Stability limits and NO emissions of premixed swirl ammonia-air flames enriched with hydrogen or methane at elevated pressures

Abdulrahman A. Khateeb^{1*}, Thibault F. Guiberti¹, Guoqing Wang¹, Wesley R. Boyette¹, Mourad Younes², Aqil Jamal², William L. Roberts¹

¹King Abdullah University of Science and Technology (KAUST), CCRC, Thuwal 23955-6900, Saudi Arabia.

²Saudi Aramco, Dhahran 31311, Saudi Arabia.

*Corresponding author email: abdulrahman.khateeb@kaust.edu.sa

Highlights

- Increasing pressure widens the range of stability of ammonia-air flames.
- For ammonia-hydrogen/methane-air flames, increasing pressure increases the ammonia fuel fraction for which the transition from flashback to rich blowout occurs.
- NO emissions from ammonia-hydrogen/methane-air flames decrease as pressure increases.
- Good NO performance is found for very lean ammonia-hydrogen-air flames under elevated pressures.

Abstract

This study reports measurements of stability limits and exhaust NO mole fractions of technically-premixed swirl ammonia-air flames enriched with either methane or hydrogen. Experiments were conducted at different pressures from atmospheric to 5 bar, representative of commercial micro gas turbines. The full range of ammonia fractions in the fuel blend, x_{NH_3} , was considered, from 0 (pure methane or hydrogen) to 1 (pure ammonia), covering very lean ($\phi = 0.25$) to rich ($\phi = 1.60$) equivalence ratios. Results show that increasing pressure widens the range of stable equivalence ratios for pure ammonia-air flames. Regardless of pressure, there is a critical ammonia fraction above which the range of stable equivalence ratios suddenly widens. This is because flashback does not occur anymore when the equivalence ratio is progressively increased towards stoichiometric and rich blowout occurs instead. This critical ammonia fraction increases

with pressure and is larger for ammonia-hydrogen than for ammonia-methane. Provided that enough hydrogen is blended with ammonia ($x_{\text{NH}_3} < 0.9$), flames with very lean equivalence ratios ($\phi < 0.7$) can be stabilized and these yield competitively low NO emissions (< 200 ppm), regardless of pressure. For this reason, very lean swirl ammonia-hydrogen-air flames are promising candidates for micro gas turbines. However, N_2O emissions have the potential to be unacceptably large for these operating conditions if heat loss is too large or residence time is too short. As a consequence, the post flame region must be considered carefully. Due to the lower reactivity of methane compared to that of hydrogen, very lean swirl ammonia-methane-air flames could not be stabilized and good NO performance is limited to rich equivalence ratios for ammonia-methane fuel blends. The equivalence ratio above which good NO performance depends on pressure and bulk velocity.

Keywords

Carbon-free, gas turbine, nitric oxide, flashback, blowout

1. Introduction

Ammonia is being considered as a sustainable energy source to fuel gas turbines because of its carbon-free nature and high hydrogen capacity of 17.8% by mass [1,2]. Relative to hydrogen, ammonia can be more readily stored, shipped, and distributed because it exists in liquid form at significantly lower pressure and temperature. The annual storage cost of ammonia is approximately \$1 per kilogram of hydrogen, compared to \$30 for hydrogen [3]. To fuel a gas turbine, ammonia can be cracked into hydrogen at the point of end use. For a fuel supply at 30 bar, this process comes with an energy penalty of around one third of the high calorific value of hydrogen [4]. Alternatively, ammonia can be used directly as a primary fuel [5–8].

Ammonia as a primary fuel suffers from its low reactivity compared to typical hydrocarbons. While stabilization of turbulent ammonia-air flames has been achieved in a few instances, e.g. in [9–14], many other experiments, e.g. [7,15–17], showed that stabilizing premixed ammonia-air flames is much more challenging than premixed methane-air flames. This issue can be mitigated by enriching ammonia with more reactive fuels such as methane or hydrogen. For example, early experiments of [7] showed that the ammonia-hydrogen-nitrogen fuel blend obtained by cracking 28% of the ammonia features the same flame-stability performance as typical hydrocarbons. More recently, the benefits of enriching ammonia have been verified for a range of different configurations [9–12,15–26]. Franco *et al.* [18] developed a novel swirl combustor and found a reasonably wide stable range when only a small addition of hydrogen is added in the ammonia-hydrogen fuel blend. In two sister studies, Khateeb *et al.* [17,19] showed that tailored ammonia-methane and ammonia-hydrogen fuel blends can actually yield broader stable ranges than pure methane, hydrogen, or ammonia. However, experiments of [17–19] were conducted at atmospheric pressure only. Stable operation of ammonia-methane-air or ammonia-hydrogen-air swirl flames

has been achieved at elevated pressures, more representative of industrial gas turbines, in e.g. [9,27]. In [27], the ammonia fraction in the ammonia-hydrogen fuel blends was not varied. In [9], the ammonia fraction in the ammonia-methane fuel blend was varied from 0 (pure methane) to 1 (pure ammonia) but effects of pressure were not isolated and examined. Studies on flame stability where the ammonia fraction is varied from 0 to 1 for atmospheric as well as elevated pressures are scarce. This paucity is addressed in this work, both for methane and hydrogen enriched ammonia fuel blends.

Another challenge associated with ammonia as a fuel is its propensity to emit large amounts of NO when burned [2,3,8]. Contrary to methane or hydrogen, most of the NO found in the exhaust of ammonia-air flames is formed via fuel NO_x pathways [28]. As a consequence, reducing flame temperature by operating lean, to penalize thermal NO_x pathways, is insufficient with ammonia-air flames to abate NO emissions below acceptable limits [29]. This strategy has been the topic of many experimental and numerical studies that examined NO formation in ammonia flames as a function of equivalence ratio [10,12,18,25,26], ammonia fuel fraction [9,17,19,30], or pressure [11,21,22,31]. In many of these studies, the OH radical was identified as one of the main drivers for NO formation. Simply put, larger OH radical concentrations lead to larger NO concentrations. This explains why very large mole fractions of NO, in excess of 1000 ppm, are usually found in the products region of slightly lean, stoichiometric, and slightly rich flames that include some ammonia in the fuel blend [28,32,33].

The intimate relationship between OH and NO also partly explains the relatively low NO mole fractions found in the exhaust of rich ammonia flames. Indeed, the abundance of NH₂ associated with rich burning promotes the consumption of OH via reaction $\text{NH}_2 + \text{OH} \leftrightarrow \text{H}_2\text{O} + \text{NH}$ [34]. In addition, NO is directly consumed via reaction $\text{NH}_2 + \text{NO} \leftrightarrow \text{H}_2\text{O} + \text{N}_2$ [28,35]. While rich burning

benefits NO performance, a globally-rich operation must be avoided to avoid harmful unburned NH₃ emissions and efficiency penalties. Therefore, two-stage combustors have been successfully developed, in which a first locally-rich stage precedes a second locally-lean stage, yielding globally-lean operation [10,12,14,22,26].

Because two-stage combustors are inherently more complex than single stage combustors, efforts were also made to identify lean operating conditions capable of competitively low NO emissions. While such conditions are yet to be found for pure ammonia or ammonia-methane blends, recent studies [19,24,30] showed that very lean ammonia-hydrogen-air flames can exhibit NO mole fractions in the exhaust of a few hundreds of ppm or less. However, these studies were not conducted at elevated pressures representative of commercial gas turbines. Very lean ammonia-hydrogen-air flames are promising candidates for gas turbines because elevating pressure is expected to abate NO emissions even further. Indeed, the reaction rate of reaction OH + H + M $\leftrightarrow$ H₂O + M that consumes OH increases with increasing pressure [11,31].

However, very lean ammonia-hydrogen-air flames may suffer from other limitations. For example, recent studies [12,26] showed that N₂O emissions rapidly increase if the equivalence ratio is sufficiently decreased. This is important because N₂O is a very potent greenhouse gas [36,37], around 250 times more effective than CO₂. As such, one must be careful not to cancel benefits associated with carbon-free fuels by releasing large amounts of N₂O to the atmosphere. Evidently, some trade-off exists between NO performance and N₂O performance for flames fueled by blends including ammonia and this warrants further studies. An example of recent effort on this topic is an experimental study of Okafor *et al.* [12] that showed that, besides equivalence ratio, heat loss and residence time in the combustion chamber are two important parameters influencing NO and N₂O emissions in premixed ammonia-air flames.

The objectives of the present study are similar to those of [17,19] but now for flames at elevated pressures, more representative of practical gas turbines. We aimed to understand how modifying the composition of the ammonia-hydrogen or ammonia-methane fuel blend affects the stability limits and NO emissions of premixed swirl flames, from very lean to rich equivalence ratios. A generic swirl combustor, also comparable to that found in [17,19], was adopted and slightly modified to fit in KAUST's high-pressure combustion duct (HPCD) [38]. Flame stability limits and NO emissions were measured at atmospheric pressure and at elevated pressures up to 5 bar, typical of industrial micro gas turbines. N₂O emissions were also considered. This study covers the full range of ammonia fractions (from 0 to 1) in the ammonia-hydrogen or ammonia-methane fuel blends.

2. Experimental setup

Figure 1 shows the schematics of the generic swirl combustor used in this study. It is the same as in [17,19] except for the combustion chamber, which now features a square-cross section and four flat quartz windows. This modification was done to improve optical access and facilitate eventual laser diagnostics in future studies.

Figure 1: Schematics of the generic swirl combustor (left) including dimensions (middle) and fit in the HPCD (right). All dimensions are in mm.

This combustor was designed for a maximal thermal power of $P_{th} \sim 30$ kW. The combustion chamber is 390 mm long and 160 mm wide. The four flat quartz windows providing optical access are 160 mm long and 150 mm wide. A converging stainless-steel chimney sits on top of the combustion chamber to accelerate the flow of exhaust gases and prevent the recirculation of ambient air into the combustion chamber.

In this study, only air was injected into the plenum through the two axial inlets a at the bottom of the assembly. A premix of fuel and air was injected through the four tangential inlets b , which are regularly distributed azimuthally. Because of this tangential injection, swirl was imparted to the flow [39]. The swirl number, dictated by the ratio of the tangential momentum m_{θ} to the axial momentum m_A [40,41] can be calculated with equation 7 available in [41]. In this study, the swirl number was fixed to $S_g = 1$. However, effects of the bulk velocity were of interest and the bulk velocity was varied. Because both the bulk velocity and pressure were varied, the bulk Reynolds number at the injector's throat also varied. It is defined here as follows:

$$\text{Re} = \frac{\rho d u_b}{\mu} \quad (1)$$

where u_b is the bulk velocity at the injector's throat, μ and ρ stand the dynamic viscosity and density of the reactants, respectively, and d refers to the diameter of the injector's throat, here 44 mm.

To allow operation at elevated pressure, the swirl combustor was mounted in KAUST's high-pressure combustion duct (HPCD) (see Fig. 1). Details about the HPCD are available in [38] and only its main features are described here. The HPCD is a 316L stainless-steel duct with an inner diameter of 410 mm and a length of ~8 m. It is designed to sustain 40 bar pressure at 250 °C. It is air-cooled and its pressure was increased and regulated by flowing cooling-air and adjusting pressure drop in its exhaust. The HPCD is fitted with 6 UV-grade fused silica windows for flame monitoring, optical diagnostics, and ignition. The flame was ignited through one of these optical windows, as well as through one of the combustion chamber's quartz plate, using a laser-induced spark.

Various mixtures of ammonia-hydrogen-air and ammonia-methane-air were examined, spanning the full range of ammonia volume fractions in the fuel blend from $x_{NH_3} = 0$ (no ammonia) to 1 (only ammonia). Mixtures with some nitrogen addition to the ammonia-hydrogen fuel blend were also examined. The hydrogen:nitrogen volume ratio was always 3:1 to mimic ammonia cracking. Ammonia fractions in the fuel blend ranging from 0 to 1 were tested for both ammonia-hydrogen-air and ammonia-methane-air flames and for 1, 2, 3, 4, and 5 bar pressure. The bulk jet velocity was varied from $u_b = 1.4$ m/s to 1.8 m/s and the Reynolds number was varied from $\text{Re} = 4000$ to 20,000.

Due to the large number of parameters investigated in this work (fuel blend composition, equivalence ratio ϕ , pressure, bulk velocity, and Reynolds number), it was not practical to test all possible combinations. Therefore, carefully-selected subsets of all possible combinations were investigated to isolate effects of relevant parameters. For example, stability limits were explored for all fuel blends and pressures but only for $u_b = 1.4$ m/s. Effects of the bulk velocity were only examined at 2 bar and for an ammonia-methane fuel blend with $x_{NH_3} = 0.80$. Similarly, exhaust NO emissions were measured for a large but limited number of operating conditions covering the range of interest. The tested conditions for stability limits or exhaust NO emissions, are summarized in Table 1. Effects of the fuel blend composition on exhaust NO emissions were exhaustively analyzed with this combustor for ammonia-hydrogen-air and ammonia-methane-air flames at atmospheric pressure in [19] and in [17], respectively. In the present study, exhaust NO emissions are investigated with an emphasize on effects of pressure and equivalence ratio instead.

Table 1: Operating conditions: fuel blends, bulk velocities, pressures, equivalence ratios, and the range of ammonia fuel fractions considered for stability limits and NO emissions.

	Fuel blend	u_b (m/s)	P (bar)	ϕ	Range of x_{NH_3} for stability limits measurements	Range of x_{NH_3} for NO emissions measurements
1	NH ₃ -CH ₄	1.40	1 – 5	0.5 – 1.6	0 – 1	×
2	NH ₃ -CH ₄	1.40	1 – 4	1.1 – 1.3	×	0.80
3	NH ₃ -CH ₄	1.40 – 1.80	2	1.1 – 1.3	×	0.80
4	NH ₃ -H ₂	1.40	1 – 5	0.2 – 1.6	0 – 1	×
5	NH ₃ -H ₂	1.40	1 – 4	0.5 – 0.9	×	0.75 – 0.90
6	NH ₃ -H ₂ -N ₂	1.40	1, 3	0.2 – 1.6	0 – 1	×
7	NH ₃ -H ₂ -N ₂	1.40	2 – 4	0.5	×	0.75

The flow rates of fuels and air were prescribed with digital mass flow controllers (BROOKS Instruments SLA series). These were calibrated in-house with a gas flow calibrator (MesaLabs

ML-1020) prior to the experiments, leading to an accuracy better than 1%. This means that the uncertainties of equivalence ratio, bulk velocity, and fuel blend composition were 1.7% in the worse-case-scenario. Stability limits, namely lean blowout, flashback, and rich blowout, were measured with the same method as in [17,19]. For illustration purposes, time-averaged broadband flame images were recorded with a DSLR camera with an exposure time of 1/1.3 seconds, an aperture of $f/13$, and an ISO number of 200.

To measure NO emissions, a quartz sampling probe was mounted through the exhaust chimney, 372 mm downstream of the injector's outlet. The probe was connected to a Testo-350 flue gas analyzer through a flange that replaced one of the HPCD windows. The probe's inlet diameter was smaller than 1 mm followed by an expansion to 2 mm to reach sonic conditions and quench chemical reactions [42]. The sensitivity of the gas analyzer was ~ 100 ppm, and its precision was approximately $\pm 1\%$. For calibration, different mixtures of 99.9% pure nitrogen with NO mole fractions of 500/1500/3000 ppm were used. For comparisons between cases with different equivalence ratios to be fair, NO mole fractions were corrected for a 6% O_2 mole fraction. Measurements were repeated at least three times for each condition, and reproducibility was $\sim 5\%$ on average. Variability for each condition is expressed by error bars in all following plots.

3. Results and discussion

Stability limits measured for operating conditions listed in Table 1 are reported and discussed in Sec. 3.1. Mostly for illustration purposes, time-averaged broadband images of flames within these stability limits are shown in Sec. 3.2. Finally, exhaust NO emissions for select cases are reported and discussed in Sec. 3.3.

3.1 Stability limits

3.1.1 Ammonia-methane-air flames

Figure shows the measured stability limits of ammonia-methane-air swirl flames for the full range of ammonia fuel fractions. These stability limits are plotted for 1, 2, 3, 4, and 5 bar for $u_b = 1.40$ m/s and $S_g = 1.00$. Typical of premixed swirl flames and as in [17,19], stability limits are bounded by rich blowout (Fig. 2 top), flashback (Fig. 2 middle), and lean blowout (Fig. 2 bottom). Trends obtained for 1 bar (black squares) are comparable to those found for at 1 bar in [17,19]. The stability limits are slightly different because, while the injector dimensions and swirl number are the same, the combustion chamber and the bulk velocity changed a little. However, discussions provided in [17,19] to explain stability limits still apply and the reader is referred to [17,19] for details. In short, the following features stand out at 1 bar:

- The equivalence ratios at lean blowout and flashback increase when the ammonia fuel fraction increases. This is because increasing the ammonia fuel fraction at a constant equivalence ratio decreases reactivity and, in turn, decreases flame speed.
- The width of the range of stable equivalence ratios is roughly constant and narrow ($\Delta\phi \approx 0.1$) for $0 \leq x_{NH_3} < 0.60$.
- For $x_{NH_3} \sim 0.60$, a transition occurs and flashback does not occur for $x_{NH_3} > 0.60$, regardless of equivalence ratio. Rich blowout occurs instead, albeit at a much larger equivalence ratio. Note that the equivalence ratio at flashback for $x_{NH_3} = 0.60$ is close to stoichiometric, roughly yielding the maximum flame speed possible for this ammonia fuel fraction as well as any larger ammonia fuel fraction [43]. Therefore, for $x_{NH_3} > 0.60$, a comparable flame speed, required to trigger flashback, cannot be reached for any equivalence ratio and rich flames may be stabilized by progressively increasing equivalence ratio past stoichiometric.

Figure 2 also shows that trends of stability limits with ammonia fuel fraction are very similar at all pressures, up to 5 bar. However, the equivalence ratios at lean blowout and flashback decrease with pressure for all ammonia fuel fractions. In addition, the critical ammonia fuel fraction yielding transition from flashback to rich blowout increases with pressure, from $x_{\text{NH}_3} = 0.60$ at 1 bar to $x_{\text{NH}_3} = 0.75$ at 5 bar. Because the bulk velocity is the same in all conditions plotted in Fig. 2, these two observations suggest that, for a given equivalence ratio and ammonia fuel fraction, the turbulent flame speed increases with pressure. Experiments and simulations from [44] show that the laminar burning velocity of ammonia-methane-air flames decreases with pressure. Therefore, trends of stability limit with pressure observed in Fig. 2 are attributed to the increase of Reynolds number, which increases velocity fluctuations and turbulent flame speed. Provided that enough ammonia is introduced in the fuel blend, Fig. 2 shows that substituting ammonia for methane widens stability limits for all pressures between 1 and 5 bar. To illustrate, the widest range of stable equivalence ratios is found for $x_{\text{NH}_3} = 0.8$ and 5 bar and is almost $\Delta\phi = 0.7$. Both lean and rich pure ammonia-air flames can be stabilized with widths of the stable range of $\Delta\phi \sim 0.3$ at 1 bar to $\Delta\phi \sim 0.6$ at 5 bar.

Figure 2: Equivalence ratio at rich blowout (top), flashback (middle), and lean blowout (bottom) as a function of the ammonia fuel fraction for ammonia-methane-air flames for pressures ranging from 1 to 5 bar ($u_b = 1.40$ m/s and $S_g = 1.00$).

3.1.2 Ammonia-hydrogen-air flames

Figure shows the measured stability limits of ammonia-hydrogen-air swirl flames for the full range of ammonia fuel fractions. Again, these stability limits are plotted for 1, 2, 3, 4, and 5 bar for $u_b = 1.40$ m/s and $S_g = 1.00$. Trends are similar to those found for ammonia-methane blends in Fig. 2. In addition, results obtained for 1 bar (black squares) are compatible with those found at 1 bar for the same fuel blends and a slightly different combustor in [17,19]. Compared to ammonia-methane blends, the main differences are: (1) equivalence ratios at lean blowout and flashback are

much smaller for ammonia-hydrogen and (2) the critical ammonia fuel fraction yielding transition from flashback to rich blowout is larger for ammonia-hydrogen. Both observations can be explained by the much larger reactivity of hydrogen compared to methane, which carries over to ammonia-hydrogen blends. It is also interesting to note that the range of stable equivalence ratios is very narrow ($\Delta\phi \approx 0.05$) for $0 \leq x_{\text{NH}_3} < 0.50$.

Regarding the effects of pressure, the same observations can be made for ammonia-hydrogen and ammonia-methane. However, pressure effects seem less pronounced for ammonia-hydrogen than for ammonia-methane. For ammonia-hydrogen, increasing pressure promotes flashback and retards lean blowout only if $x_{\text{NH}_3} > 0.75$. Increasing pressure also retards the transition from flashback to rich blowout as the ammonia fraction is increased. Transition occurs for $x_{\text{NH}_3} = 0.80$ at 1 bar and $x_{\text{NH}_3} = 0.90$ at 5 bar. Provided that enough ammonia is introduced in the fuel blend, substituting ammonia for hydrogen widens stability. The widest range of stable equivalence ratios is found for $x_{\text{NH}_3} = 0.85$ and 1 bar and is $\Delta\phi \sim 0.9$.

Another important feature of these ammonia-hydrogen-air swirl flames is that very lean ($\phi \sim 0.3$) flames can be stabilized with this burner even when non-marginal amounts of ammonia ($x_{\text{NH}_3} = 0.40$) are blended into the fuel. This is not the case for ammonia-methane-air flames with, for example, a minimum stable equivalence ratio of $\phi \sim 0.6$ for $x_{\text{NH}_3} = 0.40$. This feature will prove useful later in this manuscript as competitively low NO emissions will be reported for the very lean ammonia-hydrogen-air swirl flames.

Figure 3: Equivalence ratio at rich blowout (top), flashback (middle), and lean blowout (bottom) as a function of the ammonia fuel fraction for ammonia-hydrogen-air flames for pressures ranging from 1 to 5 bar ($u_b = 1.40$ m/s and $S_g = 1.00$).

3.1.3 Ammonia-hydrogen-nitrogen-air flames

Arguably, a very convenient way of producing an ammonia-hydrogen fuel blend is via partial dissociation (also referred to as cracking) of ammonia. However, regardless of how much ammonia is dissociated, the resulting blend includes nitrogen in addition to hydrogen, with a 3:1 nitrogen to hydrogen volume ratio. For this reason, it is useful to examine the stability limits of ammonia-hydrogen-nitrogen-air flames featuring a 3:1 nitrogen to hydrogen volume ratio. Figure 4 shows the measured stability limits of ammonia-hydrogen-nitrogen-air swirl flames for the full range of

282 ammonia fuel fractions for 1 and 3 bar ($u_b = 1.40$ m/s and $S_g = 1.00$). All the above discussions on
 283 stability limits as a function of ammonia fraction and pressure still apply. The swirl combustor
 284 used in this study allows stabilizing ammonia-hydrogen-nitrogen-air flames for large ranges of
 285 ammonia fraction and equivalence ratio at atmospheric and elevated pressure.

286
 287 Figure 4: Equivalence ratio at rich blowout (top), flashback (middle), and lean blowout (bottom)
 288 as a function of the ammonia fuel fraction for ammonia-hydrogen-nitrogen-air flames at 1 and 3
 289 bar ($u_b = 1.40$ m/s and $S_g = 1.00$).

290 For comparison purposes, Fig. 5 shows stability limits measured at 3 bar for ammonia-
 291 hydrogen-nitrogen (red) and ammonia-hydrogen (black). Equivalence ratios at lean blowout and
 292 flashback are consistently, but somewhat marginally, smaller for ammonia-hydrogen than for

ammonia-hydrogen-nitrogen. This behavior was also observed at 1 bar in [19] and it was explained by considering trends of laminar burning velocity with nitrogen addition and equivalence ratio.

Figure 5: Equivalence ratio at rich blowout (top), flashback (middle), and lean blowout (bottom) as a function of the ammonia fuel fraction for ammonia-hydrogen-air and ammonia-hydrogen-nitrogen-air flames at 3 bar ($u_b = 1.40$ m/s and $S_g = 1.00$).

3.2 Flames images

During experiments, while the flames' stability limits were mapped over a large parameter space, images of a subset of the stable flames were taken with a DSLR camera. These images are shown here to highlight the effects of ammonia substitution, equivalence ratio, and pressure on the flames' color. Note that the color and white balance were not calibrated and that exhaustive discussions on chemiluminescence properties of these flames are not targeted at this stage.

The five rows in Fig. 6 show time-averaged broadband flame images. Each row should be analyzed individually as it is designed to isolate the effect of a given operating parameter (except for row 1 where both ammonia fraction and equivalence ratio are varied). The thermal power P_{th} is stated below each image. Note that all stable flames investigated here take a V-shape, typical of non-adiabatic swirl combustors [45,46]. However, these feature a different size, angle at the base, and lift-off distance depending on the fuel blend, equivalence ratio, and pressure. The directional sensitivity of these geometrical parameters is consistent with previous literature and expectations and is not described in detail here.

From left to right, row 1 of Fig. 6 shows the effect of increasing the ammonia fraction from 0 to 1 in the ammonia-methane fuel blend at 3 bar. Note that, due to stability limits, it was not possible to keep the equivalence ratio constant. Consistent with expectations [47], the flame's blue color (attributed mainly to CH^* chemiluminescence) is progressively replaced by a yellow color (attributed to NH_2^* and H_2O^* [31,48]) when ammonia is added to the fuel blend. Interestingly, the yellow color first emerges from the most downstream regions of the flame when small amounts of ammonia are introduced. For $x_{NH_3} = 0.80$ and above, the whole flame is yellow and the blue color typically associated with hydrocarbons flames is not visible anymore.

Row 2 of Fig. 6 shows the effect of increasing pressure from 1 to 5 bar for stoichiometric ammonia-methane-air flames with $x_{\text{NH}_3} = 0.80$. All these flames are yellow. The chemiluminescence intensity increases with pressure. This is expected because the amount of fuel being burned and the flame's thermal power increase with pressure. The flame contour is less sharply defined at elevated pressure compared to atmospheric. This is because increasing pressure at a fixed bulk velocity increases the Reynolds number and increases, in turn, the thickness of the flame brush. Row 3 of Fig. 6 also shows the effect of increasing pressure but for stoichiometric pure ammonia-air flames. Similar observations can be made.

Row 4 of Fig. 6 shows the effect of increasing pressure from 1 to 5 bar for very lean ($\phi \sim 0.3$) ammonia-hydrogen-air flames with $x_{\text{NH}_3} = 0.40$. Even though the ammonia fraction in the fuel blend is substantial, these flames are not yellow but appear white instead. This white color is not typically associated with ammonia flames but it has been observed before in [19,24]. If both the equivalence ratio and ammonia fraction are sufficiently increased to $\phi \sim 0.5$ and $x_{\text{NH}_3} = 0.70$, respectively (see row 5 of Fig. 6), the yellow color is clearly visible.

Figure 6 highlights the richness of the chemiluminescence signature of flames with fuel blends including ammonia. Currently, how the chemiluminescence signature changes with ammonia fraction, equivalence ratio, pressure, etc. is not well understood and this warrants further studies.

Figure 6: Time-averaged broadband images of: **Row 1:** ammonia-methane-air flames at 3 bar for $x_{\text{NH}_3} = 0$ to $x_{\text{NH}_3} = 1$ and different equivalence ratios; **Row 2:** ammonia-methane-air flames at $\phi = 1$ and $x_{\text{NH}_3} = 0.8$ for 1 to 5 bar; **Row 3:** ammonia-air flames at $\phi = 1$ and $x_{\text{NH}_3} = 1.0$ for 1 to 5 bar; **Row 4:** ammonia-hydrogen-air flames at $\phi = 0.30$ and $x_{\text{NH}_3} = 0.40$ for 1 to 5 bar; **Row 5:** ammonia-hydrogen-air flames at $\phi = 0.50$ and $x_{\text{NH}_3} = 0.70$ for 1 to 5 bar.

3.3 NO emissions

Experiments described above demonstrate that it is possible to stabilize pure ammonia-air, ammonia-methane-air, and ammonia-hydrogen-air swirl flames with a combustor operating at pressures representative of current commercial micro gas turbines and originally designed for methane-air flames. However, before such fuel blends can be labeled as viable candidates for commercial micro gas turbines, it is necessary to evaluate their NO exhaust emissions levels and the efforts required to meet the regulations.

3.3.1 Rich equivalence ratios

Previous literature [17], has shown that rich premixed ammonia-methane-air swirl flames are capable of achieving competitively low NO emissions. However, this is not true for stoichiometric and lean equivalence ratios. Data also show that very lean ammonia-methane-air flames would possibly emit little amounts of NO but these flames cannot be stabilized due to low chemical reactivity and flame speed [49]. For instance, data of Fig. 2 show that, regardless of pressure, ammonia-methane-air flames with equivalence ratios lower than $\phi \sim 0.6$ cannot be stabilized because of lean blowout. Unfortunately, $\phi \sim 0.6$ is not low enough to abate NO emissions below acceptable levels [26,50].

Consequently, efforts have been made to develop two-stage combustors in which ammonia-methane-air [26], and ammonia-air mixtures [10,12,14,26] are first burned locally rich while maintaining globally lean operation. It is verified in what follows that the present combustor can be used as the first stage because it provides low NO emissions in addition to stable flames. Figure 7 shows the measured NO mole fraction (in ppm and corrected for 6% O₂) in the exhaust gases of ammonia-methane-air flames as a function of equivalence ratio for pressures ranging from

1 to 4 bar, $x_{\text{NH}_3} = 0.80$, and $u_b = 1.40$ m/s. The NO mole fractions reported in this study at 1 bar are globally larger than the ones reported in [17,19], for the same equivalence ratio and ammonia fraction. The combustion chambers and bulk velocities are different, leading to different heat loss and residence time. Heat loss and residence time are two important parameters, which were shown to influence NO production significantly [12,26]. Therefore, differences between present data and that reported in [17,19] are difficult to interpret.

Figure 7: Measured NO mole fraction in the exhaust of rich ammonia-methane-air flames as a function of equivalence ratio ($1.10 \leq \phi \leq 1.30$) for pressures ranging from 1 to 4 bar for $x_{\text{NH}_3} = 0.80$ and $u_b = 1.40$ m/s.

Consistent with previous literature [12,17,26], the NO mole fraction decreases monotonically when the equivalence ratio increases above $\phi = 1.10$. In [25,28,34], this behavior was explained by the increasing concentration of NH_2 radicals that promotes the consumption of OH via reaction $\text{NH}_2 + \text{OH} \leftrightarrow \text{H}_2\text{O} + \text{NH}$ and that of NO via reaction $\text{NH}_2 + \text{NO} \leftrightarrow \text{H}_2\text{O} + \text{N}_2$. Also in agreement with prior literature [2,14,26,31,44,51], increasing pressure decreases the NO mole fraction, regardless of equivalence ratio. According to [31], this is because the OH radical pool gets smaller as pressure increases reducing, in turn, NO production.

Consequently, the equivalence ratio above which NO emissions may be considered acceptable depends on pressure. For argument's sake, let us consider NO mole fractions below ~100 ppm as acceptable. Then, above 3.5 bar, an equivalence ratio of $\phi = 1.25$ or higher is desired. At 2.5 bar, the equivalence ratio must be larger than $\phi = 1.30$. This critical equivalence ratio is even larger at 1 bar. Comparable results were obtained by Somarathne *et al.* [51] who reported a simulated 144 ppm NO mole fraction in the exhaust of ammonia-air flames for $\phi \geq 1.25$ and 5 bar. Also, Valera-medina *et al.* [15] reported NO mole fractions below 100 ppm for equivalence ratios in excess of $\phi \approx 1.3$ in ammonia-methane flames at 2 bar.

For the data plotted in Fig. 7, the pressure is increased at constant bulk velocity. This implies that the flame's thermal power increases linearly with pressure and that, in turn, the relative influence of heat loss decreases with pressure [52]. In [12,26], authors report that NO production is inhibited by heat loss, suggesting that increasing pressure could promote higher NO emissions. This is not the trend displayed in Fig. 7 indicating that heat loss has a smaller influence on NO emissions than pressure for the combustor examined here.

Experiments of [12,26] also show that increasing the residence time in the primary zone, where the ammonia-air flame burns locally rich, allows reducing NO emissions. This suggests that flow time scales and how these compare to the relevant chemical time scale play a role in controlling NO emissions. To test this with the present combustor, NO mole fractions in the exhaust of ammonia-methane-air flames were measured for different bulk velocities ranging from $u_b = 1.40$ m/s to 1.80 m/s, $x_{\text{NH}_3} = 0.80$ and 2 bar. Results are plotted in Fig. 8 as a function of equivalence ratio. Trends of NO mole fraction with equivalence ratio are not modified by the bulk velocity. However, regardless of equivalence ratio, increasing the bulk velocity reduce the NO mole fraction. For example, The NO mole fraction decreases from ~4000 ppm to ~3300 ppm when

the bulk velocity is increased from $u_b = 1.40$ m/s to 1.80 m/s at a constant equivalence ratio of $\phi = 1.10$. In addition, the equivalence ratio above which the NO mole fraction remains below ~ 100 ppm decreases from $\phi = 1.30$ for $u_b = 1.40$ m/s to $\phi = 1.25$ for $u_b = 1.80$ m/s. Increasing the bulk velocity decreases flow time scales, such as the total residence time in the combustion chamber or time scales associated with turbulent eddies. While it is not clear at this stage which time scales play the largest role in controlling exhaust NO emissions in this combustor, data show that decreasing flow time scales reduce NO emissions. Note that increasing bulk velocity decreases the residence time yielding possibly a larger amount of unburned ammonia. This is a possible reason for the lower NO mole fractions in Fig. 8. Furthermore, increasing bulk velocity increases the flame's thermal power and, in turn, the temperature in the combustion chamber. This factor may also account for some of the differences in NO mole fractions displayed in Fig. 8.

Figure 8: Measured NO mole fraction in the exhaust of ammonia-methane-air flames as a function of equivalence ratio ($1.10 \leq \phi \leq 1.30$) for bulk velocities ranging from $u_b = 1.40$ m/s to 1.80 m/s for $x_{\text{NH}_3} = 0.80$ and 2 bar.

Data presented in Figs. 7 and 8 show that the critical rich equivalence ratio above which NO performance is competitive depends on pressure and residence time. Therefore, this equivalence

ratio is configuration dependent, which likely explains why discrepancies are found in the literature [15,17,26,49].

3.3.2 Lean equivalence ratio

To avoid efficiency penalties associated with unburned ammonia, strategies involving local rich burning of ammonia-methane-air or ammonia-hydrogen-air must also feature a subsequent lean combustion stage. This is to ensure globally-lean operation. Such a two-stage strategy has been shown to perform well [26]. However, it is worth verifying if simpler and more compact single-stage combustors relying on locally-lean burning could also perform well.

Data of [17,19] show that good NO performances cannot be obtained for lean premixed ammonia-methane-air swirl flames. This is because very lean flames, which would potentially emit small amounts of NO, cannot be stabilized due to lean blow-out. Therefore, the successful development of a competitive single stage combustor fueled with ammonia-methane mixtures is unlikely. However, data of [19,30] and [24] show that a NO mole fraction of a few hundred ppm or below can be achieved at atmospheric pressure with lean premixed ammonia-hydrogen-air swirl flames, provided that enough hydrogen is introduced in the fuel blend so that equivalence ratio can be low enough. For example, in [19,30] for $x_{\text{NH}_3} = 0.90$, flames could be stabilized with equivalence ratios down to $\phi = 0.60$, with a NO mole fraction in the exhaust measured to only ~110 ppm. For $x_{\text{NH}_3} = 0.70$, flames with $\phi = 0.40$ were stable, with a NO mole fraction of ~100 ppm. Such very lean flames could be stabilized because of the much larger reactivity of hydrogen compared to methane. Low NO mole fractions can be explained by the concentration of OH radicals that otherwise positively contribute to the formation of NO via fuel NO pathways [28].

In the present study, this behavior is verified at different pressures. Figure 9 shows the measured NO mole fraction in the exhaust of ammonia-hydrogen-air flames as a function of equivalence ratio ($0.70 \leq \phi \leq 0.90$) for 1, 2, 3, and 4 bar and $x_{\text{NH}_3} = 0.90$. The smallest equivalence considered is $\phi = 0.70$ because flames with $\phi < 0.70$ could not be stabilized for all pressures. Trends of NO mole fraction with lean equivalence ratio are not modified with pressure. Similar to rich cases described above, increasing pressure reduces the NO mole fraction. For $\phi = 0.70$, a NO mole fraction below 200 ppm is found for all pressures, confirming that lean ammonia-hydrogen-air flames are potential candidates for gas turbine applications.

Figure 9: Measured NO mole fraction in the exhaust of lean ammonia-hydrogen-air flames as a function of equivalence ratio ($0.70 \leq \phi \leq 0.90$) for pressures ranging from 1 to 4 bar for $x_{\text{NH}_3} = 0.90$ and $u_b = 1.40$ m/s.

3.3.3 ‘Very’ lean equivalence ratio

If the hydrogen fraction in the fuel is increased above 10%, flames with equivalence ratios even smaller than $\phi = 0.60$ can be stabilized (see Fig. 3). These conditions also lead to competitive

NO emissions as shown in Fig. 10 that plots the measured NO mole fraction in the exhaust of ammonia-hydrogen-air flames as a function of pressure (2 to 4 bar) for different very lean equivalence ratios ($\phi = 0.50$ or 0.55) and different ammonia fractions. All conditions considered exhibit a NO mole fraction below 200 ppm. For these conditions, the effect of pressure is marginal. The smallest NO mole fraction measured is ~ 100 ppm and is found for $\phi = 0.55$ and $x_{\text{NH}_3} = 0.85$, across all pressures. The largest NO mole fraction measured is ~ 160 ppm and is found for $\phi = 0.50$ and $x_{\text{NH}_3} = 0.75$. Figure 10 also shows the measured NO mole fraction for $\phi = 0.50$ and $x_{\text{NH}_3} = 0.75$ but with nitrogen introduced in the fuel blend with $3\text{H}_2:1\text{N}_2$ (back squares). Compared to the case without nitrogen, the NO mole fraction is smaller, around 120 ppm. This behavior is also attributed to the lower concentration of OH radicals due to N_2 dilution.

Figure 10: Measured NO mole fraction in the exhaust of ammonia-hydrogen-air flames as a function of pressure (2 to 4 bar) for different very lean equivalence ratios ($\phi = 0.50$ or 0.55) and ammonia fractions and $u_b = 1.40$ m/s.

Measurements of [12,26] and simulations of [14] clearly show that N_2O emissions may become large if the ammonia-methane-air or ammonia-hydrogen-air flames are operated with a too low equivalence ratio. This is problematic because N_2O is a very potent greenhouse gas, around

250 times more effective than CO₂. To illustrate, an ammonia-hydrogen-air flame with around 240 ppm of N₂O in the exhaust would have roughly the same global warming impact than a methane-air flame with an equivalence ratio of $\phi = 0.60$. Therefore, it is critical to verify that the benefit of very lean burning in terms of NO performance is not offset by poor N₂O performance. Unfortunately, the N₂O mole fraction could not be measured at the time of the experiments and one has to rely on the results of flame simulations. In this study, 1-D adiabatic and unstrained premixed laminar flames were computed with ANSYS Chemkin [53] and the detailed chemistry mechanism due to [54], which was optimized for ammonia.

In a 1-D adiabatic and unstrained premixed laminar flame, the N₂O mole fraction increases sharply and peaks near the location of maximum heat release. However, the N₂O progressively decreases in the post-flame region through reaction with H radicals and thermal decomposition [12,26]. For example, for the very lean operating conditions plotted in Fig. 10, the N₂O mole fractions computed in the post-flame region, 2 cm away from the flame front, do not exceed 10 ppm. However, real combustion chambers are not adiabatic and the residence time of burned products in regions featuring high temperature may be too small for thermal decomposition of N₂O to complete. Such effects of heat loss and residence time on N₂O formation in ammonia-air flames were nicely highlighted in [12]. Therefore, it is worth examining the worst-case-scenario, occurring if burned products are quenching immediately downstream of the reaction zone. In such case, the N₂O mole fraction in the exhaust would be close to the peak N₂O mole fraction found across a 1-D adiabatic laminar flame.

Figure 11 plots the computed peak N₂O mole fraction in 1-D adiabatic and unstrained premixed laminar flames for the same very lean conditions found in Fig. 10. The peak N₂O mole fraction is always above 800 ppm. These values are very large compared to 240 ppm, the value that would

yield roughly the same global warming impact as a methane-air flame with an equivalence ratio of $\phi = 0.60$. Of course, an N_2O mole fraction in the exhaust equal to that of the peak is a very unlikely scenario because some consumption of N_2O will occur in the post-flame region. However, consistent with measurements of [12], these simulations show that careful treatment of heat loss and residence time in the combustion chamber is necessary if very lean ammonia-hydrogen-air flames are to be considered for gas turbines.

Figure 11: Computed peak N_2O mole fraction in 1-D adiabatic unstrained premixed laminar ammonia-hydrogen-air flames as a function of pressure (2 to 4 bar) for different very lean equivalence ratios ($\phi = 0.50$ or 0.55).

4. Conclusions

The stability limits and exhaust NO emissions of premixed ammonia-air swirl flames enriched with either methane or hydrogen were measured at atmospheric and elevated pressures, up to 5 bar. One key aspect of this study is that the full range of ammonia fractions in the fuel, from pure ammonia to pure methane/hydrogen, was considered. The main findings are:

- Across the full range of ammonia fractions, increasing pressure promotes flashback and retards lean blowout. Increasing pressure also retards the transition from flashback to rich blowout as the ammonia fraction is increased.
- Increasing pressure, up to 5 bar, widens the range of stable equivalence ratios of swirl ammonia-air flames without methane or hydrogen addition.
- Provided that enough hydrogen is blended with ammonia ($x_{\text{NH}_3} < 0.9$), flames with very lean equivalence ratios ($\phi < 0.7$) may be stabilized.
- Equivalence ratios at lean blowout and flashback are consistently, but somewhat marginally, smaller for ammonia-hydrogen than for ammonia-hydrogen-nitrogen flames.
- Very lean ammonia-hydrogen-air flames yield competitively low NO emissions (< 200 ppm). This was verified for different pressures between 1 and 4 bar.
- Due to the lower reactivity of methane compared to that of hydrogen, very lean ($\phi < 0.7$) swirl ammonia-methane-air flames featuring a significant fraction of methane cannot be stabilized. As a consequence, good NO performance is limited to rich equivalence ratios and a two-stage combustion process is required to ensure globally-lean operation. The equivalence ratio above which good NO performance is found depends on pressure and bulk velocity.

545 **Acknowledgments**

546 Thanks to Saudi Aramco research and development center for funding this project under
547 research agreement number RGC/3/3837-01-01 and to the King Abdullah University of Science
548 and Technology (KAUST) under grant number BAS/1/1370-01-01.

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