Stability Limits and Exhaust Emissions from Ammonia Flames in a Swirl Combustor at Elevated Pressures

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ABSTRACT

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Intimate knowledge of ammonia fueling gas turbines is of crucial importance for power generation sectors, owing to its carbon-free nature and high hydrogen capacity. Anticipated challenges include, among others, the difficulty to stabilize ammonia flames and on top of that the propensity of ammonia flames to produce large quantities of nitrogen monoxide emissions. In gas turbine devices, combustion in practice occurs in a turbulent swirl flow and at elevated pressure conditions. The stability of ammonia flames and the production of NO emissions are sensitive to such parameters. This body of work focuses on the development of a swirl combustor for investigating behaviors of flame stability limits and of NO emissions from the combustion of ammonia fuel with mixtures of hydrogen or methane at atmospheric and elevated pressure conditions. Ammonia-hydrogen-nitrogen fuel blends are also examined to mimic ammonia decomposition mixtures, always maintaining the 3:1 hydrogen:nitrogen volume ratio.

First, the stability limits of technically-premixed ammonia-air flames at atmospheric pressure conditions are measured in a laboratory-scale swirl combustor, ~30kW thermal power, for a wide range of ammonia fractions in methane or hydrogen fuel blends. Data show that increasing the ammonia addition increases the equivalence ratio at the lean
blowout limit but also reduces the flames’ propensity to flashback. If the volume fraction of ammonia in the fuel blend exceeds a critical value, experiments also show that increasing the equivalence ratio at a fixed bulk velocity does not yield flashback and rich blow-out occurs instead. This significantly widens the range of equivalence ratios yielding stable ammonia flames. The critical ammonia volume fraction is a function of the Reynolds number.

Next, the flame stability limits of ammonia-air flames at pressures up to 5 bar are shown for a wide range of the aforementioned fuel blends. The swirl combustor is slightly modified to fit in the high-pressure combustion duct at KAUST. Regardless of the fuel blend, increasing the pressure increases the propensity to flashback if the bulk velocity remains constant. Pure ammonia-air flames are stable under elevated pressures, and the stable range of equivalence ratio becomes wider as the pressure increases.

Lastly, exhaust NO mole fractions at atmospheric and elevated pressures up to 4 bar are measured from a wide range of ammonia-air flames with mixtures of hydrogen or methane. The NO emissions are measured for large ranges of equivalence ratios, ammonia fractions, and pressures. Regardless of the ammonia fraction, data show that competitively low NO emissions occur for slightly rich equivalence ratios, which is consistent with earlier studies. Good NO performance is also found for very lean ammonia-hydrogen-air mixtures, regardless of the pressure. NO mole fractions for lean ammonia mixtures can be reduced as pressure increases, demonstrating the strong potential of fueling gas turbines with ammonia-hydrogen mixtures.
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<td>DSLR</td>
<td>digital single-lens reflex</td>
</tr>
<tr>
<td>FL</td>
<td>flashback limit</td>
</tr>
<tr>
<td>FLR</td>
<td>flammability limit range</td>
</tr>
<tr>
<td>FTA</td>
<td>fuel to air</td>
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<tr>
<td>GCF</td>
<td>gas conversion factor</td>
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<tr>
<td>HPCD</td>
<td>high-pressure combustion duct</td>
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<tr>
<td>LBL</td>
<td>lean blowout limit</td>
</tr>
<tr>
<td>LCA</td>
<td>life cycle analysis</td>
</tr>
<tr>
<td>LFL</td>
<td>lower flammability limit</td>
</tr>
<tr>
<td>MFC</td>
<td>mass flow controller</td>
</tr>
<tr>
<td>mGT</td>
<td>micro gas turbine</td>
</tr>
<tr>
<td>NCV</td>
<td>net caloric value</td>
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<tr>
<td>NO</td>
<td>nitrogen monoxide</td>
</tr>
<tr>
<td>PPM</td>
<td>parts per million</td>
</tr>
<tr>
<td>RANS</td>
<td>Reynolds averaged navier-stokes</td>
</tr>
<tr>
<td>RBL</td>
<td>rich blowout limit</td>
</tr>
<tr>
<td>TGM</td>
<td>toxic gas monitoring</td>
</tr>
<tr>
<td>UFL</td>
<td>upper flammability limit</td>
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<tr>
<td>UV</td>
<td>ultraviolet</td>
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LIST OF SYMBOLS

\( x_{\text{NH}_3} \) \hspace{1cm} \text{Ammonia volume fraction in the fuel blend}

\( m_A \) \hspace{1cm} \text{Axial momentum}

\( u_b \) \hspace{1cm} \text{Bulk velocity}

\( \rho \) \hspace{1cm} \text{Density}

\( \mu \) \hspace{1cm} \text{Dynamic viscosity}

\( \varphi \) \hspace{1cm} \text{Equivalence ratio}

\( t \) \hspace{1cm} \text{Exposure time}

\( S_g \) \hspace{1cm} \text{Geometric swirl number}

\( d_A \) \hspace{1cm} \text{Injection throat inner diameter}

\( S_l \) \hspace{1cm} \text{Laminar burning velocity}

\( S_T \) \hspace{1cm} \text{Turbulent burning velocity}

\( M_f \) \hspace{1cm} \text{Mass flow rate of fuel}

\( P \) \hspace{1cm} \text{Pressure}

\( \text{Re} \) \hspace{1cm} \text{Reynolds number}

\( r_0 \) \hspace{1cm} \text{Tangential inlet radius}

\( m_{\theta} \) \hspace{1cm} \text{Tangential momentum}

\( P_{\text{th}} \) \hspace{1cm} \text{Thermal power}

\( A_t \) \hspace{1cm} \text{Total area of tangential inlets}

\( V_{\text{NH}_3} \) \hspace{1cm} \text{Volumetric flow rate of ammonia}

\( V_f \) \hspace{1cm} \text{Volumetric flow rate of fuel}

\( V_{\text{H}_2} \) \hspace{1cm} \text{Volumetric flow rate of hydrogen}

\( V_{\text{CH}_4} \) \hspace{1cm} \text{Volumetric flow rate of methane}
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Chapter 1

Introduction

1.1 Problem considered

Global warming is one of the greatest challenges that humanity is facing. Mitigation of global warming must be achieved by a combination of strategies including the improvement of energy efficiency and the reduction of the emissions of greenhouse gases, in particular, carbon dioxide. There is a strong potential of greenhouse gases emissions reductions via the use of eco-friendly technologies, among others, those relying on renewable energy sources.

However, the power produced from the renewable resources is intermittent and issues related to the storage of electricity currently limit renewables potential [1]. Therefore, converting the renewable energy into hydrogen (H₂) should be considered, and which can play an important role in supporting the growth of renewables [2].

In 2017, renewable energy consumption is approximately 18% from the total share of energy consumption [3]. This consumption is growing through renewable energy applications, and therefore contributing to a larger portion of the total energy demand. However, fossil foils remain on the top in providing the utmost energy needs, yielding more CO₂ emissions.

In 2015, Paris agreement on climate change addressed the transition to low-carbon economy aimed at reducing greenhouse gas emission by at least 45% by 2030 compared to 2010 and net zero emissions by 2050 [4]. Meeting the agreement’s target is challenging,
but can be achieved by a combination of strategies including the reduction of the emission of greenhouse gases owing to combustion activity. Reducing greenhouse gas emission can be reached by the use of renewable energy sources, such as solar and wind. Renewable energy is promising to decarbonize parts of the typical energy systems and to meet the net zero emission target. This can be met from utilizing the renewable energy to produce hydrogen from electrolysis and from natural gas with carbon capture technologies.

However, in comparison to typical hydrocarbons, hydrogen has a poor energy density and must be compressed or liquified to remain as a competitive energy storage. This raises challenges related to cost and safety [5]. To mitigate this disadvantage, hydrogen carriers should be considered. Amongst the available options, ammonia in a liquid form is a promising carbon-free hydrogen carrier promoting cost-effective storage and distribution of renewable energy in large quantities.

Therefore, it is of crucial importance to facilitate the growth of renewable energy applications beside the development of carbon capture technologies. Here, we are interested in the pre-combustion decarbonization which covers production of carbon-free fuels such as ammonia from renewable energy sources for fueling gas turbines.

1.2 Potential of carbon-free fuels

Hydrogen can be stored chemically in a liquid hydrogen carrier such as ammonia, NH₃. Due to the use of ammonia in most fertilizers, infrastructure for its production and distribution is widely available [6–8]. In addition, the volumetric energy density of ammonia is large, roughly half of that of ethanol. Ammonia can be synthesized from hydrogen and air, and can be easily liquified at 8 bar under room temperature conditions.
In addition, ammonia is one of the most productive substances in the world [7], and has been consumed in large quantities because of its high production of about 170 million tons per year, approximately 2% of the global energy production in 2018 [8]. This makes ammonia a good candidate as a chemical storage of renewable energies. Furthermore, ammonia is expected to play a key role as an alternative fuel for power generation. However, the body of knowledge related to the application of ammonia to an actual combustor as a fuel is limited, with relatively a few available publications.

1.3 Literature survey

1.3.1 Ammonia combustion

Ammonia utilization for carbon-free combustion and for the reduction of NO emissions has recently received a great attention despite its combustion and safety concerns. In fact, ammonia enrichment of hydrocarbon fuels can enhance the combustion temperature and emissions. This idea is not new.

Early research studies in the field of ammonia combustion were published during the 1960s, demonstrating that ammonia has a higher ignition energy than conventional hydrocarbon fuels such as methane [10–13]. Verkamp et al. [11] investigated the flammability limits of pure ammonia in a flat flame burner, concluding that the equivalence ratio range (Δφ) yielding stable ammonia-air flames is quite narrow with Δφ ≈ 0.73 while that of methane-air flames is Δφ ≈ 1.15. Pratt [12] experimentally studied ammonia combustion in a gas turbine, concluding that burning ammonia is difficult due to the slow chemical reaction between the NH₃ substance and air. Furthermore, the complete combustion of ammonia requires a longer residence time, and therefore a lower amount of
air should be supplied compared to hydrocarbons [10]. To mitigate the low reactivity of ammonia, it was reported that 28% dissociation of ammonia can solve this issue [11].

SPG Advanced Propulsion Energy [14,15] invested in producing commercial systems for ammonia combustion. They summarized the main challenges associated with the development of ammonia combustion technologies, including: (1) low chemical reactivity, (2) low combustion temperature, (3) flame instability, (4) large quantity of NO production.

Recently, Hayakawa et al. [16] investigated the laminar burning velocity ($S_l$) of pure ammonia flames. The maximum laminar burning velocity of ammonia is $S_l = 7.00$ cm/s, about one fifth the $S_l$ of methane $S_l = 35$ cm/s. Furthermore, Han et al. [17], studied the laminar burning velocities of NH$_3$ in air blended with H$_2$, CO and CH$_4$, concluding that the low burning velocity of pure ammonia can be mitigated by the fuel mixtures considered, and H$_2$ is the most effective amongst the available additives.

Beside the ammonia challenges of low reactivity, NO formation is relatively high in ammonia combustion with air. The chemical reaction of ammonia can produce all three types of NO; thermal-NO, prompt-NO, and fuel-NO. However, mainly fuel-NO is formed because of the fuel-bond nitrogen within the NH$_3$ compound, which is completely different from the NO formation in hydrogen-air and in hydrocarbon-air combustion [18]. Therefore, even today, the use of ammonia as fuel in the field of combustion has not been widely considered. However, by the unique features previously mentioned, NH$_3$ has a high potential as a carbon-free fuel for practical combustors.

More recent work on fundamental combustion characteristics of pure ammonia have been carried out [9,19–23]. Hayakawa et al. [9] experimentally investigated flame stability and
emission characteristics from swirl stabilized ammonia-air premixed flames. They show, in a swirl combustor at various equivalence ratio and inlet flow velocity, stabilized ammonia-air premixed flame without any additives, even though the laminar burning velocity of ammonia is slow. They also found that under rich conditions the NO concentration decreased and ammonia concentration increased, while operating at an equivalence ratio around $\phi \approx 1.15 - 1.20$ the NO and ammonia emission are in the same order. Okafor et al. [22] succeeded to archive low NO and high combustion efficiency using pure ammonia in a micro gas turbine combustor. They demonstrated that, while operation close to stoichiometric benefits combustion efficiency, lower NO emissions can be achieved for slightly rich equivalence ratio $\phi \approx 1.10$. However, it is difficult to directly apply pure ammonia in the current gas turbine combustors because they are designed for natural gas. Therefore, the partial replacement of natural gas by ammonia in a gas turbine combustor should be considered.

Several studies have been performed on the stability of ammonia-methane-air premixed flames [24–26]. However, these studies targeted a specific concentration of ammonia in the methane-air mixture, there is no study spanning the full range of methane-air to ammonia-air premixed flame, which is important to design premixed type gas turbine combustors. Valera-Medina et al. [25] have been working on ammonia-methane blends for gas turbines combustion, and which show that mitigation of the low reactivity and NO production of pure ammonia can be achieved with the ammonia-methane-air blends. They identified regions where low emissions and high power are produced by a reaction balance between methane and ammonia at slightly rich conditions $\phi \approx 1.10$ hence similar equivalence ratio to what was achieved with pure ammonia [16,23]. Ito et al. [26] suggested
two-stage combustion systems to achieve low emissions and high combustion efficiency
where that is difficult to achieve in a single stage combustor.

Beside methane-ammonia mixtures, hydrogen additions on ammonia-air is a promising
 technique to enhance the reaction since hydrogen has a much faster laminar burning
 velocity than ammonia [27–30]. Ichikawa et al. [27] showed that the laminar burning
 velocity becomes the same order as that of conventional hydrocarbon flame when the
 hydrogen fraction in the ammonia-hydrogen mixture is 0.40 at stoichiometry. A group in
 Cardiff University, Wales [28] have also been working on ammonia-hydrogen mixtures for
gas turbine combustion. They performed experiments employing 0.50 volume fraction of
hydrogen in ammonia-hydrogen blend under lean conditions. They showed that the NO
emissions were extremely high while flame stability was compromised to a very narrow
 equivalence ratio range. Further work by the same group [29] performed experiments of
0.70 volume fraction of hydrogen in ammonia-hydrogen mixture under rich conditions.
The results demonstrate that this blend has a great potential as a fuel substitute with
reasonable combustion stability and significant reduction of emissions.

Being able to stabilize swirl flames fueled by ammonia is not practically relevant if
emissions, including NO, are too large. The propensity of ammonia-air flames to yield
large NO emissions is then another challenge associated with the use of ammonia as a fuel
[23]. In the recent years, the NO chemistry in ammonia-air, ammonia-methane-air, and
ammonia-hydrogen-air flames has received as much, if not more, attention than flame
stabilization [31–34]. When ammonia is present, NO can be produced through the three
classical chemical pathways; thermal-NO, prompt-NO, and fuel-NO [18]. Due to the
presence of nitrogen in ammonia, the fuel-NO pathway can play a large role, which is not
the case for methane and hydrogen, potentially yielding exhaust NO emissions far exceeding current regulations. Consistent across different fuel blends and burner configurations, experiments [20,23,31,32] and simulations [33,34] demonstrated that burning ammonia blends at lean equivalence ratios typical of gas turbines yields very poor NO performances [20,23,31–34]. However, resorting to slightly rich equivalence ratios allows recovering acceptable NO performances in par with that of lean premixed methane-air flames [31]. If associated with a secondary combustion stage, rich burning of ammonia blends then becomes an acceptable strategy [35].

A few studies have also reported that progressively decreasing equivalence ratio below $\phi \approx 0.8$-0.9 allows improving NO performances [9,28,31,36–38]. However, due to stability limits, NO emissions much below 500 ppm could not be evidenced for ammonia-air and ammonia-methane-air premixed flames for any lean equivalence ratio [31,36,37]. Because ammonia-hydrogen blends are more reactive, much leaner flames could be stabilized [28] and NO concentrations in the order of 100 ppm were reported for 50ammonia-50hydrogen and $\phi \approx 0.4$. However, only one fuel blend composition has been examined in [28]. Burning very lean ammonia-hydrogen mixtures seem to be another promising way of abating NO emissions, with the added benefit of not requiring a secondary combustion stage.

**1.3.2 Combustion in gas turbine applications**

Power generation sectors traditionally utilized gas turbines with combustors generating non-premixed flames. However, this type of combustors is not preferable anymore due its high production of NO emissions. Therefore, researchers have been developing combustors that host lean premixed flames to meet the NO emissions restrictions [39–42]. Since
1980’s, lean premixed combustors have been used in gas turbines for power generation. However, they still face two main challenges; dynamic instability and static instability. To mitigate combustion instabilities, hydrogen enrichment and swirl flow can be imparted. The combustion instabilities can be attributed to either the design of combustor confinement or to the heat released by combustion [43,44]. Instabilities by lean premixed flames are attributed mainly to operating close to the blow-off limits [45,46] and to small volume of heat release by combustion.

Maintaining a stable premixed flame is not a straightforward task due to challenges associated with flame instabilities. The main factors affecting flame instability include combustor design, fuel composition, oxidizer composition, turbulence level, fuel and air injection method, and interaction of neighboring flames [47]. Dynamic stability challenges are related to thermo-acoustic phenomenon, and this may lead to a hardware damage. Static stability challenges are related to flame flashback and blowout, and this may limit flame operability window.

Flames blowout if they propagate in the direction of the flow until physically disappear. This happens when the flow velocity of the fuel and air mixture exceeds the flame burning velocity. This means that the flame blowout occurs if the flow residence time is greater than that required for chemical reaction. Different theories have been developed to better understand the flame blowout correlations [48–51]. The blowout is defined as the ratio of residence to chemical timescale, this is known as the Damkohler number [52,53]. Lieuwen et al. [54] studied the effects of fuel composition on combustor static instability, i.e. blowout and flashback. They found that blowout occurs at \( \phi = 0.17 \) for pure hydrogen flame, whereas blowout occurs at \( \phi = 0.3 – 0.5 \) for blends of CO and CH4. A summary of
relevant studies on the blowout static instability can be found in [3]. Flashback is the opposite phenomenon of blowout, and it occurs if the flame propagates upstream of the jet flow direction. This is because the flow velocity is smaller than the flame burning velocity, and this may seriously damage the combustor hardware. The main reasons behind a flame flashback include low flow velocity of the fuel mixture [55], turbulent flame propagation due to fast chemical reaction of the mixture [56,57], dynamic instability [58,59], and combustion induced vortex breakdown which occurs at excessive swirl numbers [60,61].

Swirl flow technique is widely used to deter flame blowout and flashback instabilities [62–66]. The swirl flow can be generated from tangential injection of the combustible mixture [67], axial vane swirlers [68], radial vane swirlers [69], and mechanical spinners [70,71]. The main idea of using the swirl flow is contained in increasing the kinetic energy through flow expansion. This creates a central recirculation zone (CRZ), see Figure 0.1. A corner of outer recirculation zone is also created between the expanding swirling flow and the combustor corner. The swirl strength is defined differently and known as swirl number [72]. However, a common definition is the ratio of the fuel-air mixture angular momentum to the axial thrust [3]. Therefore, the simplest technique to create swirl is to split inlet flow into axial and tangential injections. This way has an advantage of varying the swirl number by simply changing the ratio between the flow split.
Jerzak and Kuznia [73] investigated the effect of swirl number on the blowout and flashback limits of premixed flames. They used three swirl numbers 0.69, 1.16, and 1.35, and the study concluded that a wider operability window is observed at a higher swirl number. Syred et al. [74] also studied the effect of swirl numbers ranging from 0.8 to 1.46 of hydrogen-methane mixture. They reported that increasing the swirl number enhances the flashback limit, but worsens the blowout limit. A similar study conducted on syngas for two swirl numbers of 0.71 and 0.97, and this agrees with [74]. Furthermore, swirl flow can also improve NO and CO emissions. Kim et al. [75] investigated the effect of vortex generator on premixed flame behavior in a gas-turbine combustor. The study revealed that using vortex generator can reduce the emissions of NO by 21% and of CO by 13%.

1.3.3 Ammonia in gas turbine combustors

Bull [76] (1964) worked on the development of an ammonia-burning gas turbine engine showing that ammonia is a satisfactory substitute for hydrocarbon fuels. He concluded that ammonia combustion is possible but with a lower flammability range and a larger burner size compared to hydrocarbons due to its low heating value. He also added that the fuel consumption of ammonia, relative to hydrocarbons and at a similar power output, is
approximately 2.25 times greater by weight and 2.82 times greater by volume. Therefore, ammonia burners should be designed differently from those for hydrocarbons.

Verkamp et al. [11] (1967) studied ignition energy, quenching distance, flame stability limits and gas turbine burner performance of ammonia-air and of dissociated ammonia mixtures. They concluded that because ammonia has a slow chemical kinetics, it would burn at only one-half air-flow velocity possible with hydrocarbons yielding a narrower stability range. They also reported that the minimum ignition energy, quenching distance, and flame-stability properties of 28% dissociated ammonia were approximately equal to these same properties of methane. Therefore, 28% dissociated ammonia could be used as a substitute fuel in gas-turbine-combustion systems optimally sized for hydrocarbon fuels.

Pratt [13] (1967) investigated scaling and combustion of ammonia in a gas turbine combustors. He reported that the final size of the burner is equally limited by chemical reaction kinetics and turbulent diffusion. The low chemical reaction between ammonia and air requires lower air flow velocity to allow sufficient residence time. Therefore, a unique technique may be required to achieve proper mixing between cold reactants and hot products. Reducing the Reynolds number to achieve a longer residence time is not ideal solution because it leads to less efficient mixing and combustion efficiency. However, solutions could be associated with reducing fuel nozzle to create more vigorous jet, and to use two parallel combustors instead of a large one.

Valera-Medina et al. [77] (2015) examined combustion stability and emissions from ammonia with mixtures of methane or hydrogen in gas turbines. This study reported that efficient combustion with high power is possible from the ammonia mixtures, but for a
narrow range of equivalence ratio. They also observed low concentration of OH radicals at high hydrogen content which is associated with the high NH\textsubscript{2} production.

Somarathne et al. [78] (2016) performed numerical investigation on the combustion characteristics of turbulent premixed ammonia-air flame in a swirl burner. The numerical study realized that ammonia flames can be stabilized with the use of additives. In addition, the results show that initial temperature of 500K and equivalence ratio of around 1.2 gives the minimal NO and NH\textsubscript{3} emissions from the tested flames. This study demonstrated a strong potential for ammonia fuel in a gas turbine.

Valera-Medina et al. [25] (2017) obtained experimental and numerical calculations to progress towards optimization of fuel injection and fluid stabilization from ammonia-methane flames in a swirl burner. This study considered ammonia as the primary fuel and found that a lower swirl and a different injection strategy are necessary for an optimized power generation. This is mainly because of the ammonia flame instabilities, which is significantly large. The study also concluded that fully premixed injection strategy that works for hydrocarbons is not appropriate for ammonia fuel.

Hayakawa et al. [9] (2017) performed experiments to investigate the stability and emissions from premixed ammonia-air flame in a swirl burner. This experimental work shows that ammonia-air flames can be stabilized for a range close to the ammonia flammability range. In rich ammonia flames, NO and NH\textsubscript{3} emissions are reasonably low and found in the same order for a specific equivalence ratio around 1.05 from experiments and 1.2 from one-dimensional simulations.
Xiao et al. [79] (2017) evaluated various numerical reaction models for ammonia-methane in gas turbines. The assessment concluded that Tian mechanism is the most appropriate for NH₃-CH₄ combustion. They also revealed that pressure has a more prominent effect than initial temperature on reducing emissions. This finding is promising for ammonia as a fuel in gas turbines.

Somarathne et al. [21] (2017) performed numerical study to investigate the effect of pressure and secondary injection on emissions from the combustion of ammonia-air in a gas turbine like combustor. The results agree with [79] on the decrease of NO and NH₃ emissions as pressure increases. The lowest NO was found for equivalence ratio around 1.2, which agrees with that in [9].

Kurata et al. [19] (2017) investigated two-stage combustion strategy on the performance and emission from ammonia-methane swirl flames in a gas turbine burner. The results agree with that from the numerical study in [21], demonstrating a strong potential of second stage combustion in reducing NO emissions from ammonia flames.

Valera-Medina et al. [28] (2017) performed a preliminary study on lean premixed combustion of ammonia with hydrogen in a gas turbine swirl burner. They reported that hydrogen additions lead to a narrow operability window due to its high propensity to flashback. They also found that good NO performance can be achieved from 50:50 NH₃:H₂ for ‘very’ lean equivalence ratio. This finding is promising for low NO emissions from ammonia fuel in gas turbines without the need for second stage combustion.
Kurata et al. [20] (2019) continued the previous work in [19] focusing on the development of a wide operable range of rich-lean low NO burner for ammonia fuel gas turbines. They succeeded using this concept to burn ammonia as a single fuel over a wide range of power and rotational speeds. The NO emissions were also reduced to one-third that of a base system. The new technology used in this study shows a strong potential to realize low NO ammonia single fueled power generation.

Somarathe et al. [80] (2019) conducted a numerical study to investigate the effect of various thermal boundary conditions and high pressure on emissions of turbulent non-premixed ammonia swirl flames. They observed that NO emission from ammonia combustion is a function of temperature and pressure, and its production is largely dependent on the local OH concentration. The numerical results show with wall heat losses that the NO emission remarkably decreases. However, the unburned NH$_3$ increases due to the lower concentration of OH in the flame which plays a vital role in the ammonia oxidation.

Valera-Medina et al. [29] (2019) performed a similar study that reported in [25] but with ammonia-hydrogen mixtures. They found it difficult to stable the flame with ammonia concentration lower than 70%, which is possible in case of ammonia with methane. The study also insisted on the need of finding new injection techniques to reduce emissions of NO and unburned ammonia.

Okafor et al. [31] (2020) controlled the NO and other emissions from ammonia-methane flames in micro gas turbine combustors. This study clearly shows the benefit of two-stage combustion over a single stage combustion in meeting significantly low NO emissions such as 49 ppm and high combustion efficiency at 2.5 bar. The optimum low NO primary zone
was found for equivalence ratio vary from 1.30 to 1.35 while the overall equivalence ratio was around 0.5.

Vigueras-Zuniga et al. [81] (2020) conducted a numerical work on ammonia-hydrogen blends for gas turbine systems to assess the potential effects of high pressure and inlet temperature. This study is first of its kind showing the impact of operating conditions on the formation of NO emissions. The results show that wall heat losses are of crucial importance in increasing ammonia reactivity, which has a clear effect on ammonia and NO emissions. Furthermore, complete reaction produces large quantities of water and nitrogen at a higher temperature. The study proposed a secondary stage combustion to minimize ammonia slip and NO emissions at high pressures and inlet temperatures.

Okafor et al. [82] (2020) investigated the influence of wall heat loss and pressure on emission characteristics from ammonia-air swirling flames, using three cylindrical combustor confinements with different heat loss rates. The study reported that wall heat loss is more dominant than pressure in controlling NO, NH₃, and N₂O emissions from ammonia combustion. They observed lower NO emission as heat loss increases but that promoted N₂O and ammonia emissions, which agrees with emission trends reported in [80,81].

Franco et al. [83] (2020) designed a novel swirl burner for ammonia combustion and tested its flame stability. They suggested the need of a longer residence time and a small addition of hydrogen to ensure stable combustion and a reasonable flame stability range. The study concluded that simple and cheap systems can utilize this novel burner, ensuring flame stability and NO emissions control.
1.4 Objectives

1.4.1 General objectives

It is of crucial importance to design carefully a combustor with good flame stability range and to assure flame stability through applying a well fuel-air mixing strategy. Swirl flame combustors have well demonstrated making flames more stable by reducing the flame jet velocity \([85,86]\). They also enhance the fuel-air mixing rate by introducing local pre-mixing inside the combustor \([87]\). Also, the swirl increases the fluid residence time yielding a longer combustion time of the fuel mixture \([88]\). Therefore, swirl flames have been used in gas turbine engines and industrial combustors \([87,89–92]\). For the aforementioned reasons, we have designed a swirl flame type combustor to conduct this research work.

Swirl flames are more stable in comparison with jet-flames. However, they can still experience combustion instability leading to lean blowout, flashback, or rich blowout phenomena. If the flame strain rate exceeds the flame extinction limit, local extinction starts along the flame sheet yielding lean blowout \([93]\). Swirl flame can also propagate upstream of the combustion chamber and stays inside the combustor where a flammable mixture is existed. This is called a flame flashback, and it can be induced by different mechanisms \([94]\). The rich blowout is a result of excessive flame stretch in the stabilization region \([95]\). In the work presented here, we try to interrupt the flame stability by changing the fuel-air equivalence ratio gradually. At a certain point, one of the three phenomena should take place. The equivalence ratio at that point is recorded as a flame stability limit.

The flame stability limit can be affected by different variables. Here, we study the effect on flame stability if we change one of following variables: (1) ammonia additions in the
fuel-air mixture, (2) swirl number, (3) Reynolds number, (4) bulk velocity, and (5) elevated pressures. Flame stability measurement is the main objective of this research work. The fuel mixtures are pure ammonia, ammonia with methane, or ammonia with hydrogen. We also investigate effects of nitrogen additions on ammonia-hydrogen-air flames by keeping a 3:1 hydrogen:nitrogen volume ratio. This mixture should provide better understanding of flame stability from ammonia decomposition mixtures.

The second major objective of this work is the measurements of NO emissions from the combustion of ammonia flame in mixtures of methane or hydrogen. This is done by utilizing high-tech emissions analyzers. This work should provide pollutant emissions data from a wide range of ammonia flames with mixtures of methane or hydrogen seeking conditions where NO concentration is in acceptable legislation range. The results from this study should provide a better insight on how to achieve stable flames with low NO production from fueling gas turbine combustors with ammonia fuel mixtures.

1.4.2 Specific objectives

Demonstrating the feasibility of combusting ammonia fuel in mixtures of methane or hydrogen in a micro gas turbine-like combustor. This specific objective should be satisfied by meeting the following scope of work:

- Design and construction of a reduced scale gas turbine swirl combustor which is compatible for ammonia fuel.
- Model swirl combustor experiments
  - Operate the swirl combustor with methane fuel to establish a baseline for operability range and emissions.
Operate the swirl combustor with ammonia in mixtures of methane and report operability window range and emissions.

Operate the swirl combustor with ammonia in mixtures of hydrogen and report operating range and emissions.

- Flame stability map generation
  - Perform flame stability testing at 5 bar for each of the fuel mixtures at various conditions to generate flame stability map.
  - Measure NO emissions from ammonia blended flames at elevated pressures.

1.5 Thesis outline

This research document contains seven main chapters. These chapters are; 1) introduction, 2) materials and methods, 3) stability limits at atmospheric pressure 4) stability limits at elevated pressures, 5) exhaust emissions, 6) lessons learned and 7) closure. The first chapter is an introduction for this work, starting with explaining a problem considered that this work should contribute in solving. We introduced a carbon-free fuel, ammonia, as a possible solution to reduce carbon dioxide emissions, though ammonia has some combustion challenges. The first chapter provides a literature survey on the research work in the field of ammonia combustion and gas turbine applications, even though, the body of information is scarce and more research work should be done.

Chapter 2 provides information on the materials and methods used to perform the experimental work. The selection of fuel mixtures blended with ammonia are discussed first. Then followed by the design specifications and materials selection of KAUST swirl combustor. In this work, the experiments were performed at two different pressure
conditions: 1) at atmospheric pressure and 2) at elevated pressures. The experimental setup for each condition is discussed separately. The experimental procedure and safety are discussed later and followed by the experimental techniques and uncertainties.

Chapter 3 provides a suitable understanding of KAUST combustor’s behavior and how to choose an appropriate swirl number and Reynolds number for further examination. It also shows the effects of ammonia additions to fuel mixtures of methane and of hydrogen on the flames’ topology and on stability limits. Chapter 4 is similar work to the one has been provided in chapter 3, but the experiments pressure conditions are different. While the experiments in chapter 3 were performed at atmospheric pressure, the one in chapter 4 were performed at elevated pressures. This chapter provides information on the effects of ammonia additions on the flame stability at up to 5 bar pressure conditions.

Chapter 5 covers the exhaust emissions, mainly NO, from flames tested in chapter 3 and 4. It is shown how ammonia additions, equivalence ratio, bulk velocity, and pressure can promote the production of NO. Before closing this dissertation work, we have added chapter 6 which covers lessons learned from this experimental journey. Relatively, a few students have handled ammonia as a fuel in a swirl burner. Therefore, we have considered adding chapter 6 to help those interested in ammonia combustion avoiding the mistakes that we have gone through. The lessons learned are not just stories to tell but instead providing recommendations and solutions for expected challenges associated with ammonia combustion. Lastly, chapter 7 provides conclusions from the whole experimental work. It also provides future work and recommendations with possible solutions for the problem considered and discussed in chapter 1.
Chapter 2

Materials and methods

In this chapter materials and methods for the experimental work are discussed in details. The selection of fuel mixtures blended with ammonia are discussed in Sec. 0. The following section, Sec. 0, shows design specifications and materials selection of KAUST swirl combustor. In this work, the ammonia flame experiments were performed under different pressure conditions and can be divided into two main parts: 1) atmospheric pressure and 2) elevated pressures. The experimental setup for the atmospheric pressure is different from that at elevated pressures. Both experimental setups are discussed in Sec. 0.

The experimental procedure and safety are presented in Sec. 0 and the experimental techniques and uncertainties are discussed in Sec. 0.

2.1 Selection of ammonia fuel mixtures

Ammonia is the main fuel investigated in this research work and the flames are either pure ammonia or ammonia blended in fuel mixtures. However, enabling ammonia for gas turbines is challenging because: (1) the chemical reactivity of ammonia is very low compared to hydrogen and natural gas [11,12] leading to slow consumption rates and (2) ammonia-air flames have a large propensity to produce harmful NO emissions [20,23,31–34,38]. However, recent experiments in laboratory-scale swirl burners at atmospheric [9,19,25,29,77] and elevated pressure [9,34,36,79,84] and industrial micro gas turbines [20,22,31] demonstrated that it is possible to stabilize turbulent swirl flames from pure ammonia or ammonia mixtures of methane [19,25,31,34] or of hydrogen [28,29]. Here, we blended ammonia in mixtures of methane or hydrogen fuels to demonstrate the feasibility
of combusting ammonia fuel in a micro gas turbine. Because the decomposition of ammonia produces a hydrogen-nitrogen blend with a 3:1 volume ratio, we have also measured stability limits and NO emissions for ammonia-hydrogen-nitrogen fuel blends. Hence, the three ammonia mixtures examined in this study are: 1) ammonia-methane-air, 2) ammonia-hydrogen-air, and 3) ammonia-hydrogen-nitrogen-air covering a wide range from pure ammonia to zero ammonia in the fuel mixture.

Table 0.1 shows the relevant fundamental combustion characteristics of ammonia compared to methane and to hydrogen. The densities of ammonia and methane are slightly similar, at 1 bar and in gas phase. However, the heating value of ammonia is 19 MJ/kg which is less than half of that of methane 50 MJ/kg. At atmospheric pressure, the maximum laminar burning velocity of ammonia is only $S_l \approx 7.00 \text{ cm/s}$ [6], about one fifth that of methane with $S_l \approx 35 \text{ cm/s}$ and significantly small compared to $S_l \approx 350 \text{ cm/s}$ for a stoichiometric hydrogen-air mixture [6]. The flammable range of ammonia-air flames is quite narrow with $\Delta \phi \approx 0.83$ compared to $\Delta \phi \approx 1.21$ for methane-air flames and to $\Delta \phi \approx 8.71$ for hydrogen-air flames [11].

Table 0.1. Fundamental combustion characteristics of ammonia, methane, and hydrogen. Data are taken from [6,77].

<table>
<thead>
<tr>
<th></th>
<th>Unit</th>
<th>NH₃</th>
<th>CH₄</th>
<th>H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Autoignition temperature</td>
<td>K</td>
<td>930</td>
<td>859</td>
<td>810</td>
</tr>
<tr>
<td>Adiabatic flame temperature (@ $\phi = 1$)</td>
<td>K</td>
<td>1850</td>
<td>2223</td>
<td>2328</td>
</tr>
<tr>
<td>Density ($\rho$)</td>
<td>kg/m³</td>
<td>0.73</td>
<td>0.66</td>
<td>0.08</td>
</tr>
<tr>
<td>Flammability limit range ($\Delta \phi$)</td>
<td>-</td>
<td>0.83</td>
<td>1.21</td>
<td>8.71</td>
</tr>
<tr>
<td>Heating value</td>
<td>MJ/kg</td>
<td>19</td>
<td>50</td>
<td>120</td>
</tr>
<tr>
<td>Laminar burning velocity ($S_l$)</td>
<td>cm/s</td>
<td>7</td>
<td>35</td>
<td>350</td>
</tr>
</tbody>
</table>
2.1.1 Ammonia-methane-air

Figure 0.1 shows flammability limits of ammonia-methane-air mixtures as a function of equivalence ratio. As mentioned earlier, see Table 0.1, the flammability limit range of methane is larger than that of pure ammonia mixture. Figure 0.1 shows the effect of ammonia additions on reducing the flammability range of methane-air mixtures. Increasing the ammonia additions increases the equivalence ratio of the lower flammability limit from \( \phi = 0.48 \) for \( x_{\text{NH}_3} = 0 \) to \( \phi = 0.63 \) for \( x_{\text{NH}_3} = 1 \). The equivalence ratio of the upper flammability limit, on the other hand, decreases with more ammonia additions from \( \phi = 1.69 \) for \( x_{\text{NH}_3} = 0 \) to \( \phi = 1.46 \) for \( x_{\text{NH}_3} = 1 \). Hence, the equivalence ratio range of pure ammonia is approximately two-third that of pure methane.

Figure 0.1. Flammability limits of ammonia-methane-air mixtures as a function of equivalence ratio, lower flammability limits (square) and upper flammability limits (circle) are calculated from [11].
Figure 0.2 shows the laminar burning velocity of stoichiometric ammonia-methane-air mixture as a function of $x_{NH3}$. The data are presented from measurement of Han et al. [17] and Okafor et al. [37]. The data show that the laminar burning velocity of stoichiometric methane-air flames is approximately five times larger than that of ammonia-air flames. At atmospheric pressure conditions, one can observe that ammonia addition on methane-air mixture decreases almost linearly. The laminar burning velocity of the flame drops from $S_l \approx 35.00$ cm/s for $x_{NH3} = 0$ to $S_l \approx 7.00$ cm/s for $x_{NH3} = 1$. It is worth mentioning that at elevated pressures conditions, the laminar burning velocity of ammonia-methane-air mixtures decreases as pressure increases [96].

![Figure 0.2. Laminar burning velocity of stoichiometric ammonia-methane-air flames as a function of $x_{NH3}$ at atmospheric pressure. Data from Han et al. [17] and Okafor et al. [37].](image-url)
2.1.2 Ammonia-hydrogen-air

Figure 0.3 shows flammability limits of ammonia-hydrogen-air mixtures as a function of equivalence ratio. As mentioned earlier, see Table 0.1, the flammability limit range of hydrogen fuel is significantly greater than that of pure ammonia fuel. Figure 0.3 shows the effect of ammonia additions on reducing the flammability range of hydrogen-air fuel. Increasing ammonia additions increases the equivalence ratio of the lower flammability limit from $\phi = 0.18$ for $x_{\text{NH}_3} = 0$ to $\phi = 0.63$ for $x_{\text{NH}_3} = 1$. The equivalence ratio of the upper flammability limit, on the other hand, decreases dramatically with more ammonia additions from $\phi = 8.84$ for $x_{\text{NH}_3} = 0$ to $\phi = 1.46$ for $x_{\text{NH}_3} = 1$. The large difference between the ammonia and hydrogen flammability range shows a great potential in enhancing the flammability range of ammonia, which can be achieved from blending ammonia with hydrogen-air mixtures.
Figure 0.3. Flammability limits of ammonia-hydrogen-air mixtures as a function of equivalence ratio, lower flammability limits (square) and upper flammability limits (circle) calculated from [11].

Figure 0.4 shows laminar burning velocity of stoichiometric ammonia-hydrogen-air mixture as a function of $x_{\text{NH}_3}$. The data are presented from measurement of Han et al. [17], Okafor et al. [37], and Kumar et al. [97]. The data shows that the laminar burning velocity of stoichiometric hydrogen-air flames is significantly greater than that of ammonia-air flames. At atmospheric pressure conditions, one can observe that ammonia addition on hydrogen-air mixture decreases dramatically the laminar burning velocity of the flame from $S_l \approx 250.00 \text{ cm/s for } x_{\text{NH}_3} = 0$ to $S_l \approx 50.00 \text{ cm/s for } x_{\text{NH}_3} = 0.60$. The slope then decreases at a slower rate until reaching $S_l \approx 7.00 \text{ cm/s for } x_{\text{NH}_3} = 1$. One can observe that the laminar burning velocity of ammonia-hydrogen-air mixture for $x_{\text{NH}_3} \approx 0.60$ is similar to that of methane-air mixture. At elevated pressures conditions, the laminar burning velocity of ammonia-hydrogen-air mixtures decreases as pressure increases [27].
Figure 0.4. Laminar burning velocity of stoichiometric ammonia-methane-air flames as a function of $x_{NH3}$ at atmospheric pressure. Data from Han et al. [17], Okafor et al. [37], and Kumar et al. [97].

2.2 KAUST swirl combustor

A laboratory-scale generic swirl combustor was designed, constructed, and used to perform the experimental work reported in this study. The combustor main features are shown in this section. The design concept of our combustor has been integrated from a well-known swirl combustor design which is called “University of Michigan Swirl Burner” [91] as shown in Figure 0.5. This combustor has been used since the 1980s in the research field of swirl flame stability. It has been proven that its swirl flow can enhance flame stability five times more compared to that of a jet flame [91]. The main differences between this design and ours are the central fuel line, fuel-air injection method, and the burner throat shape. The Michigan’s burner has a divergent shape with an angle while our combustor has a straight throat shape.
Figure 0.5. Schematic of the university of Michigan swirl burner, showing the throat shape and fuel-air injection lines [91].

KAUST swirl combustor has initially been developed for swirl flames of highly oxygenated fuels and it has been modified to accommodate ammonia-air flames. Details about this combustor are available in [98] and [99] and only the modified combustor’s main features are described here. The combustor’s design specifications are described in Sec. 0, while the materials selections are described in Sec. 0.

2.2.1 Design specifications

Figure 0.6 shows an exploded view of KAUST swirl combustor. Figure 0.6 (1) shows the combustor throat outlet and how its diameter can be easily adjusted by replacing this part. However, we have fixed the diameter to 44 mm for all experimental work reported in this document. This decision was made after testing flame topology and stability operating range from different throat diameters and also a divergent shape. The throat is sitting on a
base, see Figure 0.6 (2). The main body of the combustor has three sections; upper, middle, and lower. Figure 0.6 (3) shows the upper body and its two inlets $c$. In our experiments, we completely blocked these inlets and no-flow gases were injected from inlet $c$. Figure 0.6 (4), shows the middle body, 80 mm in diameter, and it has four tangential inlets $b$ with 6.25 mm inner diameter. Inlets $b$ are regularly distributed azimuthally and located 140 mm upstream of the combustor outlet. Figure 0.6 (5) shows how the three main bodies are fixed together using screws. A ceramic honeycomb of 20-mm thickness is located 80 mm downstream of inlets $a$ and sets inside the lower main part, see Figure 0.6 (6). The third main body is the lower part Figure 0.6 (7), 80 mm in diameter, and it has two inlets $a$ with 6.25 mm inner diameter.

Figure 0.6. Exploded view of KAUST swirl combustor showing its main parts and inlets.
2.2.2 Materials selection

Ammonia is corrosive when used on industrial materials such as copper and brass. Therefore, selecting compatible materials with ammonia is of crucial importance. In alignment with the comprehensive list reported in [6] for material compatibilities of ammonia, we have carefully selected the following materials for our combustor. Table 0.2 shows the effect of corrosion on only those materials that we used in our work.

Table 0.2. Materials compatibilities of ammonia, showing the effect of corrosion [6].

<table>
<thead>
<tr>
<th>Material</th>
<th>Ammonia corrosion effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>No effect</td>
</tr>
<tr>
<td>Buna N (Nitrile)</td>
<td>Minor effect – slight corrosion or discoloration</td>
</tr>
<tr>
<td>Ceramic</td>
<td>Minor effect – slight corrosion or discoloration</td>
</tr>
<tr>
<td>PTFE/Teflon</td>
<td>No effect</td>
</tr>
<tr>
<td>Quartz</td>
<td>No effect</td>
</tr>
<tr>
<td>Stainless steel 316</td>
<td>No effect</td>
</tr>
</tbody>
</table>

- **Aluminum** is a very desirable metal because it is more malleable and elastic compared to steel. Aluminum can go places and create shapes that steel cannot, often forming deeper or more intricate spinning. However, Aluminum melts at a low temperature of approximately 660°C. Therefore, we selected Aluminum to make only the three main parts of the main body of the combustor that do not have a direct contact with flame, part number 3, 4, and 7 in Figure 0.6.

- **Buna N (Nitrile)** is good for sealing materials. Buna is used for gaskets and valve seats in mass flow controllers. It is also used as gaskets for back pressure regulators.
Ceramic materials are good insulators. Thus, we made the flame confinement from ceramic to reduce conductive heat losses through the combustion, which affects flame stability. In addition, reducing enthalpy losses as burned gases travel through the combustion chamber permits accurate pollutant species concentration measurements, even if samples are collected at the combustion chamber exit. We also used a ceramic honeycomb, Figure 0.6 (6), to uniformly distribute air flow from inlet a.

PTFE/Teflon is used for fuel-air tubing for experiments performed at atmospheric pressure.

Quartz are used to visualize the flame inside the ceramic confinement, quartz windows were selected over BK7 glass to allow laser diagnostics in the UV range. Quartz materials also allow using laser ignition source to safely ignite fuel mixtures for experiments performed at elevated pressures.

Stainless steel 316 can resist higher temperature 1400-1450°C comparing to Aluminum 660°C. Thus, we selected stainless steel 316 for parts 1 and 2 in Figure 0.6 (throat and throat base) which may have a direct contact with flames.

2.3 Experimental setup

Two experimental setups for experiments at atmospheric pressure and at elevated pressures conditions are described here. Each setup has its own swirl combustor and flame confinement wall. While the combustors’ design specifications are similar, the confinements have a different shape and size. More details are provided in this section.
2.3.1 Atmospheric pressure experiments

Figure 0.7 shows schematic of experimental setup for experiments performed at atmospheric pressure. The swirl flame combustor shows where reactants are injected in the plenum; (a) two axial air inlets, (b) four tangential fuel-air inlets. The dimensions are in mm. The swirl combustor is located inside an enclosure, and it is sealed to prevent any gas leakage. The top of the enclosure is connected to a vacuumed exhaust line to accelerate exiting toxic gases from the laboratory. Fuel gas cylinders, located outside the laboratory, are connected to the swirl combustor through Teflon tubes which are compatible with ammonia. An air compressor is also located outside the room and it feeds the combustor through pressurized stainless-steel lines with a pressure set up point at 6 bar. Figure 0.7 shows that the flame is confined in a cylindrical ceramic wall to minimize heat loses. The cylindrical ceramic wall is 330-mm in length and it has a diameter of 152 mm. A spark ignition is located inside the ceramic confinement to ignite the fuel mixture and it is controlled remotely through a pressing switch. Quartz windows are inserted in the ceramic wall to provide visual access to the flames. A refractory material chimney rests on top of the ceramic confinement. On top of the chimney, a stainless-steel probe is located for gas sampling. The probe is connected to a thermally-insolated line with a temperature setup point 150°C to prevent water condensation, and it feeds a gas sampling analyzer (Horiba, model VA-3000, chemiluminescent sensor). A vacuum pump sits inside the Horiba system and its suction flow rate is 1 liter per minute.
Figure 0.7. Schematic of the atmospheric pressure swirl flame combustor showing where reactants are injected in the plenum; (a) two axial air inlets, (b) four tangential fuel-air inlets (dimensions are in mm).

Figure 0.8 shows the main components from the experimental setup at atmospheric pressure. Mass flow controllers are set to control four main gas lines, axial air, tangential air, ammonia, and a fuel line which could be either hydrogen or methane. The four lines are connected to the burner and their configurations are as described earlier. Controlling the flow of the gases is of crucial importance and the flame stability is strongly dependent on the MFCs. For instance, a flashback can easily takes place while amending the MFCs set points if the time response of the fuel MFC is faster than that of ammonia. Therefore, a well-controlled and automated control system is suggested. Such as using a LabView software. Another important factor which can affect flame stability and NO emissions is wall heat loss from associated with flame confinements [82]. Okafor et al. [82] investigated three flame confinements and each has a different wall heat loss rate. They concluded that controlling the heat loses can reduce NO emissions. Here, we have used a thick ceramic confinement with only a slight slots of quartz windows for visualization access.
2.3.2 Elevated pressures experiments

Figure 0.9 shows schematic of the high-pressure combustion duct (HPCD) at KAUST and it shows the swirl flow combustor located inside the duct. The HPCD is designed for experiments on turbulent and at elevated pressures conditions. Details about the HPCD are available in [100] and only the main features are described here.
Figure 0.9. Schematic of the high-pressure combustion duct at KAUST, showing the swirl flame combustor position.

The HPCD is a 316L stainless-steel tube with an inner diameter of 450 mm and it is 7500 mm in length. The duct can be pressurized using air co-flow and a back-pressure regulator. The HPCD is designed to hold air pressure at 40 bar and at 250°C temperature. This temperature seems to be a low limit for experiments with high thermal power. Hence, the HPCD should be upgraded to handle a much higher temperature than the 250°C. It has 6 optical access quartz windows to allow visualizing the flame and also can be used for laser ignition and laser diagnostic techniques. The flame can be ignited through one of the optical windows via a laser-induced spark inside the HPCD.
Figure 0.10 shows schematic of the swirl flow combustor inside the HPCD showing where reactants are injected in the plenum; (a) two axial air inlets, (b) four tangential fuel-air inlets.

The combustor in Figure 0.10 is similar to that used for experiments at atmospheric pressure and shown in Figure 0.7. However, its outlook and its confinement were amended to be compatible with the HPCD. The dimensions are in mm. The swirl flame is confined in a square-shape confinement with 160 mm inner diameter. The confinement has 4 quartz windows, 150 mm in length, to allow optical access. The corners of the square are 4 stainless steel columns, 300 mm in length, to hold the windows. A stainless-steel chimney sets on top of the windows and it is supported by the 4 columns. A sampling quartz probe is placed 370 mm downstream of the combustor’s outlet and it is connected to Testo-300
flue gas analyzer. The probe inner diameter is 1 mm and it expands to 2 mm to accelerate the sampling gas flow and to minimize chemical reactions of the exhaust gases inside the probe [101].

Figure 0.11 shows the HPCD and the swirl burner used for the experiments at elevated pressures. Here, the control of all gases is automated utilizing a LabView software remotely and from a control room. The software can control not only the flow rates of air and fuel but also the pressure inside the HPCD. Therefore, experiments at the HPCD are well controlled and margin of error is significantly small. The burner here is similar that used for atmospheric pressure as described earlier. However, the confinement is completely different in shape and materials. This confinement is made from stainless steel with a square shape and a relatively large optical quartz window. Hence, results from atmospheric pressure experiments cannot be compared to those from this experimental setup.

Figure 0.11. Experimental setup at elevated pressures showing main components.
2.4 Experimental procedure

This section provides details on how the fuel-air system is connected to the swirl combustor. It also provides the theoretical equations that are of interest. For instance, how the swirl number, Reynolds number, bulk velocity, and ammonia mole fraction are measured. Ammonia is a toxic fuel; hence following a safety procedure is important. Here, some safety procedure details are provided.

2.4.1 Flow control

Figure 0.12 shows computational fluid dynamics simulation of KAUST swirl combustor for methane-air mixture. The model used is k-epsilon and the two equations are species transport and momentum.

Figure 0.12 Non-reactive RANS simulations of KAUST swirl combustor for methane-air mixture.

The RANS simulation shows that the air and fuel are technically premixed with good uniformity of gas flow distribution at the combustor outlet. The oxygen concentration is slightly larger at the central line while slightly larger concentration of fuel at the boundary...
lines. However, the simulation shows that the mixture inhomogeneities at the injection plane is smaller than 3.5 %.

Figure 0.13 shows flow chart of the fuel-air mixtures leaving gas cylinders and passing through mass flow controllers to the swirl combustor. We can clearly see how the fuel-air are mixed and injected into the swirl combustor. Initially, methane-air mixture was selected as a baseline to test the combustor operability and to better understand the effect of the swirl number and bulk velocity on swirl flames at atmospheric pressure conditions.

Reactants are injected into the plenum via two axial inlets installed at the bottom of the assembly (inlets $a$ in Figure 0.6) and four tangential inlets (inlets $b$ in Figure 0.6). Only air flows through inlets $a$ while a mixture of fuel and air flows through inlets $b$. The flame is confined to mitigate heat losses and flat quartz windows are mounted to provide optical access to the flame. Swirl is imparted to the flow because of tangential injection [102]. The swirl number can be adjusted by varying tangential momentum $m_\theta$ and the axial momentum $m_A$. The swirl number is defined here by Equation (1) [86,103]:

![Flow chart of the fuel-air mixture set up showing how the fuel and air are mixed and injected into the swirl combustor.]
\[ S_g = \frac{\pi r_0 d_A}{2 A_t} \left( \frac{m_\theta}{m_\theta + m_A} \right)^2 \]  

(1)

where \( r_0 \) stands for the radius of each tangential inlet, \( d_A \) is the diameter of the injector throat, and \( A_t \) denotes the total area of the four tangential inlets. Effects of the Reynolds number on the flames’ topology and stability limits are of interest. The Reynolds number is defined here with bulk flow properties:

\[ \text{Re} = \frac{\rho d_A u_b}{\mu} \]  

(2)

where \( \rho \) stands for the density of the fuel-air mixture, \( d_A \) is the diameter of the injector throat (44.4 mm), \( u_b \) stands for the bulk velocity at the injector throat, and \( \mu \) is the dynamic viscosity of the fuel-air mixture. At elevated pressures conditions, the bulk velocity is of interest. Hence, it can be calculated from equation (2) as follows.

\[ u_b = \frac{\text{Re} \mu}{\rho d_A} \]  

(3)

Different ammonia additions to methane-air, hydrogen-air, and hydrogen-nitrogen-air mixtures are examined, spanning the full range of ammonia fuel fractions from \( x_{NH3} = 0.00 \) where there is no ammonia in the fuel mixture to 1.00 when it is a pure ammonia fuel mixture. The ammonia fuel fraction is adjusted by varying the ratio of the volumetric flow rate of ammonia \( V_{NH3} \) to the volumetric flow rate of the other fuels \( V_f \), where \( f \) can be either methane, hydrogen, or hydrogen:nitrogen in 3:1 ratio. The ammonia fuel fraction value is defined here by Equation (4):

\[ x_{NH3} = \frac{V_{NH3}}{V_{NH3} + V_f} \]  

(4)
The flow rates of ammonia, methane, and air are prescribed with digital mass flow controllers (MKS Instruments) with an accuracy better than 2%. The MFCs are calibrated with nitrogen (N₂) as a basis gas. Therefore, a gas correction factor (GCF) is used to indicate the ratio of flow rates of different gases. The GCF at atmospheric pressure and at 273K temperature is provided by the MKS instruments manufacturer for each gas and it is 0.72 for methane, 1.01 for hydrogen, and 0.73 for ammonia. Note that the GCF varies as ambient pressure and temperature conditions change.

Equation (5) shows that the equivalence ratio is defined as the ratio of the actual fuel to air concentrations to the ratio of the fuel to air concentrations at stoichiometry. Stoichiometric combustion occurs when all oxygen and fuel are consumed in the reaction. In this experimental work, the equivalence ratio is of crucial importance as flame stability limits and NO exhaust emissions are mainly reported in its function.

\[ \varphi = \frac{F_TA}{F_TA_{st}} \]  

(5)

Because the objective of this study focuses on ammonia as a fuel for power generation equipment, the thermal power is of interest. The thermal power can be calculated by Equation (6)

\[ P_{th} = \sum_{f=1}^{n} M_f \cdot NCV_f \]  

(6)

where \( M_f \) is the mass flow rate of the fuel mixture and \( NCV_f \) stands for the mixture net caloric value. Table 0.1 shows that the caloric value of hydrogen is large \( NCV_{H2} = 120 \) MJ/kg comparing to that of ammonia \( NCV_{NH3} = 18.8 \) MJ/kg, while the methane caloric value is about three times more than the values of ammonia.
2.4.2 Safety

The combustor is located in a confined space and all flow gases are directed to an exhaust system. There were also ammonia sensors to detect even small gas leak as low as 5 ppm. As indicated in [6], there is no lasting effect on short exposure of 400-700 ppm of ammonia, but it is dangerous and may be fatal if someone exposed to 2000-4000 ppm for less than half an hour. Therefore, extra care and safety procedures should be applied when dealing with ammonia and its combustion products.

2.5 Data measurements and uncertainties

This section provides details on the operation and practical aspects for experiments reported in this document. It provides a detailed technique on measuring flame stability limits and on measuring ammonia NO exhaust emissions.

2.5.1 Flame stability limits

The fuel-air flow and injection methods are crucial for investigating flame stability limits. In our work, a fraction of the total air is perfectly mixed with the fuel blend prior to injection via inlets $b$, while mixing with the remaining air, injected through inlets $a$, occurs within the combustor, see Figure 0.6. Therefore, it is possible that the reactant mixture is not perfectly premixed at the injection plane. However, it was verified using non-reactive RANS simulations that the mixture inhomogeneities at the injection plane was smaller than 3.5 %, see Figure 0.12. One may refer to these flames as technically-premixed and the equivalence ratio ($\phi$) mentioned in what follows stands for the global equivalence ratio. Furthermore, careful examination of the time-averaged broadband flame images (shown
later) confirm that if inhomogeneity exists, it is not large. Such images are recorded with a
digital single lens reflex camera (DSLR Nikon D700, AF-S NIKKOR 24-70 mm F2.8G
ED), for exposure times ranging from \( t = 0.60 \) to 2.00 seconds, an aperture of \( f/7.1 \), and an
ISO number of 250. Note, the flame images reported in this work and in one figure has the
same exposure time, aperture and ISO number.

Each fuel-air mixture is initially ignited at an equivalence ratio slightly higher than that of
the lean blowout limit. To measure stability limits, the fuel and air flow rates are
progressively adjusted with a rate of change of \( \varphi \approx 0.01 \) per second until lean blowout, rich
blowout, or flashback occurs. For each test, measurements are repeated at least three times.
Because the flame stability is sensitive to the flow rates, a LabVIEW software is used to
adjust the fuel-air flow rates simultaneously. The user can input fuel mole fraction and/or
fuel-air equivalence ratio. Based on the input values, the LabVIEW changes the fuel-air
mass flow rates immediately. Therefore, the LabVIEW control system increases the
accuracy of the measured flame stability data and minimizes experimental error.

### 2.5.2 Exhaust NO emissions

Because ammonia is a toxic gas and its combustion produces harmful emissions, it is vitally
important to accurately measure the exhaust NO concentrations. The combustion products
of ammonia mixtures are sampled on the centerline of the combustor at the chimney’s
outlet, 450 mm downstream of the injection plane, using a stainless-steel probe for
experiments performed at atmospheric pressure. By probing samples at different radial
locations of the chimney’s outlet, it was verified that the stream of exhaust products is
uniform. The stainless-steel probe, featuring a 4-mm inner diameter and an 80-mm length,
is connected to a thermally-insulated flexible tube that feeds a gas analyzer (Horiba, model VA-3000, chemiluminescent sensor). The flexible tube is heated to 150°C to prevent water condensation. At elevated pressure conditions, the sampling probe is made from quartz materials to resist higher thermal conductivity. It is located approximately 370 mm downstream of the injection plane. The quartz probe is 1 mm in diameter and it expands to 2 mm, allowing the sampling flow to be accelerated [101].

Mixtures of nitrogen (99.9% purity) with 500/1500/3000 ppm NO concentrations are used for calibration. For each test condition, measurements are repeated at least three times and reproducibility is within 5% of the mean. The sensitivity of the gas analyzer is around 100 ppm, and its precision is approximately ±1%. To allow fair comparisons between rich and lean cases with different air dilutions for experiments performed at atmospheric pressure, NO mole fractions are normalized for a 6% O₂ mole fraction following the procedure described by [104]. For elevated pressures, Testo-300 flue gas analyser is used and NO measurements are reported as per the device readings. The readings were confirmed by repeatability of at least three times and by only measuring NO concentrations below the device maximum range.
Chapter 3

Stability limits at atmospheric pressure

3.1 Introduction

Understanding effects of ammonia addition on flame stability limits requires a well-characterized reference. Here, mixtures of methane and air, that do not include ammonia, are used as a baseline. Flame topology and stability limits are measured for a wide range of swirl number and Reynolds number.

Measurements are first conducted for baseline methane-air mixtures to provide a suitable understanding of the combustor’s behavior as well as choosing an appropriate swirl number and Reynolds number for further examination. Effects of ammonia addition on the flames’ topology and on stability limits are examined later. This work has been published in the experimental thermal fluid science journal entitled “Stability limits and exhaust NO performances of ammonia-methane-air swirl flames” [38].

For reference and also to facilitate comparisons with methane fuel blend, ammonia-hydrogen blends are of interest here. Therefore, stability limits are measured for methane-hydrogen blends. Then, stability limits of ammonia-hydrogen-air and ammonia-hydrogen-nitrogen-air flames are discussed. This work has been published in the international journal of hydrogen energy entitled “Stability limits and NO emissions of technically-premixed ammonia-hydrogen-nitrogen-air swirl flames” [105].
3.2 Methane-air flames

Baseline methane-air flames are first examined. Figure 0.1 shows time-averaged broadband images of methane-air flames for five different swirl numbers ranging from $S_b = 0.50$ to $1.50$ for a Reynolds number $Re = 5000$ and an equivalence ratio $\phi = 0.60$. The exposure time is set to $t = 2.00$ seconds.

Figure 0.1. Time-averaged broadband images of methane-air flames for five different swirl numbers ranging from $S_b = 0.50$ to $1.50$ for $Re = 5000$ and $\phi = 0.60$.

While all the swirl flames feature a conical V shape, increasing the swirl number increases the flame’s base angle and makes the flame more compact. This is an expected feature. Since the fuel mass flow rate and equivalence ratio ($\phi$) are kept constant, the more intense chemiluminescence (here mainly from the CH* radical) observed for the largest swirl number highlights how increasing the swirl number increases the volumetric heat-release rate.

Figure 0.2 shows the measured stability limits (red and black symbols) of methane-air flames as a function of the swirl number for different Reynolds number ($Re = 4000, 6000$, and $8000$). The flammability limits of methane-air mixtures are also provided (lower and upper black solid lines) and the gray area is the flammable range. Consistent with expectations, the swirl flames’ stability limits are within the flammable range. However,
the stable range (dark gray area) is a very small subset of the flammable range and is limited
to lean equivalence ratios. Comparisons of square, circle, and triangle symbols shows that
the stability limits are fairly independent of the Reynolds number if $S_g \leq 1$. Data also shows
that stability limits are not a strong function of the swirl number. However, the flame
topology varies with the swirl number, see Figure 0.1. The range of stable equivalence
ratios is smallest for $S_g = 0.75$ and largest for $S_g = 1.50$ but, overall, lean blowout occurs
for $\phi \approx 0.5$ and flashback occurs for $\phi \approx 0.7$. The swirl number $S_g = 0.75$ roughly
corresponds to the largest swirl number for which part of the flame is still located inside of
the injection tube and is also expected to be close to the swirl number yielding vortex
breakdown [106]. The sudden change of flame structure, most-likely associated to vortex
breakdown, may explain the reduced stable range found for $S_g = 0.75$. Velocity fields were
not measured in this study and this hypothesis cannot be verified.
Figure 0.2. Stability limits of methane-air swirl flames as a function of the swirl number for $\text{Re} = 4000$ (square), $\text{Re} = 6000$ (circle), and $\text{Re} = 8000$ (triangle). The gray area corresponds to the flammable range. The dark gray area shows the stable range.

With this swirl combustor and methane-air mixtures, the lean blowout occurs at an equivalence ratio close to the lean flammability limit and flashback also occurs for rather lean mixtures, yielding a narrow stable range. However, less reactive ammonia-methane-air mixtures are targeted in this study and these are expected to be less prone to flashback.

Based on Figure 0.2, values $S_g = 1.00$ and $\text{Re} = 5000$ yield a suitable flame topology - the flame is compact and not protruding inside the injection tube - and are therefore selected for the remaining of this study. However, effects of varying Reynolds number on flame stability limits and NO emissions are reported for selected cases.

Figure 0.3 shows the measured stability limits (circle and square symbols) of methane-hydrogen-air flames for methane volume fractions in the fuel blend ranging from $x_{\text{CH}_4} = 0$ (pure hydrogen) to 1 (pure methane) for $S_g = 1.00$ and a Reynolds number $\text{Re} = 5000$. 
Circle and square symbols correspond to flashback and lean blowout, respectively. Consistent with expectations, the stable range (dark gray area) is a subset of the flammable range, depicted by the light gray area. The equivalence ratio of both flashback and lean blowout limits increase nearly linearly as the methane fraction increase. The equivalence ratio at lean blowout is \( \varphi = 0.17 \) for pure hydrogen and \( \varphi = 0.52 \) for pure methane. The equivalence ratio at flashback increases from \( \varphi = 0.27 \) for pure hydrogen to \( \varphi = 0.67 \) for pure methane. The range of stable operation marginally widens when the methane fraction increases but it is always around \( \Delta \varphi \approx 0.15 \). Overall, switching from methane to hydrogen displaces the stable range of equivalence ratios but does significantly narrow the operability range of this swirl combustor. Results of Karim et al. [107] clearly show that enriching methane with hydrogen improves reactivity and increases the flame speed across the whole range of equivalence ratios. Therefore, progressively increasing the methane fuel fraction for the methane-hydrogen-air swirl flames examined here reduces the flashback propensity and promotes lean blowout. This is why the equivalence ratio of both flashback and lean blowout limits increase when methane progressively replaces hydrogen in Figure 0.3.
Figure 0.3. Stability limits of methane-hydrogen-air flames. The flame stable zone bounded by flashback (circle) and lean blowout (square) limits.

3.3 Ammonia-methane-air flames

3.3.1 Effects of ammonia addition on stability limits

Effects of ammonia addition on the flames’ topology and stability limits of methane-air are now examined. Figure 0.4 shows time-averaged broadband images of ammonia-methane-air flames for different ammonia additions. The thermal power, equivalence ratio, and camera’s exposure time are all varied in Figure 0.4 (see Table 0.1) so quantitative comparisons are not meaningful. The swirl number is fixed to $S_g = 1.00$ and the Reynolds number is fixed to $Re = 5000$. Note that it is not possible to stabilize flames with $x_{NH3} = 0$ and $x_{NH3} = 1$ for the same equivalence ratio due to different stability limits range (shown later in Figure 0.5). Ammonia addition does not seem to have a large influence on the global flame structure. However, one can observe the orange-yellow color that increases
in intensity with increased ammonia addition. This color is mainly attributed to the NH$_2$ ammonia alpha band and water spectra [36], and it is sometimes referred to as nitrogen glow [108].

Table 0.1. Thermal power ($P_{th}$), equivalence ratio ($\phi$), and camera’s exposure time ($t$) for broadband images of ammonia-methane-air flames shown in Figure 0.4.

<table>
<thead>
<tr>
<th>$x_{NH3}$</th>
<th>$P_{th}$ (kW)</th>
<th>$\phi$</th>
<th>$t$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>5.00</td>
<td>0.58</td>
<td>2.00</td>
</tr>
<tr>
<td>0.25</td>
<td>5.50</td>
<td>0.64</td>
<td>1.30</td>
</tr>
<tr>
<td>0.50</td>
<td>6.00</td>
<td>0.71</td>
<td>1.00</td>
</tr>
<tr>
<td>0.75</td>
<td>6.50</td>
<td>0.86</td>
<td>0.77</td>
</tr>
<tr>
<td>1.00</td>
<td>7.00</td>
<td>0.92</td>
<td>0.63</td>
</tr>
</tbody>
</table>

Figure 0.4. Time-averaged broadband images of ammonia-methane-air swirl flames for $x_{NH3} = 0.00$ to 1.00 and for $S_g = 1.00$ and Re = 5000.

Figure 0.5 shows flammability and stability limits of ammonia-methane-air flames for ammonia additions ranging from $x_{NH3} = 0.00$ to 1.00. The swirl number is fixed to $S_g = 1.00$ and the Reynolds number is fixed to Re = 5000. Note that the flammability limits are not measured here and are linearly interpolated between that reported in the literature for methane-air and ammonia-air mixtures (see Table 0.1). The flammable range (gray area) narrows as ammonia addition is increased. Replacing methane by ammonia in the fuel mixture reduces the equivalence ratio ($\phi$) of the rich flammability limit from $\phi = 1.69$ to
\( \phi = 1.46 \), while the equivalence ratio (\( \phi \)) of the lean flammability limit increases from \( \phi = 0.48 \) for methane-air to \( \phi = 0.63 \) for ammonia-air [77].

Figure 0.5. Stability limits of ammonia-methane-air swirl flames as a function of the ammonia fuel fraction. The dark gray area shows the flame stability range bounded by lean blowout (triangles), flashback (circles), or rich blowout (squares).

Figure 0.5 shows that the range of stable equivalence ratios widens with ammonia addition and that it becomes relatively large for \( x_{\text{NH}_3} \geq 0.5 \), where some transition occurs. In contrast with methane-air mixtures (see Figure 0.2), stability is now bounded by three different limits; lean blowout limit (triangles), flashback limit (circles), and now rich blowout limit (squares) is introduced. Consistent with expectations and with lean flammability limits (lower black solid line), the equivalence ratio at lean blowout increases regularly with ammonia addition. It is \( \phi = 0.50 \) for pure methane (\( x_{\text{NH}_3} = 0.00 \)) and \( \phi = 0.79 \) for pure ammonia (\( x_{\text{NH}_3} = 1.00 \)). Up until \( x_{\text{NH}_3} = 0.50 \), the equivalence ratio at flashback also increases regularly with ammonia addition. The rate of increase of the equivalence ratio
yielding flashback is larger for $x_{\text{NH}_3} > 0.40$ than for $x_{\text{NH}_3} < 0.40$. The equivalence ratio at flashback increases from $\varphi = 0.83$ for $x_{\text{NH}_3} = 0.40$ to $\varphi \approx 0.96$ for $x_{\text{NH}_3} = 0.50$.

In addition to the flashback limit, the rich blowout limit is also provided for $x_{\text{NH}_3} = 0.50$. This is because, depending on the test number, flashback or rich blowout occurred during measurements. This behavior is attributed to the fact that the equivalence ratio at flashback is close to stoichiometric for $x_{\text{NH}_3} = 0.50$. Han et al. [17] reported that regardless of the ammonia fuel fraction, the equivalence ratio yielding the largest laminar burning velocity is $\varphi \approx 1.05$. It can then be argued that this equivalence ratio would also yield the largest turbulent burning velocity and, in turn, would feature the largest propensity to flashback, regardless of ammonia addition. Extrapolation of the flashback limit (circle symbols) to ammonia additions larger than $x_{\text{NH}_3} = 0.50$ suggests that flashback should occur for equivalence ratios larger than $\varphi \approx 1.05$, which is not possible if flashback did not already occur for $\varphi \approx 1.05$. Figure 0.5 shows that, for $Re = 5000$, conditions are not met for ammonia-methane-air flames to flashback if $x_{\text{NH}_3} > 0.50$, and rich blowout occurs instead, at a much larger equivalence ratio. The large error bar found for the flashback limit for $x_{\text{NH}_3} = 0.50$ is due to this transitional behavior.

Consistent with rich flammability limits, the equivalence ratio at rich blowout decreases regularly with ammonia addition. It is $\varphi = 1.40$ for $x_{\text{NH}_3} = 0.50$ and $\varphi = 1.24$ for $x_{\text{NH}_3} = 1.00$. Transition from flashback to rich blowout as the ammonia addition is increased above $x_{\text{NH}_3} = 0.50$ is due to the weaker reactivity of ammonia compared to that of methane and it explains why the range of stability becomes much wider than that of methane-air when
using this swirl combustor. Additional experiments were conducted for different Reynolds numbers to assess the universality of the $x_{NH3} = 0.50$ transitional ammonia addition.

### 3.3.2 Effects of Reynolds number on stability limits

Figure 0.6 shows direct broadband images of ammonia-methane-air flames for different Reynolds numbers ranging from $Re = 3000$ to 7000, for $S_g = 1.00$, $\varphi = 1.00$, and $x_{NH3} = 0.80$. The bulk velocity increases from $u_b = 1.00$ m/s at $Re = 3000$ to $u_b = 2.33$ m/s at $Re = 7000$. The exposure time is fixed to $t = 1.30$ seconds. Figure 0.6 shows that the flame shape is fairly insensitive to the Reynolds number if $Re > 3000$. The flame length increases slowly with the Reynolds number, except for $Re = 3000$, where the flame is slightly longer than that for $Re = 4000$. This is probably due to flow laminarization. The chemiluminescence intensity is largest for the largest Reynolds number, which is associated to more intense turbulence and volumetric heat-release rate. The thermal power increases linearly with the Reynolds number. It increases from $P_{th} \approx 4.7$ kW for $Re = 3000$ to $P_{th} \approx 11$ for $Re = 7000$.

Table 0.2. Thermal power ($P_{th}$) for the broadband images of ammonia-methane-air flames shown in Figure 0.6.

<table>
<thead>
<tr>
<th>Re</th>
<th>3000</th>
<th>4000</th>
<th>5000</th>
<th>6000</th>
<th>7000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{th}$ (kW)</td>
<td>4.73</td>
<td>6.30</td>
<td>7.88</td>
<td>9.45</td>
<td>11.03</td>
</tr>
</tbody>
</table>
Figure 0.6. Time-averaged broadband images of ammonia-methane-air swirl flames Re = 3000 to 7000 and for the $S_g = 1.00$, $\phi = 1.00$, and $x_{\text{NH}_3} = 0.80$.

Figure 0.7. Flashback and rich blowout limits near the transitional behavior for Re = 3000 (green), Re = 4000 (gold), and Re = 7000 (orange). The gray area is repeated from Figure 0.5.

Figure 0.7 shows additional measured stability limits for three different Reynolds numbers Re = 3000 (green), Re = 4000 (gold), and Re = 7000 (orange). The stable range measured for Re = 5000 (gray area) is repeated from Figure 0.5 for comparison purposes. It is evident that the transitional behavior (flashback to rich blowout limit) can be found for different Reynolds number. Regardless of the Reynolds number, the largest equivalence ratio yielding flashback is close to stoichiometric. However, the transitional ammonia addition
increases when the Reynolds number decreases. It is $x_{NH3} = 0.42$ for $Re = 7000$ and $x_{NH3} = 0.70$ for $Re = 3000$. This is because decreasing Reynolds number decreases proportionally the jet velocity and yields conditions more suitable for flashback. As a consequence, flashback continues to occur for less reactive mixtures featuring a smaller turbulent burning velocity and obtained for larger ammonia additions. Note that increasing Reynolds number for a fixed fuel blend does not change the laminar burning velocity but may increase the turbulent burning velocity. This is because turbulent velocity fluctuations become larger. Figure 0.7 shows that increasing the Reynolds number retards flashback and, as a consequence, the potential increase of turbulent burning velocity with increasing the Reynolds number does not offset the increase of the fuel-air jet velocity.

To restrict the test matrix to a manageable size, stability limits for methane-ammonia blends were not measured for different swirl numbers. Nevertheless, effects of the swirl number on the sharp transition from flashback to rich blowout can be predicted. Increasing swirl number has been shown before to promote flashback in comparable combustors (see for example [109]). As a consequence, one would assume that increasing the swirl number will shift transition from flashback to rich blowout to larger ammonia additions.

### 3.4 Ammonia-hydrogen-air flames

#### 3.4.1 Effects of ammonia addition on stability limits

Figure 0.8 shows the measured stability limits of ammonia-hydrogen-air flames for ammonia fractions in the fuel blend from $x_{NH3} = 0$ (pure hydrogen) to 1 (pure ammonia), also for $S_g = 1.00$ and $Re = 5000$. Consistent with expectations, the measured stable range (dark gray area) remains a subset of the flammable zone (light gray area). Like with
methane addition, adding ammonia to the fuel blend decreases chemical reactivity and, in
turn, modifies the stability limits by increasing both the flashback and lean blowout
equivalence ratios. The equivalence ratio at lean blowout first increases almost linearly
from $\varphi = 0.17$ to $\varphi = 0.38$ between $x_{NH3} = 0$ and 0.70 but it then increases rapidly up to
$\varphi = 0.79$ for $x_{NH3} = 1.00$. Across the whole range of equivalence ratios, increasing the
ammonia fraction in the hydrogen-ammonia fuel blend decreases reactivity and flame
speed [27], which promotes lean blowout.

The behavior is different for the upper stability limit. Note that square symbols are now
plotted as well ($x_{NH3} \geq 0.7$) and these correspond to rich blowout that, in some cases, defines
the upper stability limit instead of flashback. Between $x_{NH3} = 0$ and 0.40, the equivalence
ratio at flashback increases when the ammonia fuel fraction increases. This can also be
explained by considering trends of the flame speed with increased ammonia fuel fraction
[27]. However, for $x_{NH3} > 0.50$, the equivalence ratio at flashback increases much more
rapidly compared to for $x_{NH3} < 0.50$. It increases from $\varphi = 0.47$ for $x_{NH3} = 0.50$ to $\varphi = 0.90$
for $x_{NH3} = 0.70$. The bulk velocity is comparable for all flashback conditions depicted by
circle symbols in Figure 0.8. Therefore, it can be argued that the turbulent flame speed is
also comparable at these conditions. The laminar burning velocity plays a big role in
controlling the turbulent flame speed (note that the Reynolds number is constant across all
conditions in Figure 0.8). Therefore, the non-linear trend of equivalence ratio at flashback
as a function of the ammonia fuel fraction can be explained by the typical bell shape of the
curve plotting the laminar burning velocity versus equivalence ratio and the fact that
increasing the ammonia fuel fraction decreases the laminar burning velocity [27]. As the
equivalence ratio gets closer to stoichiometric, any increment in ammonia fuel fraction
requires a larger increment in equivalence ratio to maintain the laminar burning velocity constant compared to leaner conditions. This also explains the faster increase of equivalence ratio at lean blowout for $x_{NH3} > 0.80$ compared to smaller ammonia fuel fractions. Above an ammonia fuel fraction of $x_{NH3} = 0.70$, there is yet another sudden change of behavior. For $x_{NH3} > 0.70$, flashback does not occur when the equivalence ratio is increased above $\varphi = 0.90$. Instead, rich blowout is ultimately reached for equivalence ratios larger than 1. This transition behavior from flashback to rich blowout was observed previously in [38] for the ammonia fuel fractions in exceeds of 0.5 in ammonia-methane-air flames. In [38], transition from flashback to rich blowout roughly occurs for the ammonia fuel fraction yielding flashback for $\varphi \approx 1$. This is because progressively increasing equivalence ratio above $\varphi \approx 1$ or 1.1 reduces the flame speed [17,96] and is not likely to yield flashback if it did not already occur at a higher flame speed. Here, some data interpolation suggests that transition from flashback to rich blowout also roughly occurs for the ammonia fuel fraction yielding flashback for $\varphi \approx 1$. Rich blowout occurs at an equivalence ratio close to $\varphi = 1.40$ for $x_{NH3} = 0.70$. The equivalence ratio at rich blowout decreases down to $\varphi \approx 1.2$ for pure ammonia.

Consistent with experimental observations by others [18,28–30,110–112], these flame stability measurements show that ammonia addition to hydrogen allows widening the stable range of this swirl combustor. Contrary to previous work, the whole range of ammonia fractions in the fuel blends was investigated, from pure hydrogen to pure ammonia, which allows inferring the optimal ammonia fraction for flame stability. For this swirl combustor and $Re = 5000$, the widest stable range is found for $0.70 < x_{NH3} < 0.80$. It
is $\Delta \phi \approx 0.95$ and it spans lean to rich equivalence ratios. This value is much larger than that obtained for pure hydrogen, $\Delta \phi \approx 0.08$, and pure ammonia, $\Delta \phi \approx 0.43$.

Figure 0.8. Stability limits of ammonia-hydrogen-air flames for different ammonia fractions. The stable zone bounded by rich blowout (square), flashback (circle), and lean blowout (triangle) limits.

It is also interesting to examine the flames’ topology within these stability limits. This is done here with time-averaged broadband flame images recorded with a DSLR camera. Figure 0.9 shows such images for ammonia-hydrogen-air flames for four different ammonia fuel fractions ranging from $x_{NH3} = 0.40$ to 0.70 for $\phi = 0.40$, $S_g = 1.00$, and $Re = 5000$. The exposure time is set to $t = 1/6$ seconds. The chemiluminescence intensity is largest for the largest hydrogen concatenations, while the thermal power is almost similar around $P_{th} \approx 4$ kW, see Table 0.3.
Table 0.3. Thermal power ($P_{th}$) for the broadband images of ammonia-hydrogen-air flames shown in Figure 0.9.

<table>
<thead>
<tr>
<th>$x_{NH3}$</th>
<th>0.40</th>
<th>0.50</th>
<th>0.60</th>
<th>0.70</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{th}$ (kW)</td>
<td>4.1</td>
<td>4.3</td>
<td>4.3</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Figure 0.9. Time-averaged broadband images of ammonia-hydrogen-air flames for $x_{NH3}$ ranging from 0.40 to 0.70 for $\varphi = 0.40$, $S_g = 1.00$, and $Re = 5000$.

These four flames all feature a V shape, which is very typical of premixed swirl flames in non-adiabatic combustors [113,114] and is, therefore, expected. They also have a similar size. However, the two flames with the highest hydrogen fuel fraction slightly protrude upstream, inside of the injection tube. This is consistent with their closer proximity to flashback (see Figure 0.8). It is interesting to note that these flames feature a white hue, also visible with the naked eye. A similar color has been observed before in [28], also for a very lean ammonia-hydrogen flame. This is different from the yellow hue typically associated with ammonia flames [36,38]. A comprehensive spectroscopic analysis of the chemiluminescence signature of these flames is being conducted and will be published elsewhere.

Figure 0.10 shows time-averaged broadband images of ammonia-hydrogen-air flames for four different equivalence ratios ranging from $\varphi = 0.60$ to 1.20 for $x_{NH3} = 0.80$, $S_g = 1.00$, and $Re = 5000$. The exposure time is set to $t = 1/20$ seconds. The thermal power increases
linearly as equivalence ratio increases. It increases from $P_{th} \approx 5.8$ kW for $\phi = 0.60$ to $P_{th} \approx 10.2$ for $\phi = 1.20$.

Table 0.4. Thermal power ($P_{th}$) for the broadband images of ammonia-hydrogen-air flames shown in Figure 0.10.

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>0.60</th>
<th>0.80</th>
<th>1.00</th>
<th>1.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{th}$ (kW)</td>
<td>5.84</td>
<td>7.43</td>
<td>8.88</td>
<td>10.21</td>
</tr>
</tbody>
</table>

Figure 0.10. Time-averaged broadband images of ammonia-hydrogen-air flames for $\phi$ ranging from 0.60 to 1.20 for $x_{NH_3} = 0.80$, $S_g = 1.00$, and Re = 5000.

These flames, that feature a larger equivalence ratio and ammonia fuel fraction than those of Figure 0.9, now feature the yellow color typically associated with ammonia flames. These flames also feature a V shape and are globally longer and larger than those shown in Figure 0.9.

3.4.2 Ammonia-hydrogen-nitrogen-air flames

Dissociating ammonia to produce hydrogen allows boosting the mixture’s chemical reactivity [11]. However, dissociating ammonia produces a hydrogen-nitrogen blends with a 3:1 hydrogen:nitrogen volume ratio. Therefore, ammonia-hydrogen-nitrogen fuel blends with a 3:1 hydrogen:nitrogen volume ratio should also be examined. Figure 0.11 shows the
measured stability limits of ammonia-hydrogen-nitrogen-air flames for $x_{NH3} = 0$ to 1 and $S_g = 1.00$ and $Re = 5000$. The dashed lines correspond to the stability limits of ammonia-hydrogen-air flames already shown in Figure 0.8 and are repeated for comparison purposes.

Figure 0.11. Stability limits of ammonia-hydrogen-nitrogen-air flames (3:1 hydrogen: nitrogen volume ratio). The stable zone bounded by rich blowout (square), flashback (circle), and lean blowout (triangle) limits. The dashed lines correspond to the data from Figure 0.8.

Figure 0.11 shows that nitrogen dilution does not have a drastic effect on stability limits. On average, the equivalence ratios at flashback, lean blowout, and rich blowout are only increased by $\Delta \phi \approx 0.05$. To explain these trends, Figure 0.12 plots the laminar burning velocity computed with Chemkin and the chemistry mechanism from Okafor et al. [37] as a function of equivalence ratio for different ammonia fuel fractions, with (solid lines) and without (dashed lines) nitrogen dilution. For the range of equivalence ratios relevant to the flashback limit of Figure 0.11, it can be seen that effects of nitrogen dilution (3:1 hydrogen
to nitrogen volume ratio) can always be compensated by a slight increase of equivalence ratio of around $\Delta \phi = 0.05$. This is roughly the magnitude of the shift between the curves obtained for ammonia-hydrogen and ammonia-hydrogen-nitrogen fuel blends in Figure 0.11. Of course, using laminar burning velocity data to explain the stability limits of swirl flames is approximative, especially for very lean mixtures where chemistry mechanisms are not well validated. However, these laminar burning velocity data are consistent with the fact that nitrogen dilution (3:1 hydrogen to nitrogen volume ratio) do not drastically alter stability limits in terms of equivalence ratio.

Figure 0.12 Laminar burning velocity computed with Chemkin and the chemistry mechanism from Okafor et al. [37]. Blends diluted with nitrogen (solid lines) and undiluted blends (dashed lines).
3.4.3 Effects of Reynolds number on stability limits

Stability limits are controlled by a competition between the turbulent flame speed and the local velocity field. Because both of these quantities are modified when the Reynolds number is modified, it is interesting to conduct experiments for different Reynolds numbers. Figure 0.13 shows stability limits for three different Reynolds numbers $Re = 3000$ (pentagon), $Re = 4000$ (diamond), and $Re = 7000$ (star) for ammonia-hydrogen-air flames. The stable range measured for $Re = 5000$ (dark gray area) is repeated from Figure 0.8 for comparison purposes. For $Re = 5000$ and 7000, transition from flashback to rich blowout occurs around $x_{NH3} = 0.70$. Such transition occurs at a larger ammonia fuel fraction if the Reynolds number is reduced below 5000 with $x_{NH3} = 0.80$ for $Re = 4000$ and $x_{NH3} = 0.90$ for $Re = 3000$. This can be explained as follows. When the Reynolds number increases, by definition, the bulk jet velocity increases linearly which tends to retard flashback. At the same time, when the Reynolds number increases, turbulent velocity fluctuations increase and, in turn, the turbulent flame speed increases $[115]$. While the rate of increase of the turbulent flame speed $S_T$ with turbulent velocity fluctuations $u'$ is hard to predict, it usually follows a relationship of the form $S_T = S_L (1 + C (u'/S_L)^n)$, where $n < 1$ $[115]$. Therefore, it is expected that the bulk velocity would increase faster than the turbulent flame speed when the Reynolds number is increased in this study. This is why increasing the Reynolds number retards flashback and yields transition from flashback to rich blowout at a smaller ammonia fuel fraction, i.e. a more reactive mixture. At this point, it is not clear why increasing Reynolds number above $Re = 5000$ does not decrease the transitional ammonia fuel fraction. Regardless, over the range examined in this study,
increasing the Reynolds number tends to boost the stable range of this swirl combustor for large ammonia fuel fractions.

Figure 0.13. Stability limits of ammonia-hydrogen-air flames measured near the transitional behavior for Re = 3000 (pentagon), Re = 4000 (diamond), and Re = 7000 (star). The dark gray area shows the stable range for Re = 5000 and is repeated from Figure 0.8.

3.5 Summary

This chapter shows that the laboratory-scale swirl combustor used in this study is promising to stabilize ammonia-air flames with mixtures of methane and of hydrogen for large ranges of ammonia additions and equivalence ratios at atmospheric pressure conditions. Because decomposing ammonia produces hydrogen:nitrogen mixture in 3:1 ratio, we also measured the flame stability of ammonia-hydrogen-nitrogen-air mixtures. Data shows that the range of stable equivalence ratios increases with ammonia addition, which is contrary to what typically intuited for ammonia. Progressively replacing methane/hydrogen with ammonia
increases the equivalence ratios leading to lean blowout and flashback. This is attributed
to the decreased reactivity associated to ammonia. Overall, the range of stability, in terms
of the global equivalence ratio, widens when ammonia is added. If the ammonia addition
exceeds a critical point, the most reactive mixture does not yield suitable conditions for
flashback. In this case, rich blowout defines the upper stability limit. This critical point is
a function of ammonia volume fraction and of Reynolds number. If the ammonia addition
exceeds the critical point, slightly rich mixtures with $\phi \approx 1.10$ or 1.20 are within the stable
range. This is promising because fueling the combustor with mixtures around these
equivalence ratios is expected to yield low NOx emissions. However, ammonia is known
to be prone to large NO emissions [23] and the possibility to stabilize ammonia-air flames
is not sufficient to constitute practically relevant operating conditions. It is also required
that NO emissions are comparable or smaller than that of typical methane and hydrogen
flames. Therefore, NO emissions were also measured for many of the stable conditions
reported in this chapter. A full study on NO emissions from the combustion of ammonia-air
flames is discussed in chapter 5. In real practice, gas turbines run under elevated
pressures. Therefore, the following chapter discusses flame stability limits of ammonia-air
flames with mixtures similar to those reported here but at elevated pressures up to 5 bar.
Chapter 4

Stability limits at elevated pressures

4.1 Introduction

Understanding flame stability behavior under elevated pressures is of crucial importance for ammonia as a fuel for gas turbines. In the previous chapter, the behavior of flame stability limits of ammonia with mixtures of methane and hydrogen at atmospheric pressure is discussed. The results show that introducing ammonia to the mixtures in a technically premixed combustor, enhances the flame stability range. This range is bounded by a lower limit, lean blowout, and by two upper limits which can be either flashback or rich blowout. The previous chapter shows that the transitional behavior between flashback and rich blowout varies for different fuel mixtures and Reynolds number. Here, we investigate the effects of bulk velocity and of elevated pressures on the transitional behavior of similar fuel mixtures. It is worth mentioning that the combustor used in this work is similar to that used in chapter 3 but the experimental setup is completely different, see chapter 2. Here, the swirl number is fixed at $S_g = 1.00$.

4.2 Ammonia-air flames

Figure 0.1 shows time-averaged broadband images of pure ammonia-air flames for five pressure conditions ranging from 1 to 5 bar for $\varphi = 1.00$, $u_b = 1.40$ m/s, and $S_g = 1.00$. While all flames feature a conical V-shape, the flame becomes more compact as pressure increases. The flame’s base angle slightly widens and the flame’s length increases slowly with the pressure. This is an expected feature and can be explained as follows. While the
bulk velocity is constant, the mass flow rate of the fuel-air mixture becomes larger by the
same factor as pressure. Hence, the amount of fuel-air flow rate at 5 bar is five times larger
than that at 1 bar, while the flow velocity is constant. The yellow hue is typically associated
with ammonia flames, and it is independent of pressure [36,38]. However, the
chemiluminescence intensity is largest for the largest pressure, which is associated to more
intense turbulence and volumetric heat-release rate. The thermal power increases linearly
as pressure increases. It increases from $P_{th} \approx 6.15 \text{kW}$ for 1 bar to $P_{th} \approx 30.75 \text{kW}$ for 5 bar.

Table 0.1. Thermal power ($P_{th}$) for broadband images of ammonia-air flames shown in
Figure 0.1.

<table>
<thead>
<tr>
<th>$P$ (bar)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{th}$ (kW)</td>
<td>6.15</td>
<td>12.30</td>
<td>18.45</td>
<td>24.60</td>
<td>30.75</td>
</tr>
</tbody>
</table>

Figure 0.1. Time-averaged broadband images of pure ammonia-air flames for five different
pressure conditions ranging from 1 to 5 bar for $\phi = 1.00$, $u_b = 1.40 \text{ m/s}$, and $S_g = 1.00$.

Figure 0.2 shows stability limits for pure ammonia-air swirl flames as a function of pressure
ranging from 1 bar to 5 bar for $u_b = 1.40$ and $S_g = 1.00$. The Reynolds number increases
linearly as pressure increases. It increases from $Re = 4000$ for 1 bar to 20,000 bar for 5 bar.
The grey area corresponds to the stable range bounded by the lean blowout (square) and be
rich blowout (circle) limits, see Figure 0.2. The stability range of ammonia-air flames
increases as pressure increases. The equivalence ratio of the stable range remarkably
widens from $\Delta \phi \approx 0.1$ for 1 bar to $\Delta \phi \approx 0.6$ for 5 bar. It is worth mentioning that the
ammonia-air flame at 1 bar in Figure 0.1 is close to the lean blowout limit, see Figure 0.2.
Hence, stabilizing a flame at such conditions is not practical. However, it was observed, from the results reported in the previous chapter, a better flame stability if the bulk velocity increases to \( u_b \approx 1.7 \, \text{m/s} \), equivalent to \( \text{Re} = 5000 \).

Figure 0.2. Stability limits of ammonia-air swirl flames as a function of pressure ranging from 1 to 5 bar for \( u_b = 1.40 \, \text{m/s} \) and \( S_g = 1.00 \). The grey area corresponds to the stable range bounded by lean blowout (square) and rich blowout (circle) limits.

Figure 0.1 shows that the ammonia flame at 1 bar has the largest part of the flame is still located inside of the injection tube and is also expected to be close to the velocity field yielding vortex breakdown [106]. The sudden change of flame structure, most-likely associated to vortex breakdown, may explain the reduced stable range found for ammonia flames at 1 bar and for \( u_b = 1.40 \, \text{m/s} \). Velocity fields were not measured in this study and this hypothesis cannot be verified.
4.3 Ammonia-methane-air flames

4.3.1 Effects of bulk velocity

Figure 0.3 shows time-averaged broadband images of ammonia-methane-air flames at 1 bar for six different bulk velocity conditions ranging from \( u_b = 1.00 \) to 2.00 m/s for \( x_{\text{NH}_3} = 0.60, \varphi = 0.85, \) and \( S_g = 1.00 \). While all the flames feature a conical V-shape, the base angle becomes wider with increasing the bulk velocity from \( u_b = 1.00 \) to 1.40. The flame is longer if \( u_b < 1.40 \), the flow laminarization and vortex breakdown possibly explain this feature. If \( u_b \geq 1.40 \), the flame’s base angle and flame’s length are fairly insensitive to the bulk velocity. However, the fuel-air mass flow rate and volumetric heat-release rate are largest for the largest bulk velocity. These flames feature a white hue, also visible with the naked eye. A similar color has been observed before in [28], but for a very lean ammonia-hydrogen flame. This is different from the yellow hue typically associated with ammonia flames [36,38], see Figure 0.1. Table 0.2 shows that the thermal power increases linearly as bulk velocity increases. Its value is doubled from \( P_{\text{th}} \approx 12.5 \) kW for \( u_b = 1.00 \) to \( P_{\text{th}} \approx 24.7 \) kW for \( u_b = 2.00 \). This is because the fuel mass flow rate has a linear relation with its flow velocity.

<table>
<thead>
<tr>
<th>( u_b ) (m/s)</th>
<th>1.00</th>
<th>1.20</th>
<th>1.40</th>
<th>1.60</th>
<th>1.80</th>
<th>2.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_{\text{th}} ) (kW)</td>
<td>12.5</td>
<td>14.8</td>
<td>17.3</td>
<td>19.6</td>
<td>22.4</td>
<td>24.7</td>
</tr>
</tbody>
</table>
Figure 0.3. Time-averaged broadband images of ammonia-methane-air flames as a function of bulk velocity ranging from 1.00 to 2.00 m/s for $x_{\text{NH}_3} = 0.60$, $\phi = 0.85$, and $S_g = 1.00$.

Figure 0.4 shows direct broadband images of ammonia-methane-air flames for different ammonia concentration and equivalence ratio at elevated pressure of 3 bar for $u_b = 1.40$ m/s and $S_g = 1.00$. Note that it is not possible to stabilize flames with $x_{\text{NH}_3} = 0$ and $x_{\text{NH}_3} = 1$ for the same equivalence ratio due to different stability limits (shown later). The flame’s shape is insensitive of the ammonia additions, but the flame’s length increases slowly with ammonia additions. The flame’s color completely turns from blue hue for pure methane to orange-yellow hue for pure ammonia. While the blue color is mainly attributed to the CH* radical, detailed chemiluminescence properties of ammonia flames are not available to explain the yellow-orange color. However, this color is probably attributed to the NH$_2$ ammonia alpha band and H$_2$O radical [36,108]. Table 0.3 shows the thermal power from the broadband images in Figure 0.4. The thermal power increases from $P_{\text{th}} \approx 12.7$ kW for $x_{\text{CH}_4} = 1$ to $P_{\text{th}} \approx 18.5$ for $x_{\text{NH}_3} = 1$. This is mainly because these flames reported for different fuel-air equivalence ratio, and also methane features a higher caloric value compared to ammonia at stoichiometric, see Table 0.1. The heating value of ammonia is 19 MJ/kg which is less than half of that of methane 50 MJ/kg.
Table 0.3. Thermal power ($P_{th}$) for the broadband images of ammonia-methane-air flames for a different ammonia volume fraction shown in Figure 0.4.

<table>
<thead>
<tr>
<th>$x_{NH3}$</th>
<th>0</th>
<th>0.20</th>
<th>0.40</th>
<th>0.60</th>
<th>0.80</th>
<th>1.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varphi$</td>
<td>0.60</td>
<td>0.62</td>
<td>0.65</td>
<td>0.70</td>
<td>0.80</td>
<td>1.00</td>
</tr>
<tr>
<td>$P_{th}$ [kW]</td>
<td>12.7</td>
<td>13.2</td>
<td>13.7</td>
<td>14.6</td>
<td>16.1</td>
<td>18.5</td>
</tr>
</tbody>
</table>

Figure 0.4. Time-averaged broadband images of ammonia-methane-air swirl flames for different ammonia concentrations and equivalence ratios at 3 bar for $u_b = 1.40$ m/s, $S_g = 1.00$.

Figure 0.5 shows stability limits of ammonia-methane-air flames at elevated pressure of 3 bar as a function of bulk velocity ranging from $u_b = 1.00$ to 1.40 m/s for $S_g = 1.00$.

Regardless of the bulk velocity the equivalence ratio of the lean blowout limit increases slightly with increasing the ammonia mole fraction. It increases from $\varphi \approx 0.58$ at $x_{NH3} = 0$ to $\varphi \approx 0.95$ at $x_{NH3} = 1$. This is an expected behavior, and it is attributed to the combustion characteristics of ammonia compared to that of methane, see Table 0.1. The equivalence ratio of the flammability lower limit slowly increases with ammonia additions. Figure 0.5 shows a slight effect of increasing the bulk velocity on the flashback. The equivalence ratio of the flashback limit increases almost linearly from $\varphi = 0.65$ at $x_{NH3} = 0$ to $\varphi = 77$ at $x_{NH3} = 0.60$. Then, there is a sudden increase to $\varphi \approx 1.00$ for $x_{NH3} = 0.75$ yielding a transition in behavior from flashback to rich blowout. This transition widens the stable range of the ammonia-methane-air flames. The largest stable range is $\Delta \varphi \approx 0.7$ at $x_{NH3} = 0.75$ compared to $\Delta \varphi \approx 0.1$ if $x_{NH3} < 0.75$. The equivalence ratio of the rich blowout limit decreases linearly to $\varphi \approx 1.24$ for $u_b = 1.40$ and to $\varphi \approx 1.36$ for $u_b = 1.00$ as ammonia additions increases to
$x_{\text{NH}_3} = 1$. The higher equivalence ratio for a lower bulk velocity is probably due to the flow laminarization.

Figure 0.5. Stability limits of ammonia-methane-air swirl flames at 3 bar as a function of bulk velocity $u_b = 1.00$ m/s (square), 1.20 m/s (circle), and 1.40 m/s (triangle) for $S_g = 1.00$.

4.3.2 Elevated pressures

Figure 0.6 and Figure 0.7 show time-averaged broadband images of ammonia-methane-air flames at elevated pressures ranging from 1 to 5 bar for $u_b = 1.40$ m/s and $S_g = 1.00$. Figure 0.6 shows fuel-lean conditions for $x_{\text{NH}_3} = 0.60$ at $\varphi = 0.75$, while Figure 0.7 shows fuel-rich conditions for $x_{\text{NH}_3} = 0.80$ at $\varphi = 1.10$. Regardless of pressure, equivalence ratio, and ammonia mole fraction, all flames feature a conical V-shape thanks to the swirl flow. However, it is evident that the flame’s base angle can be wider for different pressures. If the pressure increases, the flame becomes more compact. Figure 0.6 and Figure 0.7 show that the flame length increases slowly with the pressure, except for 1 bar, where the flame

...
is slightly longer than that for 2 bar. This is probably due to flow laminarization. The chemiluminescence intensity is largest for the largest pressure, which is associated to more intense turbulence and volumetric heat-release rate. Table 0.4 and Table 0.5 show the thermal power increases linearly if the pressure rises from 1 to 5 bar. For $x_{\text{NH}_3} = 0.60$, $\varphi = 0.75$, it increases from $P_{\text{th}} \approx 5.2$ kW to $P_{\text{th}} \approx 26$ kW, and it increases from $P_{\text{th}} \approx 7$ kW to $P_{\text{th}} \approx 35$ kW for $x_{\text{NH}_3} = 0.80$, $\varphi = 1.10$.

Table 0.4. Thermal power ($P_{\text{th}}$) for the broadband images of lean ammonia-methane-air flames shown in Figure 0.6.

<table>
<thead>
<tr>
<th>$P$ (bar)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{\text{th}}$ (kW)</td>
<td>5.16</td>
<td>10.33</td>
<td>15.50</td>
<td>20.66</td>
<td>25.82</td>
</tr>
</tbody>
</table>

Figure 0.6. Time-averaged broadband images of ammonia-methane-air flames for elevated pressure ranging from 1 to 5 bar for $x_{\text{NH}_3} = 0.60$, $\varphi = 0.75$, $u_b = 1.40$ m/s, and $S_g = 1.00$.

Table 0.5. Thermal power ($P_{\text{th}}$) for the broadband images of rich ammonia-methane-air flames shown in Figure 0.7.

<table>
<thead>
<tr>
<th>$P$ (bar)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{\text{th}}$ (kW)</td>
<td>6.98</td>
<td>13.96</td>
<td>20.94</td>
<td>27.92</td>
<td>34.91</td>
</tr>
</tbody>
</table>

Figure 0.7. Time-averaged broadband images of ammonia-methane-air flames for elevated pressure ranging from 1 to 5 bar for $x_{\text{NH}_3} = 0.80$, $\varphi = 1.10$, $u_b = 1.40$ m/s, and $S_g = 1.00$. 
Figure 0.8 shows stability limits of ammonia-methane-air swirl flames as a function of pressure ranging from 1 to 5 bar for $u_b = 1.40$ and $S_g = 1.00$. Overall, ammonia flames can be stable under elevated pressures thanks to the swirl flow that induced a recirculation flow downstream of the combustor. Similar studies show stable ammonia turbulent premixed and non-premixed flames in gas turbine-like combustors under high pressure [21, 25, 34, 36, 84].

Regardless of the pressure and as expected, the equivalence ratio of the lean blowout and flashback limits increase as ammonia additions slowly increase. If the pressure increases, the equivalence ratio of all stability limits decreases as the ammonia volume fraction is constant. The largest equivalence ratio difference observed between 1 and 5 bar is $\Delta \phi \approx 0.20$ for $x_{NH3} = 0.60$ at the flashback limit. Increasing the pressure significantly decreases...
the characteristic time scale of the chemical reaction and affects aerodynamic aspects of
the flame through increasing the turbulent burning velocity, yielding a flame flashback at
a lower equivalence ratio [84,116]. Because ammonia has a lower turbulent burning
velocity compared to hydrocarbons, more ammonia additions is required for the
transitional behavior (flashback to rich blowout limit) as pressure increases. The
transitional ammonia addition is $x_{\text{NH}_3} = 0.60$ for 1 bar, $x_{\text{NH}_3} = 0.70$ for 2 and 3 bar, and $x_{\text{NH}_3}$
$\approx 0.75$ for 4 and 5 bar. Regardless of the pressure, the largest equivalence ratio yielding
flashback is close to $\varphi \approx 1.00$. If there is no suitable condition for flashback, rich blowout
takes place, and it decreases with more ammonia additions. It decreases from $\varphi \approx 1.45$ for
$x_{\text{NH}_3} = 0.60$ to as low as $\varphi \approx 1.2$ for pure ammonia flames.

4.4 Ammonia-hydrogen-air flames

4.4.1 Effects of bulk velocity

Figure 0.9 shows time-averaged broadband images of ammonia-hydrogen-air flames at
elevated pressure of 3 bar for three different bulk velocity conditions $u_b = 1.40, 1.60,$ and
1.80 m/s for $x_{\text{NH}_3} = 0.80$, $\varphi = 0.60$, and $S_g = 1.00$. Figure 0.9 shows that the ammonia-
hydrogen-air flames feature conical V-shape and a yellow color, as expected. This color is
probably attributed to the NH$_2$ ammonia alpha band and H$_2$O radical [36,108]. One can
observe that the flame’s base angle widens as the bulk velocity increases. This is an
expected feature because increasing the bulk velocity yields a larger mass flow rate from
the fuel-air mixture. If the bulk velocity increases from $u_b = 1.40$ to 1.80 m/s, the flame’s
length slowly increases and the flame is slightly lifted. The flame stable range for these
flames is shown later.
Figure 0.9. Time-averaged broadband images of ammonia-hydrogen-air flames at 3 bar for $u_b = 1.40, 1.60, \text{ and } 1.80 \text{ m/s for } x_{NH3} = 0.80, \varphi = 0.60, \text{ and } S_g = 1.00$.

Figure 0.10 shows stability limits of ammonia-hydrogen-air flames at elevated pressure of 3 bar as a function of bulk velocity ranging from $u_b = 1.40$ to 1.80 for $S_g = 1.00$. One can observe that the flame stability range is fairly similar. The equivalence ratio of the lean blowout limit increases slowly from $\varphi = 0.18$ at $x_{NH3} = 0.1$ to $\varphi \approx 0.9$ at $x_{NH3} = 1$. Regardless of the bulk velocity, the equivalence ratio of the flashback limit increases with increasing the ammonia concentration from $\varphi \approx 0.24$ at $x_{NH3} = 0.1$ to $\varphi \approx 0.8$ at $x_{NH3} = 0.85$, before the transitional behavior (from flashback to rich blowout) takes place. The equivalence ratio of the rich blowout limit decreases from $\varphi \approx 1.57$ at $x_{NH3} = 0.85$ to $\varphi \approx 1.4$ at $x_{NH3} = 1$. This is an expected behavior as pure ammonia features a lower flammability limit compared to ammonia-hydrogen-air mixtures, see Table 0.1. It is worth mentioning that a larger bulk velocity may be required to observe a significant effect on the flame stability limits. However, investigating a larger bulk velocity, i.e. $u_b > 1.8 \text{ m/s}$, is not within the scope of this work. Instead studying the effect of elevated pressures on the stability limits is of crucial importance, results are shown later.
Figure 0.10. Stability limits of ammonia-hydrogen-air swirl flames at 3 bar $u_b = 1.40$ m/s (square), 1.60 m/s (circle), and 1.80 m/s (triangle) for $S_g = 1.00$.

4.4.2 Elevated pressures

Figure 0.11 and Figure 0.12 show time-averaged broadband images of ammonia-hydrogen-air flames at elevated pressures ranging from 1 to 5 bar for $u_b = 1.40$ m/s and $S_g = 1.00$. Figure 0.11 shows fuel ‘very’ lean conditions for $x_{NH3} = 0.40$ at $\phi = 0.30$, while Figure 0.12 shows flames with higher ammonia concentrations for $x_{NH3} = 0.70$ at $\phi = 0.50$. The white dished line is a reference baseline for the combustor’s outlet. It is interesting to note the color difference in these flames between a white hue and a yellow-orange hue is associated with ammonia additions. A similar white color has been observed before in [28], also for a very lean ammonia-hydrogen flame. This is different from the yellow hue typically associated with ammonia flames [36,38]. Regardless of the pressure, the flames feature conical V-shape. However, the flame lift-off height can be found for different pressure
conditions. Increasing the pressure yields an increase in the lift-off height, and the flame becomes more compact. The chemiluminescence intensity is largest for the largest pressure, which is associated to more intense turbulence and volumetric heat-release rate. Table 0.6 and Table 0.7 show the thermal power increases linearly if the pressure is elevated from 1 to 5 bar. For $x_{\text{NH}_3} = 0.40$, $\varphi = 0.30$, it increases from $P_{\text{th}} \approx 2.5$ kW to $P_{\text{th}} \approx 12.7$ kW, and it increases from $P_{\text{th}} \approx 4.2$ kW to $P_{\text{th}} \approx 21$ kW for $x_{\text{NH}_3} = 0.70$, $\varphi = 0.50$.

Table 0.6. Thermal power ($P_{\text{th}}$) for the broadband images of ammonia-hydrogen-air flames shown in Figure 0.11.

<table>
<thead>
<tr>
<th>$P$ (bar)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{\text{th}}$ (kW)</td>
<td>2.53</td>
<td>5.06</td>
<td>7.59</td>
<td>10.12</td>
<td>12.65</td>
</tr>
</tbody>
</table>

Figure 0.11. Time-averaged broadband images of ammonia-hydrogen-air flames for elevated pressures from 1 to 5 bar for $x_{\text{NH}_3} = 0.40$, $\varphi = 0.30$, $u_b = 1.40$ m/s, and $S_g = 1.00$.

Table 0.7. Thermal power ($P_{\text{th}}$) for the broadband images of ammonia-hydrogen-air flames shown in Figure 0.12.

<table>
<thead>
<tr>
<th>$P$ (bar)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{\text{th}}$ (kW)</td>
<td>4.20</td>
<td>8.40</td>
<td>12.60</td>
<td>16.80</td>
<td>21.01</td>
</tr>
</tbody>
</table>

Figure 0.12. Time-averaged broadband images of ammonia-hydrogen-air flames for elevated pressures from 1 to 5 bar for $x_{\text{NH}_3} = 0.70$, $\varphi = 0.50$, $u_b = 1.40$ m/s, and $S_g = 1.00$. 
Figure 0.13 shows stability limits of ammonia-hydrogen-air swirl flames as a function of pressure ranging from 1 to 5 bar for \( u_b = 1.40 \) and \( S_g = 1.00 \). It is evident that the flame stable range can be found for different pressure. If the ammonia mole fraction is lower than that of hydrogen, \( x_{NH3} \leq 0.5 \), the stable range is as narrow as \( \Delta \phi \approx 0.05 \). This is attributed to the high propensity to flashback due to large hydrogen concentrations in the fuel blend. In addition, increasing the pressure affects aerodynamic aspects of the flame through increasing the turbulent burning velocity, yielding a higher flame instability. On the other hand, ammonia addition reduces the flame turbulence yielding a better flame stability regardless of the pressure. If ammonia addition increasers to a certain value, there are no suitable conditions for flashback and rich blowout takes place. This transitional behavior (from flashback to rich blowout) is dependent on pressure, and it is attributed to the fact that the equivalence ratio at flashback is close to \( \phi \approx 0.8 \) regardless of the pressure and the ammonia addition. However, the transitional ammonia addition increases when the pressure increases. It is \( x_{NH3} = 0.80 \) for 1 bar and \( x_{NH3} = 0.90 \) for 4 and 5 bar. The largest stable range is observed at the transitional ammonia addition. It is approximately \( \Delta \phi \approx 0.9 \) regardless of the pressure. The rich blowout limit decreases with ammonia additions. It decreased from \( \phi \approx 1.57 \) at \( x_{NH3} = 0.8 \) to \( \phi \approx 1.2 \) at \( x_{NH3} = 1 \) for 1 bar. Increasing the pressure allow a larger stable range for ammonia-air flames, see Figure 0.2.
4.4.3 Nitrogen additions at elevated pressures

Dissociating ammonia to produce hydrogen allows boosting the mixture’s chemical reactivity [11]. However, dissociating ammonia produces a hydrogen-nitrogen blend with a 3:1 volume ratio. Blending dissociated ammonia with ammonia-air is promising for fueling gas turbines with a carbon-free fuel. Therefore, ammonia-hydrogen-nitrogen fuel blends with a 3:1 hydrogen:nitrogen volume ratio should be examined at elevated pressures.
Figure 0.14. Stability limits of ammonia-hydrogen-nitrogen-air flames at 1 bar (square) and 3 bar (circle) for $u_b = 1.40 \text{ m/s}$ and $S_g = 1.00$.

Figure 0.14 shows a comparison of measured stability limits of ammonia-hydrogen-nitrogen-air flames at 1 bar (square) and at elevated pressure of 3 bar (circle) for different ammonia fractions and for $u_b = 1.40$ and $S_g = 1.00$. The equivalence ratio of the lower blowout limit slowly increased from $\phi \approx 0.2$ for $x_{\text{NH}_3} = 0.1$ to $\phi \approx 0.95$ for $x_{\text{NH}_3} = 1$. A similar behavior is observed for the flashback limit. The equivalence ratio of both lower blowout and flashback limits decreased by an average of $\phi \approx 0.05$ as pressure increases. If ammonia addition increasers to a certain value, there are no suitable conditions for flashback and rich blowout takes place. This transitional behavior (from flashback to rich blowout) is dependent on pressure. The transitional ammonia addition increases when the pressure increases. It is $x_{\text{NH}_3} = 0.80$ for 1 bar and $x_{\text{NH}_3} = 0.85$ for 3 bar. The largest stable range is observed at the transitional ammonia addition. It is approximately $\Delta \phi \approx 0.9$ regardless of the pressure. As expected, the rich blowout limit decreases with ammonia.
additions regardless of the pressure. This is attributed to the fact that pure ammonia has a lower flammability limit compared to ammonia with mixtures of hydrogen, see Table 0.1.

4.4.4 Comparisons with ammonia-hydrogen-nitrogen-air flames

Figure 0.15 shows the measured stability limits of ammonia-hydrogen-nitrogen-air flames at 3 bar and are repeated from Figure 0.14.

Figure 0.15. Stability limits of ammonia-hydrogen-air flames without nitrogen (square) and with nitrogen (circle) at 3 bar for $u_b = 1.40$ m/s and $S_g = 1.00$.

Here, we compare the stability limits of ammonia-hydrogen-air flames without (square) and with (circle) a 3:1 hydrogen:nitrogen volume ratio. One can observe that the equivalence ratio for the stability limits is similar even with nitrogen addition. However, the transitional behavior (flashback to rich blowout) can be found different with the nitrogen addition. It is $x_{NH3} = 0.85$ for ammonia-hydrogen-air flames and $x_{NH3} = 0.80$ for
that with nitrogen addition. The largest stable range is observed at the transitional ammonia addition. It is approximately $\Delta \varphi \approx 0.9$ for flames with and without nitrogen addition.

### 4.5 Summary

The flame stability limits of ammonia-air mixtures with methane and with hydrogen were measured in a laboratory-scale swirl combustor at elevated pressures. The flame stability limits show a similar behavior to that reported in the previous chapter at atmospheric pressure. However, the pressure effect on the flame stability here is evident. Gradually replacing methane/hydrogen with ammonia increases the equivalence ratios leading to lean blowout and to flashback. This is attributed to the decreased reactivity associated with ammonia addition. If the fuel mixture does not yield suitable conditions for flashback, rich blowout takes place. This transitional behavior (flashback to rich blowout) is a function of the ammonia volume fraction in the fuel mixture and of pressure. At a fixed pressure, ammonia-methane-air flames yield a wider stability range in comparison to ammonia-hydrogen-air flames. This is attributed to the rapid reactivity associated with hydrogen flames. If the pressure increases, regardless of the fuel mixture, more ammonia volume fraction is required to avoid flame flashback. Slightly rich ammonia mixtures with $\varphi \approx 1.10$ or 1.20 and at elevated pressures, 5 bar, are within the stable range. Operating the combustor around these equivalence ratios is expected to yield low NO emissions. On the other hand, ammonia-hydrogen-air flames with and without nitrogen addition are stable for ‘very’ lean equivalence ratio. These flames are also expected to produce low NO emissions as shown in Chapter 5. The largest stable range is observed at the transitional ammonia
addition on methane and on hydrogen mixtures. It is approximately \( \Delta \phi \approx 0.9 \) regardless of the pressure.
Chapter 5

Exhaust emissions

5.1 Introduction

The swirl combustor used in this study allows stabilizing ammonia-methane-air and ammonia-hydrogen-air flames for a wide range of ammonia additions and equivalence ratios at atmospheric pressure, chapter 3, and at elevated pressures, chapter 4. It is worth mentioning that the range of stable equivalence ratios increases with ammonia addition, which is contrary to what typically intuited for ammonia. However, ammonia is known to be prone to large NO emissions [23] and the possibility to stabilize ammonia flames is not sufficient to constitute practically relevant operating conditions. It is also required that NO emissions are comparable or smaller than that of typical methane-air flames. Therefore, the mole fractions of NO emissions are discussed here for selected stable flames from chapter 3 and chapter 4, and as a function of ammonia fraction and equivalence ratio. The NO measurements are reported at atmospheric and at elevated pressures conditions. To allow fair comparisons between rich and lean cases with different air dilutions, NO mole fractions are normalized for a 6% O₂ mole fraction following the procedure described by [104]. This normalization is only applied on measurements at atmospheric pressure conditions.
5.2 Ammonia-methane-air flames

5.2.1 NO emissions

Figure 0.1 shows measured exhaust NO mole fractions as a function of equivalence ratio for four different ammonia additions $x_{\text{NH}_3} = 0.50, 0.60, 0.80,$ and $1.00$ for $S_g = 1.00$ and $Re = 5000$. Note that for each ammonia addition, the range of available equivalence ratios is limited by the flames’ stability limits (see Figure 0.5).

Figure 0.1. Measured exhaust NO concentration in (ppm) for $x_{\text{NH}_3} = 0.50$ (square), 0.60 (circle), 0.80 (triangle), and 1.00 (diamond) for $S_g = 1.00$ and $Re = 5000$.

In this study, the largest measured NO mole fraction is 6540 ppm and it is reported for $x_{\text{NH}_3} = 0.50$ and $\phi = 0.85$. A few conditions yield NO concentrations smaller than the analyzer’s sensitivity $\sim$100 ppm. For $x_{\text{NH}_3} = 0.60$, the NO concentration increases when the equivalence ratio increases from $\phi = 0.70$ to $\phi = 0.85$. Although some data points are
missing due to blowout, this trend most likely applies as well to the other ammonia
additions investigated here: \(x_{\text{NH}_3} = 0.50, 0.80, \) and \(1.00\). For \(\phi > 0.85\), the NO concentration
decreases as the equivalence ratio decreases. The NO concentration is smaller than
100 ppm for \(x_{\text{NH}_3} = 0.50\) and \(\phi = 1.10\). These trends are compatible with that recently
measured in similar premixed swirl flames by Okafor \textit{et al.} [31]. Overall, reasonably low
NO concentrations (< 100 ppm) can only be found for rich equivalence ratios, and this is
consistent with previous studies [9,31].

Figure 0.1 also shows that for a fixed equivalence ratio, the NO concentration decreases as
the ammonia addition increases. For \(\phi = 0.85\), increasing the ammonia addition from \(x_{\text{NH}_3}
= 0.50\) to \(1.00\) decreases the NO concentration by a factor of \(~6\) from 6540 ppm to
1025 ppm. Effects of the ammonia addition are further analyzed with Figure 0.2 that plots
the measured NO concentration as a function of ammonia addition for different
equivalence ratios \(\phi = 0.70, 0.85, 1.00, \) and \(1.05\). For \(x_{\text{NH}_3} > 0.50\) and \(\phi \geq 0.70\), the NO
concentration consistently decreases with ammonia addition. For \(\phi = 0.70\), the NO
concentration increases slightly when the ammonia addition increases from \(x_{\text{NH}_3} = 0.20\) to
0.50. These trends are in agreement with those reported earlier by others [19,32,117].

Figure 0.1 shows that pure ammonia-air flames have better NO performances compared to
ammonia-methane-air flames across a large range of equivalence ratios. This is an expected
feature and reported earlier in the literature [23,96,118]. This behavior is attributed to the
role of OH radicals in the NO chemical pathways of ammonia-methane-air flames. Large
OH radical concentrations promote the oxidation of \(\text{NH}_2\) and \(\text{NH}\) radicals leading to NO
production [119,120]. The production of OH radicals is smaller in pure ammonia-air flames
than in ammonia-methane-air flames, yielding lower NO concentrations. Similarly, large OH radical concentrations are found for slightly lean equivalence ratios ($\phi \approx 0.85$) compared to rich cases, promoting NO. These slightly lean equivalence ratios do not lead to large NO concentrations in methane-air flames because NH$_2$ and NH radicals are not present.

Table 0.1 shows that ammonia at a fixed equivalence ratio features a lower adiabatic flame temperature compared to methane. Therefore, it is reasonable to think that increasing ammonia addition at a fixed equivalence ratio reduces the temperature downstream of the swirl flame. As a consequence, it is possible that thermal NOx pathways also play some role in the reduction of the NO concentration observed in Figure 0.2. However, revealing the relative contribution of thermal NO production to the total NO production requires a detailed analysis of all chemical pathways and is beyond the scope of this study.
Figure 0.2. Measured exhaust NO concentrations in (ppm) for $\phi = 0.70$ (diamond), 0.85 (pentagon), 1.00 (right-pointing triangle), and 1.05 (left-pointing triangle) for $S_g = 1.00$ and Re = 5000.

Figure 0.2 shows that good NO performances are obtained for slightly rich mixtures and Figure 0.5 shows that these equivalence ratios yield stable flames for a large range of ammonia additions. Therefore, these operating conditions are practically relevant. This was also reported before [9] for a subset of the operating conditions examined here. However, a second combustion stage is required to burn the excess ammonia and avoid efficiency and unburned ammonia emissions penalties [21,31]. Figure 0.2 also shows that good NO performances cannot be obtained for non-marginal ammonia additions and lean equivalence ratios. Even though the NO concentration decreases when the equivalence ratio becomes small enough (most-likely due to a reduced OH radical concentration), blowout occurs before good NO performances can be recovered. The trade-off between NO and unburned ammonia emissions implies that the current combustor performs
optimally for $\varphi \sim 1.10$ for ammonia additions in excess of 50%. Recent work by Valera-Medina \textit{et al.} [28] suggests that blending ammonia with hydrogen instead of methane alleviates this issue because flames with very lean equivalence ratios may be stabilized due to the highest reactivity of hydrogen. Measuring the NO performances for hydrogen-ammonia-air mixtures with this swirl combustor is discussed later in this chapter.

\subsection*{5.2.2 $O_2$ concentrations}

Figure 0.3 shows measured excess oxygen in exhaust gas from ammonia-methane-air flames as a function of equivalence ratio for $x_{NH3} = 0.50$ (square), $x_{NH3} = 0.60$ (circle), and $x_{NH3} = 0.80$ (triangle) and for $S_g = 1.00$ and Re = 5000. Regardless of the ammonia volume fraction in the fuel mixture, the oxygen concentration decreases with increasing the equivalence ratio. It decreases from 6\% for $\varphi = 0.70$ to less that 1\% for stoichiometric. At a fixed equivalence ratio, the oxygen concentration is larger for mixtures with $x_{NH3} = 0.80$ in comparison to $x_{NH3} = 0.50$. 
Figure 0.3. Measured exhaust O$_2$ concentrations for ammonia-methane-air flames for $x_{\text{NH}_3} = 0.50$ (square), 0.60 (circle), and 0.80 (triangle) and for $S_g = 1.00$ and $Re = 5000$.

5.2.3 CO$_2$ concentrations

Figure 0.4 shows measured CO$_2$ concentrations for ammonia-methane-air flames as a function of equivalence ratio for $x_{\text{NH}_3} = 0.50$ (square), $x_{\text{NH}_3} = 0.60$ (circle), and $x_{\text{NH}_3} = 0.80$ (triangle) and for $S_g = 1.00$ and $Re = 5000$. The CO$_2$ concentration is almost the same for $x_{\text{NH}_3} \leq 0.60$ and $0.7 \leq \phi \leq 1$. Then, the concentration decreases linearly from 2.5% for $\phi = 1$ to 1.8% for $\phi = 1.2$. For higher ammonia concentrations, $x_{\text{NH}_3} = 0.80$, the CO$_2$ concentration has a steeper slope. It decreases from 2% for $\phi = 0.95$ to 1% for $\phi = 1.2$. At a fixed equivalence ratio, the CO$_2$ concentration decreases with ammonia additions. This is an expected feature because ammonia is a carbon-free fuel. Therefore, the CO$_2$ concentration decreases as the ammonia addition increases in the fuel mixture.
Figure 0.4. Measured CO$_2$ concentrations for ammonia-methane-air flames for $x_{NH3} = 0.50$ (square), 0.60 (circle), and 0.80 (triangle) and for $S_g = 1.00$ and $Re = 5000$.

5.2.4 CO concentrations

Figure 0.5 shows measured CO concentrations for ammonia-methane-air flames in parts per million (ppm) as a function of equivalence ratio for $x_{NH3} = 0.50$ (square), $x_{NH3} = 0.60$ (circle), and $x_{NH3} = 0.80$ (triangle) and for $S_g = 1.00$ and $Re = 5000$. Low CO concentration as low as 100 ppm is measured for lean fuel mixtures as a result of a complete combustion. At stoichiometric, the CO concentration sharply increases to a maximum value around 1400 ppm regardless of the ammonia volume fraction. This sudden increase is associated to the low oxygen concentration yielding incomplete combustion. The CO concentration decreases slightly to 1300 for $x_{NH3} = 0.80$ and 1200 for $x_{NH3} = 0.60$ as the equivalence ratio increases.
Figure 0.5. Measured CO concentrations for ammonia-methane-air flames in (ppm) for $x_{\text{NH}_3} = 0.50$ (square), 0.60 (circle), and 0.80 (triangle) and for $S_g = 1.00$ and $Re = 5000$.

### 5.3 Ammonia-hydrogen-air flames

#### 5.3.1 NO emissions

Ensuring flame stability is not sufficient in practical combustion devices. It is also necessary that harmful exhaust emissions remain within acceptable limits. For this reason, exhaust NO emissions were measured for operating conditions within the stability limits for ammonia-hydrogen-air flames. Figure 0.6 shows the measured NO mole fraction in the exhaust of ammonia-hydrogen-air flames as a function of equivalence ratio for four different ammonia fuel fractions $x_{\text{NH}_3} = 0.70$, 0.80, 0.90, and 1.00 for $S_g = 1.00$ and $Re = 5000$. To allow fair comparisons between rich and lean cases with different air dilutions, NO mole fractions are normalized for a 6% $O_2$ mole fraction following the procedure described by [104]. Note that the range of equivalence ratios accessible for each
ammonia fuel fraction is restricted by the flames’ stability limits (see Figure 0.8). Figure 0.6 shows that the range of measured NO mole fractions is large, from less than 100 ppm, for example for $\phi \leq 0.50$ or $\phi \geq 1.10$, to around 4,000 ppm for $x_{NH3} = 0.80$ and $\phi = 0.85$.

Figure 0.6 Measured exhaust NO mole fraction in ammonia-hydrogen-air flames for $x_{NH3} = 0.70$ (triangle), 0.80 (circle), 0.90 (diamond), and 1.00 (square) for $S_g = 1.00$ and $Re = 5000$. Regardless of equivalence ratio, the NO mole fraction decreases when the ammonia fuel fraction increases. Pure ammonia has a better NO performance than ammonia-hydrogen fuel blends. This feature is in agreement with the literature [23,96,121], and may have various causes. A similar trend was observed before for methane-ammonia blends [122] and was attributed to the self-inhibiting effects of ammonia on its oxidation, leading to lower NO emissions. This can also be partly explained by the larger concentration of OH radicals existing when the hydrogen fraction in the fuel is larger, which positively contribute to the production of NO [21,29,31,36,37,117,120,123]. Finally, at a given
equivalence ratio, the flame temperature decreases with ammonia addition (see Table 0.1), in turn decreasing NO production via thermal pathways [120,124], which still accounts for a fraction of the total NO production [21,29,31,36,37,117,120,123].

For any ammonia fuel fraction, relatively large NO mole fractions are found for slightly lean to stoichiometric equivalence ratios. This is consistent with many previous studies [9,21,125,22,25,28,31,36,37,84,117] and is attributed to the large OH mole fraction that contributes to NO formation via fuel NOx pathways [21,29,31,36,37,117,119,120,123]. On the other hand, low NO mole fractions (< 100 ppm) are found for very lean or rich (ϕ ≥ 1.10) equivalence ratios. Results for rich conditions are also consistent with existing literature [9,29,31] and can be explained as follows. As the equivalence ratio progressively increases towards stoichiometric and rich, the increased availability of NH₂ radicals promotes the reaction NH₂ + NO → H₂O + N₂, which consumes NO [29,120].

The very good NO emission performance found for very lean equivalence ratios is of particular interest here. Good performance has been reported before for rich equivalence ratios but this implied that a second combustion stage is required to avoid unburnt ammonia and efficiency penalties [20,31,118]. The data reported in Figure 0.6 demonstrate that stable operation with competitively good NO performance may be achieved without secondary combustion stage if sufficiently lean ammonia-hydrogen fuel blends are used. This is in line with results of [28]. Figure 0.6 also shows that some hydrogen enrichment is required to stabilize these very lean flames. With this swirl combustor, good NO performance is possible for ϕ ≤ 0.70 and x_{NH₃} = 0.90, ϕ ≤ 0.55 and x_{NH₃} = 0.80, or ϕ ≤ 0.50 and x_{NH₃} = 0.70. Note that methane enrichment instead of hydrogen enrichment did not allow stabilizing flames lean enough to achieve good NO performance in [38] even though
decreasing equivalence ratio below $\varphi \leq 0.85$ did also slightly improve performance for $x_{NH3} = 0.50$ and $x_{NH3} = 0.60$.

5.3.2 Nitrogen additions

Figure 0.7 shows the measured NO mole fraction in the exhaust of ammonia-hydrogen-nitrogen-air flames (3:1 hydrogen:nitrogen volume ratio) as a function of equivalence ratio for three different ammonia fuel fractions $x_{NH3} = 0.70$, 0.80, and 0.90 for $S_g = 1.00$ and $Re = 5000$. Again, results for ammonia-hydrogen fuel blends (dashed lines) are repeated from Figure 0.6 for comparison purposes. Figure 0.7 shows that nitrogen dilution does not drastically alter exhaust NO mole fractions. Slightly better NO performance is found for lean equivalence ratios. To corroborate these measurements, the NO concentration in the post-flame region of 1-D laminar flames has been computed with Chemkin and the detailed chemistry mechanism from Okafor et al. [37] for $x_{NH3} = 0.80$ and a range of equivalence ratios. Results obtained for ammonia-hydrogen and ammonia-hydrogen-nitrogen fuel blends are shown in Figure 0.8. Trends of computed NO concentration with equivalence ratio and nitrogen dilution in laminar flames match that measured in the swirl flames. For $x_{NH3} = 0.80$ and no nitrogen dilution, peak NO concentration occurs around $\varphi = 0.85$ in both simulations and experiments. It is 4000 ppm in the experiments and 3400 ppm in the simulations. The NO concentration drops rapidly for either leaner or richer equivalence ratios. Regardless of equivalence ratio, nitrogen dilution (3:1 hydrogen to nitrogen volume ratio) decreases NO production in the simulations. For $\varphi = 0.85$, it decreases from 3400 ppm to 3000 ppm when nitrogen is introduced. For lean conditions, measured effects of nitrogen dilution on the NO concentration are well predicted by 1-D simulations. For rich
conditions, 1-D simulations slightly over predict the decreases of NO production associated with nitrogen dilution. Regardless, it can be said that measured NO concentrations reported in Figure 0.7 are consistent with 1-D simulations.

All the conditions reported in Figure 0.7 feature an adiabatic flame temperature much below that of a stoichiometric methane-air flame, which is known to produce around 100 ppm of NO [31], mostly through the thermal NOx pathways. However, the measured exhaust NO concentration is much above 100 ppm for most conditions (except $\phi > 1.1$) reported in Figure 0.7. This shows that thermal NOx pathways can only be responsible for a marginal fraction of the total NO produced. This is consistent with the literature [21,29,31,36,37,117,119,120,123]. For most conditions reported in Figure 0.7, NO formation is mainly through the fuel NOx pathways and is sensitive to the OH concentration [21,29,31,36,37,117,120,123]. The slight reduction in NO exhaust concentration observed for ammonia-hydrogen-nitrogen compared to ammonia-hydrogen is most likely due to the reduction of OH concentration associated with N$_2$ dilution. The thermal NOx pathways are larger contributors for rich conditions with NO concentrations around or below 100 ppm [123]. Figure 0.7 demonstrates that partially cracking ammonia into hydrogen-nitrogen and tailoring “very” lean ammonia-hydrogen-nitrogen-air mixtures are promising strategies to boost flame stability and improve NO performance in swirl combustors. Note that NO$_2$ and N$_2$O were not measured in this study but are also important to consider due to their toxicity and contributions to global warming. This will be done at a later stage. This could be particularly important for the “very” lean flames, which have been shown in [31] to generate large amounts of N$_2$O.
Figure 0.7 Measured exhaust NO mole fraction in ammonia-hydrogen-nitrogen-air flames for $x_{NH3} = 0.70$ (triangle), 0.80 (circle), 0.90 (diamond), and 1.00 (square) for $S_g = 1.00$ and $Re = 5000$. Dashed lines are repeated from Figure 0.6.

Figure 0.8 NO concentration in the burned products of a laminar flames computed with Chemkin and the detailed chemistry mechanism from Okafor et al. [37].
5.3.3 Comparisons with ammonia-methane-air flames

Figure 0.9 shows the measured NO mole fraction in the exhaust of ammonia-hydrogen-air and ammonia-methane-air flames as a function of equivalence ratio for $x_{NH3} = 0.80$. These data are repeated from Figure 0.6 for ammonia-hydrogen-air and from [38] for ammonia-methane-air. For $x_{NH3} = 0.80$ and $\phi \geq 0.80$, trends and numbers of exhaust NO mole fractions are comparable for ammonia-hydrogen-air and ammonia-methane-air flames. The NO mole fraction is only slightly higher for ammonia-hydrogen fuel blends than for ammonia-methane-air fuel blends. The peak NO mole fraction is 4065 ppm for ammonia-hydrogen at $\phi = 0.80$ compared to 3750 ppm for ammonia-methane at $\phi = 0.80$. The likely reduction of NO concentration if equivalence ratio could be reduced below $\phi = 0.8$ for ammonia-methane cannot be confirmed with Figure 0.9 due to flame stability limit restrictions. However, results of [31] show that NO production also reduces in ammonia-methane-air flames if the equivalence ratio is sufficiently decreased. Trends are similar for ammonia-hydrogen and ammonia-methane because, in both cases, NO is mainly produced via fuel NOx pathways [21,29,31,36,37,117,119,120,123], except for equivalence ratios sufficiently above unity. However, while the HCN intermediate plays a large role in the formation of NO via fuel NOx pathways for ammonia-methane blends [31,120], HCN is not present with ammonia-hydrogen blends and pure ammonia and the HNO intermediate contributes instead [21,36,37,123]. Regardless, the increase of NO production observed as the equivalence ratio increases towards $\phi \approx 0.8$ is due to the increasing concentration of OH radicals that positively contributes to NO formation via fuel NOx pathways [21,29,31,36,37,117,120,123]. As the equivalence ratio exceeds $\phi \approx 0.8$ and increases
towards rich, the increased availability of NH₂ radicals promotes the reaction

\[ \text{NH}_2 + \text{NO} \rightarrow \text{H}_2\text{O} + \text{N}_2, \]

which consumes NO [29,120].

Figure 0.9 Measured exhaust NO mole fraction in ammonia-methane-air (yellow triangles) and ammonia-hydrogen-air (black circles) flames for \( x_{\text{NH}_3} = 0.80 \).

### 5.3.4 O₂ concentrations

Figure 0.10 shows measured excess oxygen in exhaust gas from ammonia-hydrogen-air flames as a function of equivalence ratio for \( x_{\text{NH}_3} = 0.70 \) (square), \( x_{\text{NH}_3} = 0.80 \) (circle), and \( x_{\text{NH}_3} = 0.90 \) (triangle) and for \( S_g = 1.00 \) and \( \text{Re} = 5000 \). Regardless of the ammonia volume fraction in the fuel mixture, the oxygen concentration decreases with increasing equivalence ratio. This is an expected feature as more oxygen is consumed with increasing the fuel to air equivalence ratio. It decreases from 15% for \( \phi = 0.40 \) to less that 1% for stoichiometric. At a fixed equivalence ratio, the oxygen concentration is quite similar for mixtures with \( x_{\text{NH}_3} \geq 0.70 \).
5.4 NO performance at elevated pressures

This research is an introductory study to investigate the feasibility of operating a micro gas turbine with ammonia fuel mixtures. Such gas turbines run at elevated pressures around 4 bar. Therefore, investigating the effect of pressures on NO performance is of crucial importance using our swirl combustor. Here, regains from the previous sections with stable flames and low NO mole fractions are studied under pressures up to 4 bar as a function of equivalence ratio. The swirl combustor confinement, fuel-air flow velocity, and flue gas analyzer are different here from those used at atmospheric pressure conditions. Therefore, comparison of our previously reported quantitative data is unmeaningful. However, it has been reported in the literature that increasing the pressure reduces the NO emissions [22,23,31,84,96]. This is because the OH radical pool decreases as pressure increases, while OH is attributed to the production of NO emissions [31]. This means lower NO mole
fractions can be achieved from our swirl combustor at elevated pressures, demonstrating a great potential for fueling micro gas turbines with ammonia fuel mixtures.

5.4.1 ‘Very’ lean equivalence ratio

Figure 0.11 shows the measured NO mole fraction in the exhaust of ammonia-hydrogen-air flames as a function of pressure for different ammonia fuel fractions $x_{\text{NH}_3} = 0.75, 0.80, \text{ and } 0.85$ and for ‘very’ lean equivalence ratios $\varphi = 0.50 \text{ and } 0.55$ for $S_g = 1.00 \text{ and } u_b = 1.40 \text{ m/s}$.

![Figure 0.11 Measured exhaust NO mole fraction in ammonia-hydrogen-air flames under pressures up to 4 bar for ‘very’ lean equivalence ratio and $u_b = 1.40 \text{ m/s}$.

To better understand the effect of nitrogen addition on ammonia-hydrogen-air flames, Figure 0.11 also shows NO mole fraction in flames with nitrogen addition (3:1 hydrogen:nitrogen volume ratio) for $x_{\text{NH}_3} = 0.85 \text{ and } \varphi = 0.50$. Here, the NO mole fraction
is independent on the pressure. However, good NO performance for ‘very’ lean equivalence ratio is reported as low as ~ 100 ppm. Such low NO mole fractions agree with our previous data at atmospheric pressure conditions [105]. The low NO concentration for the leanest equivalence ratio is attributed to the weak presence of OH radical, which promotes production of NO [31]. For a similar reason, it is evident that the NO mole fraction decreases as the ammonia volume fraction increases, see Figure 0.11. The slight reduction in NO mole fraction observed for nitrogen addition to ammonia-hydrogen is most likely due to the reduction of OH concentration associated with N₂ dilution [105].

5.4.2 Lean equivalence ratio

Figure 0.12 shows the measured NO mole fraction in the exhaust of ammonia-hydrogen-air flames for ammonia fraction $x_{NH₃} = 0.90$ under four different pressures for lean equivalence ratios ($0.70 \leq \varphi \leq 0.90$) and for $S_g = 1.00$ and $u_b = 1.40$ m/s.
Figure 0.12 Measured exhaust NO mole fraction in ammonia-hydrogen-air flames under pressures up to 4 bar and for lean equivalence ratio (0.70 ≤ \( \varphi \) ≤ 0.90), \( x_{NH3} = 0.90 \), and \( u_b = 1.40 \) m/s.

Now the effect of pressure on the NO mole fraction is evident. The NO concentration decreases as the pressure increases, and this agrees with the literature [22,23,31,84,96,126]. Duynslaegher et al. [126] reported from a simulation work on ammonia combustion at elevated pressures that both pressure and equivalence ratio have a major impact on the formation of NO due to influencing the kinetic reactions of the fuel NO formation pathways. Figure 0.12 shows a maximum NO value for equivalence ratio \( \varphi = 0.90 \) and 1 bar, and it decreases from 3637 ppm to 2230 ppm as the pressure increases to 4 bar. Good NO performance as low as ~ 200 ppm is observed for \( \varphi \leq 0.75 \) if the pressure increases to 4 bar. This can be explained as follows. The two key radical species OH and O are playing a vital role in the production of NO. As pressure increases, the reaction rate of OH + H + M \( \leftrightarrow \) H₂O + M increases significantly, yielding a lower concentration of OH radical
In addition to the OH formation, the chemical reaction time scale is reduced as pressure increases, yielding an increase in the ammonia residence time and enhancement of ammonia air mixing. This tends to a reduction of NO emissions in the exhaust of ammonia-air flames as pressure increases [21], and this is promising for fueling micro gas turbines with ammonia fuel mixtures.

5.4.3 Rich equivalence ratio

Figure 0.13 shows the measured NO mole fraction in the exhaust of ammonia-methane-air flames for ammonia fraction $x_{\text{NH}_3} = 0.80$ under high pressures up to 4 bar for rich equivalence ratios ($1.10 \leq \phi \leq 1.30$) and for $S_e = 1.00$ and $u_b = 1.40 \text{ m/s}$. Regardless of the equivalence ratio, the NO mole fraction decreases as the pressure increases. This is because of the lower OH concentration under high pressure, as explained earlier in this document and by others [21,25,36,80,84]. Figure 0.13 shows a maximum NO value for equivalence ratio $\phi = 1.10$ and 2 bar, and it decreases from 3966 ppm to 2700 ppm as the pressure increases to 4 bar. The NO concentration for equivalence ratio $\phi = 1.10$ and 1 bar exceeded the maximum limit of the flue gas analyzer $\sim 4000$ ppm, and therefore it is not reported here. Good NO performance as low as $\sim 200$ ppm is observed for $\phi \geq 1.20$ if the pressure increases to 4 bar. Similar results were obtained by Somarathne et al. [84] who reported a $\sim 144$ ppm NO performances in ammonia-air flames for $\phi \geq 1.25$ and 5 bar. Valera-medina et al.[25] also reported competitive NO emissions ($< 100$ ppm) for equivalence ratios in excess of $\phi \approx 1.3$ and for 2 bar in ammonia-methane flames. However, rich operation implies large unburned ammonia emissions and a secondary combustion stage is needed to
ensure globally-lean operation and to avoid high emissions and low efficiency penalties [20,31,34,118].

Figure 0.13 Measured exhaust NO mole fraction in ammonia-methane-air flames under pressures up to 4 bar for rich equivalence ratio (1.10 ≤ φ ≤ 1.30), xNH3 = 0.80, ub = 1.40 m/s.

Figure 0.14 shows the measured NO mole fraction in the exhaust of ammonia-methane-air flames for xNH3 = 0.80 and different bulk velocity ub = 1.40 m/s (down-pointing triangle), 1.6 m/s (triangle), 1.7 m/s (circle), and 1.8 m/s (square) for rich equivalence ratio (1.10 ≤ φ ≤ 1.30) and for Sg = 1.00 and 2 bar. Figure 0.14 shows a maximum NO value for equivalence ratio ub = 1.40 and φ = 1.10, and it decreases from 3966 ppm to 3398 ppm as the bulk velocity increases to 1.80 m/s. Good NO performance as low as ~ 200 ppm is observed for φ ≥ 1.20 if the bulk velocity increases to 1.80 m/s. This may be explained as follows. Performance of ammonia fueling gas turbines is limited by turbulent diffusion and by chemical reaction kinetics, which is relatively slow compared to hydrocarbons [13].
Therefore, the NO production is a tradeoff between residence time and mixing process. At a lower bulk velocity, the residence time is longer between ammonia and air. However, the mixing process is less efficient yielding a lower combustion efficiency. This in turn may lead to a higher NO production. Prior work [84] illustrated how a different mixing process by splitting flow of ammonia fuel can reduce NO emissions.

Figure 0.14 Measured exhaust NO mole fraction in ammonia-methane-air for $x_{\text{NH}_3} = 0.80$ and $u_b = 1.40$ m/s (down-pointing triangle), 1.6 m/s (triangle), 1.7 m/s (circle), and 1.8 m/s (square) for rich equivalence ratio ($1.10 \leq \phi \leq 1.30$) and under 2 bar.

5.5 Summary

The combustion of ammonia fuel is promoting the propensity to produce a large quantity of NO emissions. This is attributed to the nitrogen atom in the NH$_3$ compound and to the concentration of two key radical species OH and O. The NO production increases as the OH and O increase in the fuel products, and this is a function of ammonia volume fraction.
in the fuel mixture, equivalence ratio, and pressure. At a fixed equivalence ratio, increasing
the ammonia fuel fraction decreases NO emissions. Large amount of NO is associated to
slightly lean and stoichiometric ammonia flames with mixtures of methane/hydrogen. This
conclusion is consistent with previous studies by others. However, Low NO concentration
can be achieved from slightly rich, $\phi \approx 1.05$, ammonia-air mixtures with
methane/hydrogen. More importantly, very lean ammonia-hydrogen-air flames also yield
NO mole fractions limited to $\sim 100$ ppm. Adding nitrogen with a 3:1 hydrogen:nitrogen
volume ratio marginally decreases NO emissions. The NO concentration decreases as the
pressure increases, and this agrees with prior work in the literature. Good NO performance
is reported to $\sim 150$ ppm from ammonia-hydrogen-air flames for $\phi \leq 0.75$ and under
pressures up to 4 bar, demonstrating a great potential for fueling gas turbines with ammonia
fuel mixtures and with low NO emissions.
Chapter 6

Lessons learned

Ammonia combustion is relatively a new topic. Only a few detailed experimental works on burning ammonia has been published so far, and this dissertation document is one of them. Therefore, it is vital to share the main lessons learned from this work. This chapter focuses on challenges of ammonia as a fuel and its combustion, given suggestions on how to deal with these complications or even avoid them before happening.

6.1 Handling ammonia fuel

6.1.1 Enclosure, gas cabinet, and NH₃ sensor

One of the first challenges when dealing with ammonia is a safety challenge. This is because ammonia is toxic, and it may be fetal if someone exposed to 2000-4000 ppm for less than half an hour. Therefore, extra care and safety procedures should be applied when dealing with ammonia and its combustion products. Here, we suggest to always carry on and use ammonia sensor to detect NH₃ gas leakage as low as 5 ppm. We also suggest to place the NH₃ cylinder inside a gas cabinet with gas detectors. Building an enclosure over the experimental setup to include burner, confinement, and exhaust gases is another important suggestion. Figure 0.1 shows our experimental setup with and without an enclosure.
Figure 0.1. Experimental setup with and without enclosure.

6.1.2 Valves, MFC, and tubing

Ammonia is corrosive to some materials, see materials compatibilities of ammonia in [6]. Therefore, careful selection of materials in valves, MFCs, and tubing is vital. Stainless steel material and Teflon are widely used. However, they cannot be always used such as in parts especially for sealings in valves and MFCs. Therefore, a customized mass flow controller should be used to gas leakage associated with corroded materials. In our work, we used BROOKS mass flow controller model SLA5851A1BEB1C1A1, see Figure 0.2. This version has Viton as valve seat material and EPDM for other internal seals.
Figure 0.2. BROOKS mass flow controller with materials compatibility of ammonia.

6.1.3 Heating jacket and bench scale

As mentioned in chapter 2, ammonia is stored at 8 bar and at room temperature conditions. Although this low pressure has advantages on safety, transportation, and cost, it is difficult to extract NH\textsubscript{3} gas from the cylinder to the burner especially in cases at high flow rate and at elevated pressures. One way we used to overcome this challenge is a heating jacket, see Figure 0.3. We utilized a heating jacket from LMK Thermosafe with 285W/240v maximum range and fitted with 0-85°C temperature regulator. The heating jacket can also minimize cylinder frost. The frost is a result of the vaporization process, when the ammonia liquid gas draws heat from the cylinder walls to boil and vaporize.
Figure 0.3. Ammonia cylinder with a heating jacket from LMK Thermosafe.

The gauge can also face freezing problems, but the heating jacket can minimize them. Because, ammonia is stored at low pressure, 8 bar, it is difficult to read that from its pressure gauge downstream of the cylinder. This is due to most pressure gauges have a large range, and therefore 8 bar is significantly small to be detected. As a result, it is not easy to know if the cylinder is empty or full. One suggestion could be using a weight scale. The cylinder has a well-known weight, which can be subtracted from the total weight of the cylinder plus the liquid ammonia. This is an easy way to monitor the remaining amount of the fuel inside the cylinder.

6.2 Flame topology

6.2.1 Flashback

Flame flashback can damage the burner components and also propagate to the gas cylinder yielding a major explosion. In our experiments we can easily recognize a flame flashback, see Figure 0.4. Basically, the flame goes upstream of the burner outlet and stays inside the
burner geometry. Flashback is common especially in flame stability studies, such as ours. Therefore, extra care should be taken when building the experimental setup and when operating the experiments. For instance, in case of premixing ammonia with hydrogen flashback can occur at the moment of changing the flow setting points. This is because the higher reactivity of hydrogen, or sometimes simply because a slight difference in the response time from the mass flow controllers. Therefore, if the setting points are controlled manually, the fuel with slower reactivity should be set first. Also, it is important to calibrate the mass flow controllers to ensure a fast response time. In case of stability tests, changing the setting points of fuel and air should be performed in minor steps as small as 0.05 slpm per minute.

Figure 0.4. Flashback from ammonia-methane-air flame in a swirl burner.

Flame arrestor is an important component that can be added when plumbing the fuel lines, see Figure 0.5. Flame arresters protect the upstream side of a burner from flame flashbacks propagating all the way to the fuel cylinder. Therefore, it is highly recommended to be used.
6.2.2 Losing flame shape

Swirl flames are strongly attached and they can be simply distinguished by a V-shape. However, there are a few cases near to the rich blowout limit where the flame completely loses its topology. In such cases only a cloud of combustible mixture is attached, see Figure 0.6. We have observed this cloud more often for mixtures with high concentrations of ammonia, larger than 0.7 in the volume fraction. We also noticed that this phenomenon occurs when slowly increasing the equivalence ratio at the rich blowout limit. Therefore, reporting the rich blowout limit in such cases is difficult but its value can be identified as follows. The flame should be completely killed and then reignited at a specific equivalence ratio. This should be repeated for different equivalence ratios until the fuel mixture cannot be ignited anymore. This value can be reported as a rich blowout limit.
6.2.3 Burner throat

Flames take a conical V-shape in swirl burners. However, the flame shape is sensitive to the burner throat, outlet, length, diameter, and shape. Therefore, choosing the right throat is of crucial importance for flame stability measurements. Figure 0.7 shows three flames from different burner throats. A mushroom shape flame was observed from divergent throat. This flame also has an orange color as a sign of poor premixing. The divergent throat was then replaced by a straight one but half in diameter. A V-shape was observed from the straight throat. However, the flame chemiluminescence intensity is not uniformed and the flame base is inserted inside the burner. Therefore, the diameter was enlarged by a factor of two, a similar diameter to that of the divergent throat. Now, the flame features a conical V-shape and slightly lifted. Therefore, this throat was used for our stability limits experiments.

Figure 0.7. Methane-air flames using different throat burner geometry.
6.3 Emissions

6.3.1 NO measurements beyond the analyzer limit

Burning ammonia produces a large quantity of NO emissions. There are conditions where the NO is small as low as 100 ppm but in general the numbers exceed couple of thousands. NO emission analyzer systems are limited with a specific range. In our case, 4000 ppm is the maximum limit of the Testo 300 gas flue analyzer. Measuring NO emissions beyond this limit, which is expected in some cases, is difficult. However, high numbers can still be reported. One way can be done through diluting the emissions with a known concentration of N\textsubscript{2} to reduce the concentration of NO. Then, the measurements can be converted back to report the real values. On the other hand, the 4000 ppm value is significantly high. Therefore, values larger than 4000 ppm can be just reported as high values without exact numbers. It is worth mentioning here that the emission analyzers take a long time to reach steady state. Measurement should only be reported at steady state conditions. Therefore, it is highly recommended to measure all desired NO values from the same group in one time after reaching a steady state. Otherwise, the NO measurements are not simply comparable.

6.3.2 Water condensation in the exhaust line

The combustion of ammonia produces large quantities of water. Therefore, the exhaust line that is connected to the emission analyzer should be heated to certain temperature higher than water condensation point \(\approx 100^\circ\text{C}\). If water is still condensed in the lines, a water trap could be used, see Fig. XX. This trap can keep the water at a lower level pipe connected to a drain valve to remove any water accumulation.
Figure 0.8. Trap for water condensation from exhaust emissions.
Chapter 7

Closure

The research work reported in this document is now summarized. This section provides the conclusions of the main results and also clear tasks for future work in compliance with the main objectives of this study. Based on our results and the previous literature work, recommendations are also provided lately in this chapter.

7.1 Conclusions

The flame stability limits and exhaust NO emissions of technically-premixed ammonia-air swirl flames with mixtures of methane and of hydrogen were measured at atmospheric and at elevated pressures. Based on the results, cracking ammonia into hydrogen-nitrogen and fueling swirl combustors with “very” lean ammonia-hydrogen-nitrogen-air mixtures is promising because stable flames and competitively low exhaust NO emissions can be achieved with perhaps no need for a secondary combustion stage. Other harmful species such as NO\textsubscript{2} and N\textsubscript{2}O are critical but not considered here and should be done in a future work. The main finding from flame stability and NO emissions are listed below.

7.1.1 Flame stability

- The flame stability of ammonia-air flames is limited almost equally by chemical reaction (i.e. ammonia volume fraction or equivalence ratio) and by turbulent diffusion or mixing process (Reynolds number, bulk velocity, and pressure).
- Pure ammonia-air flames can be stabilized for a wide range of equivalence ratios if a swirl combustor is used.
• The range of equivalence ratio from stable pure ammonia-air flames is a function of
the pressure and of the bulk flow velocity. This range increases as pressure increases,
and a larger range observed for a larger bulk velocity at atmospheric pressure.

• It is possible to stabilize ammonia-air flames with mixtures of methane and of hydrogen
for large ranges of ammonia fuel fractions and equivalence ratios.

• Gradually replacing methane with ammonia increases the equivalence ratio leading to
lean blowout and to flashback. A similar behavior can be observed if hydrogen is
replaced by ammonia.

• The range of equivalence ratios yielding stable flames widens when ammonia is added
to methane/hydrogen fuel blend regardless of the pressure.

• Ammonia-methane-air flames feature wider stability limits than ammonia-air or
methane-air flames, and a similar behavior can be observed if methane is replaced by
hydrogen.

• Ammonia-air flames with mixtures of methane tends to have a wider flame stability
range compared to mixtures with a higher chemical reactivity, i.e. hydrogen.

• The critical ammonia addition is the smallest ammonia addition for which the most
reactive mixture does not yield suitable conditions for flashback. It is a function of the
Reynolds number, the bulk velocity, and the pressure.

• Flashback defines the upper stability limits for ammonia additions smaller than a
critical value. Above this critical ammonia addition, rich blowout controls the upper
stability limit. As a consequence, the stable range of equivalence ratios is wider for
ammonia fuel fractions exceeding this critical value.
• Regardless of the turbulent diffusion or mixing process, the largest equivalence ratio yielding flashback is slightly similar.

• The switch at the flame stability limit from flashback to rich blowout is called here a transitional behavior. It is a function of the ammonia fuel mixture, the Reynolds number, the bulk velocity, and the pressure.

• If the ammonia addition exceeds the transitional behavior point, the equivalence ratio of the lean blowout increases and that of the rich blowout decreases. As a consequence, the stability range slowly decreases.

• If the Reynolds number or bulk velocity increases, the transitional behavior occurs at a lower ammonia addition yielding a wider flame stability range.

• Increasing the pressure requires more ammonia additions for the transitional behavior to take place.

• Stable ammonia-hydrogen-air flames can be achieved for ‘very’ lean equivalence ratio as low as $\phi \leq 0.5$ for $x_{NH3} = 0.7$ even if the pressure increases to 5 bar.

• Adding nitrogen with a 3:1 hydrogen:nitrogen volume ratio to mimic ammonia cracking does not significantly alter stability limits.

• Nitrogen addition to ammonia-hydrogen-air flames slightly reduce the mixture reactivity. This may marginally alter the transitional behavior as pressure increases.

• To restrict the test matrix to a manageable size, stability limits for ammonia-air flames with methane/hydrogen blends were not measured for different swirl numbers. Nevertheless, effects of the swirl number on the sharp transition from flashback to rich blowout can be predicted.
7.1.2 NO emissions

- Ammonia-air flames with mixtures of methane/hydrogen produce a large quantity of NO emissions. This quantity is a function of ammonia volume fraction, equivalence ratio, pressure, and bulk flow velocity.

- Consistent with previous studies by others, slightly lean and stoichiometric ammonia-air flames produce large amount of NO but slightly rich ammonia-air flames yield good NO performance with NO mole fractions limited to ~100 ppm.

- At a fixed equivalence ratio and if $x_{\text{NH}_3} \geq 0.50$, the exhaust NO concentration decreases with increased ammonia addition.

- Ammonia-methane-air flames tend to produce slightly less NO emissions compared to that if methane is replaced by hydrogen. This is associated to the larger OH radical concentrations in ammonia-hydrogen flames.

- For non-marginal ammonia additions, good NO performances (relative to lean methane-air flames) are only found for slightly rich ammonia-methane-air mixtures.

- For ammonia-methane-air mixtures, decreasing equivalence ratio much below $\phi \approx 0.85$ could improve NO performances significantly but these very lean equivalence ratios cannot be reached with this swirl combustor due to lean blowout unless the methane is replaced by hydrogen.

- Good NO performance is observed for ‘very’ lean ammonia-hydrogen-air flames (for example $\phi \leq 0.70$ for $x_{\text{NH}_3} = 0.90$ or $\phi \leq 0.45$ for $x_{\text{NH}_3} = 0.70$) also yield NO mole fractions limited to ~100 ppm.

- The NO concentration decreases as the pressure increases, and this agrees with previous literature studies.
• Good NO performance as low as ~ 200 ppm can be achieved for lean ammonia-hydrogen-air flames for $x_{\text{NH}_3} = 0.9$ and $\varphi \leq 0.75$ if the pressure increases to 4 bar.

• Adding nitrogen with a 3:1 hydrogen:nitrogen volume ratio marginally decreases NO emissions regardless of the pressure.

• Competitive NO emissions (< 100 ppm) can be achieved for equivalence ratios in excess of $\varphi \approx 1.3$ and for 4 bar in ammonia-methane flames. However, rich operation implies large unburned ammonia emissions and a secondary combustion stage is needed to ensure globally-lean operation and to avoid high emissions and low efficiency penalties.

• The NO production is a tradeoff between residence time and mixing process. As a consequence, a lower NO production can be achieved as the flow bulk velocity increases.

### 7.2 Future work

The future work should be focused on the conversion of a commercial micro gas turbine to ammonia-hydrogen fuel blends. Operating a commercial micro gas turbine (mGT) with ammonia-hydrogen blends requires upgrading its combustor. At KAUST, a mGT combustor is being reverse-engineered and scaled-down to fit in the High-Pressure Combustion Duct (HPCD), featuring optical access and emission measurements. Based on HPCD results, a new mGT combustor, compatible with ammonia-hydrogen blends, will be designed and retrofitted in the mGT. The scope of our future work should include but not be limited to the followings:

• Purchase a commercial micro gas turbine 300 kW-thermal power.
• Reverse engineer the mGT combustor in a reduced scale, 75 kW-thermal power.

• Install the reduced scale combustor in the HPCD, and investigate flame stability and exhaust emissions.

• Design a new mGT combustor compatible with ammonia-hydrogen blends.

• Retrofit the new mGT combustor in the commercial mGT.

• Run the mGT with ammonia-hydrogen blends.

Lastly, a life cycle analysis (LCA) should be developed. This LCA is focusing on the viability of using ammonia and/or ammonia blends with hydrogen in utility scale gas turbines in the Kingdom of Saudi Arabia.

7.3 Recommendations

Storing hydrogen chemically in the form of ammonia is a promising solution to mitigate challenges associated with the storage and distribution of pure hydrogen. Beyond that, ammonia can be utilized as a carbon-free fuel if blended with mixtures of hydrogen. Offsetting this low reactivity by enriching ammonia with some amount of hydrogen, which is much more reactive fuel, is a promising strategy. Here, we recommend some suggestions for power generation sectors to benefit from the potential of ammonia as a fuel. Such recommendations should be first validated in a lab scale, and that is part of our future work.

The preliminary recommendations are listed below:

• Utilize ammonia as a hydrogen carrier fuel.

• Store hydrogen in the form of ammonia at the power plant sites in large vessels and in a liquid form at 8 bar.
• Decompose 10-20% of the ammonia to hydrogen:nitrogen, and this can be stored separately or blended directly with ammonia fuel.

• Use swirl flow combustor to enhance flame stability of the ammonia fuel mixtures.

• Operate gas turbines with ammonia-hydrogen-nitrogen-air mixtures in a range of $0.80 \leq x_{\text{NH}_3} \leq 0.9$.

• Operate the gas turbines with ‘very’ lean equivalence ratio as low as 0.5 to achieve good NO performance.

• Operating the gas turbines with lean equivalence ratio $\varphi \approx 0.7$ at elevated pressures is also possible to get a better combustion efficiency and a higher thermal power output. However, NO production should be always monitored.

• Consider measuring other harmful species such as NO$_2$ and N$_2$O in the exhaust emissions.

• Utilize second combustion stage if operating at rich equivalence ratio is needed.
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Appendix A. Chemical balance calculations

Here, we show how to chemically balance reactants and products from ammonia with mixtures of methane and of hydrogen.

Example 1. A mixture of 30% volume fraction of ammonia with methane.

Solution.

- mole percentage of NH\(_3\) = 0.3 \(\rightarrow x\)
- mole percentage of CH\(_4\) = 0.7 \(\rightarrow 1 - x\)

Chemical balance

\[
N_x H_{(4-x)} C_{(1-x)} + \left(\frac{9-5x}{4}\right)[O_2 + 3.76 \, N_2] \rightarrow (1 - x)CO_2 + \left(\frac{4-x}{2}\right)H_2O + 3.76 \left(\frac{8-3x}{4}\right)N_2
\]

Now, \(x\) in this chemical equation can be replaced by its value and then fuel to air equivalence ration can be calculated at stoichiometry. The calculated value can then be used to find equivalence ratios for specific mass flow rate of fuel and air.

Example 2. A mixture of 40% volume fraction of ammonia with hydrogen.

Solution.

- mole percentage of NH\(_3\) = 0.4 \(\rightarrow x\)
- mole percentage of CH\(_4\) = 0.6 \(\rightarrow 1 - x\)

Chemical balance
$$N_x H_{(x+2)} + \left( \frac{x+2}{4} \right) [O_2 + 3.76 N_2] \rightarrow \left( \frac{x+2}{2} \right) H_2 O + 3.76 \left( \frac{3x+2}{4} \right) N_2$$

Similar as the previous example, $$x$$ can be replaced in the equation and equivalence ratio can be then calculated for a specific fuel and air mass flow rate.
Appendix B. Engineering design drawings
4 x Female NPT 1/4 inch Swagelok

All Dimen. (mm)

SECTION A-A
SCALE 1 : 1.5

MATERIAL:
Aluminium

DWG NO.
Body_middle Part

8 x 3.30
M4 Thread
Thru All

8 x 10 x 5mm

8 x 3.0

6.35 Thru All

120

120
Body_Top Part_V2

MATERIAL: Stainless Steel

DO NOT SCALE DRAWING

RFS 1001902730

SCALE 1:1.5

SECTION A-A

Dimensions are in millimeters. Tolerances: linear, angular. Dimensions shown in blue, should be added or subtracted from actual dimensions.
- Stainless steel sheets welded.
- All Sheets thickness = 2 mm.
- All dimensions are mm.

1/4" (6.35 mm) stainless tube L = 100 welded in the side sheet.

CHIMNEY
Abdulrahman Alkhateeb