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1  
2 Predictions of NO and CO emissions in ammonia/methane/air  
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5 combustion by LES using a non-adiabatic flamelet generated  
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8 manifold  
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12 Takafumi Honzawa<sup>\*,a,b</sup>, Reo Kai<sup>b</sup>, Akiko Okada<sup>a</sup>, Agustin Valera-Medina<sup>c</sup>, Philip J. Bowen<sup>c</sup>,  
13 Ryoichi Kurose<sup>b</sup>

14  
15  
16 <sup>a</sup> *Fundamental Technology Department, Tokyo Gas Co., Ltd., 1-7-7 Suehiro-cho, Tsurumi-ku, Yokohama,*  
17 *Kanagawa 230-0045, Japan*

18  
19 <sup>b</sup> *Department of Mechanical Engineering and Science, Kyoto University, Kyoto daigaku-Katsura, Nishikyo-ku,*  
20 *Kyoto 615-8540, Japan*

21  
22 <sup>c</sup> *College of Physical Sciences and Engineering, Cardiff University, Queen's Building, Cardiff CF24 3AA,*  
23 *United Kingdom*  
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28 **Abstract**

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31 A large-eddy simulation (LES) employing a non-adiabatic flamelet generated manifold  
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33 approach, which can account for the effects of heat losses due to radiation and cold walls, is  
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35 applied to NH<sub>3</sub>/CH<sub>4</sub>/air combustion fields generated by a swirl burner, and the formation  
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37 mechanisms of NO and CO for ammonia combustion are investigated in detail. The  
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39 amounts of NO and CO emissions for various equivalence ratios, are compared with those  
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41 predicted by LES employing the conventional adiabatic flamelet generated manifold  
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43 approach and measured in the bespoke experiments. The results show that the amounts of  
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45 NO and CO emissions predicted by the large-eddy simulations with the non-adiabatic  
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47 flamelet generated manifold approach agree well with the experiments much better than the  
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49 ones with the adiabatic flamelet generated manifold approach. This is because the NO and  
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51 CO reactions for NH<sub>3</sub>/CH<sub>4</sub>/air combustion are quite susceptible to H and OH radicals'  
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53 concentrations and gas temperature. This suggests that it is essential to take into account the  
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61 \*Corresponding Author. Tel.: +81-90-4021-9873; fax: +81-45-500-8790  
62 Email address: honzawa.t@tokyo-gas.co.jp (Takafumi Honzawa)  
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1 effects of various heat losses caused by radiation and cold walls in predicting the NO and  
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4 CO emissions for the combustion of ammonia as a primary fuel.  
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9 Key words: Non-adiabatic flamelet generated manifold approach, NH<sub>3</sub>/CH<sub>4</sub>/air combustion,  
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11 Large-eddy simulation, Nitrogen oxides, Carbon monoxide  
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### 14 15 **Highlights**

- 16 • LES employing non-adiabatic flamelet approach is employed for NH<sub>3</sub>/CH<sub>4</sub>/air  
17 combustion.
  - 18 • Heat losses affect NO and CO emissions, which can be captured by the simulation.
  - 19 • NO and CO reactions are susceptible to H and OH concentrations and gas temperature.
  - 20 • Temperature dependency of NO reaction is different between NH<sub>3</sub>/CH<sub>4</sub>/air and CH<sub>4</sub>/air.
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### 30 31 32 33 **1. Introduction**

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35 The emissions of carbon dioxide (CO<sub>2</sub>), which induces global warming, is  
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37 increasing at a rapid rate. In Japan, 39% of CO<sub>2</sub> emissions are discharged in energy  
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39 transformation industries such as power generation plants [1], and the most are produced by  
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41 combustion of fossil fuels. The amount of the CO<sub>2</sub> emissions in gas power plants is  
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43 approximately one half of that in coal-fueled power plants [2]. Therefore, while renewable  
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45 energy plants such as solar and wind power plants increase, the demand of gas power plants  
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47 is considered to remain in order to maintain the supply of electricity. But it is necessary to  
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49 reduce the CO<sub>2</sub> emissions in gas power plants more than now.  
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55 Ammonia (NH<sub>3</sub>) combustion has recently drawn intense research interest because  
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58 of its potential to reduce CO<sub>2</sub> emissions when implemented in such power plants. NH<sub>3</sub> is  
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1 17.8% by weight hydrogen, a relatively high hydrogen ratio [3, 4]. The technologies related  
2 to its production, transportation, and storage are well established, with  $\text{NH}_3$  being the  
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4 second largest produced chemical in the world.  $\text{NH}_3$  can be also produced from renewable  
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6 energy sources [5]. In addition,  $\text{NH}_3$  can be easily liquefied and stored in the conditions of  
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8 8.5 bar at ambient temperature or 240 K at ambient pressure, which is less expensive than  
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10 liquefying pure hydrogen [6]. Therefore,  $\text{NH}_3$  has been considered as a potential source of  
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12 hydrogen and an alternative carbon-free fuel for the future. As the first step, it will be an  
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14 actual solution to mix  $\text{NH}_3$  and conventional fossil fuels in order to reduce  $\text{CO}_2$  emissions.  
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21 Considerable research on  $\text{NH}_3$  combustion has been done since the 1960s [7-9].  
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23 Experimental studies showed that the minimum ignition energy of  $\text{NH}_3$  is 16 times higher  
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25 than that of fossil fuels. At stoichiometric conditions, the quenching distance of  $\text{NH}_3/\text{air}$   
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27 was 3.5 times greater than that of propane/air [8]. Other experiments demonstrated that  
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29  $\text{NH}_3/\text{air}$  has a relatively slow chemical reaction rate, giving a laminar burning velocity of  
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31 6-8 cm/s [10], which is only one fifth that of methane ( $\text{CH}_4$ )/air. In other studies, high  
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33 production of nitrogen oxides ( $\text{NO}_x$ ) originating from nitrogen in  $\text{NH}_3$  is considered as a  
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35 problem [11-13].  
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40 In the face of such problems for  $\text{NH}_3$  combustion, some challenges for the  
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42 practical application have been conducted recently. Valera-Medina et al. [14, 15] combusted  
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44  $\text{NH}_3/\text{CH}_4/\text{air}$  in various equivalence ratios in a laboratory-scale tangential swirl burner and  
45  
46 suggested low swirl and different injection strategies to optimize gas turbines with  $\text{NH}_3$  as a  
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48 primary fuel. Kurata et al. [16] demonstrated  $\text{NH}_3/\text{CH}_4/\text{air}$  combustion employing a micro  
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50 gas turbine in the Fukushima Research Energy Institute. Hayakawa et al. [17] showed that a  
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52 specific equivalence ratio supports low emissions of nitric oxide ( $\text{NO}$ ) and  $\text{NH}_3$ .  
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56 Because  $\text{NO}_x$  emissions are strictly regulated, an optimized burner design for  $\text{NH}_3$   
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58 combustion is required. For such purposes, computational fluid dynamics (CFD) can be an  
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1 effective approach. Somarathne et al. [18] illuminated the effect of secondary air injection  
2 to reduce the amount of NO emissions. It was suggested that the equivalence ratio,  $\phi$ , at the  
3 primary zone should be controlled as  $\phi = 1.2$ . This indicates that the equivalence ratio in an  
4 ideal combustion chamber changes from a fuel-rich condition to a stoichiometric condition.  
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6 Additionally, the NO production rate is relatively slow and depends on temperature.  
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8 Therefore, to evaluate the amount of NO emissions, it is necessary to consider heat losses  
9 in combustion chambers. However, the simulations in previous researches were conducted  
10 in an adiabatic condition using detailed reaction mechanisms [18, 19]. There is no study  
11 that examined the validity of turbulence combustion models, especially flamelet  
12 approaches.  
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25 The purpose of this study is, therefore, to perform large-eddy simulation (LES)  
26 using two types of flamelet approach for NH<sub>3</sub>/CH<sub>4</sub>/air combustion in the swirl burner [15],  
27 and to validate our method by comparing the amounts of NO and carbon monoxide (CO)  
28 emissions with experimental data. At the beginning, in order to investigate an adequate  
29 mechanism for the condition of the swirl burner, some representative detailed reaction  
30 mechanisms are compared through evaluating the laminar burning velocity and the amount  
31 of NO emissions. Then, LESs with two types of flamelet approach are conducted. As a  
32 combustion model, a non-adiabatic flamelet generated manifold approach (NA-FGM),  
33 which is extended based on the conventional flamelet-generated manifold approach (FGM)  
34 [20]. The NA-FGM can consider the effects of various heat losses through radiation and  
35 cold walls. Proch and Kempf [21] employed the NA-FGM for a tabulated premixed flame.  
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37 In their approach, progress variable, progress variable variance and enthalpy difference  
38 were introduced for generating the flamelet library, whereas mixture fraction is additionally  
39 introduced in this study, in order to take into account the variation of  $\phi$ . In addition, the NO  
40 and CO reactions are discussed in non-adiabatic conditions from the viewpoint of chemical  
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## 6 **2. Numerical methods**

### 7 **2.1. Configurations of targeted chamber and swirl burner**

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10 Figure 1 shows schematics of computational domain and generic swirl burner. The  
11 detailed structure of this burner is identified in the previous studies [15, 22]. The fuel  
12 consists of 61.0% NH<sub>3</sub> and 39.0% CH<sub>4</sub> by volume, and the oxidizer is air. This fuel  
13 component gave stable NH<sub>3</sub>-based flames in the experiments, and NO and CO emissions  
14 were measured [15]. The NH<sub>3</sub>/CH<sub>4</sub>/air premixed gas is supplied from the inlet nozzle. Its  
15 equivalence ratio is set as 0.840, 1.04 and 1.31 respectively. Because the gas is completely  
16 mixed in advance, the variance of the composition is ignored. Progress variables  $C$  of any  
17 inlet gases are zero. Here,  $C$  is defined as the sum of  $Y_{H_2}$ ,  $Y_{H_2O}$ ,  $Y_{CO}$  and  $Y_{CO_2}$ .  $Y_i$  denotes the  
18 mass fraction of chemical species  $i$ . After passing through the swirler, the premixed gas is  
19 burned in the combustion chamber made of a quartz glass. The domain is divided into ~5  
20 million vertices and ~6 million cells. The small meshes are provided to resolve the  
21 turbulent eddies in the recirculating reaction zones.  
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40 As boundary conditions, the volume flow rate of fuel at the inlet is constant as  $1.35$   
41  $\times 10^{-3}$  m<sup>3</sup>/s. The inlet premixed gas temperature is 298 K, and the ambient pressure is 1 atm.  
42 If the LES/NA-FGM is employed, temperature, convection heat transfer rate, and  
43 emissivity on the walls of the combustion chamber are set to 1500 K, 10 W/m<sup>2</sup>K, and 0.8  
44 respectively. The other walls are treated adiabatically. Since these properties on the walls  
45 could not be measured in the experiment, these parameters on the boundary conditions are  
46 based on our experiences. On the other hand, the all walls are treated adiabatically if the  
47 conventional LES/FGM is employed.  
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58 Here, the swirl number,  $S_w$ , of the burner is also addressed.  $S_w$  can be defined as  
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$$Sw = \frac{G_a}{G_r r_1}, \quad (1)$$

where  $G_a$  and  $G_r$  are respectively the angular and radial momenta, and  $r_1$  is the radius of the tubular cavity of the swirler. Velocity at the slit,  $w_s$ , is expressed as  $w_s = Q/(n_s t_s L_s)$ , where  $Q$  is total volume flow rate, and  $n_s$ ,  $t_s$  and  $L_s$  are respectively the number of slits, the thickness and the longitudinal length for each slit. The angular momentum per unit volume for the premixed gas is  $\rho w_s (r_1 - t_s/2)$ . Here,  $(r_1 - t_s/2)$  is the distance between the axis and the center of the slits. Because of the above, the total angular momentum,  $G_a$ , is expressed as  $G_a = \rho Q w_s (r_1 - t_s/2) = \rho Q^2 (r_1 - t_s/2) / (n_s t_s L_s)$ . On the other hand, mean axial velocity,  $U$ , is expressed as  $U = Q / (\pi r_1^2)$ . Accordingly, the total radial momentum,  $G_r$ , is expressed as  $G_r = \rho Q U = \rho Q^2 / (\pi r_1^2)$ . Therefore,  $Sw$  is expressed as

$$Sw = \frac{1}{\pi} \frac{(r_1 - \frac{t_s}{2}) r_1}{n_s t_s L_s}. \quad (2)$$

In this study, because  $r_1 = 20$  mm,  $n_s = 9$ ,  $t_s = 5.7$  mm and  $L_s = 18.5$  mm,  $Sw$  is 1.84.

## 2.2. LES/NA-FGM

For numerical simulations of premixed combustion, premixed flamelet libraries based on the FGM [20], for which one-dimensional premixed free-propagating flame is calculated in several equivalence ratios, are often used. However, the conventional FGM has the deficiency that a set of chemical species' mass fractions at the equilibrium state of the reaction is basically stored in adiabatic conditions, so that the effect of heat loss on the change in the composition of chemical species cannot be considered. In this study, therefore, a non-adiabatic procedure, which was proposed by Kishimoto et al. [23] for generating non-premixed flamelet libraries that consider the effects of heat losses based on the flamelet/progress-variable approach [24], is employed for generating the premixed flamelet

1 library. The calculations of the one-dimensional free-propagating flames for generating the  
 2 premixed flamelet libraries for the FGM and NA-FGM are conducted by using  
 3 FlameMaster [25], for which the non-adiabatic procedure [23] is introduced.  
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8 The results of one-dimensional premixed flames calculated in physical space is  
 9 converted to low dimensional manifold parameterized by mixture fraction  $Z$ , progress  
 10 variable  $C$ , and enthalpy difference  $\Delta h$ , shown as  
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$$15 \quad \varphi = \varphi(Z, C, \Delta h), \quad (3)$$

16 where  $\varphi$  is flamelet properties such as temperature, chemical species mass fraction and so  
 17 on.  $\Delta h$  is the difference between the absolute enthalpy without heat loss in the flamelet  
 18 library and that with heat loss in the physical space at each vertex. In LES, the  
 19 Favre-filtered flamelet library can be obtained as  
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$$27 \quad \tilde{\varphi}(\tilde{Z}, \tilde{C}^{\tilde{n}_2}, \tilde{C}, \tilde{\Delta h}) = \int_0^1 \varphi(Z, C, \Delta h) P(C) dC, \quad (4)$$

28 where  $P(C)$  is the density weighted filter probability function of the progress variables,  
 29 and beta sub-filter distribution of the progress variable is shown as  
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$$35 \quad P(C; \tilde{C}, \tilde{C}^{\tilde{n}_2}) = \frac{C^{\beta_1-1} (1-C)^{\beta_2-1}}{\int_0^1 C^{\beta_1-1} (1-C)^{\beta_2-1} dC}. \quad (5)$$

36 Here,  $\beta_1$  and  $\beta_2$  are given as  
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$$39 \quad \beta_1 = \beta_1(\tilde{C}, \tilde{C}^{\tilde{n}_2}) = \tilde{C} \left( \tilde{C}^{\frac{1-\tilde{C}}{\tilde{C}^{\tilde{n}_2}}} - 1 \right), \quad (6)$$

$$40 \quad \beta_2 = \beta_2(\tilde{C}, \tilde{C}^{\tilde{n}_2}) = (1 - \tilde{C}) \left( \tilde{C}^{\frac{1-\tilde{C}}{\tilde{C}^{\tilde{n}_2}}} - 1 \right), \quad (7)$$

41 where  $\tilde{C}$  is grid scale and  $\tilde{C}^{\tilde{n}_2}$  is sub-grid scale variable component.  
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48 The numbers of grids set for  $\tilde{Z}$ ,  $\tilde{C}$ ,  $\tilde{C}^{\tilde{n}_2}$ , and,  $\tilde{\Delta h}$ , are  $100 \times 100 \times 50 \times 4$ . The  
 49 discrete points of  $\tilde{C}$ ,  $\tilde{C}^{\tilde{n}_2}$  and  $\tilde{\Delta h}$  are arranged at regular intervals. Accordingly to  $Z$ , 98  
 50 points are regularly arranged among  $Z = 0.057$  and  $Z = 0.12$ , and points of  $Z = 0.0$  for only  
 51 oxidizer and  $Z = 1.0$  for only fuel are added.  
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The governing equations for the LES employing the FGM and NA-FGM are the same. They are the conservation equations of mass, momentum, absolute enthalpy  $\tilde{h}$ , mixture fraction  $\tilde{Z}$ , and progress variable  $\tilde{C}$ , and NO mass fraction  $\tilde{Y}_{NO}$  as follows:

$$\frac{\partial \bar{\rho}}{\partial t} + \nabla \cdot (\bar{\rho} \tilde{\mathbf{u}}) = 0. \quad (8)$$

$$\frac{\partial \bar{\rho} \tilde{\mathbf{u}}}{\partial t} + \nabla \cdot (\bar{\rho} \tilde{\mathbf{u}} \tilde{\mathbf{u}}) = -\nabla \bar{P} + \nabla \cdot \bar{\boldsymbol{\sigma}} + \nabla \cdot \boldsymbol{\tau}. \quad (9)$$

$$\frac{\partial \bar{\rho} \tilde{h}}{\partial t} + \nabla \cdot (\bar{\rho} \tilde{\mathbf{u}} \tilde{h}) = \nabla \cdot (\bar{\rho} \tilde{D}_h \nabla \tilde{h}) + \nabla \cdot \mathbf{q}_h + Q_{\text{rad}}. \quad (10)$$

$$\frac{\partial \bar{\rho} \tilde{Z}}{\partial t} + \nabla \cdot (\bar{\rho} \tilde{\mathbf{u}} \tilde{Z}) = \nabla \cdot (\bar{\rho} \tilde{D}_Z \nabla \tilde{Z}) + \nabla \cdot \mathbf{q}_Z. \quad (11)$$

$$\frac{\partial \bar{\rho} \tilde{C}}{\partial t} + \nabla \cdot (\bar{\rho} \tilde{\mathbf{u}} \tilde{C}) = \nabla \cdot (\bar{\rho} \tilde{D}_C \nabla \tilde{C}) + \nabla \cdot \mathbf{q}_C + \tilde{\omega}_C. \quad (12)$$

$$\frac{\partial \bar{\rho} \tilde{Y}_{NO}}{\partial t} + \nabla \cdot (\bar{\rho} \tilde{\mathbf{u}} \tilde{Y}_{NO}) = \nabla \cdot (\bar{\rho} \tilde{D}_{Y_{NO}} \nabla \tilde{Y}_{NO}) + \nabla \cdot \mathbf{q}_{Y_{NO}} + \bar{\rho} \tilde{\omega}_{NO}. \quad (13)$$

Here,  $\mathbf{u}$  is the velocity,  $P$  is the pressure,  $\boldsymbol{\sigma}$  is the stress tensor.  $D_h$ ,  $D_Z$ ,  $D_C$  and  $D_{Y_{NO}}$  are the diffusion coefficients of  $h$ ,  $Z$ ,  $C$  and  $Y_{NO}$ , respectively, which are given as

$$D_\varphi = \frac{\mu}{Pr_\varphi}, \quad (14)$$

where  $\mu$  is dynamic viscosity, and  $Pr_\varphi$  is Prandtl number of each transport scalar  $\varphi$ .  $Pr_\varphi = 0.7$  are used for the simulations.  $\boldsymbol{\tau}$  is the subgrid-scale stress term derived from the turbulence model, and  $\mathbf{q}_h$ ,  $\mathbf{q}_Z$ ,  $\mathbf{q}_C$  and  $\mathbf{q}_{Y_{NO}}$  are the subgrid-scale terms for each scalar.  $Q_{\text{rad}}$  is the source term of radiative heat transfer.  $\bar{\varphi}$  and  $\tilde{\varphi}$  denote the LES filtering and Favre averaging of a physical quantity  $\varphi$ , respectively.  $\tilde{\omega}_C$  is the reaction rate of  $C$ . Temperature is calculated from transported enthalpy with the species mass fractions and these thermal data.

It is well-known that reactions related to NO are slow. NO concentration in the flamelet libraries is calculated at the equilibrium state. The reactions are often affected by heat losses in practical combustion chambers. In that case, the concentration is not

coincident with experimental results. Then, NO concentration is evaluated based on Ihme and Pitsch's approach [26]. They proposed the method that the forward and backward NO reaction rates are separately modeled with the reaction rates taken from the flamelet library as,

$$\widetilde{\dot{\omega}}_{NO} = \widetilde{\dot{\omega}}_{NO}^+ + \widetilde{Y}_{NO} \frac{\widetilde{\dot{\omega}}_{NO}^-}{\widetilde{Y}_{NO}^{flm}}, \quad (15)$$

where  $\widetilde{\dot{\omega}}_{NO}^+$  and  $\widetilde{\dot{\omega}}_{NO}^-$  denote forward and backward reaction rate, respectively, and  $\widetilde{Y}_{NO}^{flm}$  denotes NO mass fraction in the flamelet libraries. Therefore, for the LES/NA-FGM, the slow rate of the NO reactions in non-adiabatic conditions can be considered. On the other hand, for the LES/FGM, the rate in an adiabatic condition is considered.

### 2.3. Computational details

The governing equations are solved using an unstructured LES solver: FrontFlow/Red extended by some research institutes, including Kyoto University, referred to as FFR-Comb [23, 27, 28]. Previously, the NA-FPV was implemented to the LES solver and the accuracy of non-adiabatic procedure is validated [23]. In this study, the NA-FGM is newly implemented to the code.

A dynamic Smagorinsky model [29] is used as the turbulence model. A first-order Euler implicit method is used for time advancement, and the time step is set to  $1.0 \times 10^{-5}$  s. The flamelet libraries for the FGM and NA-FGM are built using the mechanisms developed by the University of California San Diego [30] with nitrogen chemistry [31] in this study. This mechanism has 70 species and 321 reaction steps. The reason for selecting this mechanism is expressed in section 3.1. A gray gas model is adopted as the radiation model [32]. The absorption constant is 0.10, which is determined by reference to the results of

1 RANS simulation with weighted sum of gray gasses model [33].  
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4 As ignition process, the initial value of the progress variable,  $C$ , is set to 0.5 at the  
5 region which is from 20 mm to 50 mm from the burner rim and within 15 mm from the  
6 center axis. After that, the calculations are continued until the fields reach steady state.  
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### 10 **3. Results and discussion**

#### 11 **3.1. Validation of reaction mechanism**

12 The predicted combustion behavior is strongly affected by the detailed reaction  
13 mechanism used in the LES. Therefore, in this section, the effects of the detailed reaction  
14 mechanism on the laminar burning velocity,  $S_L$ , and NO emissions are investigated in terms  
15 of one- and two-dimensional simulations, respectively. As the detailed reaction mechanism,  
16 GRI-mech 3.0 [34], and the mechanisms developed by the University of California San  
17 Diego [30] with nitrogen chemistry [31], Tian et al. [35], and Okafor et al. [36] are featured.  
18 Here, these mechanisms are respectively referred to as GRI-mech, UCSD-mech, Tian-mech,  
19 and Okafor-mech which was developed by combining GRI-mech and Tian-mech.  
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##### 40 **3.1.1. Laminar burning velocity by one-dimensional simulations**

41 One-dimensional adiabatic and unstretched laminar premixed flames of  
42  $\text{NH}_3/\text{CH}_4/\text{air}$  mixtures are calculated using ANSYS Chemkin-PRO [37]. This application is  
43 used for comparing various reaction mechanisms, because the FlameMaster cannot deal  
44 with complex mechanisms such as Tian-mech and Okafor-mech. It is found the cause that  
45 these mechanisms have  $\text{NH} + \text{NO} = \text{N}_2\text{O} + \text{H}$  as an important elementary reaction and the  
46 pre-exponential factor is negative value.  $S_L$  is defined as the velocity at the cold boundary  
47 in the computational domain.  
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58 Figure 2 shows the comparison of  $S_L$  obtained by one-dimensional calculations  
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using different detailed reaction mechanisms, together with experiments of Okafor et al. [36]. The fuel consists of 52.1% NH<sub>3</sub> and 47.9% CH<sub>4</sub> by volume, and this constituent is close to that in the swirl burner. Tian-mech overestimates  $S_L$  in the whole  $\phi$  range. Although GRI-mech shows good accuracy, the reactions related to NH<sub>2</sub>, which is an important species for the NO reactions, are not included [38]. Okafor-mech shows a good agreement in a wide range of  $\phi$ . Finally, although UCSD-mech matches the experimental results at  $\phi > 1$ , it somewhat overestimates at  $\phi < 1$ .

### 3.1.2. NO emissions by two-dimensional simulations

Two-dimensional RANS (Reynolds-Averaged Navier-Stokes) simulations are conducted in order to compare the amount of NO emissions using each reaction mechanism. There are no previous studies that evaluated the amount of NO emissions for NH<sub>3</sub>/CH<sub>4</sub>/air laminar flames, so the experiment conditions by Valera-Medina et al. [15] are taken up in order to qualitatively evaluate each reaction mechanism.

Figure 3 shows the schematic of computational domain for two-dimensional RANS simulations. The domain is divided into ~90 thousand cells. As the conditions regarding the composition of the premixed gases, its flow rate and temperature and pressure are the same in section 2.1. For the premixed gas, the uniform radial velocity,  $V$ , and uniform circumferential velocity,  $W$ , are used as the inlet boundary condition.  $V$  and  $W$  are respectively expressed as

$$V = \frac{Q}{2\pi r_1 L_s}, \quad (16)$$

$$W = \frac{Q}{n_s t_s L_s}. \quad (17)$$

Wall conditions are adiabatic and any radiation model is not employed, due to focus on the elementary adequateness of each reaction mechanism for the swirl burner. Realizable  $k$ - $\varepsilon$

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2 model [39] is employed as a turbulence model.  
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4 Figure 4 shows the comparison of temperature distributions obtained by  
5 two-dimensional RANS simulations using different detailed reaction mechanisms at  $\phi =$   
6 0.840, 1.04 and 1.31, respectively. The distributions by GRI-mech, UCSD-mech and  
7 Okafor-mech are quite similar at each  $\phi$  condition. There is great difference for only  
8 Tian-mech. Although Tian-mech overestimates laminar burning velocity, the flame is lifted  
9 up from the bottom of the burner. In the experimental study, the actual flame was not lifted  
10 up at  $\phi = 1.31$  [15]. Therefore it is assumed that Tian-mech is incompatible with the  
11 conditions of this study.  
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23 Figure 5 shows the comparison of the amounts of NO emissions obtained by  
24 two-dimensional RANS simulations using different detailed reaction mechanisms, together  
25 with experiments [15]. The NO concentrations for the whole conditions by the simulations  
26 reach the steady state before approaching the outlet boundary. All mechanisms overestimate  
27 the amounts of NO emissions in the whole  $\phi$  range in comparison with the experimental  
28 results. The amount of NO emissions using UCSD-mech is comparatively close to the  
29 experimental result except for Tian-mech. NO emissions with both of Okafor-mech and  
30 UCSD-mech are similar at  $\phi = 0.840$  and 1.04, but the amount of NO emissions at  $\phi = 1.31$   
31 with Okafor-mech is 1.55 times larger than that with UCSD-mech.  
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44 As above, because UCSD-mech has a relatively reasonable agreement among these  
45 mechanisms and can be dealt by the FlameMaster, it is employed for generating the  
46 flamelet libraries and discussing the NO and CO reactions in non-adiabatic conditions.  
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## 54 **3.2. Predictions of NO and CO emissions by LES**

### 55 **3.2.1. NO emissions**

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58 First, Fig. 6 shows the comparisons of distributions of (a) temperature, (b) axial  
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1 velocity, (c) OH mole fraction, and (d) NO mass fraction at  $\phi = 1.31$  between the LES/FGM  
2 and the LES/NA-FGM. The maximum temperature for the LES/FGM is 1974 K, the same  
3 as the adiabatic flame temperature,  $T_{ad}$ . However, the LES/NA-FGM shows 1950 K, and it  
4 is lower than the  $T_{ad}$  by 24 K by heat losses. There are no differences in terms of flow field  
5 between these approaches. The difference in OH mole fraction distributions, which is one  
6 of the most important species for the  $\text{NH}_3$  combustion, should be addressed. Once OH is  
7 produced in the LES/FGM, the concentration remains high throughout the combustion  
8 process. However, OH in the LES/NA-FGM is produced only in the flame region, and, after  
9 leaving this region, it disappears. This is the reason that the production of NO in the  
10 LES/NA-FGM is lower than that in the LES/FGM. The effects of temperature and the  
11 presence of H and OH radicals are discussed in section 3.3.1. Figure 7 shows the  
12 comparisons of axial profiles of NO concentration and temperature at  $\phi = 1.31$  between the  
13 LES/FGM and the LES/NA-FGM. NO concentrations for both approaches rapidly decrease  
14 through passing each flame zone. After that, the NO concentration for the LES/FGM  
15 remains almost the same in the downstream. This is explained by Fig. 8, which shows the  
16 correlation between production rate of NO and progress variable,  $C$ , at  $\phi = 0.840, 1.04$  and  
17  $1.31$  for  $\Delta h = 0$  (FGM). The production rate of NO in the downstream of a flame is negative  
18 at only  $\phi = 1.31$ , and when the value of  $C$  becomes its maximum, the rate is almost zero.  
19 The LES/FGM estimates the amount of NO emissions as 148 ppm in Fig. 7. However, the  
20 NO concentration for the LES/NA-FGM monotonically decreases even in the downstream  
21 of a flame, and eventually reaches 9 ppm. This value is close to 7 ppm measured in the  
22 experiments [15]. This shows the superiority of the LES/NA-FGM in estimating the amount  
23 of NO emissions, and it also shows the quantitative accuracy at  $\phi = 1.31$ .

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Second, Fig. 9 shows the comparisons of distributions of (a) temperature, (b) axial velocity, (c) OH mole fraction, and (d) NO mass fraction for the LES/NA-FGM between

1 the cases of  $\phi = 0.840$  and  $1.04$ . The maximum of OH mole fraction at  $\phi = 0.840$  and  $1.04$  is  
2 larger by approximately 15 times than that at  $\phi = 1.31$ , increasing the reactivity at these  $\phi$   
3 conditions. As a result, the NO production is quite high, especially at  $\phi = 0.840$ . Each of  
4 NO concentrations at  $\phi = 0.840$  and  $1.04$  for the LES/NA-FGM also decreases in the  
5 downstream of the flames. This is the peculiar behavior derived from the presence of heat  
6 losses, because the NO production rate in the downstream of a flame zones is almost zero  
7 in adiabatic conditions in Fig. 8.  
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18 Figure 10 shows the comparison of the amounts of NO emissions as a function of  
19  $\phi$  between the LES/FGM and the LES/NA-FGM, together with the results obtained by  
20 one-dimensional premixed flame calculations (PREMIX) and experiments [15]. For  
21 comparison, the NO concentrations at the outlet boundary for one-dimensional laminar  
22 premixed flames are also illustrated as PREMIX. The amount of NO emissions for the  
23 LES/FGM is proximate to that for the PREMIX and is higher than that of the experiment  
24 for whole  $\phi$  conditions, whereas that for the LES/NA-FGM is estimated quantitatively at  $\phi$   
25  $> 1.04$ . However, it is overestimated by more than twice, at  $\phi = 0.840$ , even when the  
26 LES/NA-FGM is employed. The reasons of the overestimation are as follows. First, the  
27 experiment at  $\phi = 0.840$  may include an uncertainty. According to the experiment, the  
28 amount of O<sub>2</sub> emissions at  $\phi = 0.840$  is approximately 4.5%. The concentration corresponds  
29 to that as  $\phi = 0.752$  if the premixed gas is completely burned. However, because the amount  
30 of NO emissions at  $\phi = 0.752$  for the LES/NA-FGM is still high in Fig. 10, it cannot be  
31 concluded that the experimental condition was equivalent to not as  $\phi = 0.840$  but as  $\phi =$   
32  $0.752$ . Second, some inaccuracies remain in UCSD-mech employed in this study.  
33 UCSD-mech overestimates  $S_L$  at  $\phi < 1$ , and the reactions concerning NO are still not  
34 validated. At  $\phi = 0.840$ , there is very few effect on the consumption rate of NO in  
35 non-adiabatic conditions in section 3.3.1. If this should be the case, it means that  
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1 UCSD-mech overestimates the NO production in a flame zone. For the quantitative  
2 prediction of NO emissions at  $\phi = 0.840$ , these unclear problems must be separately  
3 examined.  
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### 10 **3.2.2. CO emissions**

11 Because CO emissions are often problematic for practical uses because of its  
12 harmful effect on human bodies, this section deals with their evaluation. Figure 11 shows  
13 the comparisons of distributions of CO mole fraction at  $\phi = 0.840$ , 1.04 and 1.31 between  
14 the LES/FGM and the LES/NA-FGM. Once CO in the LES/FGM is produced at  $\phi = 1.04$   
15 and 1.31, the concentration remains high. This is the effect of thermal dissociation, and one  
16 part of CO<sub>2</sub> transforms into CO in high temperatures. This transformation is hardly seen in  
17 the LES/NA-FGM because of heat losses.  
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30 Finally, Fig. 12 shows the comparison of the amounts of CO emissions at  $\phi =$   
31 0.840 between the LES/FGM and the LES/NA-FGM, together with the experiments [15].  
32 The experimental results for other  $\phi$  conditions were not accurately measured because of an  
33 upper limit of equipment range. At  $\phi = 0.840$ , the amount of CO emissions in the LES/FGM  
34 is overestimated, whereas that in the LES/NA-FGM is close to the experimental result,  
35 which emphasizes that the LES/NA-FGM is a more accurate tool to determine the amount  
36 of CO emissions.  
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### 49 **3.3. Effects of heat losses on NO and CO reactions**

50 The effects of heat losses on the NO and CO reactions are investigated in detail in  
51 terms of one-dimensional premixed flame calculations below. The UCSD-mech is  
52 employed as the detailed reaction mechanism as ever. The fuel consists of 61.0% NH<sub>3</sub> and  
53 39.0% CH<sub>4</sub> by volume, and the unburned temperature and pressure are 298 K and 1 atm,  
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### 6 **3.3.1. NO reactions** 7

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9 The reactions related to NO are slower than others. Therefore, it is assumed that  
10 heat losses affect the consumption rate of NO in the downstream region of flames. Figure  
11 13 shows the time series of NO concentrations at  $\phi = 0.840$ , 1.04 and 1.31 for NH<sub>3</sub>/CH<sub>4</sub>/air  
12 combustion obtained by one-dimensional calculations in non-adiabatic conditions. Here,  
13 the downstream region of a flame is defined as the downstream side from the position that  
14 H mole fraction reaches the maximum. The all species' concentrations at the time in an  
15 adiabatic condition are used as each initial condition. Then, the change of NO  
16 concentrations is calculated under constant temperature,  $T$ , in downstream regions. Besides,  
17  $T_{ad}$  shows the adiabatic flame temperature at each  $\phi$  condition.  
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30 At  $\phi = 0.840$ , the NO concentrations are not changed other than the case of  $T =$   
31 1900 K, and it slightly decreases at  $T = 1900$  K. At  $\phi = 1.04$ , the NO concentration at  $T =$   
32  $T_{ad}$  remains over 4000 ppm. On the other hand, it dramatically decreases in non-adiabatic  
33 conditions, and especially at  $T = 2000$  K, it eventually reaches 204 ppm. As temperature  
34 becomes lower than  $T = 2000$  K, the consumption rate becomes slower, and the NO  
35 concentration at  $T = 1500$  K rather increases and heads for 6300 ppm. That is, this value is  
36 larger than that in the adiabatic condition. Finally, at  $\phi = 1.31$ , the NO concentrations  
37 become diminished as temperature decreases. In the case of  $T = 1900$  K and 1800 K, the  
38 NO concentrations gradually decrease, and they eventually reach about 6 ppm. NO  
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53 instantaneously disappears in the cases of  $T < 1700$  K.

54 For comparison, Fig. 14 shows the time series of NO concentrations at  $\phi = 0.840$ ,  
55 1.04 and 1.31 for CH<sub>4</sub>/air combustion obtained by one-dimensional calculations in  
56 non-adiabatic conditions. At  $\phi = 0.840$  and 1.04, the production rate of NO increases  
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1 through thermal NO<sub>x</sub> processes as temperature becomes higher. For CH<sub>4</sub>/air combustion,  
 2 there is no specific temperature condition which strengthens the consumption of NO, and  
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 4 this trend is different from NH<sub>3</sub>/CH<sub>4</sub>/air combustion. On the other hand, the NO  
 5  
 6 concentration decreases slowly at  $\phi = 1.31$ , and the consumption rate of NO becomes max  
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 8 at around 1900 K.  
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 12 For NH<sub>3</sub>/CH<sub>4</sub>/air combustion, Fig. 15 shows the relevant reaction path related to  
 13 the NO concentration at  $\phi = 1.31$  at the time that its consumption rate is max by  
 14 one-dimensional calculation in a non-adiabatic condition. The ambient temperature is  $T =$   
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 16 1900 K. The thickness of each arrow denotes the relative magnitude of the reaction rate.  
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 18 NO is mainly consumed through three routes, or N<sub>2</sub>O, N<sub>2</sub>H and N<sub>2</sub> route respectively.  
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37 In the N<sub>2</sub>O route, N<sub>2</sub>O changes to N<sub>2</sub> by reacting with H or OH radical. Moreover, NH<sub>2</sub> and  
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 39 NH, which are needed for above reactions, are generated from NH<sub>3</sub> and NH<sub>2</sub>, respectively.  
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 41 These reactions require H and OH radicals. Therefore, it is important for the consumption  
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 43 of NO that there are active radicals such as O and OH in non-adiabatic conditions.  
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 47 As above, the effects of heat losses on the consumption of NO are not almost  
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 49 observed at  $\phi = 0.840$ , but the NO concentration slightly decreases at only  $T = 1900$  K. At  $\phi$   
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 51 = 1.04, NO concentration decreases the fastest at  $T = 2000$  K, and as temperature becomes  
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 53 smaller, it rather increases. At  $\phi = 1.31$ , NO concentrations at  $T = 1900$  K and 1800 K  
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 55 decrease gradually to about 6 ppm, and in the cases of  $T < 1700$  K, it instantaneously  
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 57 disappears. Such heat losses and active radicals such as H and OH support the consumption  
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### 6 **3.3.2. CO reactions** 7

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9 Figure 16 shows the principal reactions of CO at  $\phi = 0.840$  for NH<sub>3</sub>/CH<sub>4</sub>/air  
10 combustion obtained by one-dimensional calculation in an adiabatic condition. The  
11 consumption rate of CO basically depends on one reaction,  
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17 OH radical is namely the most important species.  
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20 In order to evaluate the effects of heat losses, ambient temperature dependence for  
21 the consumption of CO is investigated. Figure 17 shows the time series of CO  
22 concentrations at  $\phi = 0.840$  for (a) NH<sub>3</sub>/CH<sub>4</sub>/air combustion and (b) CH<sub>4</sub>/air combustion,  
23 which are obtained by one-dimensional calculations in non-adiabatic conditions. The  
24 definition of the downstream region is the same as the previous section. For NH<sub>3</sub>/CH<sub>4</sub>/air  
25 combustion, the consumption rate of CO becomes larger with rich OH radicals under low  
26 ambient temperature. As temperature becomes lower than  $T_{ad}$ , the consumption rate of CO  
27 becomes faster, and the rate becomes max around 1500 K. At  $T = 1500$  K, the concentration  
28 reaches a few ppm within 40 ms. The consumption rate at  $T = 1200$  K becomes slower than  
29 that at  $T = 1500$  K, but the concentration reaches under 1 ppm after the passage of 200 ms.  
30 Because the required time is much larger than the reaction time of other main species, the  
31 transport equation of CO must be additionally employed in LES for the prediction of CO  
32 emissions in such non-adiabatic conditions. In other words, in this study, it is assumed that  
33 the amount of CO emissions can be evaluated without its transport equation. At  $T = 900$  K,  
34 CO reactions are completely stopped and the concentration remains quite high. Additionally,  
35 the behavior of the CO concentration for CH<sub>4</sub>/air combustion is almost the same as that for  
36 NH<sub>3</sub>/CH<sub>4</sub>/air combustion.  
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#### 4. Conclusions

In this study, a large-eddy simulation (LES) employing a non-adiabatic flamelet generated manifold approach (NA-FGM), which can account for the effects of various heat losses caused by radiation and cold walls, was applied to  $\text{NH}_3/\text{CH}_4/\text{air}$  combustion fields generated by a swirl burner, and the formation mechanisms of NO and CO for ammonia combustion were investigated in detail. The amounts of NO and CO emissions for various equivalence ratios,  $\phi$ , were compared with those predicted by LES employing the conventional adiabatic flamelet generated manifold approach (FGM) and measured in the bespoke experiments [15]. The results obtained in this study are summarized as follows.

- (1) The amounts of NO and CO emissions predicted by the LES/NA-FGM agree well with the experiments much better than the LES/FGM. This is because the NO and CO reactions for  $\text{NH}_3/\text{CH}_4/\text{air}$  combustion are quite susceptible to H and OH radicals' concentrations and gas temperature. This suggests that it is essential to take into account the effects of various heat losses caused by radiation and cold walls in predicting the NO and CO emissions for the combustion of ammonia as a primary fuel.
- (2) Regarding the NO emissions, the amount is successfully predicted using the LES/NA-FGM for  $\phi > 1.04$ , whereas it is overestimated at  $\phi = 0.840$ . This is considered to be due to the UCSD-mech used for generating the flamelet libraries. This mechanism tends to overestimate  $S_L$ , which may produce NO excessively in a flame zone.

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3  
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2 **References**  
3

- 4 [1] Y. Nojiri, S. Harasawa, E. Hatanaka, A. Hayashi, H. Ito, N. Kosaka, T. Oda, A. Osako,  
5  
6 K. Sakai, M. Yanagawa, National Greenhouse Gas Inventory Report of JAPAN (2017),  
7  
8 National Institute for Environmental Studies, Japan. ISSN: 1341-4356.  
9
- 10 [2] V. Krey, O. Masera, G. Blanford, T. Bruckner, R. Cooke, K. Fisher-Vanden, H. Haberl,  
11  
12 E. Hertwich, E. Kriegler, D. Mueller, S.Paltsev, L. Price, S. Schlömer, D. Ürge-Vorsatz,  
13  
14 D. van Vuuren, T. Zwickel, IPCC Working Group III - Mitigation of Climate Change,  
15  
16 Annex II: Metrics and Methodology (2014), available at  
17  
18 <http://pure.iiasa.ac.at/id/eprint/11109/>.  
19  
20  
21
- 22 [3] K. Goshome, T. Yamada, H. Miyaoka, T. Ichikawa, Y. Kojima, High compressed  
23  
24 hydrogen production via direct electrolysis of liquid ammonia, Int. J. Hydrogen Energy  
25  
26 41 (2016) 14529-14534.  
27  
28
- 29 [4] C. Zamfirescu, I. Dincer, Ammonia as a green fuel and hydrogen source for vehicular  
30  
31 applications, Fuel Process. Technol. 90 (2009) 729-737.  
32  
33  
34
- 35 [5] R. Michalsky, B.J. Parman, V. Amanor-Boadu, P.H. Pfromm, Solar thermochemical  
36  
37 production of ammonia from water, air and sunlight: Thermodynamic and economic  
38  
39 analyses, Energy 42 (2012) 251-260.  
40  
41
- 42 [6] S.J. yang, H. Jung, T. Kim, C.R. Park, Recent advances in hydrogen storage  
43  
44 technologies based on nanoporous carbon materials, Prog. Nat. Sci. 22 (2012) 631-638.  
45  
46
- 47 [7] F.J. Verkamp, M.C. Hardin, J.R. Williams, Ammonia combustion properties and  
48  
49 performance in gas-turbine burners, Int. Symp. Combust. 11 (1) (1967) 985-992.  
50  
51
- 52 [8] D.T. Pratt, Performance of ammonia fired gas turbine combustors, Report  
53  
54 TR-9-TS-67-5, Solar San Diego, USA (1967).  
55
- 56 [9] H. Newhall, E. Starkman, Theoretical performance of ammonia as a gas turbine fuel,  
57  
58 SAE tech. pap. 660768 (1966).  
59  
60

- 1  
2 [10]J. Li, H. Huang, N. Kobayashi, Z. He, Y. Nagai, Study on using hydrogen and ammonia  
3  
4 as fuels: Combustion characteristics and NO<sub>x</sub> formation, *Int. J. Energy Research* 38  
5  
6 (2014) 1214-1223.  
7  
8  
9 [11]O. Mathieu, E.L. Petersen, Experimental and modeling study on the high-temperature  
10  
11 oxidation of ammonia and related NO<sub>x</sub> chemistry, *Combust. Flame* 162 (2015)  
12  
13 554-570.  
14  
15  
16 [12]K. Ryu, G.E. Zaccarakis-Jutz, S.C. Kong, Performance enhancement of  
17  
18 ammonia-fueled engine by using dissociation catalyst for hydrogen generation, *Int. J.*  
19  
20 *Hydrogen Energy* 39 (2014) 2390-2398.  
21  
22  
23 [13]W.E. Lear, Ammonia-Fueled Combustion Turbines, available at  
24  
25 [https://nh3fuel.files.wordpress.com/2012/05/lear\\_nh3.pdf](https://nh3fuel.files.wordpress.com/2012/05/lear_nh3.pdf).  
26  
27  
28 [14]A. Valera-Medina, S. Morris, J. Runyon, D.G. Pugh, R. Marsh, P. Beasley, T. Hughes,  
29  
30 Ammonia, methane and hydrogen for gas turbines, *Energy Procedia* 75 (2015)  
31  
32 118-123.  
33  
34  
35 [15]A. Valera-Medina, R. Marsh, J. Runyon, D. Pugh, P. Beasley, T. Hughes, P. Bowen,  
36  
37 Ammonia–methane combustion in tangential swirl burners for gas turbine power  
38  
39 generation, *Applied Energy* 185 (2017) 1362-1371.  
40  
41  
42 [16]O. Kurata, N. Iki, T. Matsunuma, T. Inoue, T. Tsujimura, H. Furutani, H. Kobayashi, A.  
43  
44 Hayakawa, Performances and emission characteristics of NH<sub>3</sub>-air and NH<sub>3</sub>-CH<sub>4</sub>-air  
45  
46 combustion gas-turbine power generations, *Proc. Combust. Inst.* 36 (2017) 3351-3359.  
47  
48  
49 [17]A. Hayakawa, Y. Arakawa, R. Mimoto, K.D.K.A. Somarathne, T. Kudo, H. Kobayashi,  
50  
51 Experimental investigation of stabilization and emission characteristics of ammonia/air  
52  
53 premixed flames in a swirl combustor, *Int. J. Hydrogen Energy* 42 (2017)  
54  
55 14010-14018.  
56  
57  
58 [18]K.D.K.A. Somarathne, S. Hatakeyama, A. Hayakawa, H. Kobayashi, Numerical study  
59  
60

- 1 of a low emission gas turbine like combustor for turbulent ammonia/air premixed swirl  
2 flames with a secondary air injection at high pressure, *Int. J. Hydrogen Energy* 42  
3  
4  
5  
6 (2017) 27388-27399.  
7
- 8 [19]H. Xiao, A. Valera-Medina, P. Bowen, S. Dooley, 3D simulation of ammonia  
9 combustion in a lean premixed swirl burner, *Energy Procedia* 142 (2017) 1294-1299.  
10
- 11 [20]J.A. Van Oijen, L.P.H. De Goey, Modelling of premixed laminar flames using  
12 flamelet-generated manifolds, *Combust. Sci. Tech.* 161 (1) (2000) 113-137.  
13  
14  
15
- 16 [21]F. Proch, A.M. Kempf, Modeling heat loss effects in the large eddy simulation of a  
17 model gas turbine combustor with premixed flamelet generated manifolds, *Proc.*  
18 *Combust. Inst.* 35 (3) (2015) 3337-3345.  
19  
20  
21  
22
- 23 [22]J. Runyon, R. Marsh, A. Valera-Medina, A. Giles, P. Bowen, Methane-oxygen flame  
24 stability in a generic premixed gas turbine swirl combustor at varying thermal power  
25 and pressure, *ASME turbo expo.* (2015) GT2015-43588.  
26  
27  
28  
29  
30  
31
- 32 [23]A. Kishimoto, H. Moriai, K. Takenaka, T. Nishiie, M. Adachi, A. Ogawara, R. Kurose,  
33 Application of a non-adiabatic flamelet/progress-variable approach to Large Eddy  
34 Simulation of H<sub>2</sub>/O<sub>2</sub> combustion under a pressurized condition, *J. Heat Transfer* 139  
35 (12) (2017) 124501.  
36  
37  
38  
39  
40  
41
- 42 [24]C.D. Pierce, P. Moin, Progress-variable approach for large-eddy simulation of  
43 non-premixed turbulent combustion, *J. Fluid Mech.* 504 (2004) 73-94.  
44  
45  
46
- 47 [25]H. Pitsch, FlameMaster, A C++ Computer Program for 0D Combustion and 1D  
48 Laminar Flame Calculation (1998),  
49 <https://web.stanford.edu/group/pitsch/FlameMaster.htm>.  
50  
51  
52  
53
- 54 [26]M. Ihme, H. Pitsch, Modeling of radiation and nitric oxide formation in turbulent  
55 nonpremixed flames using a flamelet/progress variable formulation, *Phys. Fluids* 20  
56 (2008) 055110.  
57  
58  
59  
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- 1  
2 [27]H. Moriai, R. Kurose, H. Watanabe, Y. Yano, F. Akamatsu, S. Komori, Large-eddy  
3 simulation of turbulent spray combustion in a subscale aircraft jet engine  
4 combustor-predictions of no and soot concentrations, J. Eng. Gas Turbines Power 135  
5  
6 (2013) 091503.  
7  
8  
9
- 10 [28]S. Tachibana, K. Saito, T. Yamamoto, M. Makida, T. Kitano, R. Kurose, Experimental  
11 and numerical investigation of thermo-acoustic instability in a liquid-fuel aero-engine  
12 combustor at elevated pressure: Validity of large-eddy simulation of spray combustion,  
13 Combust. Flame 162 (2015) 2621-2637.  
14  
15  
16  
17  
18  
19
- 20 [29]M. Germano, U. Piomelli, P. Moin, W.H. Cabot, A dynamic subgrid - scale eddy  
21 viscosity model, Phys. Fluids A 3 (1991) 1760-1765.  
22  
23  
24
- 25 [30]Chemical Kinetic Mechanism for Combustion Applications, Center for Energy  
26 Research (Combustion Division), University of California at San Diego, available at  
27 [http://web.eng.ucsd.edu/mae/groups/combustion/sdmech/sandiego20161214/sandiego2](http://web.eng.ucsd.edu/mae/groups/combustion/sdmech/sandiego20161214/sandiego20161214_mechCK.txt)  
28 [0161214\\_mechCK.txt](http://web.eng.ucsd.edu/mae/groups/combustion/sdmech/sandiego20161214/sandiego20161214_mechCK.txt).  
29  
30  
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32  
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34
- 35 [31]Chemical Kinetic Mechanism for Combustion Applications, Center for Energy  
36 Research (Combustion Division), University of California at San Diego, available at  
37 [http://web.eng.ucsd.edu/mae/groups/combustion/sdmech/sandiego\\_nitrogen/NOx\\_200](http://web.eng.ucsd.edu/mae/groups/combustion/sdmech/sandiego_nitrogen/NOx_20041209/NOXsandiego20041209.mec)  
38 [41209/NOXsandiego20041209.mec](http://web.eng.ucsd.edu/mae/groups/combustion/sdmech/sandiego_nitrogen/NOx_20041209/NOXsandiego20041209.mec).  
39  
40  
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43  
44
- 45 [32]M.F. Modest, Radiative Heat Transfer, Academic Press, U.S. (2013).  
46
- 47 [33]T.F. Smith, Z.F. Shen, J.N. Friedman, Evaluation of coefficients for the weighted sum  
48 of gray gases model, J. Heat Transfer 104 (1982) 602-608.  
49  
50
- 51 [34]G.P. Smith, D.M. Golden, M. Frenklach, N.W. Moriarty, B. Eiteneer, M. Goldenberg, et  
52 al., GRI-mech 3.0, Gas Research Institute, available at  
53 [http://www.me.berkeley.edu/gri\\_mech/](http://www.me.berkeley.edu/gri_mech/).  
54  
55  
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58
- 59 [35]Z. Tian, Y. Li, L. Zhang, P. Glaborg, F. Qi, An experimental and kinetic modeling study  
60  
61  
62  
63  
64  
65

1 of premixed NH<sub>3</sub>/CH<sub>4</sub>/O<sub>2</sub>/Ar flames at low pressure, Combust. Flame 156 (7) (2009)  
2  
3  
4 1413-1426.  
5

6 [36]E.C. Okafor, Y. Naito, S. Colson, A. Ichikawa, T. Kudo, A. Hayakawa, H. Kobayashi,  
7  
8 Experimental and numerical study of the laminar burning velocity of CH<sub>4</sub>-NH<sub>3</sub>-air  
9  
10 premixed flames, Combust. Flame 187 (2017) 185-198.  
11  
12

13 [37]CHEMKIN-PRO 18.2, ANSYS, Inc.: San Diego (2017).  
14  
15

16 [38]A. Hayakawa, T. Goto, R. Mimoto, Y. Arakawa, T. Kudo, H. Kobayashi, Laminar  
17  
18 burning velocity and Markstein length of ammonia/air premixed flames at various  
19  
20 pressures, Fuel 159 (2015) 98-106.  
21  
22

23 [39]T.H. Shih, W.W. Liou, A. Shabbir, Z. Yang, J. Zhu, A new k- $\epsilon$  eddy viscosity model for  
24  
25 high reynolds number turbulent flows, Computers Fluids 24 (3) (1995) 227-238.  
26  
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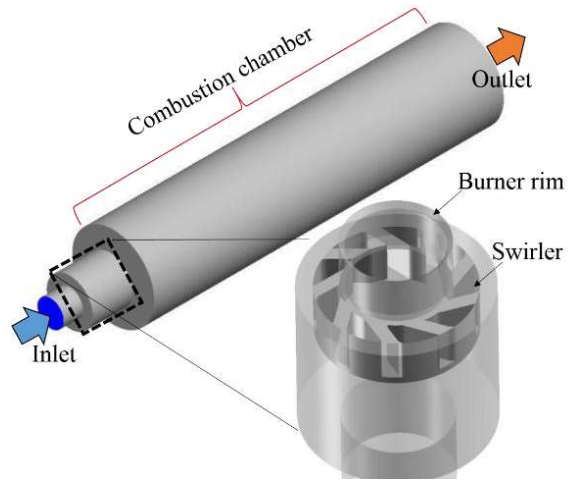


Fig. 1: Schematics of computational domain and generic swirl burner [15].

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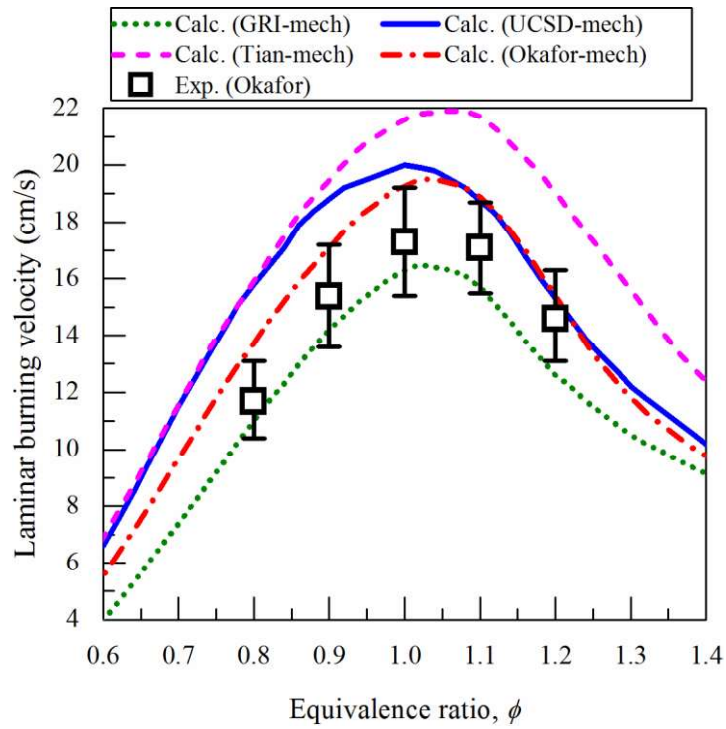


Fig. 2: Comparison of laminar burning velocities obtained by one-dimensional calculations using different detailed reaction mechanisms, together with experiments [36].

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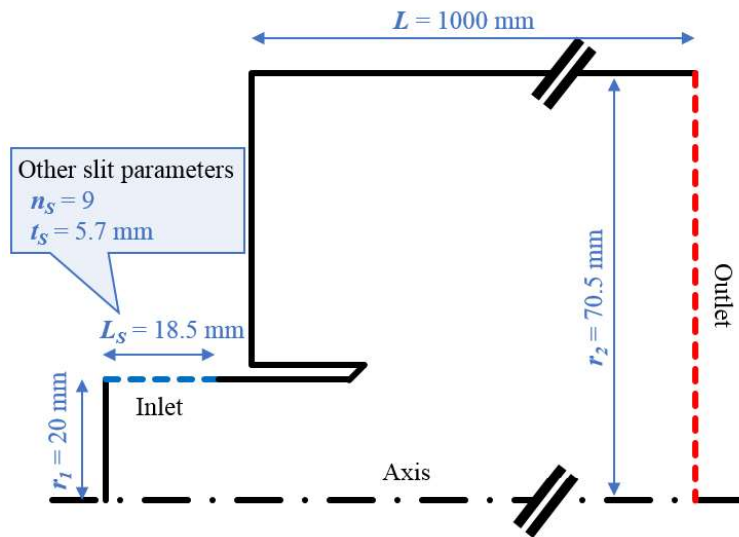


Fig. 3: Schematic of computational domain for two-dimensional RANS simulations.

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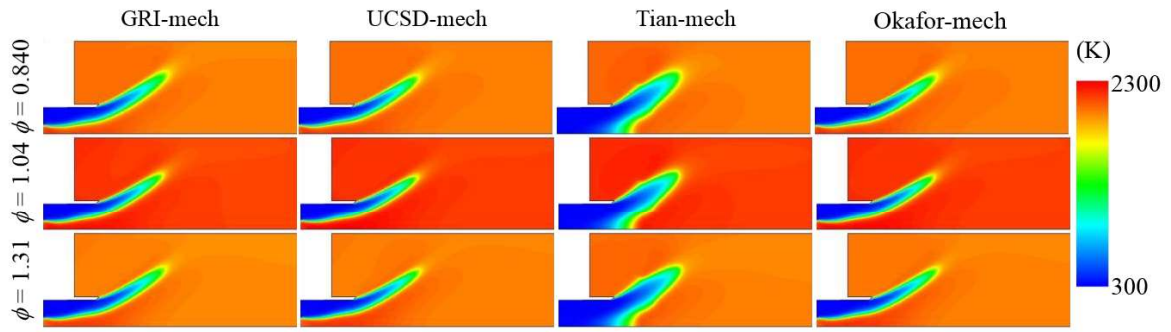


Fig. 4: Comparison of instantaneous temperature distributions obtained by two-dimensional RANS simulations using different detailed reaction mechanisms at  $\phi = 0.840$ , 1.04 and 1.31.

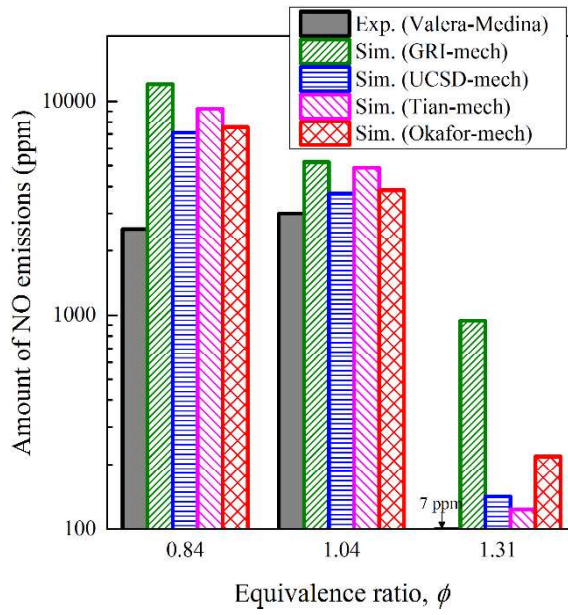


Fig. 5: Comparison of time-averaged amounts of NO emissions obtained by two-dimensional RANS simulations using different detailed reaction mechanisms, together with experiments [15].

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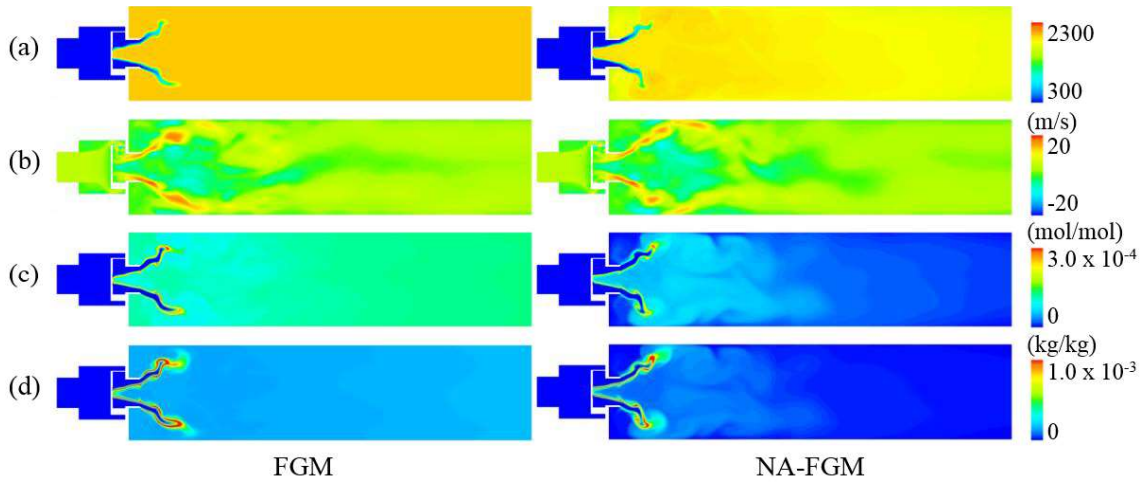


Fig. 6: Comparisons of instantaneous distributions of (a) temperature, (b) axial velocity, (c) OH mole fraction, and (d) NO mass fraction at  $\phi = 1.31$  between LES/FGM and LES/NA-FGM.



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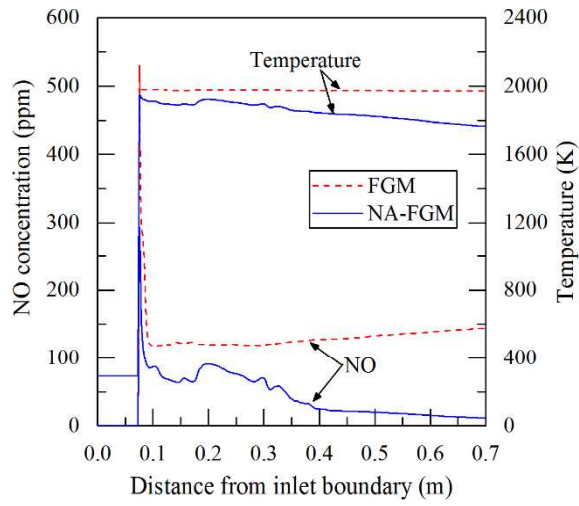


Fig. 7: Comparisons of time-averaged axial profiles of NO concentration and temperature at  $\phi = 1.31$  between LES/FGM and LES/NA-FGM.

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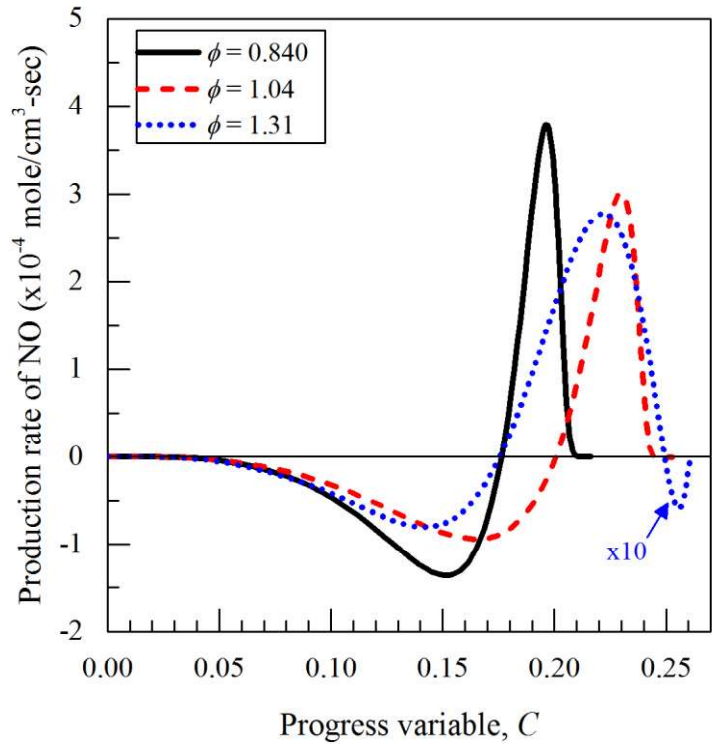


Fig. 8: Correlation between production rate of NO and progress variable,  $C$ , at  $\phi = 0.840$ , 1.04 and 1.31 for  $\Delta h = 0$  (FGM).

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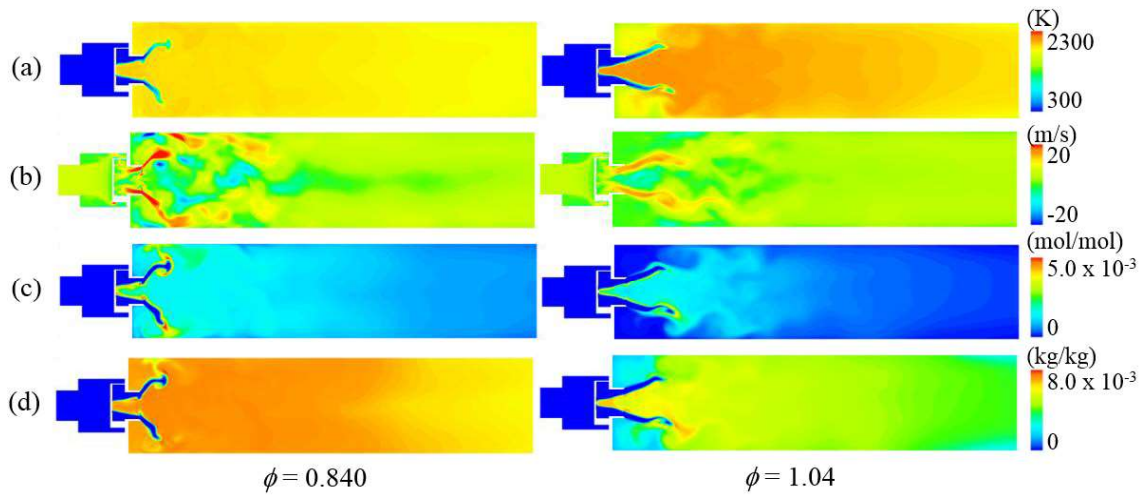
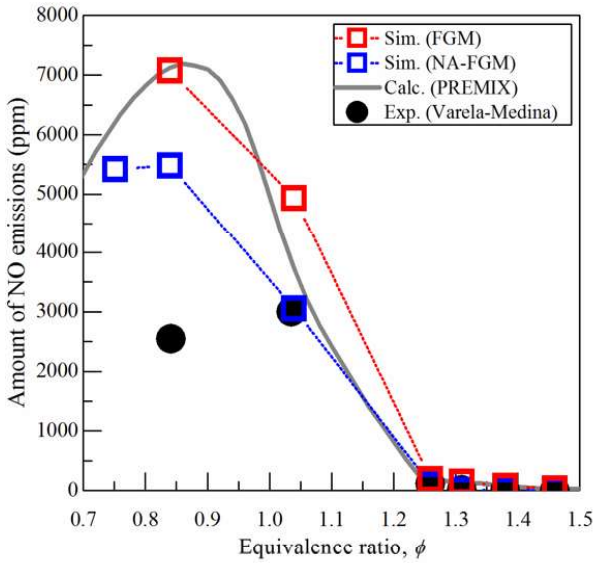


Fig. 9: Comparisons of instantaneous distributions of (a) temperature, (b) axial velocity, (c) OH mole fraction, and (d) NO mass fraction for LES/NA-FGM between the cases of  $\phi = 0.840$  and  $1.04$ .

(a)  $0.70 < \phi < 1.5$



(b)  $1.2 < \phi < 1.5$

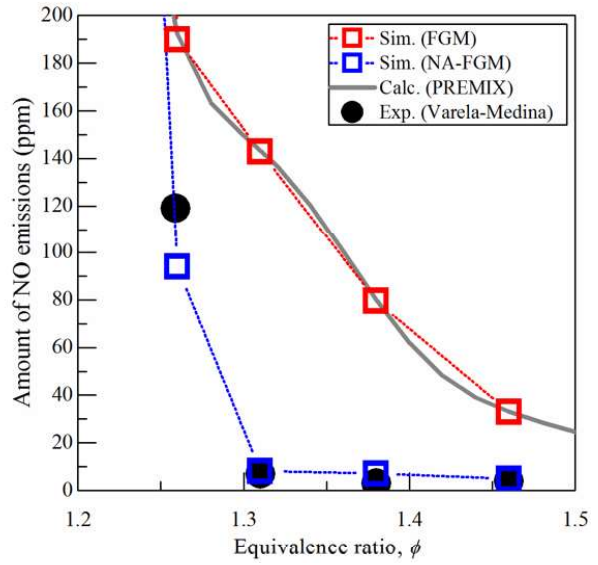


Fig. 10: Comparison of time-averaged amounts of NO emissions as a function of  $\phi$  between LES/FGM and LES/NA-FGM, together with the results obtained by adiabatic one-dimensional premixed flame calculations (PREMIX) and experiments [15]. The display ranges are (a)  $0.70 < \phi < 1.5$  and (b)  $1.2 < \phi < 1.5$ .

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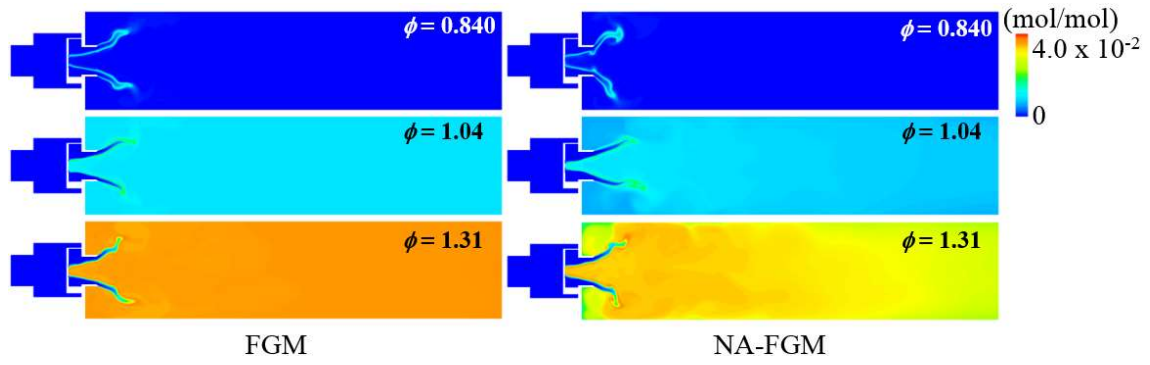


Fig. 11: Comparisons of instantaneous distributions of CO mole fraction at  $\phi = 0.840$ , 1.04 and 1.31 between LES/FGM and LES/NA-FGM.

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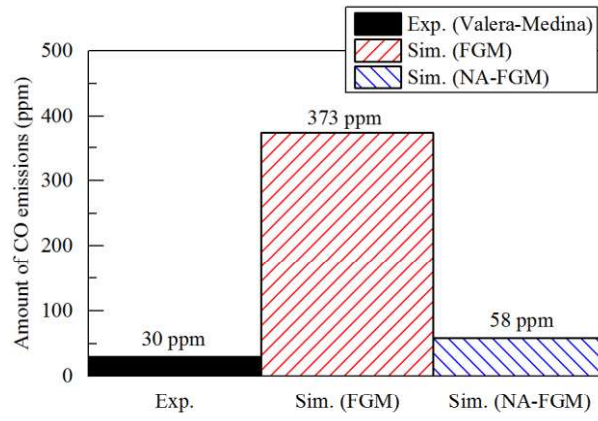


Fig. 12: Comparison of time-averaged amounts of CO emissions at  $\phi = 0.840$  between LES/FGM and LES/NA-FGM, together with experiments [15].

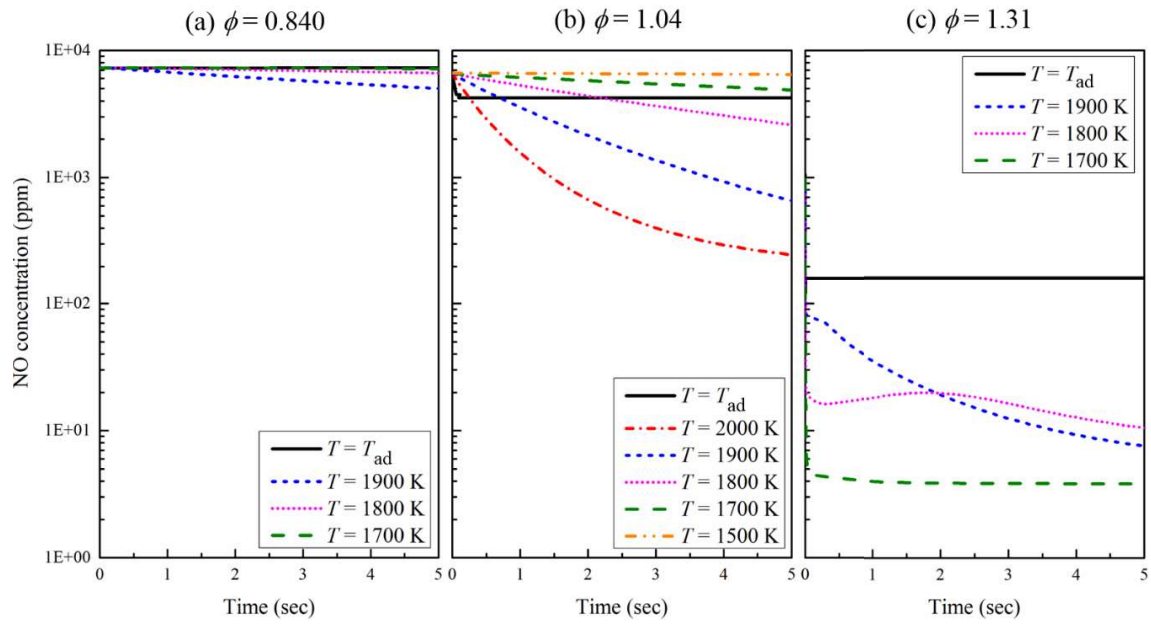


Fig. 13: Time series of NO concentrations at  $\phi = 0.840$ , 1.04 and 1.31 for  $\text{NH}_3/\text{CH}_4/\text{air}$  combustion obtained by one-dimensional calculations in various temperature conditions.

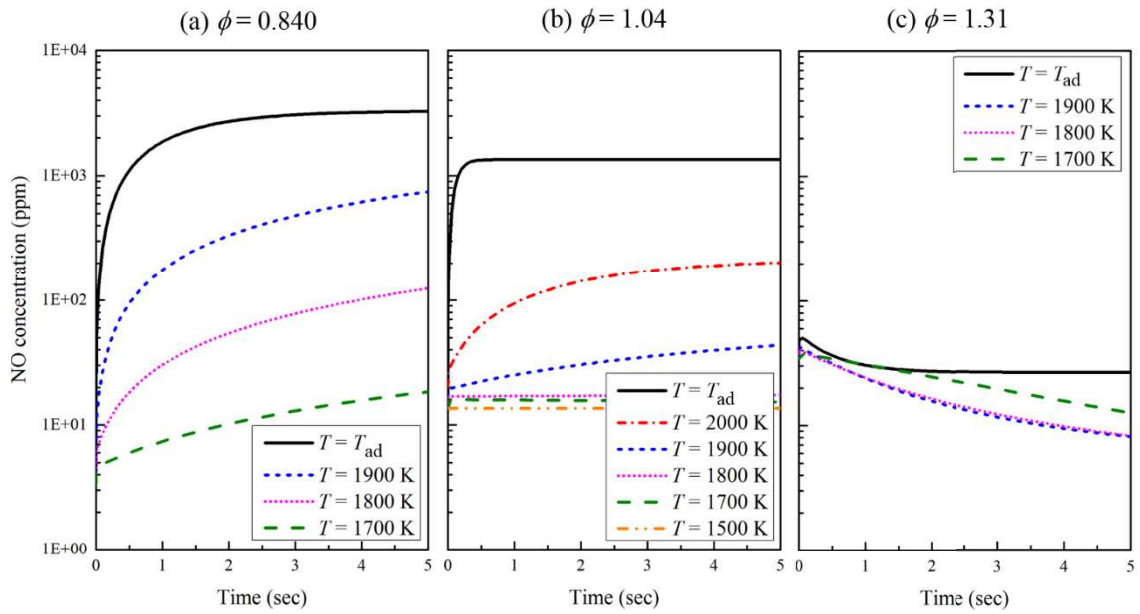


Fig. 14: Time series of NO concentrations at  $\phi = 0.840$ ,  $1.04$  and  $1.31$  for  $\text{CH}_4/\text{air}$  combustion obtained by one-dimensional calculations in various temperature conditions.



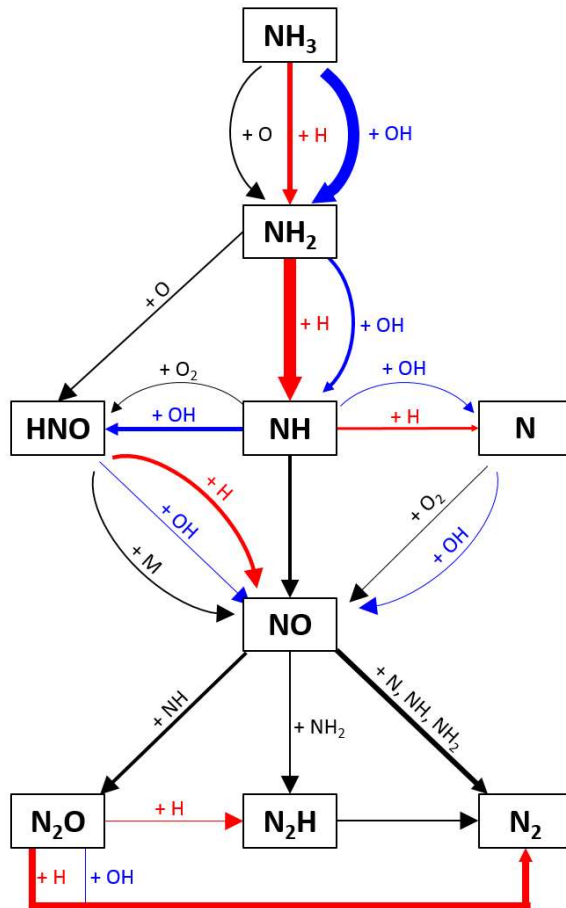


Fig. 15: Relevant reaction path related to NO concentration at  $\phi = 1.31$  for  $\text{NH}_3/\text{CH}_4$ /combustion at the time that its consumption rate is max by one-dimensional calculation in  $T = 1900$  K.

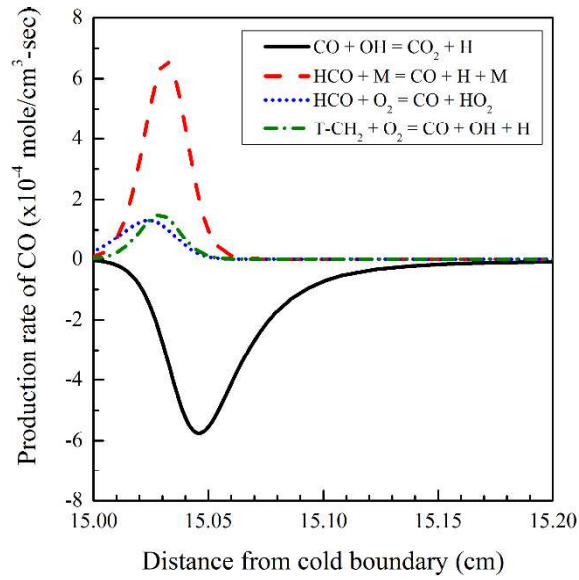


Fig. 16: Principal reactions of CO at  $\phi = 0.840$  for  $\text{NH}_3/\text{CH}_4/\text{air}$  obtained by one-dimensional calculation in an adiabatic condition.

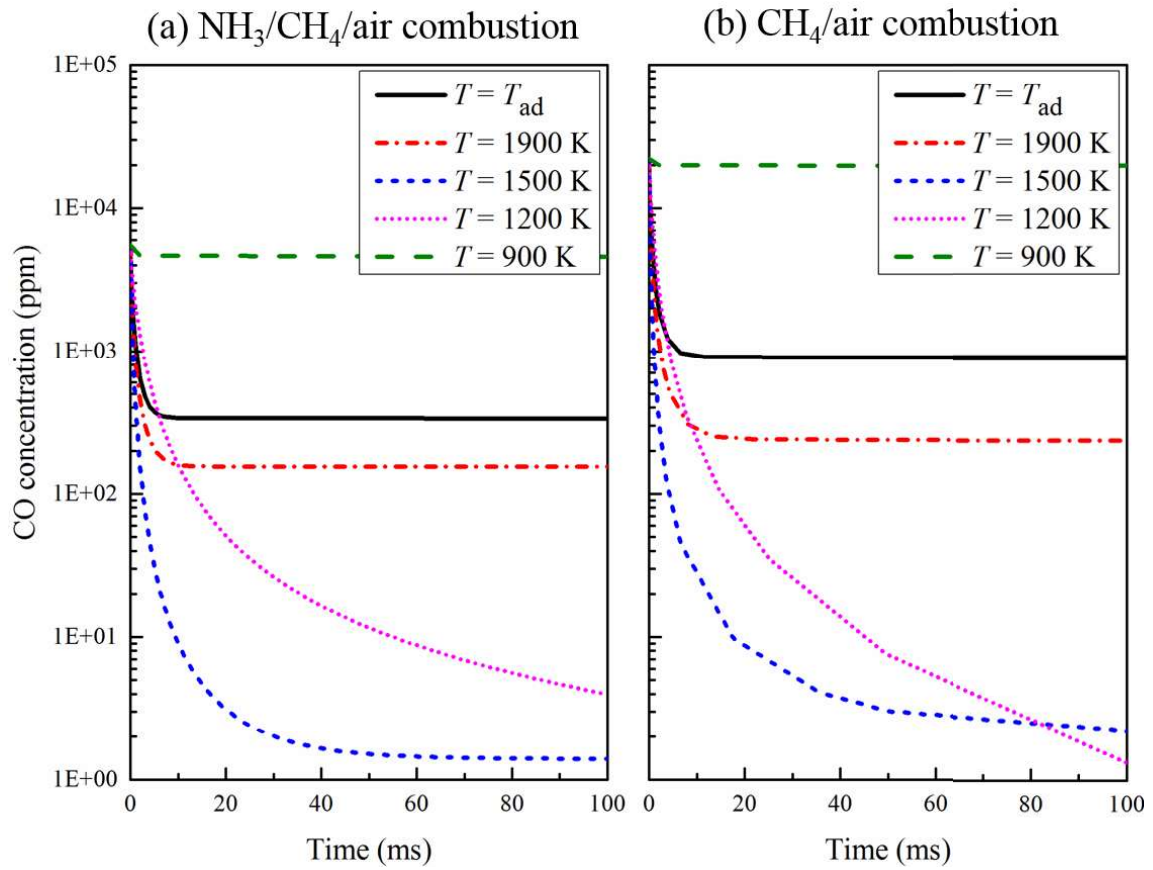


Fig. 17: Time series of CO concentrations at  $\phi = 0.840$  for (a)  $\text{NH}_3/\text{CH}_4/\text{air}$  combustion and (b)  $\text{CH}_4/\text{air}$  combustion obtained by one-dimensional calculations in various temperature conditions.