

## INFLUENCE OF PRIMARY COMBUSTION TEMPERATURE AND FLUE GAS TREATMENT ON THE BEHAVIORS OF NITRO POLYCYCLIC AROMATIC HYDROCARBONS IN MUNICIPAL SOLID WASTE COMBUSTION

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### Abstract

For understanding the formation and decomposition behaviors of nitro polycyclic aromatic hydrocarbons (nitro PAHs) in municipal solid waste (MSW) combustion, pilot-scale thermal treatment experiments were conducted. Nitro PAHs were formed mainly through the nitration of PAHs in primary combustion. While most nitro PAHs were decreased the concentrations with increasing temperatures of primary combustion (690–890 °C), concentrations of some nitro compounds, such as 1-nitropyrene and 1-nitrobenz[a]pyrene, at 790 °C were slightly higher than those at 690 °C. Most amounts of nitro PAHs, which were formed in primary combustion, were decomposed in secondary combustion at 900 °C, indicating that secondary combustion is the most effective for emission control of nitro PAHs. Nitro PAHs in bottom and fly ashes were extraordinary lower amounts than inputs. Overall decomposition efficiency of nitro PAHs in MSW combustion was more than 95%.

### Introduction

Nitro polycyclic aromatic hydrocarbons (nitro PAHs) have been of the great concerns as potential mutagens and carcinogens<sup>1</sup>. Once released into the atmosphere, nitro PAHs are highly persistent in the environment and can be transported long distances from their original sources<sup>2,3</sup>. Nitro PAHs in environment originate mainly from direct emissions from combustion sources, especially from diesel exhaust, and nitration of PAHs in the atmosphere<sup>1</sup>.

Nitro PAH emissions from municipal solid waste (MSW) incinerators have been studied using bioassay (mainly Ames test)<sup>4,7</sup>. They concluded that nitro PAHs were an important contributor to the mutagenic activity, while most of these studies did not performed the isomer-specific analysis using analytical instrument, such as GC. Results of quantitative analysis of nitro PAHs in emissions of MSW incinerators have also been reported<sup>8,9</sup>. However, they have studied the limited nitro PAHs (mainly 1-nitropyrene) in only final exit gases and ashes. To our knowledge, there is no information regarding on behaviors of various nitro PAHs in MSW incinerator.

Based on these backgrounds, we carried out the thermal treatment experiments using pilot-scale equipment to investigate the formation and decomposition behaviors of nitro PAHs in MSW combustion. In addition, effect of primary combustion temperature to nitro PAH formation was also studied.

### Materials and Methods

The thermal treatment plant equipment at National Institute for Environmental Studies, Japan, was used in this study. This plant consists of a rotary kiln primary combustion chamber, a vertical secondary combustion chamber, a gas cooling zone, a bag filter, an activated carbon adsorption tower and a wet scrubber<sup>10</sup>. Three experiments using MSW as fuels were carried out, each with a different temperature setting of the primary combustion chamber as follows: 690 °C, 790 °C and 890 °C. The experimental conditions were shown in Table 1. Flue gases were collected at four locations (kiln exit, bag filter entry [secondary combustion exit], bag filter exit, and final exit) for 4 hours after steady combustion. Sampling was basically followed the method of JIS K0311<sup>11</sup>. However, filter and

Table 1 Experimental conditions of thermal treatment plant in this study

Experimental Name		690 °C	790 °C	890 °C
Temperature (°C)	Primary combustion	679	794	898
	Secondary combustion	899	899	899
	Bag filter	149	149	149
Air flow rate in primary combustion (m <sup>3</sup> /h)		11.2	16.9	19.4
MSW feeding rate (g/h)		1,485	2,085	2,500
total MSW input (g)		5,940	8,338	10,000
Volume (g)	Bottom ash	488.9	693.0	803.9
	Fly ash	29.5	39.7	65.0
Acid gas treatment		NaHCO <sub>3</sub>	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>
Flue gas at bag exit	O <sub>2</sub> (%)	9.5	9.3	9.6
	CO (ppm*)	0	0	0
	NOx (ppm*)	22	35	30

\* Concentration normalized on 12% of O<sub>2</sub> concentration.

XAD column were set after liquid gas samplers for refusing the artificial formation of nitro PAHs during sampling. Bottom and fly ashes were collected after the end of each experiment.

The extraction of nitro PAHs as well as polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), dioxin-like polychlorinated biphenyls (PCBs) and PAHs from flue gas and ash samples were followed the methods of JIS K0311<sup>11</sup> and Noma et al.<sup>10</sup>, respectively. Activated silica-gel and multi-layered silica-gel column chromatography was used for clean-up procedure of nitro PAHs, after <sup>2</sup>H-labeled nitro PAHs were added to the extract as internal standards. Clean-up procedure of dioxin-related compounds (PCDD/Fs and DL-PCBs) was followed the methods of JIS K0311<sup>11</sup>. For analyzing PAHs, the extract was diluted and added the internal standard (<sup>13</sup>C-labeled PAHs). Identification and quantification of these compounds were performed using a GC/HRMS.

### Results and Discussion

In all the experiments, flue gases at kiln exit retained the highest concentrations/amounts of nitro PAHs as well as dioxin-related compounds and PAHs, indicating the thermal formations of these compounds in primary combustion (e.g. Fig. 5). Figure 1 shows the concentrations of nitro PAHs, PAHs, dioxin-related compounds and NOx in kiln exit gases at various temperatures of primary combustion. Concentrations of nitro PAHs were 1-4 orders of magnitude lower than those of dioxin-related compounds and PAHs. Concentrations of nitro PAH in kiln exit gases were the highest at temperatures of 690 °C, followed by 790 °C > 890 °C. Similarly, concentrations of PAHs were also decreased with increasing primary combustion temperature. In contrast, dioxin-related compounds and NOx were less variation of concentrations in three combustion experiments. Figure 2 shows the concentrations of nitro PAH compounds in kiln exit gases at various temperatures.

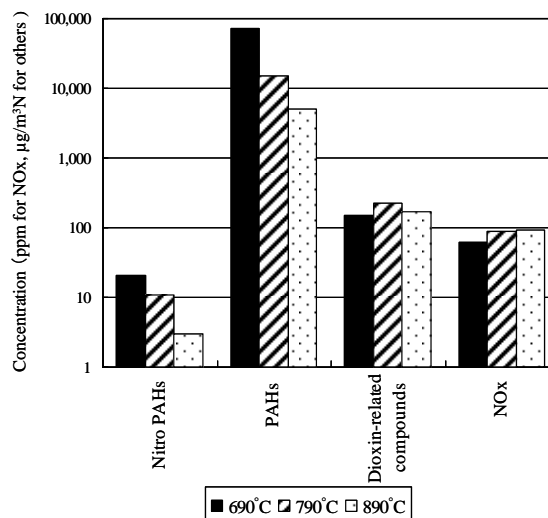


Fig. 1 Concentrations of nitro PAHs, dioxin-related compounds, PAHs and NOx in kiln exit gases at various temperatures.

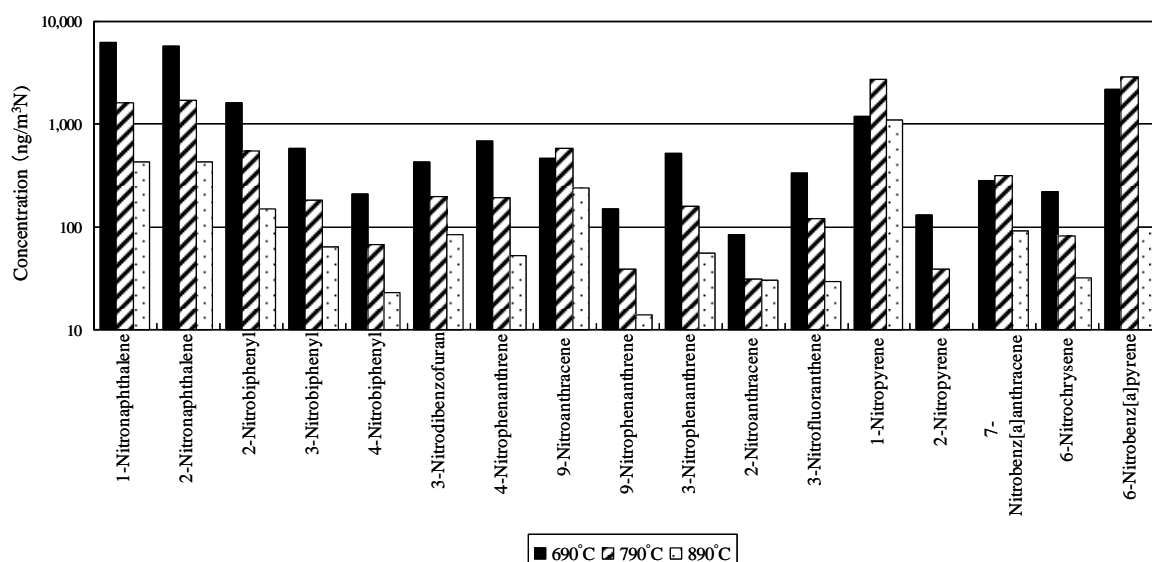


Fig. 2 Concentrations of nitro PAH compounds in kiln exit gases at various temperatures.

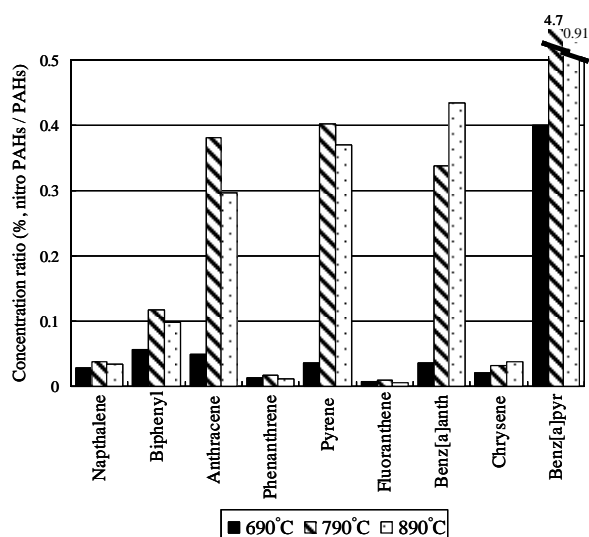


Fig. 3 Concentration ratios of nitro PAHs / PAHs in kiln exit gases.

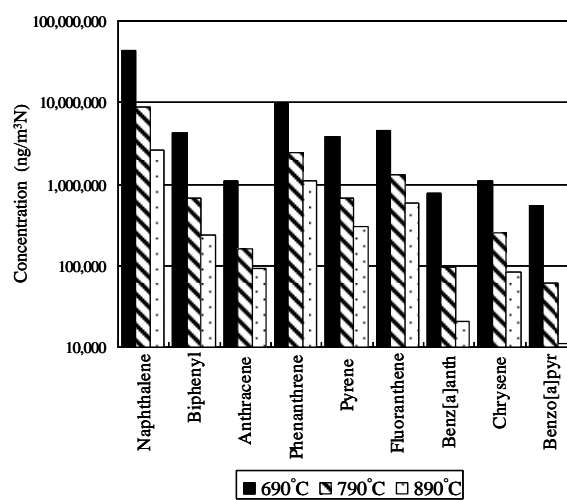


Fig. 4 Concentrations of PAH compounds in kiln exit gases.

Nitronaphthalenes were the predominant nitro compounds at primary combustion temperature of 690 °C. In contrast, 6-nitrobenzo[a]pyrene and 1-nitropyrene were the highest concentrations at 790 °C and 890 °C, respectively. While most nitro PAH compounds were decreased the concentrations with increasing temperature (Type I), concentrations of 9-nitroanthracene, 1-nitropyrene, 7-nitrobenz[a]anthracene and 6-nitrobenz[a]pyrene in kiln exit gas at temperature of 790 °C were slightly higher than those at temperatures of 690 °C (Type II). These results may be related to the reactivity of PAHs to nitration and the concentrations of parent PAHs in primary combustion. Figure 3 shows the concentration ratios of nitro PAHs to parent PAHs in kiln exit gases. These ratios of nitro PAHs in Type I were low and less variation at various primary combustion temperatures. In contrast, nitro PAHs in Type II were dramatically increased these ratios at temperatures of 790 °C and 890 °C, compared to those of 690 °C. These results indicate that parent PAHs of Type II are more reactive for nitration than those of Type I at primary combustion temperatures over 790 °C. Because naphthalene was the predominant PAH in kiln exit gases (Fig. 4) and the reactivity to nitration was almost similar among PAH compounds, except for benz[a]pyrene (Fig. 3), nitronaphthalenes were the predominant nitro PAHs at temperature of 690 °C. Because nitration of benz[a]pyrene and pyrene was extraordinary higher than those of naphthalene at temperature over 790 °C (Fig. 3), 6-nitrobenz[a]pyrene and 1-nitropyrene became to be the predominant nitro PAHs at 790 and 890 °C.

Figure 5 shows the formation and decomposition behaviors of 1-nitronaphthalene, 1-nitropyrene, dioxin-related compounds and PAHs in MSW combustion. As discussed above, thermal formations of these compounds were observed in primary combustion. Amount ratios of 1-nitronaphthalene and 1-nitropyrene in kiln exit gas to the inputs were 3.8-53, which were lower than those of PAHs (31-440) and dioxin-related compounds (520-610). This result implies that thermal formation of nitro PAHs is smaller than PAHs and dioxin-related compounds at combustion temperatures of 690-890 °C. Amounts of nitro PAHs in flue gases at bag filter entry (secondary combustion exit) were extraordinarily lower than those in kiln exit gases (Fig. 5). Similar trends were observed in PAH and dioxin-related compounds. Amount ratios of nitro PAHs in kiln exit gases to those in bag filter entry gases were 170-7,400 (Fig. 5). These results mean that most of nitro PAHs, which are formed in primary combustion, are decomposed in the secondary combustion. These suggest that secondary combustion is the most effective for emission control of nitro PAHs in MSW combustion. There was less variation of amounts of nitro PAHs, as well as dioxin-related compounds and PAHs, between flue gases at bag filter entry and bag filter exit. This may be related to less efficiency of bag filter, probably due to low concentration of fly ash in this equipment (concentration of fly ash in bag filter entry gases: 0.23-0.45g/m<sup>3</sup>N). Nitro PAHs and PAHs in final exit gases were comparable amounts to bag filter exit gases, while 95% of dioxin-related compound amounts in bag filter exit gases were removed by a carbon adsorption tower and a wet scrubber (Fig. 5). In final exit gases, amounts of

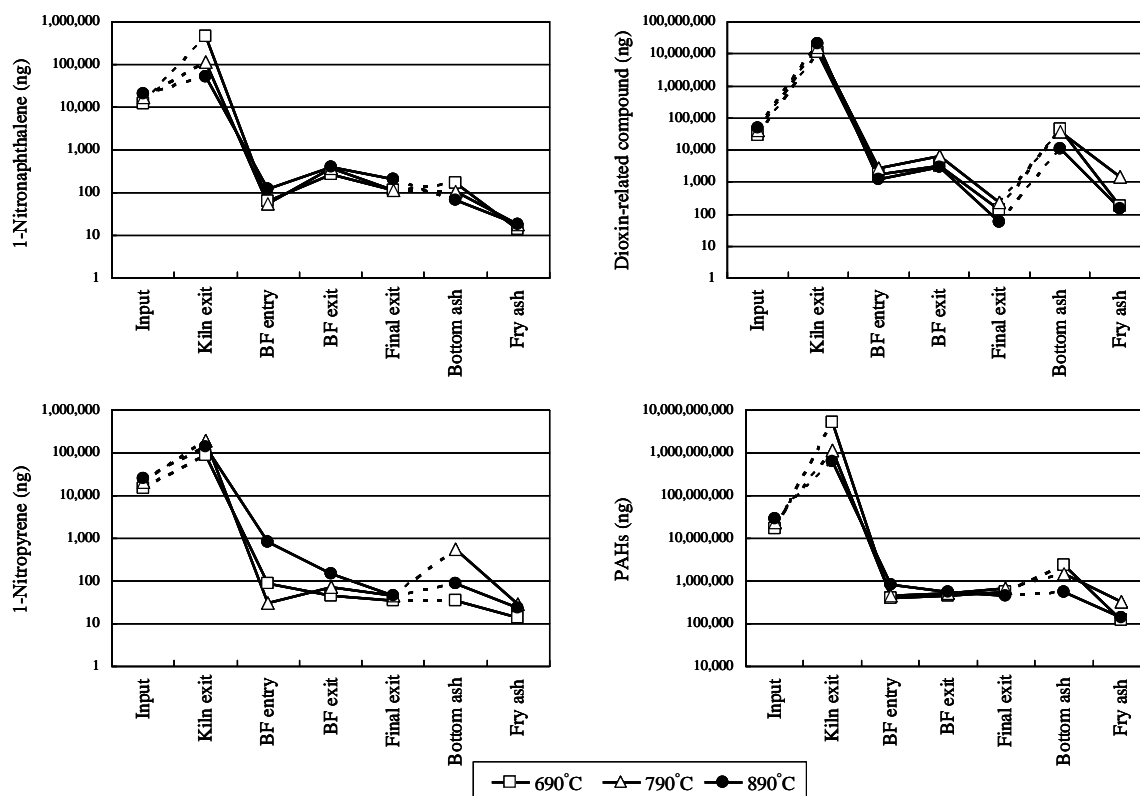


Fig. 5 Behaviors of nitro PAHs, dioxin-related compounds and PAHs in three combustion experiments.

nitro PAHs, PAHs and dioxin-related compounds were not varied with primary combustion temperatures (Fig. 5).

Nitro PAHs in bottom and fly ashes were lower amounts than inputs (Fig. 5). Overall decomposition efficiency of nitro PAHs in this study is calculated to be more than 95%, implying that emission of nitro PAHs from MSW combustion to environment can be decreased by appropriately management of incinerator condition.

#### Acknowledgements

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