1
2 **Laminar burning velocity and Markstein length of**
3 **ammonia/air premixed flames at various pressures**
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21 **Abstract**

22 Ammonia is expected to be useful not only as a hydrogen-energy carrier but also as a
23 carbon-free fuel. In order to design an ammonia fueled combustor, fundamental flame characteristics
24 of ammonia must be understood. However, knowledge of the characteristics of ammonia/air flames,
25 especially at the high pressures, has been insufficient. In this study, the unstretched laminar burning
26 velocity and the Markstein length of ammonia/air premixed flames at various pressures up to 0.5
27 MPa were experimentally clarified for the first time. Spherically propagating premixed flames,
28 which propagate in a constant volume combustion chamber, were observed using high-speed
29 schlieren photography. Results indicate that the maximum value of unstretched laminar burning
30 velocities is less than 7 cm/s within the examined conditions and is lower than those of hydrocarbon
31 flames. The unstretched laminar burning velocity decreases with the increase in the initial mixture
32 pressure, tendency being the same as that of hydrocarbon flames. The burned gas Markstein length
33 increases with the increase in the equivalence ratio, the tendency being the same as that of
34 hydrogen/air flames and methane/air flames. The burned gas Markstein lengths at 0.1 MPa are
35 higher than those at 0.3 MPa and 0.5 MPa. However, the values of burned gas Markstein length at
36 0.3 MPa and 0.5 MPa are almost the same. In addition, numerical simulations using
37 CHEMKIN-PRO with five detailed reaction mechanisms which are presently applicable for the
38 ammonia/air combustion were also conducted. However, qualitative predictions of unstretched
39 laminar burning velocity using those reaction mechanisms are inaccurate. Thus, further
40 improvements of reaction mechanisms are essential for application of ammonia/air premixed flames.

41

42 **Keywords**

43 Laminar flames, Ammonia, High pressure, Burning velocity, Markstein length, Numerical
44 simulation

45

46 1. Introduction

47 Ammonia holds promise as a hydrogen energy carrier because of its high hydrogen weight of
48 17.7% [1]. At present, ammonia is widely used as a fertilizer. Application of ammonia as a hydrogen
49 energy carrier would be useful because the infrastructure for ammonia distribution has already been
50 established and the ammonia production process, i.e., the Harber-Bosh process, is well-known.
51 Recently, a new process for producing ammonia by utilizing renewable energy sources, such as solar
52 energy, is being studied [2]. In addition, ammonia also shows promise as a carbon-free fuel.
53 However, in general, because of its lower combustion intensities, which means lower calorific value,
54 slower laminar burning velocity and narrower flammability range, ammonia has not been considered
55 as a fuel. Hence, fundamental flame characteristics of ammonia flame have been insufficiently
56 studied.

57 In order to improve the lower combustion intensities of ammonia, hydrogen-added ammonia
58 flames have been studied [3-7]. Lee et al. [3, 4] experimentally investigated the laminar burning
59 velocity of hydrogen-added ammonia/air premixed flames. They showed the laminar burning
60 velocity and Markstein numbers at the atmospheric pressure and clarified that the laminar burning
61 velocity increases and the Markstein number decreases with an increase in hydrogen concentration.
62 Kumar et al. [5] showed the laminar burning velocity of hydrogen/ammonia/air flames by
63 considering the heat loss from the flames. The application of ammonia in an actual combustor is also
64 being studied. Frigo et al. [6, 7] applied hydrogen-doped ammonia as a fuel for the spark ignition
65 engines. The power and thermal efficiencies of a hydrogen-doped ammonia fielded engine were
66 compared with those of a gasoline engine. In addition, consideration is being given to on-board
67 cracking of ammonia in order to obtain hydrogen as a flame promoter in SI engines.

68 Recently, flame characteristics of ammonia/air premixed flames have been studied. Hayakawa
69 et al. [8] experimentally and numerically investigated premixed ammonia/air laminar flames at
70 atmospheric pressure as well as at elevated pressures. Experimental and numerical observations
71 showed that the NO formation from ammonia/air flames was reduced in rich mixtures because of the

72 reduction NO by ammonia. In addition, it was also clarified that NO formation decreases with an
73 increase in pressure due to the enhancement of consumption of H and OH radicals, which play an
74 important role in NO formation.

75 Detailed reaction mechanisms of ammonia flames have been developed by Miller et al. [9] and
76 Lindstedt et al. [10], and reaction mechanisms of C reactions, including N chemistry, are also
77 available for ammonia combustion as proposed by Konnov [11] and Tian et al. [12]. However, since
78 these mechanisms were not elucidated based on ammonia/air flames, it is unclear whether they are
79 applicable for ammonia/air flames owing to insufficiency of experimental results for ammonia/air
80 combustion.

81 Laminar burning velocity is one of the most important parameters for premixed flames and for
82 confirmation of reaction mechanisms. The laminar burning velocities of ammonia/air premixed
83 flames have been investigated by Zakaznov et al. [13], Takizawa et al. [14] and Pfahl et al. [15].
84 According to their results, the laminar burning velocity of ammonia/air premixed flames is lower
85 than that of hydrocarbon flames, such as methane/air flames and propane/air flames. In studies of
86 Takizawa et al. [14] and Pfahl et al. [15], spherically propagating flames in a constant volume
87 combustion chamber were investigated for the evaluation of laminar burning velocity. Although
88 flame stretch, which causes a change in flame speed owing to thermo-diffusive effects [16], was
89 known to occur for spherically propagating laminar flames, the effects of flame stretch on flame
90 speed were not considered in these studies. In addition, all experiments were conducted at
91 atmospheric pressure.

92 Spherically propagating premixed flames in a constant volume combustion chamber have been
93 widely investigated in order to clarify the fundamental characteristics of premixed flames [17 - 20].
94 Kitagawa and Hayakawa et al. [17, 18] investigated spherically propagating laminar and turbulent
95 flames in a large constant volume combustion chamber for hydrogen and iso-octane up to initial
96 mixture pressure of 0.5 MPa. Tse et al. [19] investigated flame propagation up to 60 atm using two
97 concentric cylindrical vessels. Kelley et al. [20] proposed a non-linear relationship between flame

98 speed and flame stretch rate.

99 The Markstein length and the Markstein number are also important parameters for laminar
100 flames because these values express the role of thermo-diffusive effects. Although these values are
101 important for laminar flame characteristics, such as flame instability [21], turbulent flame
102 characteristics are also affected by the Markstein length or the Markstein number. Hayakawa et al.
103 [18] investigated the turbulent burning velocity at fixed turbulence Karlovitz numbers and showed
104 that the ratio of turbulent burning velocity to unstretched laminar burning velocity increases with a
105 decrease in Markstein number. Kobayashi et al. [22] proposed that the Markstein length affects the
106 flame surface density of the turbulent flame front via a change in the passivity of the flame front.
107 Bradley et al. [23] expressed the correlation between turbulent burning velocity and effective
108 turbulence intensity. Therefore, evaluation of the Markstein length or the Markstein number is also
109 important for an understanding of turbulent combustion.

110 The objectives of the present study were to evaluate the laminar burning velocity and the
111 Markstein length of ammonia/air premixed flames at various pressures up to 0.5 MPa. The
112 equivalence ratios were varied from 0.7 to 1.3. In addition, numerical simulations using various
113 detailed reaction mechanisms were also carried out. The results of numerical simulations are
114 compared with the experimental results in the next sections.

115

116 **2. Experimental setup and numerical method**

117 Figure 1 shows the experimental setup used in this study. Experiments were carried out using a
118 constant volume cylindrical combustion chamber. The inner diameter and length of the chamber
119 were 270 mm and 410 mm, respectively. The volume of the chamber was approximately 23 L,
120 equivalent to that of a sphere with a diameter of 355 mm. The mixture was ignited by spark
121 electrodes near the center of the chamber. The diameter of the spark electrodes was 1.5 mm and the
122 spark gap was set to 2 mm.

123 A capacitor discharge ignition (CDI) circuit was adopted for spark ignition of the mixture. The

electrostatic energy, which was charged in the capacitor in the CDI circuit, was set to 2.8 J. Although the energy of 2.8 J was different from the ignition energy and extremely larger than the minimum ignition energy of usual fuels, such as hydrocarbons [24], it was required to ensure the ignition of the ammonia/air mixture at atmospheric pressure. As described in section 4.2, the ignition-affected regimes during flame propagation were not considered in the analysis of the determination of unstretched flame speed and Markstein length. Optical windows made of quartz glass were located opposite each other and flame propagation could be observed via these two windows.

Ammonia was used as the fuel and air was used as the oxidizer. Experimental conditions are summarized in Table 1. Initial mixture pressure, P_i , and the equivalence ratio, ϕ , were varied from 0.1 to 0.5 and 0.7 to 1.3, respectively. All experiments were conducted at a temperature of 298 K. The mixture was prepared according to the partial pressure of ammonia and air. The pressure inside of the chamber was measured by a pressure sensor (P1 in Fig. 1, GE Sensing UNIC5000). Experiments were carried out at least five times for each examined condition. The unstretched laminar burning velocity and burned gas Markstein length, which will be described in section 4.2, were determined as the averaged value of the results obtained from each experiment. Experimental fluctuation was defined as the difference between maximum and minimum values of the experimental results.

Schlieren photography with a high-speed camera and a continuous light source was adopted for the flame observation. A metal halide lamp (Photron, HVC-SL) and a high-speed camera (Photron, FASTCAM SA5) were used for the schlieren system. In order to form a spotlight source, a pinhole was mounted in front of the metal halide lamp. A micro lens (Nikon, Ai AF Micro-Nikkor 200mm f/4D IF-ED) was mounted on the high-speed camera. The resolution of the schlieren photography was 768×768 and the frame rate was 1000 fps. The resolution of the schlieren images was approximately 0.1 mm/pixel. Flame propagation could be obtained up to 60 mm in diameter using the schlieren technique via two optical windows. In addition, direct color high-speed photographs were taken by a high-speed camera (Photron, FASTCAM SA-Z) with a lens (Nikon, AF-S DX

Nikkor 35mm f/1.8G). The resolution and frame rate of color imaging were 1024×1024 and 1000 fps, respectively. The spatial resolution of the direct image was approximately 0.2 mm/pixel.

The pressure inside of the chamber during flame propagation was measured by a pressure sensor (P2 in Fig. 1, Kyowa, PVL-10KD) and recorded by a memory recorder (HIOKI, MEMORY HiCORDER LR8431) with a sampling rate of 1 kHz. A pulse circuit was also adopted. When the switch was pushed, a single trigger pulse was outputted from the pulse circuit. The ignition timing of the mixture, recorded by the high-speed camera and the memory recorder started simultaneously.

Numerical simulations were also performed using a one-dimensional freely propagating laminar flame model of CHEMKIN-PRO [25]. The detailed chemical kinetics of Miller et al. [9], Lindstedt et al. [10], Konnov [11] without all carbon reactions, Tian et al. [12] and GRI-Mech 3.0 [26] were used in this study. The initial mixture temperature was set to 298 K. Pressure was varied from 0.1 to 0.5 MPa. In the case of numerical simulation, unstretched laminar burning velocity, S_L , was defined as the velocity at the cold boundary in the computational domain.

Table 2 shows the mixture and flame characteristics of ammonia/air premixed flames. Here, ρ_u and ρ_b are unburned mixture density and burned gas density, respectively. The densities were evaluated from the equilibrium calculation of CHEMKIN-PRO with thermo transport data of Tian et al. [12]. λ , c_p , α and ν are thermal conductivity, specific heat at constant pressure, thermal diffusivity and kinematic viscosity, respectively. The Lewis number of deficient components, Le , is also shown in Table 2. As shown in Table 2, the Lewis numbers of lean mixtures are lower than unity and almost constant for rich mixtures.

3. Evaluation of laminar burning velocity and Markstein length

The laminar burning velocity and the Markstein length were obtained by the following methodology. The flame radius obtained from the schlieren image, r_{sch} , was determined to be the radius of a circle whose area was equivalent to the area of the schlieren image of spherically propagating flame. In the case of spherically propagating premixed flames, the flame speed during

176 flame propagation, S_N , is evaluated by Eq. (1):

$$177 \quad S_N = \frac{dr_{sch}}{dt}, \quad (1)$$

178 where t is time.

179 Because the spherically propagating premixed flame is curved at the flame front, the effects of
180 flame stretch on flame characteristics must be considered. The flame stretch rate, ε , is determined as
181 the change in flame front area per unit area and unit time. In the case of spherically propagating
182 flames, the flame stretch rate is derived by Eq. (2):

$$183 \quad \varepsilon = \frac{1}{A} \cdot \frac{dA}{dt} = \frac{2}{r_{sch}} \cdot \frac{dr_{sch}}{dt}, \quad (2)$$

184 where A ($=4\pi r_{sch}^2$, for spherically flame) is the flame front area. In the case of non-unity Lewis
185 number flames, thermo-diffusive effects occur, and thus flame temperature as well as laminar
186 burning velocity are different from those of the unstretched flame. According to asymptotic analysis,
187 the difference between unstretched flame speed, S_S , and stretched flame speed, S_N , can be considered
188 to be proportional to the flame stretch rate, as shown by Eq. (3) [27]:

$$189 \quad S_S - S_N = L_b \cdot \varepsilon, \quad (3)$$

190 where the proportional constant L_b is the burned gas Markstein length. Thus, the unstretched flame
191 speed, S_S , can be determined by the extrapolation of $\varepsilon \rightarrow 0$ (or $r_{sch} \rightarrow \infty$). The unstretched
192 laminar burning velocity, S_L , can then be calculated by Eq. (4):

$$193 \quad S_L = \frac{\rho_b}{\rho_u} \cdot S_S. \quad (4)$$

194 Recently, Kelley et al. [20] proposed a non-linear relationship between the unstretched laminar
195 burning velocity and the stretched laminar burning velocity. In this case, the linear approximation of
196 Eq. (3) is available because the Lewis numbers of ammonia/air flames are close to unity, as shown in
197 Table 2 [28].

198

4. Experimental results

4.1. Flame observation

Figure 2 shows direct images of spherically propagating ammonia/air premixed laminar flame at elapsed time from the ignition, t , taken at 100 ms at an initial mixture pressure of 0.1 MPa at equivalence ratios of (a) $\phi = 0.8$, (b) $\phi = 1.0$ and (c) $\phi = 1.2$. Orange chemiluminescence was observed from ammonia/air premixed flames. Hayakawa et al. [8] proposed that the orange chemiluminescence was caused by the NH_2 ammonia α band spectra [29] and the superheated H_2O vapor spectra. NH_2 increases as the equivalence ratio increases, and orange chemiluminescence becomes clearer. The shape of flame at $\phi = 0.8$ was jellyfish-like at $t = 100$ ms. As described in subsection 4.2, the unstretched laminar burning velocity at $\phi = 0.8$ is very low. Therefore, buoyancy is significantly influenced, especially for this condition, and consequently changes the flame shape.

Figure 3 shows the pressure history inside the chamber, P , during flame propagation at $\phi = 1.0$ and $P_i = 0.1$ MPa. The increase of the pressure, within the observation range of 60 mm in diameter, was less than 2 % from the initial mixture pressure, P_i , because the volume of the chamber is sufficiently large compared to the visible range of schlieren photography. Therefore, the pressure in the chamber during flame propagation can be assumed to be constant within the observation range.

Figure 4 shows schlieren images of ammonia/air premixed flames at various equivalence ratios, ϕ , with elapsed time from the ignition, t , at (a) $P_i = 0.1$ MPa, (b) $P_i = 0.5$ MPa, respectively. In the case of the equivalence ratio of 0.7 at $P_i = 0.1$ MPa, a hot gas regime generated by an electric spark could be observed between the spark electrodes at $t = 0$ ms. The boundary of the hot gas regime became obscure at $t = 40$ ms. After that, the boundary of the hot gas seems to disappear at $t = 80$ ms. This denotes that the flame does not propagate throughout the chamber under this condition. A similar phenomenon was also observed at $\phi = 1.3$ and at $P_i = 0.1$ MPa. The lean and rich flammability limits of ammonia flame are $\phi = 0.63$ and $\phi = 1.4$ [30], respectively, and present experimental results were close to the lean and rich flammability limits. However, flame propagates throughout the chamber at $P_i = 0.3$ MPa and 0.5 MPa at $\phi = 0.7$ and $\phi = 1.3$, respectively.

225 According to Paschen's law, voltage at the spark increases with an increase in initial mixture
226 pressure. Ballal et al. [31] showed that the released energy of the electric spark increases with the
227 increases in pressure if the spark gap remains constant. Although the ignition energy could not be
228 evaluated in this study, it is considered to increase with an increase in the initial mixture pressure. In
229 the case of equivalence ratios of 0.8, 1.0 and 1.2, spherically propagating premixed flame propagated
230 throughout the chamber for all examined initial mixture pressure conditions. After 40 ms from
231 ignition, the flame radius at $\phi = 1.0$ was larger than that at $\phi = 0.8$ and 1.2. The center of spherical
232 flame was close to the gap of spark electrodes until $t = 20$ ms. After that, the center of spherical
233 flame moved upward in the combustion chamber. The movement of the flame center was caused by
234 buoyancy.

235 Figure 5 shows schlieren images of ammonia/air premixed flames with an equivalence ratio of ϕ
236 = 1.0 at the examined initial mixture pressure conditions. As the initial mixture pressure increased,
237 the size of spherical flame became smaller. It could be concluded that the flame speed decreases with
238 the increase in initial mixture pressure.

239 240 **4.2. Unstretched laminar burning velocity and Markstein length**

241 Figure 6 shows the relationship between the stretched flame speed, S_N , and the flame stretch rate,
242 ε , of a stoichiometric mixture at $P_i = 0.1$ MPa. Flame propagation in a constant volume combustion
243 chamber can be classified into three periods: an ignition affected period, a quasi-steady period and a
244 chamber affected period [20]. The quasi-steady period is shown by closed symbols in Fig. 6.

245 As flame propagated, flame stretch rate decreased, and then, flame speed rapidly increased at
246 about $\varepsilon = 43 \text{ s}^{-1}$. Since the inner diameter of the chamber was sufficiently large, compared with the
247 observation range, the influence of the chamber is considered to be small. As described in subsection
248 4.1, the flame speed of ammonia/air flames is very slow and thus flame shape changes from
249 spherical flame owing to buoyancy. Therefore, the change in the flame speed is caused by the
250 buoyancy, and thus the regime should be termed as a buoyancy influenced regime. In this study, the

transitions of the ignition affected regime to a quasi-steady regime and the quasi-steady regime to a buoyancy influenced regime were determined based on the flame shape and the ratio of flame propagation speed. Here, the flame shape ratio and flame propagation ratio are defined as a/b and $(dr_{sch}/dt)_t/(dr_{sch}/dt)_{t-\Delta t}$, respectively. a and b are the length of the vertical and horizontal diameters of the flame, respectively. $(dr_{sch}/dt)_t$ denotes the flame propagation speed at time t . Since the frame rate of schlieren photography was 1000 fps in this study, Δt was 1 ms.

Figure 7 shows the variations of the flame shape ratio and the moving average of the flame propagation ratio with the flame stretch rate at $P_i = 0.1$ MPa and $\phi = 1.0$. As shown in Fig. 7, in the regime which can be presumed to be a quasi-steady regime, the change in the flame shape ratio and the flame propagation ratio does not fluctuate so much. In this study, the quasi-steady regime was determined to be a regime in which the flame shape ratio and the moving average of the flame propagation ratio change smoothly. The time when the flame kernel starts the upward motion in the chamber does not correspond to the time when the flame propagation stage transitions to the buoyancy influenced regime. Although the upward movement of the flame kernel influences the propagation speed, it was considered that the influence of the upward motion was not significant. As shown in Fig. 6, the change in the stretched flame propagation speed, S_N , was well proportional to the flame stretch rate. Thus, the linear approximation by Eq. (3) was applied for the relationship between S_N and ε .

Figure 8 shows the relationship between unstretched laminar burning velocity, S_L , and equivalence ratio, ϕ . The unstretched laminar burning velocity reached its maximum value around an equivalence ratio of $\phi = 1.1$ for all examined initial mixture pressure conditions in this study. These tendencies are the same as those of hydrocarbon flames. The maximum value of the unstretched laminar burning velocity at the initial mixture pressure of 0.1 MPa was about 7 cm/s and was very low compared with that of hydrocarbon flames whose maximum value of the unstretched laminar burning velocity is about 35 cm/s. Although the flame propagated throughout the chamber at $\phi = 0.7$, 0.8 and 1.3 at $P_i = 0.3$ MPa and 0.5 MPa, the unstretched laminar burning velocity could not be

277 evaluated owing to the significant influence of buoyancy because it is presumed that the unstretched
278 laminar burning velocity is very low at these conditions.

279 The results obtained experimentally by Takizawa et al., Pfahl et al. and Zakaznov et al. are also
280 plotted in Fig. 8. Even though the effects of flame stretch were not considered in the previous results,
281 the laminar burning velocities are close to the results obtained in this study. As shown in Table 1, the
282 Lewis number of ammonia/air premixed flames is close to unity. Therefore, the flame stretch, i.e.,
283 the thermo-diffusive effects, does not change significantly in unstretched laminar burning velocity.
284 The unstretched laminar burning velocity decreased with the increases in the initial mixture pressure
285 for all examined equivalence ratios.

286 Figure 9 shows the variations of the burned gas Markstein length, L_b , with the equivalence ratio,
287 ϕ . The burned gas Markstein length increases with the increase in the equivalence ratio. The
288 tendency of the burned gas Markstein length is the same as those of hydrogen/air [32] and
289 methane/air [33], but different from that of iso-octane/air [33]. The values of burned gas Markstein
290 lengths at $\phi = 0.8$ and 0.9 are negative. As shown in Table 1, the Lewis numbers of ammonia/air
291 flames of a lean mixture are lower than unity. Thereby, the burned gas Markstein lengths at lean
292 mixtures are negative because temperature and burning velocity of stretched flames increase owing
293 to the thermo-diffusive effects. Although the value of the burned gas Markstein length at $P_i = 0.1$
294 MPa is larger than that of 0.3 and 0.5 MPa, its values at $P_i = 0.3$ MPa and 0.5 MPa are almost the
295 same.

296 Figure 10 shows the relationship between preheating zone thickness, $\delta_l (= \alpha/S_L)$, and the
297 equivalence ratio, ϕ . The preheating zone thickness is thinnest at the equivalence ratio of $\phi = 1.1$ for
298 all initial mixture pressures because the unstretched laminar burning velocity was the fastest at this
299 equivalence ratio. The preheating zone thickness decreases with the increase in initial mixture
300 pressure. The preheating zone thicknesses of methane/air premixed flames obtained by Kitagawa
301 [21] are also plotted in Fig. 10. The preheating zone thicknesses of methane/air flames are thinner
302 than those of ammonia/air premixed flames because unstretched laminar burning velocities of

methane/air flames are faster than those of the ammonia/air premixed flames.

The Lewis number of ammonia/air flames and that of methane/air flames are almost unity and the variation of Lewis number with the equivalence ratio of ammonia/air flames and that of methane/air flames are similar. In the case of the turbulent combustion, which is used in actual combustors, the thermo-diffusive effect is important for turbulent flame characteristics. Because the variation of Markstein length of ammonia/air flames and that of methane/air flames are similar, the turbulent flame characteristics are considered to be similar from the standpoint of thermo-diffusive effects. According to the Peters regime diagram [34], flame thickness is an important parameter of turbulent flame structures. Thus, the flame structure is considered to be different because the laminar flame thickness is significantly different.

Figure 11 shows the variation of unstretched laminar burning velocity, S_L , with the initial mixture pressure, P_i , at the equivalence ratios of (a) $\phi = 0.9$, (b) $\phi = 1.0$ and (c) $\phi = 1.2$, respectively. The results of numerical simulation by CHEMKIN-PRO with detailed reaction mechanisms are also plotted in Fig. 11. The calculated unstretched laminar burning velocity decreases with the increase in initial mixture pressure and is the same tendency as that of the experimental results. The calculated unstretched laminar burning velocity decreases in the order of Konnov, Lindstedt and Miller, Tian, and GRI-Mech 3.0. Most numerical simulations overpredict when compared with the experimental results. Although the results from GRI-Mech 3.0 seem to be close to the experimental results, GRI-Mech 3.0 is possibly not appropriate for the numerical simulation of ammonia flames because N reactions including NO and NH_2 reactions are insufficient.

Although some of these reactions take the ammonia reaction into consideration and are used in the study of ammonia/hydrogen/air flames [5], they have not been optimized for the ammonia/air combustion. The detailed chemical kinetics of Tian's mechanism [12] was developed based on $\text{NH}_3/\text{CH}_4/\text{O}_2/\text{Ar}$ flame at a reduced pressure condition in order to identify the detailed flame structure using tunable synchrotron vacuum ultraviolet photoionization and molecular-beam mass spectrometry. Konnov's mechanism [11] was responsible for the prompt NO formation from

hydrocarbon flames. Although the detailed chemical kinetics of Lindstedt's mechanism [10] and Miller's mechanism [9] were developed based on ammonia combustion, these mechanisms were developed considering NH_3/O_2 , $\text{NH}_3/\text{H}_2/\text{O}_2$, $\text{NH}_3/\text{NO}/\text{O}_2$ and $\text{NH}_3/\text{NO}/\text{O}_2/\text{H}_2/\text{Ar}$ flames to permit comparison with the previous experimental results. GRI-Mech [26] was optimized for natural gas combustion. Therefore, further improvement of the ammonia reaction mechanisms is essential.

5. Conclusions

The laminar burning velocity and the burned gas Markstein length of the ammonia/air premixed flames were experimentally investigated at the various pressures up to 0.5 MPa. Spherically propagating premixed flames, which propagated in a constant volume combustion chamber, were observed using high-speed schlieren photography. The equivalence ratio was varied from 0.7 to 1.3. Numerical simulation using five detailed reaction mechanisms, which can be applied to ammonia flames, were also conducted. The following results were obtained:

1. The maximum laminar burning velocity reaches its peak value around an equivalence ratio of 1.1 for all examined initial mixture pressure conditions. Unstretched laminar burning velocity of ammonia/air premixed flames decreases with an increase in the initial mixture pressure. That tendency is the same as that of hydrocarbon fuels.
2. The burned gas Markstein length increases with an increase in equivalence ratio. This tendency is the same as that of methane/air and hydrogen/air flames. The burned gas Markstein lengths of lean flames at an initial mixture pressure of 0.1 MPa are negative. The burned gas Markstein lengths at elevated pressures of 0.3 MPa and 0.5 MPa are lower than those of 0.1 MPa. However, the values of burned gas Markstein length at 0.3 MPa and 0.5 MPa are also the same.
3. Reaction mechanisms used in this study can predict the qualitative variation of the unstretched laminar burning velocity with the initial mixture pressure, i.e., the unstretched laminar burning velocity decreases with the increase in the initial mixture pressure.

355 However, those mechanisms are not applicable for quantitative prediction of unstretched
356 laminar burning velocity. Thus, further improvement of reaction mechanisms of the
357 ammonia/air flames is essential.

358

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- 440

441 **Table captions**

442 Table 1 Examined conditions.

443 Table 2 Properties of ammonia/air mixtures used in the present study.

444

Equivalence ratio, ϕ (-)	0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3
Initial mixture pressure, P_i (MPa)	0.1, 0.3, 0.5
Initial mixture temperature (K)	298

Table 1

P_i (MPa)	ϕ (-)	ρ_u (kg/m ³)	ρ_b (kg/m ³)	λ (10 ⁻³ W/m/K)	c_p (J/kg/K)	α (10 ⁻⁵ m ² /s)	ν (10 ⁻⁵ m ² /s)	Le (-)
0.1	0.7	1.101	0.182	27.21	1121	2.205	1.575	0.95
	0.8	1.091	0.167	27.31	1135	2.205	1.575	0.94
	0.9	1.083	0.155	27.41	1149	2.204	1.575	0.94
	1.0	1.074	0.146	27.50	1162	2.203	1.576	=
	1.1	1.066	0.146	27.59	1175	2.203	1.576	1.09
	1.2	1.058	0.148	27.68	1188	2.202	1.576	1.09
	1.3	1.051	0.149	27.76	1200	2.201	1.576	1.09
0.3	0.7	3.302	0.546	27.21	1121	0.735	0.525	0.95
	0.8	3.274	0.501	27.31	1135	0.735	0.525	0.94
	0.9	3.248	0.465	27.41	1149	0.735	0.525	0.94
	1.0	3.222	0.437	27.50	1162	0.734	0.525	=
	1.1	3.198	0.438	27.59	1175	0.734	0.525	1.09
	1.2	3.175	0.443	27.68	1188	0.734	0.525	1.09
	1.3	3.152	0.448	27.76	1200	0.734	0.526	1.09
0.5	0.7	5.503	0.910	27.21	1121	0.441	0.315	0.95
	0.8	5.457	0.835	27.31	1135	0.441	0.315	0.94
	0.9	5.413	0.775	27.41	1149	0.441	0.315	0.94
	1.0	5.370	0.727	27.50	1162	0.441	0.315	=
	1.1	5.330	0.729	27.59	1175	0.441	0.315	1.09
	1.2	5.291	0.738	27.68	1188	0.440	0.315	1.09
	1.3	5.254	0.747	27.76	1200	0.440	0.315	1.09

450

451

Table 2

452

453 **Figure captions**

454 Fig. 1 Schematic of experimental setup.

455 Fig. 2 Direct photograph of ammonia/air premixed flames of $P_i = 0.1$ MPa at $t = 100$ ms. (a) $\phi =$
456 0.8, (b) $\phi = 1.0$, (c) $\phi = 1.2$.

457 Fig. 3 Pressure history during flame propagation.

458 Fig. 4 Schlieren images of ammonia/air premixed flames (a) $P_i = 0.1$ MPa and (b) $P_i = 0.5$ MPa..

459 Fig. 5 Schlieren images of ammonia/air premixed flames at $\phi = 1.0$.

460 Fig. 6 Relationship between stretched flame speed, S_N , and flame stretch rate, ε .

461 Fig. 7 Variation of flame shape ratio, a/b , and moving average of flame propagation ratio,
462 $(dr_{sch}/dt)_t / (dr_{sch}/dt)_{t-\Delta t}$.

463 Fig. 8 Experimental and numerical results of the relationship between unstretched laminar burning
464 velocity, S_L , and equivalence ratio, ϕ .

465 Fig. 9 Relationship between preheating zone thickness, δ_f , and equivalence ratio, ϕ .

466 Fig. 10 Relationship between burned gas Markstein length, L_b , and equivalence ratio, ϕ .

467 Fig. 11 Variation of unstretched laminar burning velocity, S_L , with initial mixture pressure, P_i . (a) ϕ
468 = 0.8, (b) $\phi = 1.0$, (c) $\phi = 1.2$. The numerical simulations were conducted with detailed
469 chemical kinetics developed by Miller et al. [9], Lindstedt et al. [10], Konnov [11], and Tian
470 et al. [12] and with GRI-Mech 3.0 [26]. Here, all carbon reactions were removed from
471 Konnov's mechanisms.

472

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11