13th Asia-Pacific Conference on Combustion 2021
ADNEC, Abu Dhabi – UAE
4 – 9 December 2021

N_2O Production Characteristics of Ammonia/Hydrogen/Air Premixed Laminar Flames Stabilized in Stagnation Flows at Lean Conditions

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Abstract

Product gas characteristics of ammonia/hydrogen/air laminar premixed flames stabilized in stagnation flows were experimentally and numerically studied. The maximum value of NO mole fraction increased compared with pure ammonia/air flames, and a trade-off relationship between NO and unburnt NH_3 was observed. In addition, the N_2O production for very lean conditions was observed. To clarify the N_2O production mechanism in detail, numerical simulations were employed using CHEMKIN software with the reaction kinetics developed by Gotama et al. Sensitivity analysis suggested that the reactions of (R58) NH+NO = N_2O+H, (R105) N_2O+H = N_2+OH, and (R106) N_2O(+M) = N_2+O(+M) play an important role in N_2O mole fraction. Product gas characteristics of N_2O were numerically investigated for various stagnation plane temperatures and equivalence ratios. The reaction rate of R106 decreases for low stagnation plane temperature and at small equivalence ratios. It was found that the decrease in the reaction rate of R106 hinders the reduction rate of N_2O to N_2, and thus large amount of N_2O were detected. Also, the N_2O amount decreased when the stagnation plane temperatures were sufficiently high. This also suggested that the N_2O production may be restricted by a decrease in the heat loss in an ammonia-fueled combustor.

1 Introduction

Reduction in the emission of greenhouse gases, in particular carbon dioxide, is an urgent issue to prevent climate change which is a critical issue as well as one of the development targets of the sustainable development goals (SDGs). To achieve carbon neutrality by 2050, the Japanese government proposed the Green Growth Strategy. In this strategy, the application of ammonia as fuel is proposed [1]. To reduce CO_2 from combustors, many fundamental studies have been carried out [2], anticipating the application of ammonia as a fuel.

There are mainly two challenges to be solved, towards the application of ammonia in a combustor, especially for a gas turbine. One of these challenges is flame stability caused by the lower burning velocity of ammonia. The maximum laminar burning velocity of ammonia/air flame is almost 1/5 of that of methane/air flame [3]. To increase the laminar burning velocity without adding CO_2 emission, the addition of hydrogen to create ammonia/hydrogen binary fuel is promising strategy. Ichikawa et al. [4] and Gotama et al. (submitted to Combust. Flame, under review), and many other researchers proposed an increase in laminar burning velocity with an increase in the hydrogen fraction in binary fuel of ammonia/hydrogen. However, hydrogen addition changes emission characteristics, which is another challenge for ammonia application as emissions must be adhere to the emission regulation. Fuel NOx and unburnt ammonia may be formed when the combustion conditions are not appropriate [5]. Recently, Okafor et al. [6] clarified that the heat loss from the combustor increases N_2O emission. Since N_2O has a large global warming potential around of 300 [7], N_2O emission from combustor must be reduced. To do so, it is important to understand the the fundamental production mechanism of N_2O.

The objective of this study is to clarify the product gas characteristics of ammonia/hydrogen/air premixed laminar flames stabilized in a stagnation flow. The product gas characteristics are experimentally analyzed. Then, emission characteristics are discussed in detail by conducting a numerical simulation study using a detailed reaction kinetics.

2 Experimental Setup

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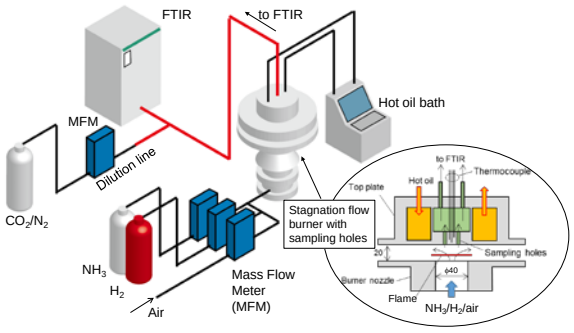

Figure 1: Experimental setup.

Figure 1 shows the schematic of the experimental setup. A similar setup was employed for the product gas analysis of ammonia/air premixed flames [5]. Ammonia and hydrogen were used as fuel, and air was used as an oxidizer. The mixtures were introduced to a nozzle burner with 40 mm outlet diameter, and a top plate being mounted 20 mm above the nozzle burner that generate a stagnation flow. There were sampling holes on the top plate, and the product gas was sucked through the holes. The product gas was introduced to an FTIR (Fourier transform infrared) gas analyzer (BOB-2000FT, Best Instruments). To avoid condensation of water inside the sampling line, the temperature of the sampling line was maintained above 100 °C. The temperature of the top plate was maintained by using hot oil supplied by the hot oil bath. Three thermocouples inserted in the top plate enabled the estimation of the surface temperature of the top plate, T_w. The value of T_w was varied depending on the equivalence ratio between and 490.7 K and 583.3 K.

The hydrogen fraction in the binary fuel, ξ_{H2}, was determined as $\xi_{H2} = [H_2]/([H_2]+[NH_3])$, here [X] represents the mole fraction of the species X [4]. The hydrogen fraction was set to 0.3 as suggested by [8] in this study. All experiments were conducted at atmospheric pressure condition. The mixture inlet temperature was 295±2 K. The mixture inlet velocity, U_{in}, was varied because the laminar burning velocity changes depending on the equivalence ratio between 23.6 cm/s and 44.5 cm/s.

A dilution sampling method was employed when the concentration of the product gas exceeded the measurement range of the FTIR gas analyzer. As shown in Fig. 1, the product gas was diluted by the dilution gas upstream of the FTIR gas analyzer. CO_2/N_2 mixture with CO_2 mole fraction of 15.9 % was employed as the dilution gas. Since CO_2 is not present in the product gas (if the CO_2 from air is neglected), CO_2 was available as a tracer species. The dilution ratio and actual concentration of the product gas were evaluated using the measured concentration of CO_2 in the mixture introduced to FTIR gas analyzer. The detailed descriptions of the dilution sampling method are available elsewhere [9].

Numerical simulations were conducted using ANSYS CHEMKIN software [10]. The premixed laminar burner stabilized stagnation flame model was used to simulate this experiment. As for the reaction model, a detailed reaction model developed by Gotama et al. (referred as Gotama Mech in this paper, submitted to Combust. Flame, under review) was employed. This reaction kinetics were validated in terms of the laminar burning velocity of ammonia/hydrogen/air flames for various equivalence ratios up to 0.5 MPa. The mixture inlet velocity and the stagnation plane temperature are required for the numerical simulation with the strain stabilized model. The estimated values of the surface temperature of the top plate and mixture inlet velocity changed depending on the equivalence ratio with experimental fluctuation. To determine the boundary condition for the numerical simulation, fitting curves by 5th and 6th polynomials were employed for T_w and U_{in}, respectively. Calculated values using the polynomials were used for the boundary condition of the stagnation plane temperature and mixture inlet velocity.

3 Results and Discussions

3.1 Experimental and Numerical Results

Figure 2 shows the measured product gas characteristics of ammonia/hydrogen/air flames in terms of equivalence ratio, ϕ. The maximum NO mole fraction, X_{NO}, of around 8700 ppm was observed at ϕ ~ 0.85. This maximum value was larger than that of pure ammonia/air premixed flames whose value was around 3500 ppm within the conditions examined by Hayakawa et al. [5]. The NO mole fraction changes non-monotonically with equivalence ratio, and almost no emission was observed around ϕ > 1.20. However, the emission of unburnt NH_3 were also increased around this equivalence ratio. At rich condition, trade-off relationship between NO and unburnt NH_3 emissions were observed. The optimal equivalence ratio at which NO and unburnt ammonia emissions reach minimum simultaneously can be determined. The optimal equivalence ratio was found to be at around ϕ ~ 1.20, and was larger than that for the case of pure ammonia/air flames [6]. As shown in Fig. 2e, hydrogen was detected in the product gas at rich condition, and hydrogen mole fraction increases with an increase in the equivalence ratio, that reached high as ~ 8% within the examined conditions in this study. The trade-off characteristics between NO and unburnt NH_3 at rich condition can be applied the rich-lean two stage combustor in ammonia-

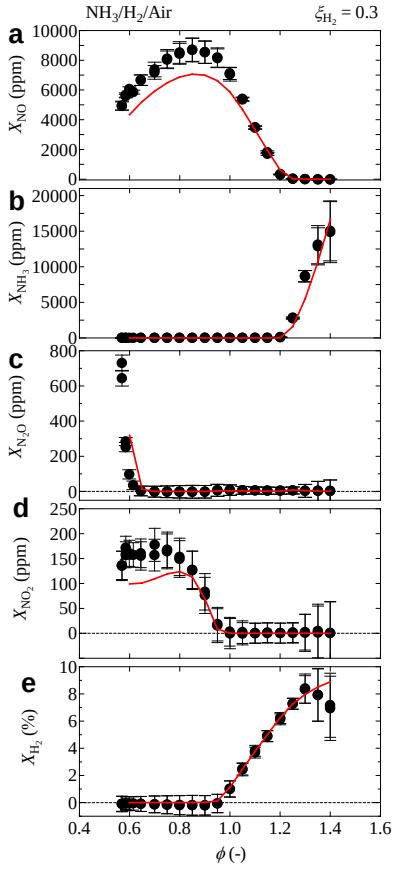

Figure 2: Experimental and numerical results of product gas characteristics of ammonia/hydrogen/air laminar premixed flames of (a) NO, (b) NH_3, (c)N_2O, (d)NO_2, and (e) H_2. Here, X_i represents the mole fraction of species i.

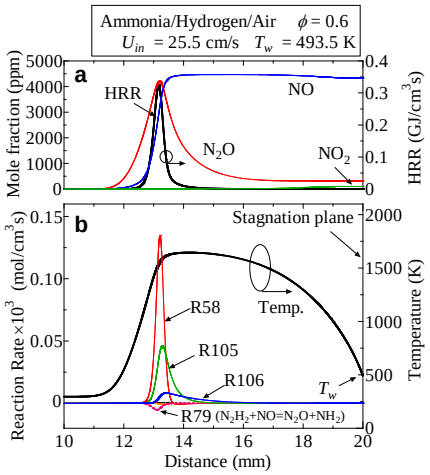

Figure 3: Flame structure of ammonia/air/hydrogen flame at ϕ = 0.6. The mixture inlet velocity and the stagnation plane temperature were the same with the experimental condition.

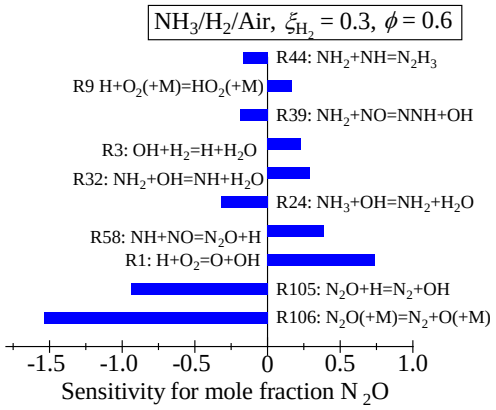

Figure 4: Sensitivities for mole fraction of N_2O for ϕ = 0.6 at the stagnation plane. The mixture inlet velocity and the stagnation plane temperature were the same with the experimental condition.

fueled gas turbine combustor to allow simultaneous reduction in NOx, unburnt ammonia, and hydrogen.

As shown in Fig. 2d, NO_2 was detected for lean condition, and the value increases around 170 ppm. It was also noted that a significant increase in N_2O was detected for lower equivalence ratio conditions of ϕ ~ 0.6 as shown in Fig. 2c. Because of the large global warming potential of N_2O, the equivalence ratio range with large N_2O production should not be employed for a combustor.

The numerical results calculated using the Gotama Mech were also shown in Fig. 2 with red curves. Although the calculated values predict slightly lower values for NO and NO_2 than the experimental values, it was considered that product gas characteristics were well predicted by the Gotama Mech.

Figure 3 shows the flame structure at ϕ = 0.6. Gotama Mech has 6 elementary reactions that express N_2O production or reduction. Figure 3b represents the reaction rate of the reactions express N_2O production or reduction in Gotama Mech. In addition, Fig. 4 shows the sensitivity of N_2O at the stagnation plane, i.e., the end point of computational domain. According to these results, it was considered that these three elementary reactions play an important role in N_2O production:

$$NH+NO = N_2O+H \qquad (R58)$$

$$N_2O+H = N_2+OH \qquad (R105)$$

$$N_2O(+M) = N_2+O(+M) \qquad (R106)$$

where R represents the reaction number in the Gotama Mech. R58 is the N_2O production path from NO, and N_2O was reduced to N_2 through R105 and R106. In this paper, these reactions were discussed to understand the N_2O production and reduction mechanisms.

3.2 Effects of Top Plate Temperature on Product Gas Characteristics

As indicated by Okafor et al. [6], N_2O emission occurs when the low temperature region exists in the combustion field due to such as heat loss. Thus, the numerical simulations were conducted for various stagnation plane temperature, T_w, with the fixed mixture inlet velocity at the equivalence ratio of ϕ = 0.6. Figure 5 shows calculated N_2O mole fraction at the stagnation point for various stagnation plane temperature at ϕ = 0.6. The mole fraction of N_2O decreased with an increase in the stagnation plane temperature, and N_2O reached almost zero for T_w > 1700 K. This indicates that N_2O emission may be restricted when heat loss can be reduced in an ammonia-fueled combustor. However, in the case of an actual combustor, wall material temperature limitations must also be considered.

Figure 6 shows the variation of the integral value of the reaction R, I_R. Here, the value of I_R was calculated using Eq. (1),

$$I_R = \int_0^L \dot{\omega}_R \, dx \qquad (1)$$

where L represents the distance from the burner outlet and the top. plate, $\dot{\omega}_R$ is the reaction rate of reaction R, and x is the distance. The value of I_{R58} represents N_2O production through R58, and I_{R105} and I_{R106} represent N_2O reductions through R105 and R106, respectively. As shown in Fig. 6b, the values of I_{R58}, I_{R105}, and I_{R106} increases with an increase in the stagnation plane temperature, T_w. Here, we consider the difference between the overall production and the overall reduction of N_2O, i.e., $I_{R58} - (I_{R105} + I_{R106})$, and the value was shown in Fig. 6a. This value decreases monotonically with an increase in T_w. Also, this value reached almost constant value for T_w > 1500 K. As shown in Fig. 5, N_2O increased when the stagnation plane temperature was lower than 1500 K. With a decrease in the stagnation plane temperature, the value of I_{R58} and I_{R105} almost linearly decreases. However, the values of I_{R106} decreases non-linearly with a decrease in T_w. The decrease in the N_2O reduction through R106 reduces at low temperature region, and large amount of N_2O remained in the product gas.

3.3 Effects of Equivalence Ratio on Product Gas Characteristics

Figure 2c represents a rapid increase in N_2O with a decrease in equivalence ratio. To clarify this characteristic, a similar analysis to section 3.2 was also conducted. Figure 7 represents the N_2O mole fraction at the stagnation plane for various equivalence ratio at the fixed stagnation plane temperature and mixture inlet velocity. The value of N_2O increases rapidly for ϕ < 0.65.

Figure 8 represents variations of the integral value of the reaction rate, I_R, in terms of the equivalence ratio, ϕ. As shown in Fig. 8a, the value of $I_{R58} - (I_{R105} + I_{R106})$ increases with a decrease in the equivalence ratio, and this value also increases

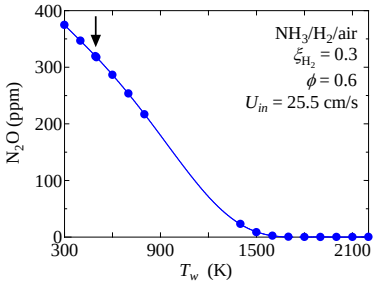

Figure 5: Effects of stagnation plane temperature on N_2O mole fraction. The condition indicated with the arrow corresponds to the stagnation plane temperature at the experimental condition. Here, no converged results were obtained between $900 < T_w < 1300$ K.

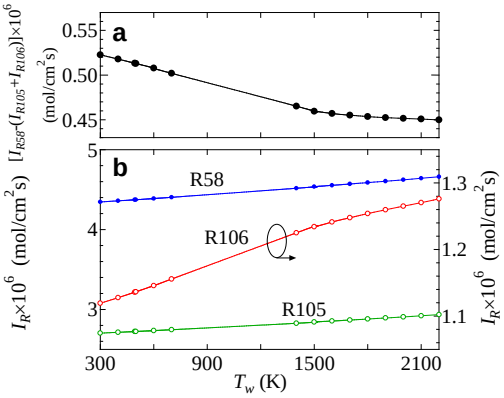

Figure 6: Integral value of the reaction rate of reaction R, I_R, in terms of the stagnation plane temperature, T_w.

rapidly for $\phi < 0.65$. This trend was well related to the N_2O characteristics shown in Fig. 7. Figure 8b shows the variations of I_R for each reaction. The value of I_{R58} and I_{R105} reduces almost linearly with a decrease in equivalence ratio. However, the values of I_{R106} were small for leaner conditions. The decrease in I_{R106} induces the increase in N_2O as shown in Fig. 7. Therefore, the importance of R106 for N_2O emissions were suggested from numerical analysis with Gotama Mech.

4 Conclusions

Product gas characteristics of ammonia/hydrogen/air premixed laminar flames stabilized in stagnation flows were experimentally and numerically investigated. It was found that the mole fractions of NO of ammonia/hydrogen/air flames are greater than that of pure ammonia/air flames. Also, a trade-off relationship between NO and unburnt NH_3 are observed at slightly rich condition, indicating that the rich-lean two-stage combustion may be applicable for this mixture. Also, N_2O, which has large global warming potential increases rapidly for very lean condition. To understand this characteristic, numerical simulation with a detailed reaction kinetic developed by Gotama et al. were conducted. The sensitivity analysis shows that these three reactions play an important role in N_2O production for the examined mixture: (R58) NH+NO = N_2O+H, (R105) N_2O+H = N_2+OH, and (R106) N_2O(+M) = N_2+O(+M). In the case of low stagnation plane temperature and/or the small equivalence ratio cases, the overall reduction rate of N_2O through R106 decreases non-monotonically with a decrease in the stagnation plane temperature and the equivalence ratio. Therefore, a decrease in N_2O reduction to N_2 through this reaction causes large emission of N_2O.

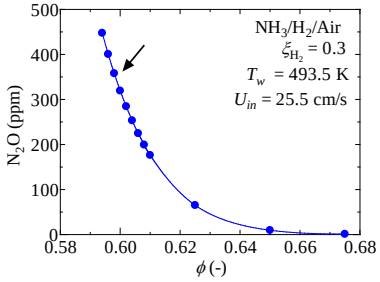

Figure 7: Effects of equivalence ratio on N_2O mole fraction. The condition indicated with the arrow corresponds to the equivalence ratio at the experimental condition.

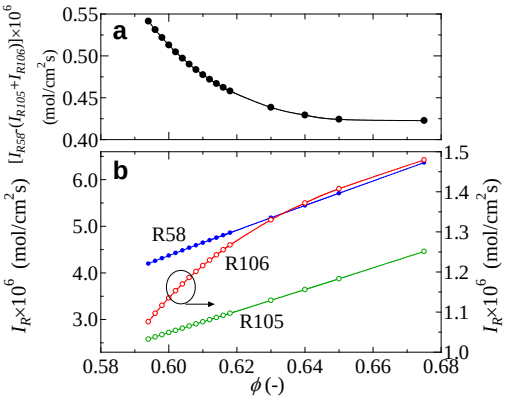

Figure 8: Integral value of the reaction rate of reaction R, I_R, in terms of the equivalence ratio, ϕ

5 Acknowledgment

This work was partially supported by the Collaborative Research Project (J21I1026) of the Institute of Fluid Science, Tohoku University, and the Suzuki Foundation.

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