G	P	G/Sum%	G	P	G/Sum%	G	P	G/Sum%	G	P	G/Sum%
<b>(ESP-1)</b>																
TeCDDs	57	<0.02	52	~0	2.0	58	3.3	2.7	50	5.2	19	2.8	87	14	4.3	77
PeCDDs	200	<0.05	140	~0	2.6	110	2.3	4.0	120	3.2	34	4.3	89	25	6.3	80
HxCDDs	410	<0.06	300	~0	3.5	210	1.6	5.8	240	2.4	54	4.5	92	43	8.5	84
HpCDDs	410	<0.05	300	~0	3.4	210	1.6	5.9	240	2.4	50	2.8	95	44	6.4	87
OCDD	300	<0.3	190	~0	5.2	180	2.8	10	240	4.2	78	2.2	97	87	5.8	94
TeCDFs	230	<0.02	200	~0	17	280	5.7	36	290	11	410	20	95	290	29	91
PeCDFs	360	<0.05	280	~0	18	370	4.7	31	420	6.7	450	23	95	350	35	91
HxCDFs	440	<0.06	320	~0	19	430	4.3	29	520	5.3	520	19	96	400	33	92
HpCDFs	260	<0.05	180	~0	13	310	4.2	23	380	5.6	400	8.7	98	360	18	95
OCDF	75	<0.3	62	~0	9.5	210	4.3	16	370	4.1	200	3.1	98	230	7.1	97
<b>(ESP-2)</b>																
TeCDDs	5.9	<0.02	4.7	~0	0.072	2.3	3.0	0.14	2.2	6.1	0.52	0.078	87	0.31	0.05	86
PeCDDs	16	<0.05	9.8	~0	0.08	2.5	3.1	0.19	2.5	7.1	0.42	0.10	81	0.30	0.061	83
HxCDDs	36	<0.06	14	~0	<0.06	2.2	~0	0.17	2.1	7.4	0.26	0.074	78	0.22	0.041	84
HpCDDs	45	<0.05	13	~0	<0.05	1.2	~0	0.14	1.1	11	0.091	<0.05	NE <sup>d</sup>	0.11	<0.05	NE
OCDD	44	<0.3	9.8	~0	<0.3	0.75	~0	0.056	0.66	7.8	<0.3	<0.3	NE	<0.3	<0.3	NE
TeCDFs	9.3	<0.02	5.3	~0	0.22	3.0	6.9	0.34	2.7	11	1.5	0.107	94	1.1	0.091	92
PeCDFs	13	<0.05	6.1	~0	0.094	2.1	4.2	0.17	1.9	8.2	0.66	0.084	89	0.48	0.075	86
HxCDFs	21	<0.06	7.3	~0	<0.06	1.5	~0	0.13	1.1	10	0.31	0.076	80	0.24	0.060	80
HpCDFs	18	<0.05	4.4	~0	<0.05	0.61	~0	0.066	0.49	12	0.083	<0.05	NE	0.084	<0.05	NE
OCDF	7.9	<0.3	1.2	~0	<0.3	<0.3	NE	<0.3	<0.3	NE	<0.3	<0.3	NE	<0.3	<0.3	NE
	Original ash (pg g <sup>-1</sup> )	300 °C			350 °C-1			350 °C-2			400 °C-1			400 °C-2		
		G <sup>e</sup>	P <sup>e</sup>	G/Sum%	G	P	G/Sum%	G	P	G/Sum%	G	P	G/Sum%	G	P	G/Sum%
<b>(CT)</b>																
TeCDDs	3000	15	2800	0.52	179	1300	12	230	1400	14	623	53	92	550	52	91
PeCDDs	3000	5.8	2900	0.20	67	1300	5.0	91	1400	6.1	277	52	84	260	45	85
HxCDDs	1700	4.3	1400	0.30	25	790	3.0	36	870	4.0	118	32	79	110	28	80
HpCDDs	260	<2	230	~0	3.5	190	1.9	4.1	200	2.0	28	9	76	25	10	72
OCDD	120	<10	110	~0	<10	110	~0	<10	120	~0	14	<10	NE	17	<10	NE
TeCDFs	1800	8.4	1600	0.51	120	1100	9.6	150	1000	13	968	88	92	850	88	91
PeCDFs	750	5.1	730	0.70	32	630	4.8	38	600	6.0	412	69	86	370	66	85
HxCDFs	280	3.6	280	1.3	9.4	360	2.5	10	360	2.8	210	52	80	180	47	79
HpCDFs	72	<2	86	~0	2.3	200	1.1	3.8	210	1.8	94	37	72	92	31	75
OCDF	23	<10	43	~0	<10	210	~0	<10	240	~0	31	27	53	41	17	71

<sup>a</sup> Concentrations of the homologs in gaseous form (ng g<sup>-1</sup>).

<sup>b</sup> Concentrations of the homologs in particle-bound form (ng g<sup>-1</sup>).

<sup>c</sup> Proportions of the homologs in gaseous form to the summed concentrations.

<sup>d</sup> Not estimated on account of severe degradation of the analytes.

<sup>e</sup> pg g<sup>-1</sup>.

PCDD/F formation occurs at low duct temperatures ( $\leq 376^\circ\text{C}$ ) and short residence times ( $< 4.6\text{ s}$ ) [31], indicating the possibility of PCDD/F formation in a modern incinerator, which has high-performance gas cooling devices. Therefore, we considered that PCDD/F synthesis on in-flight ash would proceed sufficiently even after quite a short residence time. In addition, in Japan, outdated gas treatment devices such as cyclone separators are until date being employed mainly for small incinerators, where the residence time of the collected fly ash in the separator should be clearly longer than that of modern devices. Fig. 5 shows that PCDF synthesis on N-CT ash is completed by 2 h heating at  $350^\circ\text{C}$ . In addition, the gasification and decomposition of produced PCDFs terminate after 2 h heating of N-CT at  $400^\circ\text{C}$  (see Fig. 4). On the basis of these data and our consideration that all reactions (synthesis, gasification, and decomposition) would proceed sufficiently on in-flight ash in a real post-combustion zone, we set the heating period to 2 h, which has also been employed in many previous experimental studies on fly ash [32–35].

We set the sample quantity as low as possible, that is, 0.1 g for highly contaminated ESP-1 and ESP-2, and 0.5 g for weakly contaminated CT, on the basis of the results in Fig. 2, which indicate that a lower sample amount leads to higher thermal activity in fly ash. B/W rate was set to  $1.6\text{ L min}^{-1}\text{ g}^{-1}$  (that is,  $160\text{ mL min}^{-1}$  for ESP-1 and ESP-2, and  $800\text{ mL min}^{-1}$  for CT); temperature was set to 250, 300, 350, and  $400^\circ\text{C}$ .

Table 3 shows the gas-particle partitions of PCDD/Fs for three fly ash samples by treatment. Transition of total amounts of each homolog varied, indicating the difference in the degree of formation and decomposition among the samples resulting from the difference in properties of the ash. However, similar results were obtained on gas-particle partitions. No gaseous PCDD/Fs were detected at 250 and  $300^\circ\text{C}$ , whereas a small amount of gasification was observed at  $350^\circ\text{C}$ . Moreover, 53–98% of total amounts of PCDD/Fs gasified at  $400^\circ\text{C}$  treatment for all samples. These results indicate that PCDD/Fs in fly ash are gasified in the range of  $350\text{--}400^\circ\text{C}$ . The results obtained are apparently different from those by Altwicker et al. [22] and Addink et al. [23], most probably because of the difference in various experimental conditions as well as the difference in properties of the examined fly ash samples.

As stated above, the thermal treatment conditions (heating period) employed in this study were determined mainly on the basis of the results of the experiments conducted at  $350^\circ\text{C}$ , and thus may not be optimum at other temperatures. It is certain that the optimum heating period varies with parameters such as temperature, gas flow rate, or manner of packing of ash in the heating tube. The gaseous form ratios of PCDFs at  $400^\circ\text{C}$  treatment shown in Table 3 may be overestimated due to the long heating period. It is important in the future to establish thermal treatment conditions which accurately simulate the conditions in the post-combustion zone of a modern incinerator.

In summary, our results indicate that PCDD/Fs in fly ash start to gasify at around  $350^\circ\text{C}$ , and this implies that the gaseous form would be dominant for flue gas whose temperature is over  $350^\circ\text{C}$  regardless of fly ash concentration. However, as stated

in Section 1, the distribution of PCDD/Fs will be influenced by various properties of the flue gases as well as their vapor pressures, and thus estimation of the distribution should not be based only on the gas temperature. In future, it will be necessary to evaluate gas-particle partition using fly ash samples with various properties and to estimate the relationship between partition and the various properties as well as the temperature. Furthermore, establishing an accurate estimation method of gas-particle partition of PCDD/Fs in flue gas by quantitative analysis is also necessary.

#### 4. Conclusion

The results of this study revealed that gasification behavior of PCDD/Fs in fly ash depends on various experimental conditions such as gas flow rate, treatment weight of ash or heating period, and treatment temperature. The time course evaluation of PCDF amounts in the gaseous form and in the particle-bound form revealed that their gaseous form ratios depend on the extent of three reactions (i.e., formation, gasification, and decomposition) simultaneously occurring in fly ash during thermal treatment. In addition, the presence of two forms of de novo formed PCDFs in fly ash, that is, a readily gasified form and a hard-to-gasify form, was also indicated. These findings are important because they provide helpful information for the determination of treatment conditions in thermal experiments on fly ash.

Under our treatment conditions, we confirmed that PCDD/Fs in fly ash gasified at  $350\text{--}400^\circ\text{C}$ , implying that their gaseous form would be dominant in flue gas whose temperature is above that range regardless of fly ash concentration.

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