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# An Investigation of Ammonia Primary Flame Combustor Concepts for Emissions Reduction with OH\*, NH<sub>2</sub>\* and NH\* Chemiluminescence at Elevated Conditions

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## Abstract

With developing interest in NH<sub>3</sub> as a prospective energy carrier, combustor designs and fuelling concepts require optimisation to reduce NO<sub>x</sub> emissions. Through the introduction of staged combustor concepts, pathways have previously been identified that limit NO<sub>x</sub> production whilst improving combustor efficiency and reducing unburned NH<sub>3</sub>. However, the efficacy of secondary air staging is sensitive to the primary flame behaviour, and whilst low NO<sub>x</sub> emissions can be achieved at rich conditions, high unburned NH<sub>3</sub> leads to greater global NO<sub>x</sub> concentrations from downstream production. Here, time-resolved OH\*, NH<sub>2</sub>\* and NH\* chemiluminescence were employed together *for the first time* for NH<sub>3</sub>-air and NH<sub>3</sub>-H<sub>2</sub>-air flames to investigate a primary flame configuration that produced the lowest combined emissions concentration. A generic, fuel-flexible burner was developed to enable partial and full premixing, together with operation of a swirl-stabilised non-premixed flame. Initially, NH<sub>3</sub>-H<sub>2</sub>-air flames were employed in a range of configurations and produced markedly different chemiluminescence and emissions results as functions of global equivalence ratio. The performance of a pure NH<sub>3</sub>-air flame was subsequently investigated and compared to

the blended fuel results. Optical trends complemented changes in sampled exhaust emissions, enabling analysis of intermediate chemistry. Burner inlet temperature and pressure were then increased proportionally to maintain equivalent bulk nozzle exit velocities. Contrasting trends were identified as functions of fuel composition and equivalence ratio, with a comprehensive database of optical and analytical results generated. Results obtained for NH<sub>3</sub>-H<sub>2</sub>-air suggest the most favourable configuration resulted from a partially premixed flame employing H<sub>2</sub> as a pilot, operating under rich conditions ( $\Phi=1.2$ ). However, at higher temperatures and pressures, the trends observed for non-premixed NH<sub>3</sub>-air flames will lead to superior performance, particularly with a small increase in equivalence ratio.

**Keywords**

Ammonia, Turbulent premixed flames, Chemiluminescence, Staged combustion, Chemical kinetics

## 1. Introduction

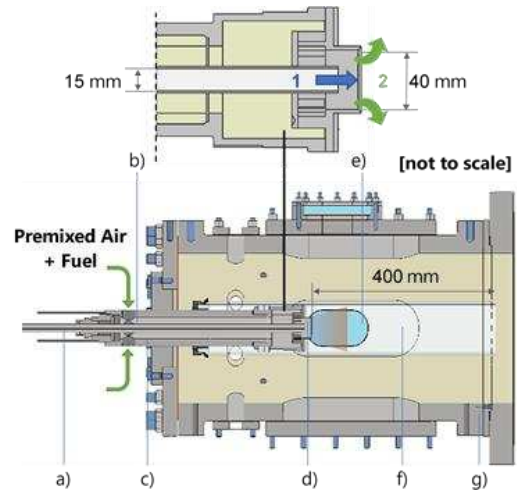
With favourable storage and transportation characteristics, there is developing interest in  $\text{NH}_3$  as a prospective energy carrier [1,2] and a cost-effective mechanism for storing  $\text{H}_2$ . The potential exists to directly supply power systems with  $\text{NH}_3$ , avoiding  $\text{H}_2$  conversion and presenting several combustion research challenges [2-6].  $\text{NH}_3$  reactivity is comparatively poor, with combustion enhanced by thermolysis to form  $\text{H}_2$  [7-9], additional supplementary fuels [8-12], or preheating. More significant is the propensity for excessive  $\text{NO}_x$  production [12-15] from fuel-bound nitrogen. Lean, low-temperature combustor strategies for  $\text{NO}_x$  reduction are ineffective for  $\text{NH}_3$ , with previous studies demonstrating successful concepts including humidification [3] and staging [14-15], alongside an increase in combustor pressure [3,16-17], making the prospective application of  $\text{NH}_3$  more conducive to gas turbine operation.

Recent research has investigated low- $\text{NO}_x$   $\text{NH}_3$  combustors [3,14,17], exploring staged concepts in detail and contrasting against  $\text{CH}_4$ -air flames [15,18]. Through the optimised introduction of staged secondary-air, pathways have been identified that limit  $\text{NO}_x$  production, whilst improving combustor efficiency through reducing unburned  $\text{NH}_3$  [3,14,17,18]. However, detailed experimental studies with  $\text{NH}_3$  flames remains limited, particularly at elevated inlet conditions, and an optimised primary flame configuration that provides both low  $\text{NO}_x$  and  $\text{NH}_3$  will greatly impact the understanding and influence of downstream staging. The purpose of this study, expanding on recent findings [3], is to investigate the primary flame, exploring  $\text{NO}$  reduction pathways through the detailed optical investigation of distinct combustor concepts, and mechanisms of fuel delivery for pure  $\text{NH}_3$  and  $\text{NH}_3/\text{H}_2$  blends. A fuel-flexible generic swirl burner was employed in several configurations, using swirl-stabilised premixed and non-premixed  $\text{NH}_3$ -air flames, alongside partial-premixing of  $\text{NH}_3$  and  $\text{H}_2$ . Regions of reacting  $\text{OH}^*$ ,  $\text{NH}_2^*$  and  $\text{NH}^*$  were visualised using Abel deconvoluted high-speed chemiluminescence for the first time with  $\text{NH}_3$  flames, and compared against emissions produced. Elevated inlet conditions of temperature and pressure were subsequently investigated to indicate the change in primary flame behaviour.

## 2. Experimental Facility and Diagnostics

### 2.1 Pressurised Optical Combustor

The swirl burner employed in previous studies [3,19,20,22] was modified, as presented in the cross-sectional view in Fig.1, with a central injection lance (Fig.1a) added to facilitate fuel injection into the annular swirling flow. The lance internal diameter was sized to give approximately equal axial jet velocities (flow-path 1 in Fig. 1) to the outer swirling flow (flow-path 2) for the range of equivalence ratios specified. Premixed reactants entered the inlet plenum (Fig.1b) with all flows metered using Coriolis mass-flow control ( $\pm 0.35\%$ ). The plenum body was preconditioned to the specified inlet temperature ( $T_x$ ) using electric preheaters and compressed air, dried to a dew point of  $-17^\circ\text{C}$ . From the premix chamber (Fig.1c), reactants leave the swirler exit nozzle ( $r=20\text{mm}$ ) through a single radial-tangential swirler (Fig.1d) with a geometric swirl number of  $S_g=0.8$ , using the central injection lance as a bluff-body. Quartz windows (Fig.1e) allowed optical access into a high-pressure optical casing (Fig.1g) with high-speed chemiluminescence measurements taken perpendicular to the reactant flow direction. The flame was housed within cylindrical quartz confinement (Fig.1f) at an expansion ratio of 2.5 from the nozzle. The system was pressurised to each specified condition ( $P_x$ ) using a water-cooled back-pressure valve. Greater detail of the experimental setup is provided in other works [19-20,22].



**Fig.1 Burner assembly**

## 2.2 Emissions

Combustor exhaust gas emissions were sampled downstream of the quartz confinement using a 9-hole equal-area probe, water-conditioned with a heat exchanger to regulate sample temperature (433K) following specifications in ISO-11042 [21]. The pump, filter block and sample lines were also maintained at 433K. NO<sub>x</sub> (NO and NO<sub>2</sub>) concentrations were quantified using heated vacuum chemiluminescence (Signal 4000VM). Unburned NH<sub>3</sub> measurements were obtained by redirecting sample through an NO converter (Signal 410) to measure unreacted concentrations (80% conversion efficiency). All NH<sub>3</sub> and NO<sub>x</sub> concentrations were measured hot/wet and normalised to equivalent dry conditions (Eqn. (9) in ISO-11042). Dry O<sub>2</sub> concentrations were quantified using a paramagnetic analyser (Signal 9000MGA) and used to subsequently normalise NO<sub>x</sub> to equivalent 15% O<sub>2</sub> (Eqn. (10) in ISO-11042). After changing experimental conditions, burner temperatures, pressures, flows and emissions were monitored and, once stable, held for a minimum of 60 samples to be taken. Systematic uncertainties comprising analyser specification, linearisation and span gas certification were combined with any fluctuations in measurement to give the total uncertainty represented by the plotted error bars.

## 2.3 Chemiluminescence

Time-resolved chemiluminescence measurements were conducted at each experimental condition, targeting three electronically-excited intermediate chemical radicals within NH<sub>3</sub>-air and NH<sub>3</sub>-H<sub>2</sub>-air flames, namely OH\*, NH<sub>2</sub>\* and NH\*. These measurements were taken utilising a combination of Phantom v1212 high-speed CMOS camera, Specialised Imaging SIL40HG50 high-speed image intensifier, UV lens (78 mm, f/11), and narrow bandpass filters selected specifically for each radical species. Further information on this specific high-speed imaging setup is found in other works [22]. While the authors have previously conducted OH\* chemiluminescence measurements in NH<sub>3</sub>-based flames [3,12], focusing specifically on the well-known A<sup>2</sup>Σ<sup>+</sup>-X<sup>2</sup>Π OH\* system [23] using a 315 nm (±15 nm FWHM) bandpass filter as in this study, only a select few experimental studies have conducted NH<sub>2</sub>\* and NH\* chemiluminescence measurements, typically confined to canonical reactors [24-27] or shock tubes [28-29] rather than premixed or diffusion NH<sub>3</sub> swirl flames, where NH<sub>2</sub> and NH intermediate chemistry is key to NH<sub>3</sub> oxidation [1-3]. For NH<sub>2</sub>\* measurements in this

study, a single peak of the  $\text{NH}_3$   $\alpha$  band was selected at 630 nm [23,26] using a bandpass filter centred at 632 nm ( $\pm 10$  nm FWHM). For  $\text{NH}^*$  measurements, the  $\text{A}^3\Pi\text{-X}^3\Sigma^-$  system was selected at 336 nm [23-25, 27-29] using a bandpass filter centred at 337 nm ( $\pm 10$  nm FWHM). Filter specifications provide nominal values, however filter transmission curves encompass expected  $\text{OH}^*$ ,  $\text{NH}^*$ , and  $\text{NH}_2^*$  wavelengths with minimal overlap. Transmission of the  $\text{NH}^*$  filter below 327 nm is  $<0.1\%$ , well away from the 309 nm  $\text{OH}^*$  peak. At the peak  $\text{NH}^*$  wavelength of 336 nm, the  $\text{OH}^*$  filter transmittance is  $\sim 1\%$ .  $\text{H}_2\text{O}$  interference in the  $\text{NH}_2^*$  signal was expected to be minimal as shown in [30]. The system was calibrated for the spectral efficiencies of both camera and intensifier, alongside the employed filters, UV lens, and optical windows. The transmission efficiency ratios of  $\text{OH}^*/\text{NH}_2^*$  and  $\text{NH}^*/\text{NH}_2^*$  were respectively calculated as 1.9:1 and 5.7:1 at peak emission wavelengths, with further detail included in supplemental material.

The frame rate deployed was 4000 Hz, with the image intensifier gated at  $10\mu\text{s}$  and the intensifier gain held constant throughout. A scaled target image provided the image resolution, equal to 4.6 pixels/mm, resulting in a field of view of 75mm (axial, y) by 100mm (radial, x) relative to the edge and centreline of the burner exit nozzle, respectively. For images presented herein, each instantaneous chemiluminescence image was filtered using a 3x3 pixel median filter and temporally averaged from 2000 images. The temporally-averaged images were then background corrected and processed using a modified Abel inversion algorithm to provide an axisymmetric planar representation of the electronically-excited radical species distribution within the swirling flow field [31]. Quantification of the chemiluminescence signal was further conducted using an integral intensity, e.g.  $I_{\text{OH}^*}$  as described by Runyon et al. [31].

Proportionality between electronically excited and ground state species with the spectroscopic flame response is complicated by influences such as radiation losses and quenching. Previous works have employed a directly proportional response relating  $\text{NH}^*$  to  $\text{NH}$  and  $\text{NH}_2^*$  to  $\text{NH}_2$  in  $\text{NH}_3$  dissociation [32], however proportionality is not assumed in this paper. Instead, only a positive correlation between emitting

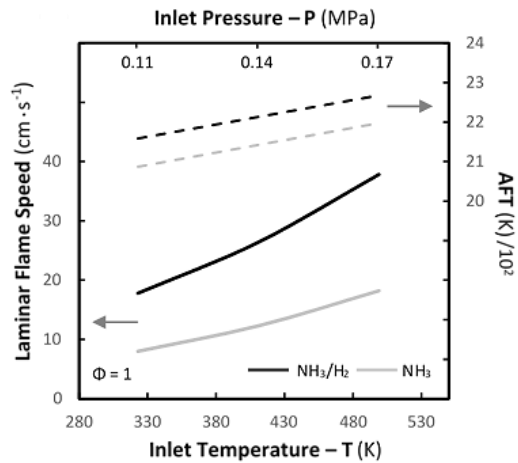
and ground state radicals is applied, and that more emitting species suggests increased ground state population [29,33,34].

### 3. Experimental Specification

Initial experiments were undertaken using a 70/30%<sub>vol</sub> ratio of NH<sub>3</sub>-H<sub>2</sub>, having demonstrated favourable stability in previous work [3] and shown to exhibit comparable behaviour to CH<sub>4</sub>-air [35]. A fully premixed flame was obtained by directing all reactants to the outer swirling flow (flow-path 2 - Fig.1). The fuel streams were then separated for the partially premixed configuration, with H<sub>2</sub> directed to the central diffusion jet (flow-path 1 - Fig.1) and NH<sub>3</sub> premixed with air in the outer swirling airflow (arrangement denoted 'H<sub>2</sub>Diff'). H<sub>2</sub> and NH<sub>3</sub> were subsequently interchanged, with the former directed to the swirling premixed flow ('NH<sub>3</sub>Diff'). Data-points were specified for a change in global equivalence ratio ( $\Phi=0.9-1.2$ ) by varying the swirling air flow rate with each flame configuration, capturing emissions and optical data. It should be noted that changing  $\Phi$  will provide small changes in swirl/recirculation, and whilst flow field effects are unquantified, changes in flame shape are visualised via chemiluminescence. Baseline inlet conditions of temperature ( $T_1$ ) and pressure ( $P_1$ ) were specified at 323K and 0.11MPa. Ambient conditions were elevated with a constant T/P ratio, retaining quasi-steady nozzle outlet velocities and combustor residence time for each configuration and  $\Phi$ . The elevated temperature conditions were specified as 411K and 499K ( $T_2, T_3$ ), corresponding to respective elevated-inlet pressures of 0.14MPa and 0.17MPa ( $P_2, P_3$ ). Taking the stoichiometric fully premixed case as an example; swirler nozzle bulk outlet velocities were maintained with Reynolds numbers reducing from  $\sim 15,200$  at  $T_1/P_1$ , to  $\sim 11,200$  at  $T_3/P_3$ . H<sub>2</sub> supply was subsequently removed and a comparison made between premixed/non-premixed NH<sub>3</sub>-air flames, with fuel-flow increased to maintain a constant net thermal power of 25kW<sub>th</sub> – equivalent to the NH<sub>3</sub>-H<sub>2</sub> case (based on proportional fuel LHV). Whilst significant results are presented and discussed, the full experimental dataset of inlet conditions and results is provided in the supplemental material.



### 3.1 Chemical Kinetics Modelling



**Fig.2 Changes in modelled  $S_L$  (solid) and AFT (dotted) for each fuel at the specified conditions ( $\Phi=1$ )**

Chemical kinetics were modelled using CHEMKIN-PRO, with the PREMIX reactor used to simulate changes in laminar flame speed ( $S_L$ ). Solutions were based on an adaptive grid, with multi-component transport properties and new schemes for convective flux. The equilibrium tool was used to generate adiabatic flame temperatures (AFT), under conditions of constant pressure/enthalpy. Each simulation employed the NH<sub>3</sub> reaction mechanism from Okafor et al. [11] comprising

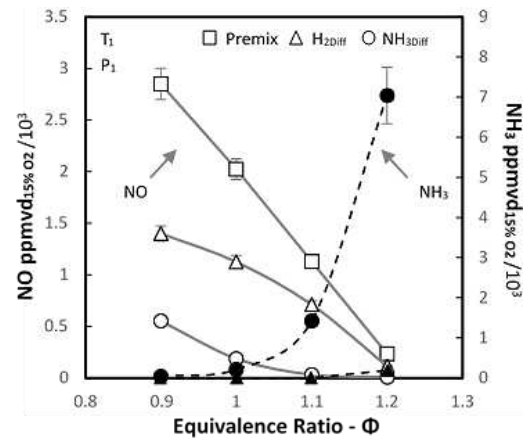
59 chemical species and 356 reactions. Changes in  $S_L$  and AFT are shown at  $\Phi=1$  and changing T/P in Fig.2, for the premixed NH<sub>3</sub>-air and NH<sub>3</sub>-H<sub>2</sub>-air cases. Even at the lowest inlet temperatures, AFT is sufficient to facilitate thermal NO<sub>x</sub> formation [36] and was shown to vary by ~80K across the specified experimental range for both fuel mixtures. Pure NH<sub>3</sub>-air flame temperatures were ~70K lower than each equivalent NH<sub>3</sub>-H<sub>2</sub>-air condition. The low  $S_L$  for NH<sub>3</sub> is highlighted in Fig. 2 and is predicted to approximately double with the addition of 30% H<sub>2</sub> for all equivalent cases of T/P. The highest  $S_L$  at T<sub>3</sub>/P<sub>3</sub> highlighted the potential for flashback with NH<sub>3</sub>-H<sub>2</sub>-air and relatively low nozzle velocities.

## 4. Results

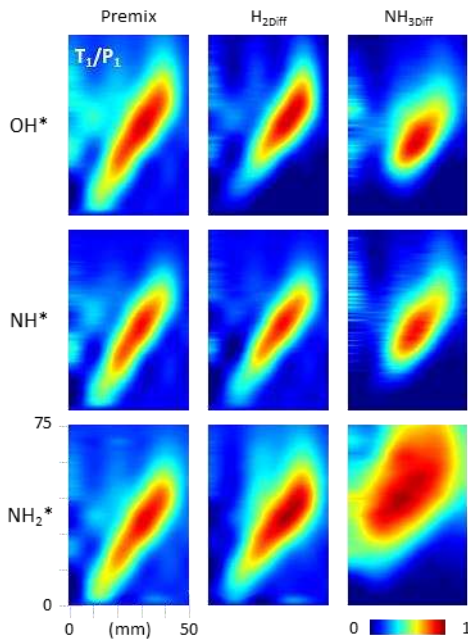
### 4.1 NH<sub>3</sub>-H<sub>2</sub>-air flames

Sampled concentrations of NO and NH<sub>3</sub> from the fully premixed, H<sub>2</sub>Diff, and NH<sub>3</sub>Diff flames are shown in Fig. 3 for change in  $\Phi$  at T<sub>1</sub>/P<sub>1</sub>. NO<sub>2</sub> is not plotted - or NH<sub>3</sub> for the premixed case - as measured concentrations were negligible compared to NO; the data is provided in the supplemental material. Note - lean premixed CH<sub>4</sub>/air in the same facility gave ~5-30 ppmvd<sub>15%O<sub>2</sub></sub>.for an AFT range of ~1800-2200K [22]. A near order of magnitude increase in NO concentration produced by the

premixed flame is observed, compared to the NH<sub>3</sub>Diff regime. Local NH<sub>3</sub>-rich zones lead to increased production of NH<sub>2</sub>\* within the NH<sub>3</sub>Diff flame, as evidenced in the Abel-transformed chemiluminescence shown in Fig.4 ( $\Phi=1$ ) - one half of the planar representation is shown, with x= 0 corresponding to the burner



**Fig.3 Sampled NO (empty) and NH<sub>3</sub> (filled) emissions for each NH<sub>3</sub>-H<sub>2</sub> flame configuration at T<sub>1</sub>/P<sub>1</sub>**

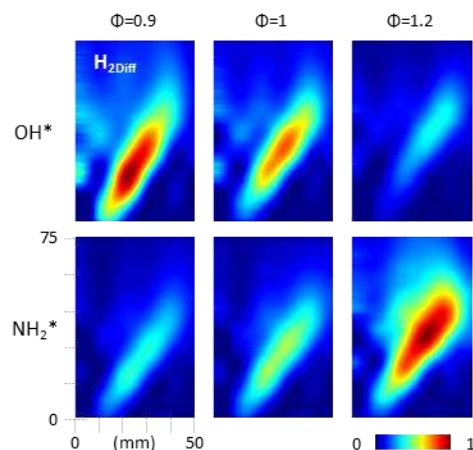


**Fig.4 Abel transformed NH\*, OH\* and NH<sub>2</sub>\* chemiluminescence for each NH<sub>3</sub>-H<sub>2</sub> flame configuration at T<sub>1</sub>/P<sub>1</sub>.**  
(colourmap normalised to image max)

centreline and flow from the bottom up. Measured intensities of NH<sub>2</sub>\* were significantly higher than both OH\* and NH\* (even accounting for the increase in quantum efficiency with the UV-enhanced photocathode of the intensifier), though with the colourmap presented, profiles are normalised to the maximum in each image to show the change in topology for each configuration. Each flame stabilises along the shear layer of zero axial velocity [19,22], with the flame brush thicker and structure markedly different for the partially premixed cases. Significantly greater NH<sub>2</sub>\* intensities were evident post-flame for the NH<sub>3</sub>Diff case, when compared to

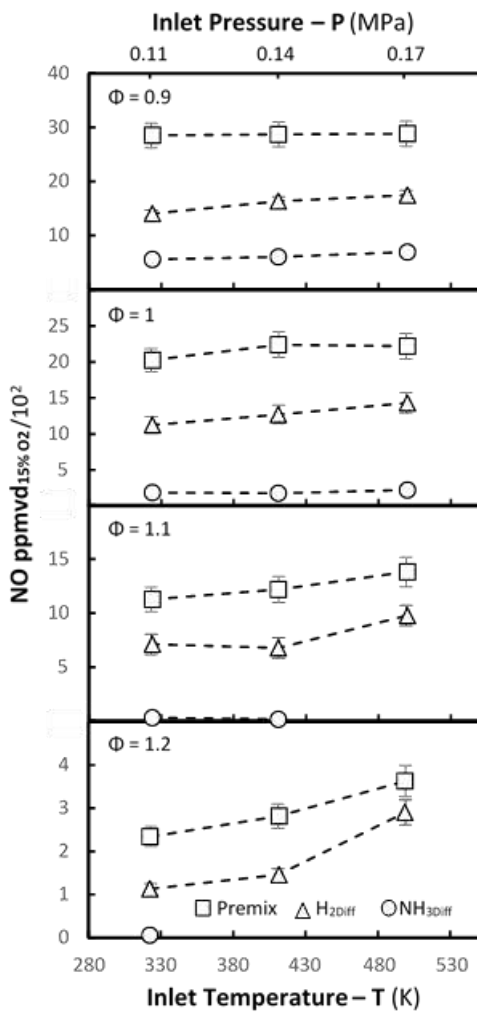
the other regimes.  $\text{NH}_2$  is noted as being key for enhancing NO consumption through the chain carrying reaction  $\text{NH}_2 + \text{NO} \leftrightarrow \text{NNH} + \text{OH}$ , and the terminating reaction  $\text{NH}_2 + \text{NO} \leftrightarrow \text{H}_2\text{O} + \text{N}_2$  [3]. OH and O are also important for the respective oxidation of NH and  $\text{NH}_2$  to NO via HNO and the reaction  $\text{HNO} + \text{OH} \leftrightarrow \text{NO} + \text{H}_2\text{O}$  [2]. With a positive correlation between ground state and excited species, enhanced  $\text{NH}_2^*$  and reduced regions of  $\text{OH}^*$  evident in Fig.4 complement the reduction in NO concentrations shown in Fig. 3 for the  $\text{NH}_{3\text{Diff}}$  case. The change in each chemiluminescence intensity distribution was quantified by calculating the integral intensity [31] for each species, with values of  $I_{\text{NH}_2^*}$  for  $\text{NH}_{3\text{Diff}}$  a factor of 3.7 greater than the equivalent premixed flame. The  $\text{H}_{2\text{Diff}}$  flame behaves as an intermediate between the other two configurations, with  $\text{NH}_2^*$  and  $\text{OH}^*$  chemiluminescence profiles demonstrating transitional behaviour as seen with measured NO. The distribution of  $\text{NH}^*$  appears to closely match the deconvoluted  $\text{OH}^*$  profiles, while ground state OH and NH are related by the primary production pathway:  $\text{NH}_2 + \text{OH} \leftrightarrow \text{NH} + \text{H}_2\text{O}$ .

A pronounced decrease in NO with increasing  $\Phi$  is also evident in Fig. 3, as previously observed [3]. This results from a combination of reduced thermal formation with the Zel'dovich mechanism, the availability of OH for  $\text{NH}_3$  oxidation [16,18], and enhanced NO consumption with  $\text{NH}_2$ . Figure 5 shows the change in  $\text{OH}^*$  and  $\text{NH}_2^*$  chemiluminescence profiles for a sample  $\text{H}_{2\text{Diff}}$  flame with change in  $\Phi$  at  $T_2/P_2$ . The colourmaps in these images have been normalised to the maximum for each species dataset



**Fig.5 Abel transformed  $\text{OH}^*$  and  $\text{NH}_2^*$  chemiluminescence for the  $\text{H}_{2\text{Diff}}$  flame configuration at  $T_2/P_2$**   
(colourmap normalised to species dataset max)

to emphasise the change in excited radical intensity with  $\Phi$ . A complementary trend is seen again between the reduction of  $\text{OH}^*$ , an increase in  $\text{NH}_2^*$  intensity, and a drop in NO (data shown for  $T_2/P_2$  in Fig. 6). As modelled in Section 3.1, AFT is highest for the  $\Phi=1$  case, and expected to reduce by  $\sim 80\text{K}$  to near equivalent values for both  $\Phi=0.9$  and 1.2. The influence of rising AFT was investigated in further detail, by increasing  $T_1/P_1$  to  $T_3/P_3$ . The change in sampled NO concentrations for each  $\text{NH}_3\text{-H}_2\text{-air}$  flame configuration is plotted



**Fig.6 Sampled NO emissions for each NH<sub>3</sub>-H<sub>2</sub> flame configuration and  $\Phi$  at elevated inlet conditions**

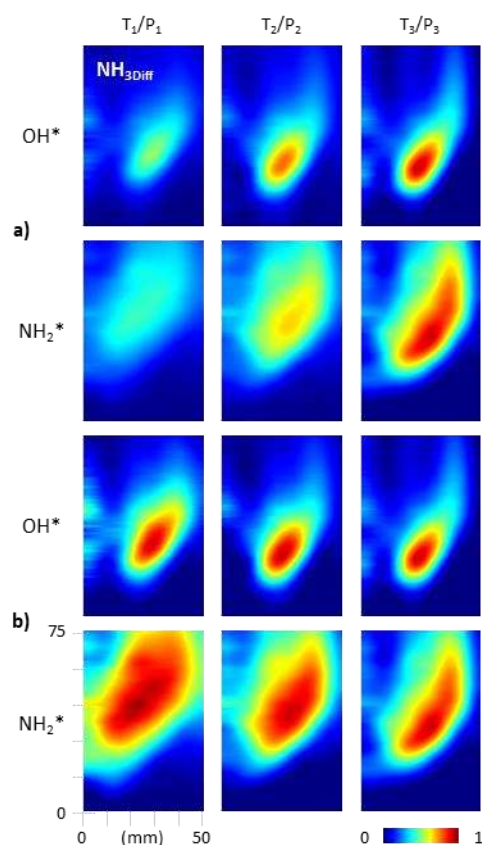
against increasing inlet conditions in Fig. 6, for distinct  $\Phi$ . The observed trend is for increased NO production with inlet temperature, as would be expected from enhanced thermal NO<sub>x</sub> formation. However, this is diminished due to the NO reduction induced by rising inlet pressure – resulting in increased NH<sub>2</sub> from HNO/OH and third-body H<sub>2</sub>O production from OH, as has been previously shown for NH<sub>3</sub>-H<sub>2</sub>-air flames by the authors [3]. This pressure effect is seemingly overcome by enhanced OH production at elevated temperature through  $H+O_2 \leftrightarrow O+OH$  and  $2OH \leftrightarrow O+H_2O$ , and increased Zel'dovich production via  $N+O_2 \leftrightarrow NO+O$  and  $N+OH \leftrightarrow NO+H$  [36] - taking  $\Phi=1$  as an example, Zel'dovich reaction rates were simulated to rise by factors of  $\sim 3$  with the specified elevation in conditions (note - Kobayashi et al. [2] demonstrated effective NO consumption via  $N_2+O \leftrightarrow NO+N$  for NH<sub>3</sub>-air flames). The relative trends observed in Fig. 6 appear to be more

pronounced at richer conditions; as for the leaner cases OH fractions are higher so enhanced NO production from rising temperature is diminished. It should be emphasised, the decoupled dominant reactions highlighted for changes in NO formation with temperature and pressure have been reported for NH<sub>3</sub>-H<sub>2</sub> flames [3,9,14], and this work was specified to highlight that influences are competing as T/P increase together as may be expected with practical systems. A comparison between changes in OH\* and NH<sub>2</sub>\* chemiluminescence is shown in Fig.7 for the  $\Phi=1$  NH<sub>3</sub>Diff flame and increasing T/P. To demonstrate the differences in flame topology and chemiluminescence intensity with T/P, colourmaps are normalised to the maximum in both species' dataset (Fig.7a) and each image (Fig.7b). The OH\* and NH<sub>2</sub>\* chemiluminescence intensities are shown to rise with increasing temperature and pressure. However, the flame structure is also

shown to contract with increasing inlet conditions (Fig.7b).

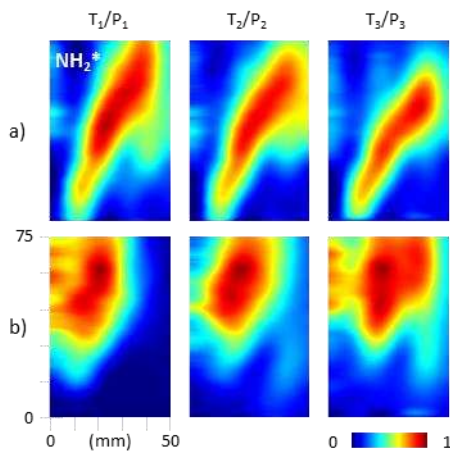
This results from enhanced reactivity from increasing temperature, and the reduction in flame thickness induced from increasing pressure. It should be noted the increase in collisional quenching resulting from a rise in pressure would be expected to reduce observed chemiluminescence [33,37], however the inverse is observed resulting from increased production from changes in intermediate chemistry and an increase in flame temperature. Emissions data could not be collected at the richest conditions for the  $\text{NH}_{3\text{Diff}}$  flame at elevated temperature and pressure – the reduction in outlet velocities with decreasing airflow led to a change in flame mode, and effective flashback into the burner nozzle with premixed  $\text{H}_2$ . To sustain a rich  $\text{NH}_{3\text{Diff}}$  flame at elevated conditions an increase in nozzle outlet velocity is required, and therefore thermal power; this is outside the scope of

this study. The  $\text{NH}_{3\text{Diff}}$  flame produced significantly higher  $\text{NH}_3$  emissions than the other two configurations, rising with increasing  $\Phi$ . This is simulated to primarily result from the elevated  $\text{NH}_2$  concentrations, with the respective third body and branching reactions  $\text{NH}_2 + \text{H} + \text{M} \leftrightarrow \text{NH}_3 + \text{M}$ , and  $2\text{NH}_2 \leftrightarrow \text{NH}_3 + \text{NH}$ . With the change in experimental configuration, there exists the potential for fluid dynamic influences to contribute to enhanced exhaust  $\text{NH}_3$ , however measured exhaust  $\text{O}_2$  concentrations at stoichiometric conditions were similar for all flame configurations and T/P, suggesting sufficient mixing of reactants. Excessive  $\text{NH}_3$  emissions from the primary flame will lead to increased aggregate  $\text{NO}_x$  production in a staged configuration. Whilst the  $\text{NH}_{3\text{Diff}}$  flame provided the lowest  $\text{NO}$  emissions,  $\text{NH}_3$  concentrations meant that optimal (combined  $\text{NO}$  and  $\text{NH}_3$ ) performance was achieved with the  $\text{H}_{2\text{Diff}}$  flame at  $\Phi = 1.2$ , with a marginal difference compared to the fully premixed case.

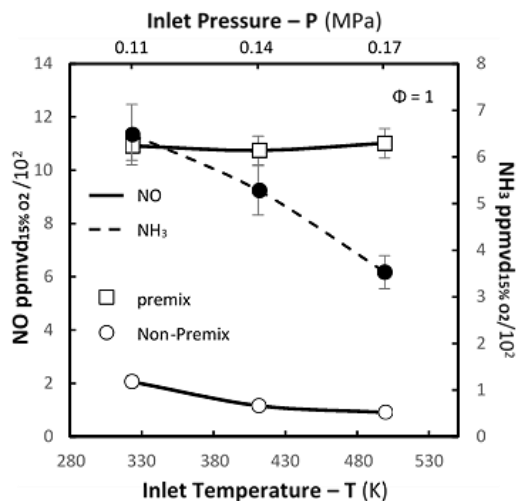


**Fig.7** Abel transformed  $\text{OH}^*$  and  $\text{NH}_2^*$  chemiluminescence for the  $\Phi=1$   $\text{NH}_{3\text{Diff}}$  flame configuration for increasing inlet conditions. (colourmaps normalised to species dataset max (a) and image max (b))

## 4.2 NH<sub>3</sub>-air Flames



**Fig.8** Abel transformed NH<sub>2</sub>\* chemiluminescence for the  $\Phi=1$  NH<sub>3</sub>-air with premixed (a) and non-premixed (b) flames (colourmaps normalised to image max)



**Fig.9** Sampled NO (empty) and NH<sub>3</sub> (filled) emissions for each NH<sub>3</sub>-air flame configuration with increasing inlet condition

For practical systems there are advantages of operating with NH<sub>3</sub>-air flames only. Hence, further studies were undertaken with both non-premixed and premixed configurations (respective fuel flow paths 1 and 2 in Fig.1). At lower temperatures, ignition could not be achieved with NH<sub>3</sub>/air alone, and H<sub>2</sub> addition was required. The H<sub>2</sub> was subsequently removed after flame stabilisation. At T<sub>3</sub>, the stoichiometric NH<sub>3</sub>-air flame ignited in both configurations without H<sub>2</sub> addition. A comparison of Abel transformed NH<sub>2</sub>\*

chemiluminescence from  $\Phi=1$  premixed and non-premixed NH<sub>3</sub>-air flames is shown in Fig. 8. For the premixed regime, as inlet temperature and pressure rise, the flame compresses, retreating upstream in the flow and expanding radially – as would be expected with increased reactivity and reduced flame thickness, with NH<sub>2</sub>\* chemiluminescence in the outer recirculation zones reduced. Conversely, for the non-premixed case, higher NH<sub>2</sub>\* intensities initially appear near the centreline, then as T increases, NH<sub>2</sub>\* within the flame brush radially thickens and higher intensities are established in the outer recirculation zone. These opposing trends are

matched in the emissions data shown in Fig. 9. With an increase in T/P, the premixed NH<sub>3</sub>-air flame exhibits the same behaviour as NH<sub>3</sub>-H<sub>2</sub>-air, and gives a small increase in NO. For the non-premixed flame however, NO is shown to approximately halve across the specified range. In the premixed case it is suggested that enhanced mixing leads to increased OH production at elevated conditions, supported by kinetic modelling

and chemiluminescence (available in the full dataset). However, for the non-premixed case reduced relative OH production allowed the  $\text{NH}_2$ /pressure effect (described in the section 4.1) to dominate. There is also a noticeable reduction in  $\text{NH}_3$  emissions with an increase in T/P for the non-premixed case (premixed case not presented as concentrations were negligible). This is modelled to result from a switch in the  $\text{NH}_3 + \text{H} \leftrightarrow \text{NH}_2 + \text{H}_2$  reaction, producing  $\text{NH}_3$  at lower temperatures and reversing to consume it with a rise in temperature. This also contributes to the enhanced production of  $\text{NH}_2$  and reduction in NO.

## 5. Conclusions

A combination of time resolved OH\*, NH<sub>2</sub>\* and NH\* chemiluminescence was employed for the first time with NH<sub>3</sub> flames. The optical techniques were used to investigate a primary flame configuration that produced the lowest combined concentrations of NO and NH<sub>3</sub> for two fuels: pure NH<sub>3</sub> and NH<sub>3</sub>/H<sub>2</sub> (70/30%vol). Results highlighted that NH<sub>2</sub>\* intensity is a good marker for NO consumption in rich NH<sub>3</sub> flames. Measured intensities elucidated changes in sampled exhaust emissions, supporting detailed analysis of intermediate chemistry.

A generic, fuel-flexible burner was developed that enabled partial and full premixing of fuels, together with a swirl-stabilised diffusion flame. The facility was used with a combination of NH<sub>3</sub>-H<sub>2</sub>-air flames, with markedly different results obtained for each configuration as a function of  $\Phi$ . Partial premixing of H<sub>2</sub>, with non-premixed NH<sub>3</sub>, provided to the lowest measured NO concentrations, an order of magnitude below the fully premixed case, but also produced more unburned NH<sub>3</sub>. The performance of a pure NH<sub>3</sub>-air flames was also investigated, showing an order of magnitude reduction in NO between premixed and non-premixed configurations.

Conditions of temperature and pressure were scaled in proportion to maintain equivalent bulk nozzle exit velocities with contrasting trends identified as functions of fuel composition and  $\Phi$ : For NH<sub>3</sub>-H<sub>2</sub>-air flames, an increase in T/P led to a rise in measured NO. However, across the specified range, NO concentrations halved for non-premixed NH<sub>3</sub>-air and reached lower NO concentrations than any other stoichiometric case.

To optimise the primary flame for staged combustion, the lowest combination of NH<sub>3</sub> and NO was achieved as a function of equivalence ratio. Previous studies have suggested  $\Phi=1.2-1.3$  for premixed flames, or mildly rich ( $\Phi=1-1.1$ ) for diffusion [3,15,17,19]. Results obtained for NH<sub>3</sub>-H<sub>2</sub>-air suggest the most favourable configuration resulted from the partially premixed H<sub>2</sub>Diff flame with the lowest combination of NO and NH<sub>3</sub> achieved at  $\Phi=1.2$ . It is acknowledged that at higher temperatures and pressures, the trends observed for the non-premixed NH<sub>3</sub> flame will lead to superior performance, particularly with a small increase in  $\Phi$ , and will be the subject of future study.



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## Figure Captions

Fig.1 Burner assembly

Fig.2 Changes in modelled  $S_L$  (solid) and AFT (dotted) for each fuel at the specified conditions ( $\Phi=1$ )

Fig.3 Sampled NO (empty) and NH<sub>3</sub> (filled) emissions for each NH<sub>3</sub>-H<sub>2</sub> flame configuration at  $T_1/P_1$

Fig.4 Abel transformed NH\*, OH\* and NH<sub>2</sub>\* chemiluminescence for each NH<sub>3</sub>-H<sub>2</sub> flame configuration at  $T_1/P_1$ .

(colourmap normalised to image max)

Fig.5 Abel transformed OH\* and NH<sub>2</sub>\* chemiluminescence for the H<sub>2</sub>Diff flame configuration at  $T_2/P_2$

(colourmap normalised to species dataset max)

Fig.6 Sampled NO emissions for each NH<sub>3</sub>-H<sub>2</sub> flame configuration and  $\Phi$  at elevated inlet conditions

Fig.7 Abel transformed OH\* and NH<sub>2</sub>\* chemiluminescence for the  $\Phi=1$  NH<sub>3</sub>Diff flame configuration for increasing inlet conditions. (colourmaps normalised to species dataset max (a) and image max (b))

Fig.8 Abel transformed NH<sub>2</sub>\* chemiluminescence for the  $\Phi=1$  NH<sub>3</sub>-air with premixed (a) and non-premixed (b) flames (colourmaps normalised to image max)

Fig.9 Sampled NO (empty) and NH<sub>3</sub> (filled) emissions for each NH<sub>3</sub>-air flame configuration with increasing inlet condition

## Supplemental Material

Experimental data