Analysis of NO$_x$ Formation Behavior in Waste Combustion

～Development of three-dimensional analysis with detailed reaction mechanism～

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Abstract

Most of nitric oxide (NO$_x$) generated by waste combustion is fuel NO$_x$ whose starting material is nitrogen in waste. In order to minimize NO$_x$ generation, two-stage combustion is applied, however its reaction mechanism is complex. Numerical analysis of NO$_x$ formation in waste combustion requires detailed reaction model, which makes computational cost too large and difficult to conduct three-dimensional analysis. A newly developed reduced mechanism was applied to three-dimensional computational fluid dynamics (CFD) analysis, and confirmed the consistency between analysis and experimental data. The results of NO$_x$ concentration of analysis showed good agreement with experimental data of them in multiple operating conditions. We introduce the contents as a design and development tool.

1　Introduction

Nitrogen oxide (NO$_x$) is produced in the combustion process at Waste-to-Energy (WtE) plants. Nitric oxide (NO) makes up the largest proportion of NO$_x$ originated in the combustion process. When released into the atmosphere, it is oxidized to highly toxic nitrogen dioxide (NO$_2$). As NO$_x$ is also responsible for pollution in the form of acid rain and the formation of photochemical oxidants[1], rules on emission have been set by national and local governments. While Japan's Air Pollution Control Law specifies a limit for emissions of 250 ppm (corrected to a residual oxygen concentration of 12%. In this paper, NO$_x$ concentrations are given on this basis unless otherwise stated.), a lot of local municipalities apply their own more stringent emission standards. Table 1 lists the characteristics of two ways in which NO$_x$ can be removed from flue gas: selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR). Each has its own advantages – good NO$_x$ removal efficiency in the case of SCR and cost and energy use in the case of SNCR – and the equipment is selected that best suits the circumstances, such as the permitted level of NO$_x$ emissions. Another approach is to use more advanced combustion control to reduce the amount of NO$_x$ produced. This can allow the cost and energy efficiency benefits of SNCR to be taken advantage of even at plants subject to strict rules on NO$_x$ emissions.

Table 1 Methods of NOₓ reduction in flue gases

Method	Summary	Advantages	Disadvantages
Selective catalytic reduction (SCR)	• Reaction of NOₓ with ammonia using a catalyst • Reaction temperature ≥ 180 °C	• Good NOₓ removal	• Requires steam to reheat flue gas from about 160 °C to 180 °C or more
Selective non-catalytic reduction (SNCR)	• Ammonia or urea solution sprayed directly into combustion chamber to react with NOₓ at temperatures of between 800 and 900 °C	• Does not require reheating of flue gas • Simple equipment	• Low level of NOₓ removal makes it inadequate for achieving tight emission standards

The shaft-furnace type gasification and melting system, known as a Direct Melting System (DMS), is one type of WtE plant constructed by Nippon Steel Engineering (NSE) in the past. The production of NOₓ in this system occurs in the independent combustion chamber located downstream of the gasifier. In the design of combustion chambers, NSE has for more than 20 years been making use of simulation by computational fluid dynamics that also incorporates the combustion process, in order to optimize combustion performance and temperature distributions. However, given the complex reaction pathways involved in its formation, extending the scope of simulation to include NOₓ has remained impractical due to the heavy computational load. Accordingly, to provide a tool for determining combustion chamber designs and operating practices that will minimize the amount of NOₓ produced by combustion, NSE has developed an analytical technique that considers the three-dimensional behavior of NOₓ formation in the combustion chamber.

2 Combustion Chamber in Shaft-Furnace Type Gasification and Melting System

Figure 1 shows a schematic diagram of the gasification and melting furnace and independent combustion chamber that form part of the shaft-furnace type gasification and melting system. Waste is fed into the gasification and melting furnace from the top of the gasifier. After its moisture content evaporates as steam in the drying and preheating zone, the waste falls slowly in the furnace, then the combustibles are thermally decomposed and gasified. Incombustibles and fixed carbon remaining after thermal decomposition move to the bottom of the furnace, and then fall into the combustion zone and melting zone together with the coke and limestone fed from the ceiling. The coke
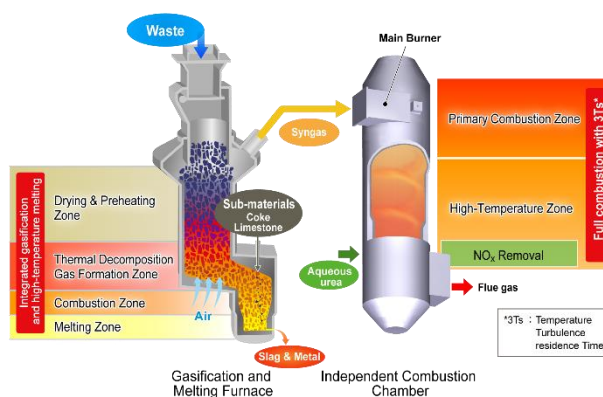

Figure 1 Gasifier and independent swirl combustion chamber of direct melting system

is combusted with the air and oxygen supplied through the tuyeres (blow nozzles) at the bottom of the furnace to form a high-temperature melting zone that melts all of the ash content. The molten materials, the fluidity of which is kept moderate, are discharged from a tap hole at the bottom of the furnace and quenched by jet-water. Generated granular slag and metal are completely recycled after magnetic separation.

Meanwhile, syngas that forms in the gasifier is supplied to the downstream combustion chamber where it is ignited in the main burner. The main burner is positioned so as to generate swirl flow with turbulence, which makes the syngas well-mixed with the combustion air in the chamber to achieve full combustion. Dioxins are fully broken down in this process, both because a high level of mixing is achieved at high temperature (approximately 1,000 °C) and because the mixture is held in this high-temperature zone for long enough to provide adequate combustion. Furthermore, when SNCR is used for NOₓ removal, aqueous urea or ammonia is supplied to the high-temperature zone. A key feature of this shaft-furnace type gasification and melting system is that the combustion chamber and the gasification and melting furnace are separate, with independent control of each, achieving both full gasification and melting, and full

combustion. In particular, because the combustion chamber mainly burns gas, combustion performance is superior to solid fuel combustion, in terms of easier control of the air ratio.

NSE uses two-stage combustion to reduce the amount of NO_x produced in the combustion chamber. This involves fuel-rich combustion in the first stage (an excess air ratio of about 0.8) to suppress the formation of NO_x, and then adding air in the second stage to complete combustion. The efficacy of two-stage combustion has been demonstrated both in plant trials and by numerical analysis using a simplified model[2].

3 NO_x Formation Mechanism and Analysis Method

The NO_x formed during combustion can be split into three categories based on the mechanism by which it forms: [1] Fuel NO_x, [2] Thermal NO_x, and [3] Prompt NO_x. Table 2 lists their respective characteristics. Of these, the bulk of NO_x formed in the combustion chamber is considered to be fuel NO_x. Nitrogen makes up about 1% of municipal solid waste by weight, with nitrogen compounds such as NH_3 being formed by the thermal decomposition of waste. These nitrogen compounds are oxidized in the combustion chamber to form fuel NO_x. Because of the extreme complexity of the reaction pathways for fuel NO_x, detailed chemical kinetics is needed to simulate it numerically. A numerical analysis of the reaction field with detailed chemical kinetics simulates the various different reactions taking place at the atomic level in the actual combustion process. It means solving the simultaneous equations for the concentration of each chemical species using the reaction rates for each elemental reaction. While the accuracy is high, so too is the computational load. The second category, thermal NO_x,

is formed by atmospheric nitrogen (N_2) bonding with oxygen. The rate of thermal NO_x formation rises sharply above 1,500 °C. Because the temperature in the combustion chamber does not exceed about 1,200 °C, the amount of this type of NO_x formed is considered to be low. The third category, prompt NO_x, is formed by the oxidation of the HCN formed by atmospheric N_2 reacting with CH radicals from the fuel. As a high concentration of H_2O reduces the amount of prompt NO_x[4], the combustion of syngas is considered to produce only small amounts of this type of NO_x due to it containing a lot of H_2O from the waste.

To confirm that the bulk of the NO_x formed in the combustion chamber is in fact fuel NO_x, an analysis using detailed chemical kinetics of the combustion of waste in which the pyrolysis gas does not contain any nitrogen compounds found that it resulted in an NO_x concentration of less than 1 ppm. As an actual combustion chamber generates between 50 and 200 ppm of NO_x, this result indicates that little thermal and prompt NO_x is generated. Similarly, Figure 2 (cited from the literature) shows how the amounts of NO_x produced by the different mechanisms vary with temperature in the combustion of waste. These data also indicate that fuel NO_x accounts for the bulk of the NO_x produced by the shaft-furnace type gasification and melting system in which combustion takes place at temperatures of less than 1,200 °C.

Accordingly, detailed chemical kinetics is required for numerical analysis of the behavior of NO_x formation in the combustion chamber, but as noted above it imposes a high computational load. To perform a three-dimensional analysis of an actual-size combustion chamber is not practical. For this reason, the authors set out to reduce the detailed reaction model used in the analysis to reduce its computational load.

Table 2 Classification of NO_x by mechanism of formation

Name	Typical reaction	Characteristics	Numerical analysis
[1] Fuel NO_x	Decomposition and oxidation of nitrogen compounds in fuel	• Formed from nitrogen in fuel	• Requires detailed chemical kinetics • High computational load
[2] Thermal NO_x	$N_2 + O \rightarrow NO + N$ $N + O_2 \rightarrow NO + O$ $N + OH \rightarrow NO + H$	• Increased formation at high temperature (> 1500 °C) • Formed from atmospheric N_2	• Can be calculated for overall reaction • Low computational load
[3] Prompt NO_x	$N_2 + CH \rightarrow HCN + N$ Decomposition and oxidation of HCN	• Generated by excess fuel • Reduced by presence of H_2O • Formed from atmospheric N_2	• Requires detailed chemical kinetics • High computational load

Figure 2 Temperature dependence of various NOₓ formation mechanisms in waste incineration[5]

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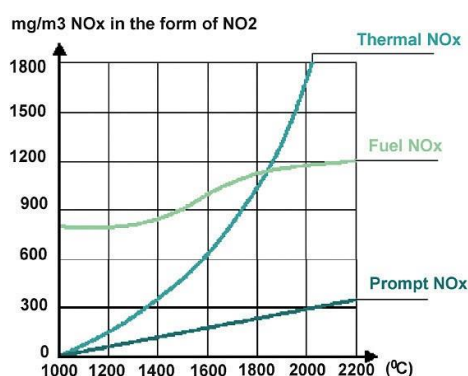
4 Reduction of Detailed Reaction Model for Fuel NOₓ

Kilpinen 97[6] was selected as the detailed reaction model for expressing the behavior of fuel NO_x. This reaction model is based on a combustion reaction in which hydrocarbons with one or two carbon atoms are combusted in the presence of nitrogen compounds. As experimental data has been used to confirm the model's integrity with regard to the breaking down of NH_3 by partial combustion, it is considered to be suitable for use with the two-stage combustion of pyrolysis gas produced from waste. While GRI-Mech 3.0[7] is a widely used reaction model for the analysis of gas combustion by detailed chemical kinetics, it has been demonstrated that Kilpinen 97 is better suited to the qualitative modeling of the NO_x produced by the combustion of pyrolysis gas that contains NH_3 under a wide range of conditions[8]. However, because Kilpinen 97 includes 57 chemical species and 353 elementary reactions, the calculation time is very long if used for the three-dimensional combustion analysis of a large model such as a combustion chamber.

While the detailed reaction model includes a large number of elementary reactions and chemical species, these include some that affect parameter such as flame temperature and the concentration of chemical species by such a small extent that they can be ignored. To focus on the concentration of NO and temperature in the combustion analysis, elementary reactions that have little influence on them may be eliminated. As sensitivity analysis is a way to assess these influences, the following formula was used to calculate sensitivity coefficients.

$$S_i = \frac{A_{f,i}}{\phi} \frac{\partial \phi}{\partial A_{f,i}} \qquad (1)$$

Here, S_i is the sensitivity coefficient for scalar quantity ϕ (NO mole fraction or temperature) for elementary reaction i and $A_{f,i}$ is the frequency factor for elementary reaction i. The Kilpinen 97 reaction model was then reduced by eliminating those reactions that these sensitivity coefficients indicated had a low impact on NO concentration and temperature.

Table 3 lists the conditions for the sensitivity analysis. Flexible control of the excess air ratio is enabled with the combustion chamber constructed by NSE. Accordingly, the sensitivity analysis was performed for excess air ratios from 0.5 to 1.5 to ensure the accuracy of the NOx analyses over a wide range of excess air ratios.

Cantera[9], software for chemical reaction analysis, was used to perform the numerical calculations, including sensitivity analysis. Kilpinen 97 was modified to use data formats that can be read by Cantera and incorporated into the analysis. The procedure was as follows.

[1] Cantera was used to perform sensitivity analyses for combustion at each excess air ratio (0.5 to 1.5).

[2] For NO mole fraction and temperature respectively, the sensitivity coefficient with highest absolute value across all excess air ratios was set as the sensitivity coefficient for each elementary reaction.

[3] For NO mole fraction and temperature respectively, the sensitivity coefficients were normalized such that the largest coefficient from step [2] across all reactions had the value 1.

[4] The sensitivity coefficients for NO mole fraction and temperature obtained in step [3] above were sorted by value and the elementary reactions excluded one by one, starting from the reaction with lowest coefficient value. The chemical species that were no longer needed were also excluded.

Table 3 Conditions for sensitivity analysis

Analysis software	Cantera 2. 3. 0
Reactor model	Perfectly stirred reactor (adiabatic)
Fuel	Syngas from melting furnace
Excess air ratios	0.5, 0.7, 1.0, 1.5
Monitoring value	NO concentration, temperature

[5]   The calculation of step [1] was repeated for the new reaction model (with elementary reactions and chemical species reduced) and the difference from the original reaction model was determined.

[6]   If exclusion of an elementary reaction resulted in a large difference between models, this indicated that the reaction was important and so it was restored, and the next reaction was excluded.

Figure 3 and Figure 4 show sensitivity coefficients for typical elementary reactions. The reaction numbers in these figures correspond to those in Table 4. The absolute values of the sensitivity coefficients of elementary reaction 1 for temperature and that of elementary reaction 2 for NO molar fraction were respectively the largest across all reactions. Elementary reaction 1 is the main reaction of combustion. As O and OH radicals influence NO generation, it had a high sensitivity coefficient with respect to NO. In contrast, elementary reaction 2 is between chemical species that do not contribute significantly to the combustion reaction and therefore its sensitivity coefficient with respect to temperature was low. Moreover, whereas elementary reactions 1 and 3 only had high sensitivity coefficients with respect to NO when the excess air ratio was 0.5, elementary reactions 2 and 4 had high sensitivity coefficients regardless of excess air ratio. This signifies that the important elementary reactions under lean and rich combustion conditions are different. While elementary reactions 5 and 6 were initially excluded because they had low sensitivity coefficients for both NO molar fraction and temperature, the check calculation result after excluding elementary reaction 5 differed by a large amount. Although elementary reaction 5 is not a rate-limiting reaction for combustion, it could not be excluded because to do so interrupted the reaction pathway.

The model that resulted after excluding as many elementary reactions as possible had 40 chemical species and 134 reactions. Table 5 lists the results before and after reaction model reduction. The analysis was performed for excess air ratios of 0.5 to 1.5, with results of the before and after reaction models showing good agreement for NO concentration and temperature. It was anticipated that this would shorten the computation time while still achieving

the objective of studying the behavior of NO_x formation in the combustion chamber.
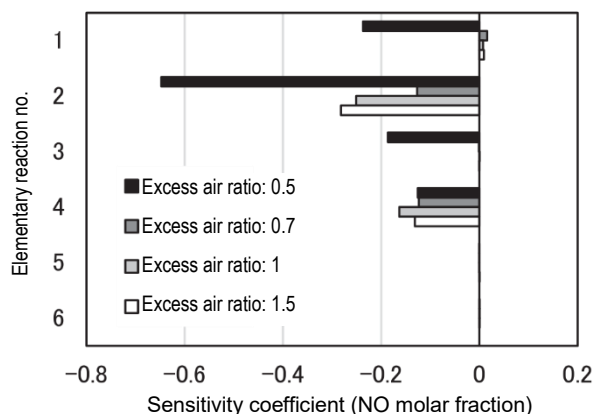

Figure 3 Sensitivity coefficients for typical reactions with respect to NO molar fraction
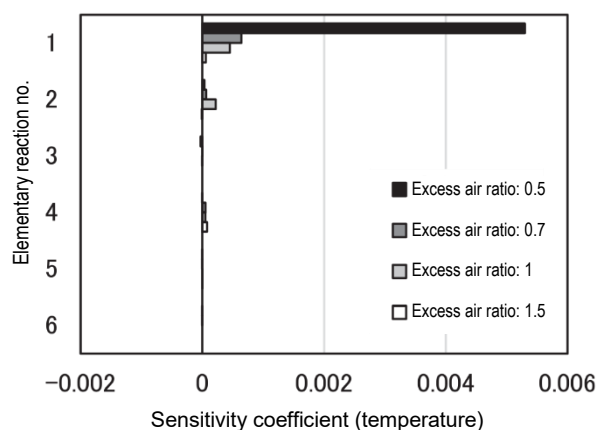
Figure 4 Sensitivity coefficients for typical reactions with respect to temperature

Table 4 Chemical equations for elementary reactions in Figure 3 and Figure 4

No.	Chemical equation
1	$O + OH \Leftrightarrow H + O_2$
2	$HCCO + NO \Leftrightarrow HCNO + CO$
3	$CH_3 + N \Leftrightarrow H_2CN + H$
4	$NH + NO \Leftrightarrow N_2O + H$
5	$CH_2O + OH \Leftrightarrow HCO + H_2O$
6	$NCN + OH \Leftrightarrow HCN + NO$

Table 5 Results of analysis before and after reaction model reduction

	Excess air ratio	[1] Before reduction (57 chemical species, 353 reactions)	[2] After reduction (40 chemical species, 134 reactions)	[3] Difference ([2]/[1]-100%)
NO concentration (ppm, wet)	0.5	5.66	5.35	-6%
	0.7	109	117	8%
	1.0	389	415	7%
	1.5	351	381	8%
Temperature (°C)	0.5	1122	1126	0%
	0.7	1356	1356	0%
	1.0	1575	1574	0%
	1.5	1337	1336	0%

5 Application to Three-Dimensional Analysis

The reduced reaction model was combined with computational fluid dynamics (CFD) to perform a three-dimensional combustion analysis of an actual-size combustion chamber. Table 6 lists the analysis conditions. Actual plant measurements were made by varying the excess air ratio of primary air to change the amount of NO_x formed in the combustion chamber and these conditions were then analyzed in a three-dimensional simulation with detailed chemical kinetics to enable comparison of the measured and calculated results.

Table 7 lists the amounts of NO_x produced. The calculated NO_x concentrations were of a similar order to the measured values and replicate the effect whereby reducing the primary excess air ratio reduces the amount of NO_x produced. The computation time for the simplified reaction model was reduced by approximately half compared to the model before simplification. The calculated and measured concentrations differed by around 50 to 70%. The reasons for this are considered to be the use of a turbulence model with a low computational load that has inferior accuracy, and because the quantity of nitrogen compounds in the syngas was higher than the actual plant. While more work is needed to enable quantitative prediction of NO_x concentration, the method still provides a practical tool with a low computational load for studying ways of improving low-NO_x combustion.

Figure 5 shows the distributions of O_2 concentration, NO formation rate, heat of reaction, and NO concentration. These results show that reducing the primary air reduces the concentration of O_2 and expands the extent of reducing atmosphere in the main combustion region. A comparison of the distributions for NO formation rate and heat of reaction shows that the NO formation rate is high at locations where the heat of reaction is high, indicating that NO is formed by combustion. Also, the more the primary excess air ratio is reduced, the larger the extent within the main combustion region where the NO formation rate becomes negative (where the decomposition of NO is

Table 6 Conditions for three-dimensional NO_x analysis

Analysis software	ANSYS FLUENT 18. 2
Turbulence model	Realizable k—ε model
Turbulent combustion model	Eddy dissipation concept (EDC) model
Reaction model	Reduced Kilpinen 97 (40 chemical species, 134 reactions)
Primary excess air ratio	0.85, 0.98, 1.18

Table 7 Comparison of flue gas NO_x concentration with results of three-dimensional NO_x analysis and actual plant

Primary excess air ratio		0.85	0.98	1.18
NO_x concentration (ppm)	[1] Measured	64	73	99
	[2] Calculated	110	120	150
	[3] Difference ([2]/[1]-100%)	72%	64%	52%

promoted). Due to this effect, the NO concentration at the combustion chamber outlet was suppressed as the primary excess air ratio reduced.

6 Future Plans

While the behavior of NO_x formation in the combustion chamber was successfully simulated, issues remain with the quantitative accuracy of the NO_x concentration. There is a need to look more closely at the turbulence model and the quantity of nitrogen compounds in the syngas to reduce the difference between calculated and measured values. The aim is to utilize this tool to further reduce of NO_x formation by optimizing combustion chamber design and condition of air supply. Plans also include extending the analysis to NSE's technology for stoker-type incineration.

7 Conclusion

Reduction of a detailed reaction model which requires high computational load succeeded in roughly halving its calculation time, and as a result that was suitable for the three-dimensional analysis of the behavior of NO_x formation in the combustion chamber that forms part of the shaft-furnace type gasification and melting system. The analysis results replicated the trend in flue gas NO_x concentration under different conditions in which the primary excess air ratio was varied, successfully determining the distribution of NO_x concentration in the combustion chamber. The intention is to use this analytical model to further improve of low-NO_x combustion.

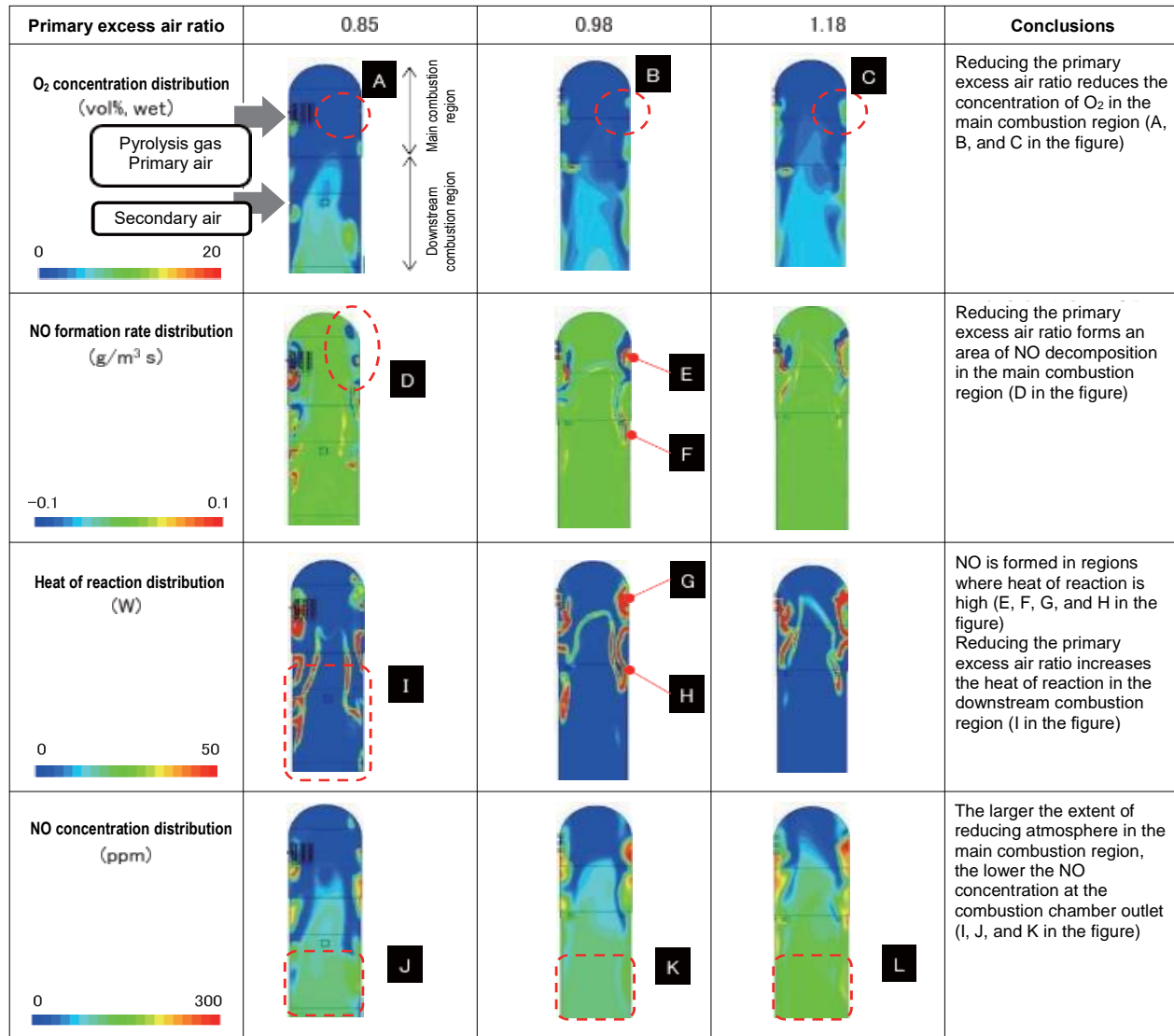| Primary excess air ratio	0.85	0.98	1.18	Conclusions
O₂ concentration distribution (vol%, wet) — Pyrolysis gas Primary air / Secondary air — 0 … 20 — Main combustion region / Downstream combustion region	A	B	C	Reducing the primary excess air ratio reduces the concentration of O₂ in the main combustion region (A, B, and C in the figure)
NO formation rate distribution (g/m³ s) — −0.1 … 0.1	D	E, F		Reducing the primary excess air ratio forms an area of NO decomposition in the main combustion region (D in the figure)
Heat of reaction distribution (W) — 0 … 50	I	G, H		NO is formed in regions where heat of reaction is high (E, F, G, and H in the figure) Reducing the primary excess air ratio increases the heat of reaction in the downstream combustion region (I in the figure)
NO concentration distribution (ppm) — 0 … 300	J	K	L	The larger the extent of reducing atmosphere in the main combustion region, the lower the NO concentration at the combustion chamber outlet (I, J, and K in the figure)

Figure 5 Results of three-dimensional NOₓ analysis: contours of O₂ concentration, heat of reaction, NO formation rate, and NO concentration

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