Influence of Chlorine Forms and Dechlorination on Dioxins Formation/Suppression in the Combustion Processes

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Abstract
Chlorine sources, forms and chlorine concentration of combustion materials are considered to be the most important factors influencing the formation of dioxins/furans (Dioxins) in the combustion processes. Therefore, one of the effective methods to suppress the formation of Dioxins is expected to dechlorinate from combustion materials at high temperatures. In the present work, effects of chlorine sources, forms and chloride concentration on the formation of Dioxins and effect of the dechlorination on the suppression of Dioxins formation in the combustion process have been investigated in the combustion furnace of a laboratory scale at 1073 K.

The concentration of Dioxins formation is nearly proportional to the chloride content of combustion materials under the conditions of the same chlorine sources and forms, and besides, its concentration is significantly influenced by chlorine sources, i.e. organochlorine compound or inorganic chloride. Furthermore, even in the case of inorganic chloride, Dioxins of high concentration are formed under the existence of the active chlorine with high reactivity such as chlorine ion in the hydrate, made from salt and flour. On the other hand, Dioxins are hardly formed by the dechlorination from combustion gas and fly carbonaceous matters with CaO chips put in the combustion furnace.

Introduction
It is well known that the main source of formation of dioxins/furans (Dioxins) is combustion processes such as municipal and industrial waste incinerations. The formation causes of Dioxins in the incineration processes are a partly incomplete combustion in a combustion zone and a de novo synthesis in a flue or an electric precipitator under the cooling process of an exhaust gas. It is very difficult to avoid the combustion with the existence of chlorine in the municipal waste incineration, because it is considered that the main source of chlorine is not only poly vinyl chloride (PVC) but also inorganic chloride such as sodium chloride [1,2]. Many studies [1–7] have been done to suppress the formation of Dioxins and their emission in combustion processes. Most of the studies have focused on the de novo synthesis of Dioxins at nearly 573 K in cooling processes [6,7].

Chlorine sources and forms are considered to be the most important factors in the formation of Dioxins due to the fact that Dioxins are organochlorine compounds. In the present work, effects of chlorine sources and forms on the formation of Dioxins and effect of dechlorination from combustion materials on the suppression of Dioxins formation in the combustion processes have been investigated through combustion experiments on the formation of Dioxins in the combustion furnace of a laboratory scale at 1073 K.

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Experimental

Figure 1 shows a schematic layout of the combustion furnace. The reaction tube, made of SUS 316 with 157 mm I.D., was heated by an electric furnace with three-divided heating parts to obtain a long isothermal zone by controlling each temperature separately. The temperature in the reaction tube was controlled at 1073 K, which was general combustion temperature in municipal waste incineration. The isothermal zone at 1073 ± 10 K, in which a part of an exhaust pipe was included, was 250 mm long as shown in Fig. 1. Combustion materials, such as PVC powders, fine powders of carbon (C powders), the mixture of PVC and C powders, the mixture of NaCl and flour powders, and the mixture of NaCl and polyethylene powders (PE powders), were fed together with O₂-N₂ gas mixtures by the fixed quantity feeder, which was installed in the upper part of the reaction tube. The combustion zone is designed to be composed of the primary combustion part and the secondary combustion part. This primary combustion part is for the preheating, the gasification and the combustion of the combustion materials, and the secondary combustion part is within a bed packed with alumina balls, where gas and unburnt materials are well mixed and combusted by heat exchange. Gas flow rates of O₂, H₂, Cl₂ and N₂ were controlled by the respective mass flow controllers. Total flow rate of the supplied gas mixtures of O₂ and N₂ was constantly set to be 2 L/min (s.t.p.). Residence time of the gas in the isothermal zone at 1073 K within the reaction tube is calculated to be about 22 s under the present experimental conditions, when gas stream is assumed to be a plug flow.

In the present experiments, Dioxins were hardly formed by the de novo synthesis under the cooling process of the exhaust gas, because the exhaust gas was rapidly cooled by injection directly into two impingers filled with distilled water kept at 278 K (a gas sampling system for Dioxins) [5]. The methods of gas sampling and chemical analysis for Dioxins were conformed to JIS K 0311-1999. To monitor the combustion conditions, the main compositions of the exhaust gas were continuously measured by using a gas-mass analyzer.

Results and discussion

1. Dioxin’s concentration under each experimental condition

Experimental conditions, and Dioxin’s and gas concentrations in the exhaust gas are summarized in Table 1. The feed rate of combustion materials is 0.1 g/min in the case of 100 mass% PVC powder for Run Nos. 2 and 3. Each molar feed rate of C, H and Cl for Run Nos. 1, 5 and 6 are almost the same as those in the case of 100 mass% PVC powder. The molar feed Cl rate for Run Nos. 4 and 7 are 1/40 and 1/100 times as much as that for the others, respectively. In the present experiments, the feed rates of combustion materials were ranging from 0.04 to 0.2 g/min as shown in Table 1. These feed rates were determined from the reason that the combustion materials were able to burn out with the amount of 5 vol% O₂ in the supplied gas of 2 L/min (s.t.p.). Two kinds of the supplied gas compositions were set as follows:

1) 40 vol% O₂ - 60 vol% N₂,
2) 5 vol% O₂ - 95 vol% N₂

It is important to investigate whether Dioxins are formed or not under the combustion conditions without any organic compound. The combustion experiment was carried out using H₂, Cl₂, O₂ gases and C powder with the size of 60 µm at 1073 K under the incomplete combustion conditions (Run No. 1). TEQ (Toxic Equivalent Quantity) and total Dioxin’s concentrations were 1.3 ng·TEQ/m³ (s.t.p.) and 44 ng/m³ (s.t.p.), respectively. Therefore, it is confirmed that Dioxins are formed at 1073 K under the incomplete combustion conditions even without organic compounds, but Dioxin’s concentration can be considered to be very
Table 1  Experimental conditions, and Dioxin’s and gas concentrations in exhaust gas.
Combustion temperature: 1073 K, Supplied gas flow rate: 2 L/min (s.t.p.)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Supplied gas compositions (vol%)</th>
<th>Exhaust gas compositions (vol%)</th>
<th>[Combustion materials: powder]</th>
<th>Cl feed rate (mol/min)</th>
<th>TEQ (ng-TEQ/m³)</th>
<th>Total (ng/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5%O₂-95%N₂</td>
<td>0.1 3.7 0.7</td>
<td>[Active C+H₂, Cl₂ gases]</td>
<td>1.6×10⁻¹</td>
<td>1.3</td>
<td>44</td>
</tr>
<tr>
<td>2</td>
<td>5%O₂-95%N₂</td>
<td>0.2 3.0 1.5</td>
<td>[100 mass% PVC]</td>
<td>1.6×10⁻¹</td>
<td>230</td>
<td>14,000</td>
</tr>
<tr>
<td>3</td>
<td>40%O₂-60%N₂</td>
<td>0 4.0 35</td>
<td>[100 mass% PVC]</td>
<td>0.1</td>
<td>4.7</td>
<td>120</td>
</tr>
<tr>
<td>4</td>
<td>40%O₂-60%N₂</td>
<td>0 4.0 35</td>
<td>[5 mass% PVC+95 mass% C]</td>
<td>0.04×10⁻³</td>
<td>0.13</td>
<td>7.1</td>
</tr>
<tr>
<td>5</td>
<td>5%O₂-95%N₂</td>
<td>0.05 3.8 0.9</td>
<td>[NaCl+PE]</td>
<td>0.14</td>
<td>1.7</td>
<td>110</td>
</tr>
<tr>
<td>6</td>
<td>40%O₂-60%N₂</td>
<td>0 4.0 35</td>
<td>[NaCl+Flour]</td>
<td>1.6×10⁻³</td>
<td>19</td>
<td>750</td>
</tr>
<tr>
<td>7</td>
<td>40%O₂-60%N₂</td>
<td>0 4.0 35</td>
<td>([1/100] NaCl+Flour)</td>
<td>0.016×10⁻³</td>
<td>0.57</td>
<td>11</td>
</tr>
</tbody>
</table>

low values under the complete combustion conditions [5].

Run Nos. 2 and 3 show the experimental results in the case of 100 mass% PVC powders (the size of 200 μm). Concentrations of CO, CO₂ and O₂ in the exhaust gas of Run No. 2 under the incomplete combustion conditions were about 0.2, 3 and 1.5 vol%, respectively. TEQ and total Dioxin’s concentrations of Run No. 2, in which many fly carbonaceous matters were included in the exhaust gas, were as high as 230 ng-TEQ/m³ (s.t.p.) and 14,000 ng/m³ (s.t.p.). Run No. 3 shows the formation of Dioxins under the complete combustion conditions with 100 mass% PVC. In this case, O₂ concentration of the exhaust gas was about 35 vol% and CO could not be detected. TEQ and total Dioxin’s concentrations of the exhaust gas of Run No. 3 including a few fly carbonaceous matters were 4.7 ng-TEQ/m³ (s.t.p.) and 120 ng/m³ (s.t.p.). These values are two orders of magnitude smaller than those under the incomplete combustion conditions using 100 mass% PVC (Run No. 2). The fly carbonaceous matters in the exhaust gas observed by SEM are fine particles with the sizes of about 0.5 to 40 μm, and their surface is smooth such as liquid [5]. It is found that these fly carbonaceous matters contain precursor such as phenol, benzene, biphenyl, naphthalene, anthracene, and their chlorides. The number of these fly carbonaceous matters is nearly proportional to Dioxin’s concentration under the condition with the same combustion material [5]. It may be considered that Dioxins are mainly formed on the surface of the fly carbonaceous matters [5].

The influence of chlorine concentration on the formation of Dioxins was investigated by using the mixture of 5 mass% PVC powder and 95 mass% C powder under the complete combustion conditions (Run No. 4). The chlorine concentration is 1/40 times in comparison to the case of 100 mass% PVC (Run No. 3), because the feed rate of the mixture was set half as large as that for Run No. 3. TEQ and total Dioxin’s concentrations in the exhaust gas of Run No. 4 were as low as 0.13 ng-TEQ/m³ (s.t.p.) and 7.1 ng/m³ (s.t.p.) as shown in Table 1. The Dioxin’s concentration is approximately proportional to the chlorine concentration of the combustion materials, because TEQ and total values are about 1/40 and 1/20 times in comparison to the case of 100 mass% PVC (Run No. 3), respectively.

2. Influence of chlorine sources and forms on the formation of Dioxins
Run No. 5 is the combustion experiment of the mixture composed of NaCl and PE powders (the size of 180 μm) used as inorganic chloride and organic compound, respectively. Total Dioxin’s concentration in the exhaust gas is 110 ng/m³ (s.t.p.), which is about 1/130 times as large as that under the same incomplete combustion conditions using 100 mass% PVC (Run No. 2). The fly carbonaceous matters include little active Cl with high reactivity such as Cl bond in PVC on the surface and in itself, because NaCl in the combustion...
Influence of Chlorine Forms and Dechlorination on Dioxins Formation/Suppression in the Combustion Processes

materials is thermodynamically stable chlorine source. Comparison among Run Nos. 1, 2, 3 and 5 reveals that the formation of Dioxins is significantly influenced by the existence of active Cl such as Cl bond in the fly carbonaceous matters.

Influence of chlorine forms on the concentration of Dioxins formation was investigated by using NaCl as follows: Flour and NaCl were dissolved in distilled water to mix them well, where each molar ratio of C, H and Cl was almost the same as those for 100 mass% PVC powder. After the mixture was dried in air for 20 days, it was pulverized to be the size of about 200 µm. These particles still include a hydrate. TEQ and total Dioxins’ concentrations of Run No. 6 are 19 ng-TEQ/m$^3$ (s.t.p.) and 750 ng/m$^3$ (s.t.p.), which are higher than those for Run No. 3 in the case of 100 mass% PVC under the same complete combustion conditions. Such a high concentration of Dioxins may be due to the fact that the fly carbonaceous matters formed in the combustion process include active Cl with high reactivity on the surface and in itself, because many chlorine ions exist in a hydrate made from salt and flour.

To investigate the influence of NaCl concentration on the formation of Dioxins, the same hydrate but the chlorine concentration of 1/100 times as large as the case of Run No. 6 was combusted under the complete combustion conditions; this experiment is Run No. 7. TEQ and total Dioxin’s concentrations in the exhaust gas of Run No. 7 are 0.57 ng-TEQ/m$^3$ (s.t.p.) and 11 ng/m$^3$ (s.t.p.) as shown in Table 1. The Dioxin’s concentrations are approximately proportional to the NaCl concentration of the combustion materials, because these values are two orders of magnitude smaller than those for Run No. 6. Thus it can be regarded that our daily meals using salt also play an important role for the formation sources of Dioxins in the municipal waste incinerator.

3. Comparison of Dioxin’s concentration formed under different chlorine sources and forms

Figure 2 summarizes effects of chlorine sources and forms on the concentration of Dioxins at 1073 K. As described above, Dioxin’s concentrations under the complete combustion conditions were two orders of magnitude smaller than those under the incomplete combustion conditions in the case of 100 mass% PVC. In Fig. 2, therefore, Dioxin’s concentrations of Run Nos. 1 and 5 under the incomplete combustion conditions are divided by 100 and designated as Nos. 1’ and 5’, so that the resultant values can be compared to Dioxin’s concentrations of Run Nos. 3 and 6 under the complete combustion conditions. The combustion of mixture of NaCl and PE (No. 5’) shows low Dioxin’s concentration. The formation of Dioxins is high in the case of the combustion using PVC as an organochlorine compound. Even in the case of inorganic chloride (NaCl), Dioxins of very high concentration are formed under the existence of active Cl in the hydrate making as Run No. 6.

Chlorine sources and forms are the most important factors in the formation of Dioxins. The concentration of Dioxins formation is significantly influenced by chlorine sources, i.e. organochlorine compound or inorganic chloride. Even in the case of inorganic chloride, Dioxins of very high concentration are formed under the existence of the active Cl with high reactivity such as Cl ion in the hydrate. The concentration of Dioxins is greatly governed by whether active Cl with high reactivity still exists or not on the surface and in itself of the fly carbonaceous matters formed in the combustion processes.

4. Effect of dechlorination from combustion materials on the concentration of Dioxins formation

The packed bed with alumina balls ($\text{Al}_2\text{O}_3$) was used for well gas mixing and heat exchange in the present experiments (see Fig. 1). TEQ and total Dioxin’s concentrations of the exhaust gas under the complete combustion conditions with 100 mass% PVC of Run No. 3 were 4.7 ng-TEQ/m$^3$ (s.t.p.) and 120 ng/m$^3$ (s.t.p.).

To investigate the effect of dechlorination from
combustion gas and the fly carbonaceous matters on the concentration of Dioxins formation, CaO chips with the size of $4 \times 5 \times 2.5$ mm were put in a height of 110 mm instead of alumina balls within the combustion tube. Other experimental conditions are the same as those for Run No. 3. It is expected that most of chlorine in combustion gas and the fly carbonaceous matters are fixed as the thermodynamically stable CaCl$_2$ by CaO. Figure 3 shows the experimental result; TEQ and total Dioxin’s concentrations of the exhaust gas including a few fly carbonaceous matters are fixed as the thermodynamically stable CaCl$_2$ by CaO. Figure 3 shows the experimental result; TEQ and total Dioxin’s concentrations of the exhaust gas including a few fly carbonaceous matters are extremely low, i.e. 0.007 ng-TEQ/m$^3$ (s.t.p.) and 0.67 ng/m$^3$ (s.t.p.). By the dechlorination from combustion gas and the fly carbonaceous matters with CaO chips put in the combustion furnace, Dioxins are hardly formed even in the combustion of 100 mass% PVC with high possibility of Dioxins formation.

Conclusions

Effects of chlorine sources, forms and dechlorination on formation/suppression of Dioxins have been investigated by the use of the electric furnace of a laboratory scale at 1073 K. The conclusions obtained are as follows:

(1) The concentration of Dioxins formation is significantly influenced by the chlorine sources, that is Dioxin’s concentration formed under the combustion of organochlorine compound (PVC) is higher than that of inorganic chloride (NaCl).

(2) Even in the case of inorganic chloride (NaCl), the formation of Dioxins is greatly governed by the chlorine forms such as Cl ion in the hydrate made from NaCl and flour.

(3) By the dechlorination from combustion materials with CaO chips put in the combustion furnace, Dioxins are hardly formed even in the combustion of 100 mass% PVC with high possibility of Dioxins formation.

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References