

A Study on N₂O Formation/Destruction Behavior in Sewage Sludge Combustor

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1 Introduction

Generally sewage sludge is incinerated in a fluidized-bed combustor after dehydrating process in Japan. Since sewage sludge contains less chlorine and heavy metals in comparison with municipal solid waste (MSW), it is necessary to remove only NO_x and SO_x from the exhaust gas. In addition, owing to low combustion temperature and self-denitration effect, NO_x concentration in the exhaust gas of sewage sludge combustor is relatively low and removal of SO_x can be easily achieved with a wet scrubber using NaOH.

However, there is a need to pay attention to production of N₂O, whose emission characteristics have been found to be dependent on temperature. It is reported that N₂O is likely to be emitted in the sewage sludge combustors because of low combustion temperature [1, 2]. Since N₂O has 300 times the greenhouse effect than CO₂, it is urgent task to respond quickly for reduction of N₂O. Currently, tries to raise combustion temperature in sewage sludge combustors have been promoted in Japan [3]. This leads to increase in the auxiliary fuel consumption such as kerosene or digester gas, which are not desirable in terms of energy saving and economy. Although it is desirable to take measures on the basis of experimental results using actual sewage sludge combustors, this requires a large amount of cost and time.

Numerical simulation based on chemical kinetic modeling is expected to be a powerful tool for analysis to improve combustions condition despite ignoring spatial distributions of temperature, pressure, and concentration of chemical species. In this case, the numerical results have to be verified under actual combustion conditions. While comparison between the numerical and experimental results has been done in coal combustion, there are few studies on sewage sludge combustion at the present.

In the present work, to study formation and destruction behavior of N₂O, exhaust gas measurement was carried out in fluidized-bed sewage sludge combustors under various conditions, especially focused on temperature and HCN concentration. The measurement results were compared with numerical ones based on chemical kinetic modeling to check availability of numerical simulation as an analysis tool to improve combustions condition and to suppress N₂O emission.

2 Experimental

Exhaust gas measurement was conducted in 2 actual sewage sludge combustors of the waste water treatment plant and 1 pilot plant combustor. Overview and operating condition is shown in Table 1. These three combustors are fluidized-bed type, which are usually used at sewage sludge combustors. Figure 1 shows a schematic diagram of the fluidized-bed type combustor.

Table 1. Overview and operating condition of combustors.

Combustor		A	B	Pilot Plant C
Incinerated	-	Dehydrated cake of sewage sludge	Dehydrated cake of sewage sludge	Dehydrated cake of sewage sludge
Water	%	78.8	83.5	73.2
Combustible	dry %	80.1	82.7	80.9
Ash	dry %	19.9	17.3	17.0
C	dry %	42.5	44.6	43.3
H	dry %	6.1	6.2	6.2
N	dry %	4.4	7.6	4.5
O	dry %	26.5	23.5	28.5
S	dry %	0.6	0.8	0.5
LHV	MJ/kg	1.8	1.0	2.8
Feed rate	kg/h	4,500~5,000	840~1,000	50~80
Auxiliary fuel	-	Heavy oil (Bunker A)	Kerosene	kerosene
Air ratio	-	1.3	1.3	1.3
Fluidized air temperature	degrees Celsius	650	650	550
Freeboard temperature	degrees Celsius	830~890	830~910	865~895

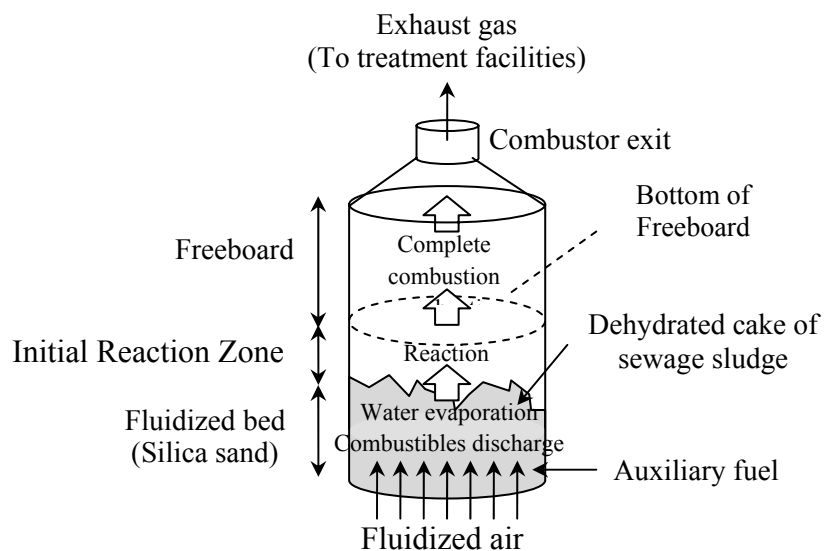


Figure 1. Schematic diagram of fluidized bed combustor.

In the experiment, operating conditions of the combustors was essentially the same with those in the actual sewage treatment plant. Auxiliary fuel feed rate was controlled to keep constant temperature from 700 to 800 degrees Celsius at the fluidized bed. Air feed rate was adjusted so that excess air ratio is constant of 1.3. Since gas treatment facilities downstream from the combustor exit are different by each plant, species concentration and temperature measured at the combustor exit and freeboard were evaluated. Species concentration of the collected gas was measured by a conventional gas-chromatograph analyzer. Temperature was measured by thermo-couples (type-K).

3 Numerical simulation

Numerical simulation based on chemical kinetic modeling of N₂O formation/destruction at the freeboard was carried out to analyze the experimental results. In the simulation, initial conditions were specified using the measured values at the actual lower freeboard condition as shown in Table 2, except for concentrations of CH₄ and H₂, which were estimated from some previous reports [4, 5]. As for numerical codes, DARS-basic (CD-adapco Japan) and Cantera [6] were used. Simulation was carried out under constant-pressure, adiabatic kinetics zero-dimensional reactor model. At the actual freeboard of sewage sludge combustor, combustion reaction proceeds mainly under gas-phase, however ash and char particles exist in some small measure. The present numerical simulation aimed to check availability as an analysis tool to improve combustions condition, not to model all the phenomena proceeding in the combustor.

Table 2. Initial condition of numerical simulation.

Elements	Unit	Value
Pressure	MPa	0.1
Temperature	degrees Celsius	780~900
O ₂	dry%	5.6
CO	dry%	0.1
CO ₂	dry%	11.8
N ₂	dry%	82.3~82.4
NO	dry-ppm	500
HCN	dry-ppm	0~200
NH ₃	dry-ppm	100
N ₂ O	dry-ppm	0~300
CH ₄	dry-ppm	200
H ₂	dry-ppm	510
H ₂ O	%	45

Reaction mechanisms used were "Leeds mechanism" and "Konnov mechanism". The former is combination of "The Leeds methane oxidation mechanism version 1.5" and "The Leeds NOx mechanism v2.0", and includes 56 species (H/O/C/N) and 341 reactions [7]. In previous report, numerical results which were based on Leeds mechanism agree well with measurement results in an actual MSW combustor [8]. The present study and previous report have common features; main target of chemical species is nitrogen oxide, and the exhaust gas contains large amount of water vapor. In addition, Konnov mechanism is also used for comparison. It is based on modified version of "Konnov mechanism Release 0.5" by Konnov, and includes 129 species (H/O/C/N) and 1230 reactions [9].

4 Results and Discussion

4.1 Relationship between temperature and N₂O concentration

Figure 2 shows relationship between temperature and N₂O concentration at the combustor exit. Here, "free-board temperature" means the highest temperature in several measurement points at the freeboard. It is clearly demonstrated that N₂O emission characteristics are dependent on temperature. Especially for combustor B, the temperature dependency of N₂O formation is most obvious as a result of the wide temperature range. N₂O destruction is significant at higher temperature, which is very similar to the trend indicated in previous reports [10], while NOx concentration is inversely correlated to N₂O concentration. This is because thermal NOx is dominant.

From these results, raising temperature is found to be effective in order to reduce N₂O emissions, to such an extent that NOx emission is still moderate value.

However, temperature requires to be less than or equal to a critical value depending on the combustor. For example, the critical temperature is 850 degrees Celsius at combustor A to keep N₂O concentration less than 50 ppm, while 910 degrees Celsius is needed at combustor B, and 810 degrees

Celsius at pilot plant C. This discrepancy is related to the fact that the flow velocity in the combustor differs. Then it is necessary to consider the effects of gas residence time in the free-board in which the flow undergoes some predefined temperature range. Figure 3 shows relation between N₂O concentration and the calculated residence time for temperature of 850 degrees Celsius or higher. N₂O concentration at the combustor exit monotonically decreases with increase in the residence time, for all the combustors. These results suggest that the residence time of at least 4 seconds at the free-board is required to achieve N₂O emission less than 50 ppm at the combustor exit.

In Figure 3, the solid line denotes the calculated results on the effects of the residence time on N₂O concentration. In this calculation, Leeds mechanism is used and the temperature, N₂O and HCN concentrations are 850 degrees Celsius, 300 ppm, and 150 ppm, respectively. The experimental results show that N₂O concentration ranges from 100 ppm to 200 ppm at the residence time of 2 seconds and that it is lower than 50 ppm at 4 seconds, which agrees well with the calculated result indicating 100 ppm at 2 seconds and 40 ppm at 4 seconds. Although species concentrations of the exhaust gas in the actual combustors are not exactly the same those given as the initial conditions in the numerical simulation, the both results demonstrates the same tendency. From this, it is found that numerical simulation using Leeds mechanism is able to reproduce approximate conditions of actual combustors in the temperature range around 850 degrees Celsius.

Figure 4 shows the calculated results for various temperatures, namely 800, 850, and 900 degrees Celsius. Other initial conditions are the same as in the Figure 3. It is clearly shown that N₂O destruction rate is faster as temperature become higher. If the temperature at the free-board is over 900 degrees Celsius, the residence time of only 2 seconds is required to achieve N₂O emission less than 50 ppm at the combustor exit. Applying this result to fluidized-bed combustors, it is possible to reduce N₂O concentration with a shorter combustor, if the combustion temperature is higher. However, in this case, increase of auxiliary fuel consumption, thermal-NO_x emissions, and thermal load to heat exchangers are problems to be solved. If sufficient residence time is ensured, reduction of N₂O is possible, which causes longer combustors leading to increase in construction or maintenance cost. From the practical viewpoint, it can be said that to ensure the residence time of 4 seconds at 850 degrees Celsius is a reasonable guideline to reduce N₂O emission.

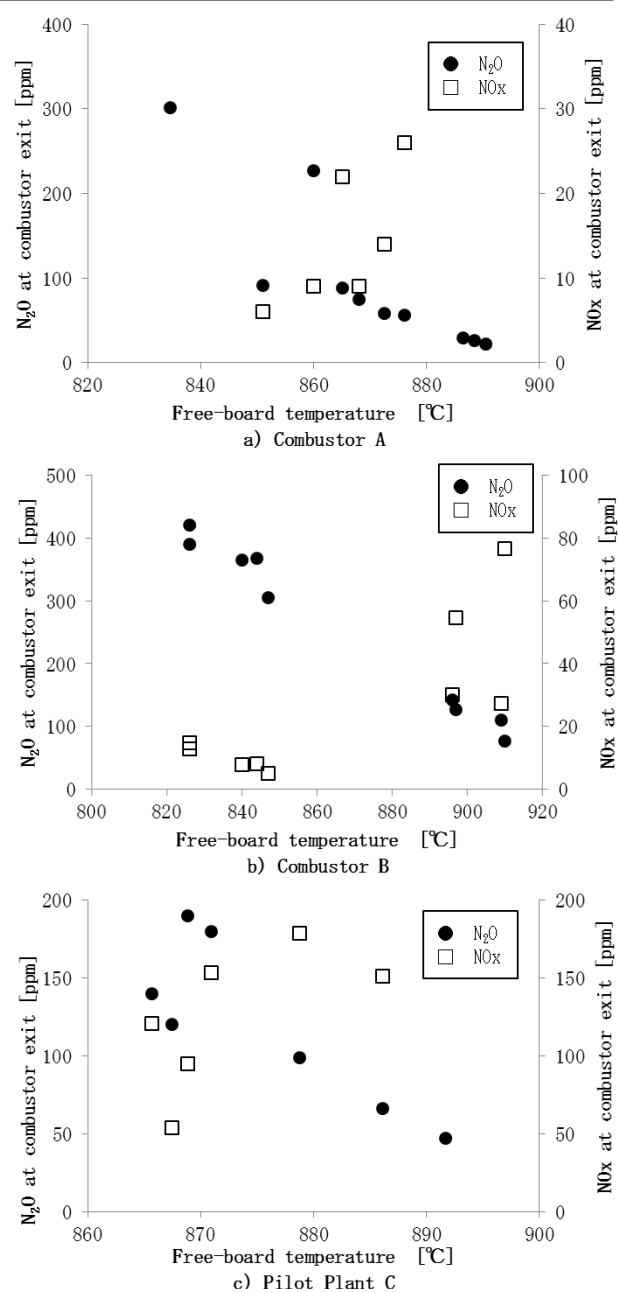


Figure 2. Relationship between temperature and N₂O concentration at combustor exit.

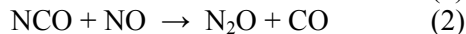
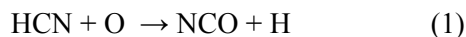
4.2 Effects of HCN on N₂O formation

It is reported that HCN plays a role of precursor in N₂O formation [11]. Figure 5 shows relationship between HCN concentration at the lower free-board and N₂O concentration at the combustor exit in the combustor A. In these tests the plant was operated so that the free-board temperature was kept constant at 850±20 degrees Celsius. The data plots are categorized into two groups; one is the lower free-board temperature of 780±10 degrees Celsius (N₂O of 300 ppm) and the other is 800±10 degrees Celsius (N₂O of 100 ppm). It is found that there is a positive correlation between HCN concentration at the lower free-board and N₂O concentration at the combustor exit. Destruction rate of N₂O can be treated as almost constant, because the free-board temperature did not change through the tests. This result, therefore, indicate that the higher temperature causes the larger formation of N₂O by oxidation.

Solid lines in Figure 5 show the calculated results concerning effects of HCN on N₂O formation using Leeds mechanism. Initial temperature, HCN and N₂O concentration were set as the above-mentioned experimental values. Residence time was assumed to be 6 seconds according to the test conditions. Comparing the experimental and calculated results, their qualitative trends agree well for in the temperature of 800±10 degrees Celsius. However, for the temperature of 780±10 degrees Celsius, the calculated N₂O concentration is lower than the experimental ones. This discrepancy is discussed in the next sub-section.

4.3 Validity of Reaction Mechanism

Usually N₂O formation from HCN is treated via NCO as follows [12]:



In recent years, the following reactions concerning HCN and NO formation via NCN have been proposed [9]:



Since Leeds mechanism does not include NCN in the chemical species, the reactions (3)-(5) are not reflected in the calculated results shown in Figure 5. Then, numerical simulation

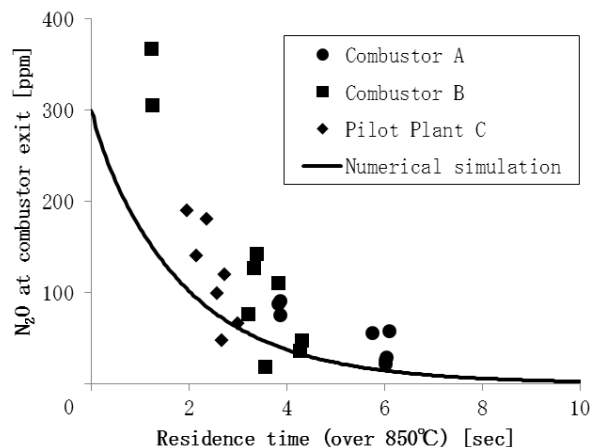


Figure 3. Relationship between residence time for 850 degrees Celsius or higher and N₂O concentration

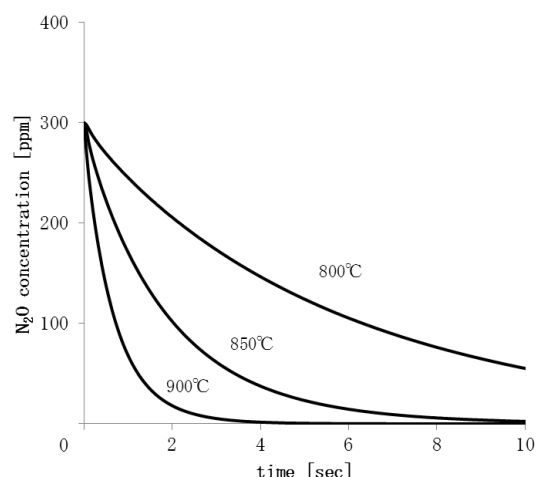


Figure 4. Calculated N₂O concentration vs. residence time.

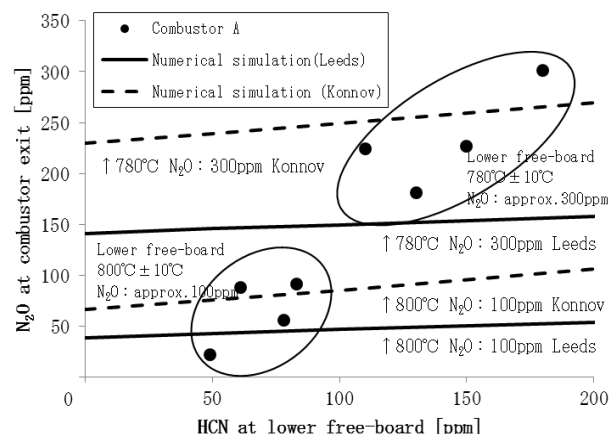
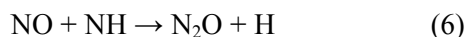


Figure 5. Comparison of experimental and calculated results on effects of HCN concentration at the lower free-board to N₂O concentration at the combustor exit.

was carried out using Konnov mechanism which includes NCN and the calculated results are denoted by the dotted line in Figure 5. The calculated N₂O concentration with Konnov mechanism shows higher N₂O concentration in the entire range of the initial HCN concentration and agrees well with the experimental results. However, it must be noted that the calculated N₂O concentrations using Konnov mechanism according to Figure 3 and Figure 4 are higher several tens of percent than the experimental results. This suggests availability of Konnov mechanism for temperature around 800 degrees Celsius or less, while Leeds mechanism is valid for around 850 degrees Celsius. Governing reaction in Leeds mechanism is reaction (2), however in Konnov mechanism is the following reaction.



The differences of the calculated results between two reaction mechanisms are mainly due to different temperature dependence of reaction (2) and (6). Proper selection of chemical kinetic model according to temperature range is critical to serve calculated results as an analysis tool to improve combustion conditions.

5 Summary

- (1) The exhaust gas residence time of at least 4 seconds at the free-board in which temperature is over 850 degrees Celsius is required to achieve N₂O emission less than 50 ppm at the combustor exit.
- (2) There is a positive correlation between HCN concentration at the lower free-board and N₂O concentration at the combustor exit. The higher temperature causes the larger formation of N₂O by oxidation.

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