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S. Zitouni, Pierre Brequigny, Christine Mounaïm-Rousselle. Turbulent Partially Cracked Ammonia/air Flames in Spherical Vessel. Twentieth International Conference on Flow Dynamics, Nov 2023, Sendai, Japan. hal-04402596

HAL Id: hal-04402596

<https://hal.science/hal-04402596>

Submitted on 18 Jan 2024

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Turbulent Partially Cracked Ammonia/air Flames in Spherical Vessel

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ABSTRACT

The partial dissociation of the Ammonia molecule appears as a potentially interesting strategy not only to enhance Ammonia's combustion properties but also to guarantee flexibility for power production. Using the spherical expanding flame configuration, laminar burning velocities, Markstein lengths and turbulent flame speeds were measured for cracking ratios ranging from 10 to 40%, and 3 equivalence ratios of 0.8, 1.0 and 1.2. It was observed that lean mixtures exhibit the greatest increase in turbulent to laminar velocity ratio given the same turbulent intensity. This is was potentially due to opposite stretch related behaviour as well as preferential diffusional instability effects. Measurements presented herein correlate well with a Lewis Number weighted turbulent flame speed scaling law.

1. Introduction

Ammonia (NH_3) has emerged in recent years as a promising zero-carbon hydrogen (H_2) carrier, due to its several advantages, notably in terms of ease of storage, established distribution and transport infrastructures. It is gaining considerable attention as a promising alternative to carbon-based fuels but there remain several practical combustion challenges. NH_3 exhibits slow laminar burning velocities, a narrow flammable range and high ignition energy, potentially yielding poor flame stabilisation and extinction characteristics resulting in local or global extinctions. A potential NH_3 combustion enhancement strategy is the partial fuel dissociation (or 'cracking', referred herein as PCA, for Partially Cracked Ammonia) of NH_3 , which is different to co-firing with more reactive fuel as hydrogen or increasing the oxygen content. NH_3 can be converted to H_2 and Nitrogen (N_2) with or without the use of catalysts at temperatures of 425 – 500 °C, with conversion efficiencies reaching 98 – 99% [1].

Although a potentially interesting strategy, experimental and kinetic studies focusing on combustion characteristics of partially cracked NH_3 /air mixtures remain limited and a such there seems to be a practical necessity in enhancing fundamental knowledge, ultimately leading to the development of combustors offering greater flame stability and reduced pollutant emissions. In this regard, the measurement of the laminar burning velocity (S_L^0), a fundamental physicochemical property of any premixed air-fuel mixture and central parameter in turbulent modelling, is essential. Han et al. [2], measured the S_L^0 of pre-dissociated NH_3 /air flames, using the heat flux method at 1 atm and 298 K, across a wide range of equivalence ratios ($\phi = 0.6 - 1.6$) and dissociation ratio $\gamma = 2.5 - 50\%$. Undertaking a thorough kinetic analyses they underlined that $\text{NH}_3/\text{H}_2/\text{N}_2$ /air flames have approximately the same S_L^0 reaction sensitivities than those of NH_3/H_2 /air flames. Lesmana et al. [3] measured the S_L^0 of PCA ($\gamma = 0 - 37.5\%$) at normal temperature and pressure using a Bunsen burner, across a narrow ϕ range ($\phi = 0.9 - 1.2$). The study underlines that S_L^0 peaks at $\phi=1.10$ at those conditions. Furthermore, they attribute the increase in S_L^0 with increasing cracking ratio to an enhancement of key radical production, notably OH, O, H and NH_2 due to the increasing presence of H_2 . Mei et al. [1], using the spherically expanding

flame configuration measured the S_L^0 of PCA blends, across a wide range of ϕ (0.7 – 1.4) and γ (10 – 80%), up to unburnt pressures of 10 bars. The work underlines that the peak S_L^0 of a PCA 40% flame is close to that of methane (CH_4), at 1 bar and 298K. Of interest, the study observed cellular instabilities at larger γ (>40%) as well as at higher pressures. By and large the aforementioned studies cover the limited peer-reviewed literature available for laminar PCA flame measurements.

With respect to studies focusing on the turbulence flame interaction of PCA flames, there appears to be a gap in knowledge with no studies found, to the authors best knowledge. Relative to S_L^0 , the turbulent burning velocity (S_T) is enhanced due to flame stretch and wrinkling induced by the turbulence, with potential enhanced mixing resulting in an increase in combustion efficiency. The very different characteristics of NH_3 (low S_L^0 coupled with a large flame thickness (δ_L)) relative to H_2 (high S_L^0 and thin δ_L) result in significant differences in relative chemical time scales (ratio of S_L^0/δ_L). As a consequence, the turbulent burning of NH_3 leads to higher turbulence Karlovitz numbers (Ka) [4].

Recent turbulent combustion experiments, based on blending NH_3 with CH_4 or H_2 underline the role of preferential-diffusion and flame stretch upon NH_3 based flames. For example Ichimura et al. [5] investigated NH_3 /air flames at various turbulent intensities (u'), finding that mixtures on the lean side were more difficult to extinguish than rich fuel conditions, due to potential thermo-diffusive instability strengthening lean NH_3 /air mixtures. Similarly, Xia et al. [6] underlined that due to thermo-diffusional instabilities, a higher ratio of S_T/S_L^0 under the same turbulence stretch arises for lean oxygen-enriched NH_3 flames, than for rich conditions. Likewise, Lhuillier et al. [7] investigated NH_3/H_2 and NH_3/CH_4 (up to 15% vol. of H_2 or CH_4) turbulent flame propagation under engine related conditions (445K, 0.54 MPa). They reported a decreasing and increasing S_T/S_L^0 ratio upon CH_4 and H_2 addition respectively, induced by the different stretch-related behavior and opposite Lewis Number (Le) and Markstein Length (L_b) of these mixtures.

In light of the scarcity of the studies relating to laminar and turbulent flame speed measurements of ammonia/air flames and especially for PCA/air flames, it thus motivates the present study to assess the potential

effects of thermal-diffusionally instabilities upon various PCA flames, across a wide range of equivalence ratios, and various turbulent intensities.

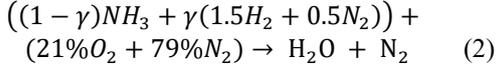
2. Experimental Set-up and Conditions

2.1 Laminar Flame Set-up and Conditions

Laminar flame speed measurements were performed using a constant-volume spherical vessel. Details of the experimental apparatus and post-processing techniques can be found in [8], updated for NH₃ specifications in [9]. Measurements of the mixtures were performed at initial conditions of 298 K (± 3 K) and 0.1 MPa ($\pm 1 \times 10^{-3}$ MPa). The quasi-steady non-linear relation between the stretched flame speed and stretch was employed [10] – rearranged with the error used for least square regression – to estimate the extrapolated unstretched flame speed and corresponding Markstein Length (L_b). In order to obtain representative values of laminar flame speed, the adiabatic expansion ratio ($\sigma = \rho_b/\rho_u$, with ρ_u , and ρ_b , the unburnt and burnt gas densities, respectively) was considered. In this work, the definition of the dissociation ratio (γ) is defined as:

$$\gamma = \frac{[\text{NH}_3]_{\text{cracked}}}{[\text{NH}_3]_{\text{init}}} = 2[\text{H}_2]/(3[\text{NH}_3] + 2[\text{H}_2]) \quad (1)$$

where $[\text{NH}_3]_{\text{cracked}}$ and $[\text{NH}_3]_{\text{initial}}$ are the concentrations of cracked NH₃ and initial NH₃, respectively, with $[\text{H}_2]$ and $[\text{NH}_3]$ are the mole fractions of the H₂ and NH₃ in the partially dissociated fuel mixture. The equivalence ratios, ϕ of PCA/air mixtures are evaluated as per Eqn. 2:



For the laminar measurements, ϕ was varied from 0.6 – 1.4, with γ varied from 0 – 40%, with 3 – 5 nominally identical experiments conducted per condition.

2.2 Turbulent Flame Set-up and Conditions

The combustion vessel described in Section 2.1 was employed equipped with six four-blade fans, located in a regular hexahedral configuration, creating a near-isotropic and homogeneous turbulent region (HIT) within a diameter of 40 mm of the vessel center. The turbulence intensity (expressed as $u' = Af_0$, where $f_0 = (w/60)$ and A , a constant = 0.0098 m) and integral length scale ($L_T = 2.63$ mm) of the non-reacting turbulence flow field were evaluated using 2D image velocimetry (PIV). The centrally ignited flames were measured using a Z-Schlieren configuration, recorded using a Phantom V1610 high-speed camera, set to capture 10,000 fps and facilitating a spatial resolution of 0.098 mm/pixel. Details of the apparatus, turbulence parameters and experimental procedure have previously been introduced in [8,11]. The flame propagation rates were determined by edge-detection algorithms written in a bespoke MATLAB script. By assuming a spherical flame shape, from the binarized flame contour images, the instantaneous surface equivalent flame radii, defined as $R_s = (A/\pi)^{1/2}$, where A represents the burnt gasses area was determined. An equivalent flame propagation velocity with respect to the burnt side was derived as $S_T = (dR_s)/dt$. The experimental data range with $\langle R_s \rangle$ ranging from 5 to 20 mm to minimise the effects of ignition energy, wall confinement and to stay within the HIT zone. To facilitate the comparison of S_T among different fuel mixtures, a

volume-averaged flame speed was adopted as done in [12,13], defined as per Eqn. 3:

$$S_{T,\text{mean}} = \frac{3 \int_{\langle R_s \rangle_1}^{\langle R_s \rangle_2} \langle R_s \rangle^2 \left(\frac{d\langle R_s \rangle}{dt} \right) d\langle R_s \rangle}{\sigma(\langle R_s \rangle_2^3 - \langle R_s \rangle_1^3)} \quad (3)$$

Where σ is the thermal expansion ratio, $\langle R_s \rangle_1$ and $\langle R_s \rangle_2$ are 5 and 20 mm, respectively. For turbulent experiments, ϕ was varied from 0.8, 1.0 and 1.2, with γ varied from 10 – 40%, whilst two turbulent intensities were investigated, $u' = 0.63$ and 1.13 m/s. Finally, 5 – 7 nominally identical experiments were conducted per condition, with error bars representing the standard deviation.

3. Results and Discussion

All experiments performed under turbulent conditions are plotted on the Peters-Borghi diagram in Fig. 1. Most of the present experiments are located within the thin reaction zone, with increasing cracking ratio (increasing H₂ content) resulting in a downwards shift towards the corrugated flamelets, due to a much greater S_L^0 . Noteworthy, mixtures with $\gamma < 20\%$ cross the $Da = 1$ limit, with $\gamma > 20\%$ exhibiting a $Da > 1$.

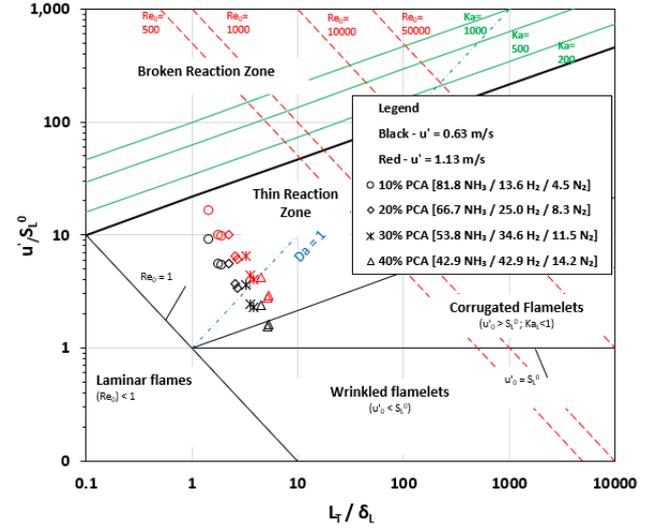


Fig. 1 Present experimental conditions on Peter-Borghi diagram [14].

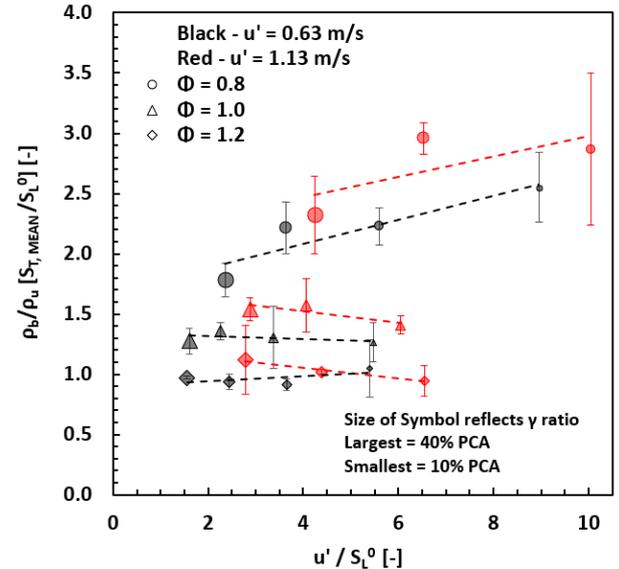


Fig. 2 Variation of $\rho_b/\rho_u[S_{T,\text{mean}}/S_L^0]$ as a function of u'/S_L^0

for all conditions.

The relationship between u'/S_L^0 and $\rho_b/\rho_u[S_{T,\text{mean}}/S_L^0]$ is illustrated in Fig. 2 for all conditions, with the size of symbols reflecting the γ ratio (biggest equates to $\gamma = 40\%$, smallest $\gamma = 10\%$), and the colour code the turbulent intensity (u'). It should be underlined that an increase in u'/S_L^0 is analogous to an increasing turbulent Karlovitz Number (Ka). As can be seen in Fig. 2, for the smallest u' ($u' = 0.63$ m/s) the $\rho_b/\rho_u[S_{T,\text{mean}}/S_L^0]$ ratio for the lean cases ($\phi = 0.8$) increases with u'/S_L^0 as γ decreases, whilst the $\rho_b/\rho_u[S_{T,\text{mean}}/S_L^0]$ remains stable with increasing u'/S_L^0 and γ for both the stoichiometric and rich ($\phi = 1.2$) cases. As the u' is increased, the lean cases maintain the same above-mentioned trend, whilst stoichiometric and fuel rich blends display a decreasing $\rho_b/\rho_u[S_{T,\text{mean}}/S_L^0]$ ratio with u'/S_L^0 with decreasing γ . Similar behavior has previously been reported in NH_3/air flames, with Ichimura et al. [5] reporting mixtures on the lean side where more difficult to extinguish than on the rich side, owing to preferential-diffusional instability. Similarly, Xia et al. [6] reported higher S_T/S_L^0 ratios for lean oxygen enriched NH_3 flames for the same turbulence than under rich conditions. Hashimoto et al. [15] reported similar findings for CH_4/NH_3 flames. As such, it appears that the consideration of thermal-diffusional instabilities greatly contributes to the ability of predicting turbulent flame behavior of NH_3 based fuels.

In premixed flames, instabilities can result from both preferential-diffusional and hydrodynamic (Darrieus-Landau) instabilities. The Markstein Length (L_b) indicates the response of the flame to stretch, and thus a good indicator of a flame's propensity to instability. Fig. 3 illustrates the variation of $\rho_b/\rho_u[S_{T,\text{mean}}/S_L^0]$ as a function of L_b , with L_b measured from the laminar flame experiments. Clearly, an increasing L_b equates to a decrease in the velocity ratio. All lean PCA flames exhibited a negative L_b , displaying a higher S_T/S_L^0 ratio for similar u'/S_L^0 ratios than PCA blends exhibiting positive L_b . It should be noted that a negative L_b response equates to an acceleration of the flame under increasing stretch (turbulent) conditions and thus seems to corroborate with the trends measured in Fig. 2. Furthermore, PCA blends at stoichiometric and rich conditions exhibit a L_b close or around 0, meaning that the flame is relatively free from stretch effects, in agreement with the relatively small change in the velocity ratio with increasing u'/S_L^0 of those blends in Fig. 2, even with increasing u' .

Although L_b remains a valid qualitative evaluator of the turbulent flame-stretch interaction, the Lewis Number (Le) defined as the ratio of thermal to mass diffusivity of the deficient reactant, strongly influences the burning rate of stretched flames, with both L_b and Le interrelated. Flames with $Le > 1$ exhibit greater relative thermal diffusivity, displaying a reduction in burning rate with increasing stretch (turbulent intensity), and conversely flames with $Le < 1$ show a relative acceleration with increasing stretch [16]. The relationship between the Lewis number (Le_{eff}) and the velocity ratio of the all the present experiments is illustrated in Fig. 4. Note that

details of the evaluation of Le_{eff} are available in [17].

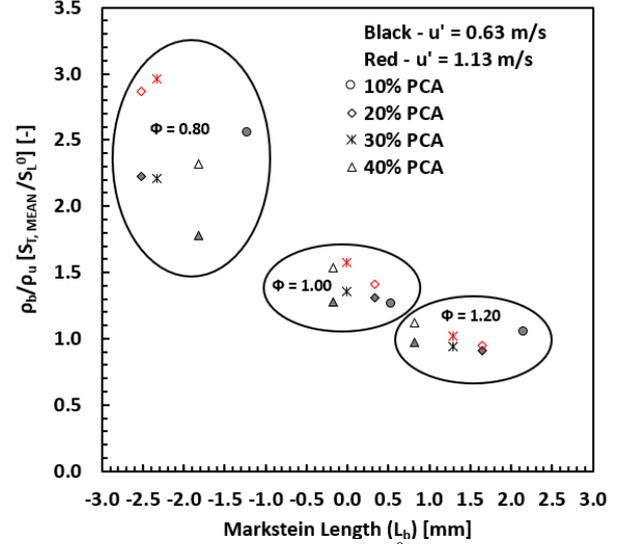


Fig. 3 Variation of $\rho_b/\rho_u[S_{T,\text{mean}}/S_L^0]$ as a function of Markstein Length (L_b) for all conditions.

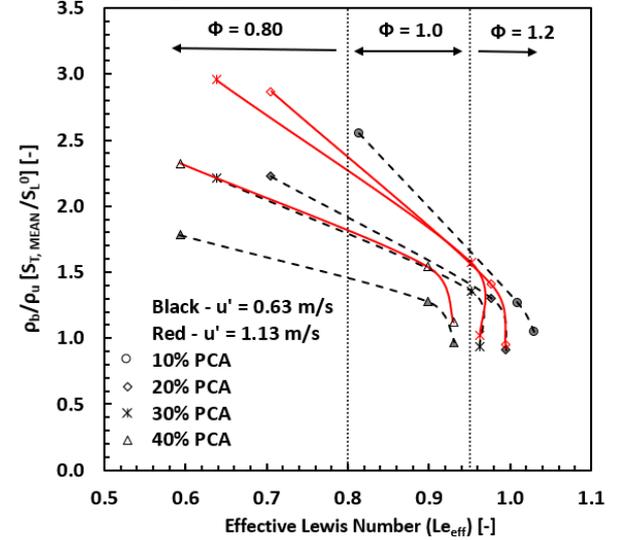


Fig. 4 Variation of $\rho_b/\rho_u[S_{T,\text{mean}}/S_L^0]$ as a function of effective Lewis Number (Le_{eff}) for all conditions.

As can be seen from Fig. 4, the lean PCA flames display the lowest Le_{eff} ($Le_{\text{eff}} < 0.8$) whilst exhibiting the greatest S_T/S_L^0 for the same u' . Conversely, stoichiometric and fuel rich PCA flames have similar Le_{eff} ($0.9 - 1.05$), and display nominally similar resistance to turbulence, as illustrated in Fig. 2. These trends are most likely due to the influence of the thermal-diffusional instability on turbulent NH_3 based flames. For the lean PCA flames, that have a $Le_{\text{eff}} \ll 1$, it is likely that the local burning velocity is enhanced in the convex structure of the flame, due to the imbalance in the mass diffusion of the reactants, which is much greater than the thermal diffusion from the burned to the unburnt area. Additionally, a change in the local flame temperature is expected, with an increase and decrease in the convex and concave area, respectively. Ultimately, the overall burning intensity is enhanced due to preferential-diffusional preferences enhanced by the turbulent eddies in the lean PCA flames, in good agreement with the trends

presented in Fig. 2.

It is interesting to note the rapid increase in the velocity ratio with decreasing Le_{eff} , exhibiting a ‘bending motion’, as displayed in Fig. 4. Moreover, considering that the PCA mixtures investigated have a wide range of Le_{eff} ($\sim 0.6 - 1.05$) and cross the $Da = 1$ limit (see Fig. 1), it seems of interest to compare a literature proposed correlation that incorporates the influence of Le . The establishment of a unified scaling law for S_T incorporating the influence of Le is till an open issue, with numerous studies proposing various scaling laws. Recently, Dai et al. [18] studies the effects of Le on turbulent expanding $NH_3/H_2/air$ mixtures and proposed various correlations. Comparing a large data-set including lean H_2/air ($Le < 1$), lean C_3H_8/air flames ($Le < 1$), CH_4/air ($Le \sim 1$), and rich $NH_3/H_2/air$ flame (50/50, $\phi = 1.3$, $Le > 1$), they proposed a number of correlations in the form of:

$$(S_T/S_L^0) = A [(u'/S_L^0)] Le^{-B} \quad (4)$$

With $A = 2.42 - 2.63$ and $B = 0.44 - 0.47$.

Fig. 5 illustrates this correlation against results presented in this work. Due to space requirements, other literature datasets have not been superimposed on Fig.5. Nevertheless, the PCA flames investigated show good agreement with the above correlation, with the pre-factor A and power exponent B falling within the range proposed by Dai et al. [18], 2.628 and 0.486, respectively, with an R^2 value exceeding 0.89. It should be noted the mixtures displaying the lowest Le ($Le < 0.7$, red symbols) start deviating from the proposed correlation. Yet, the agreement is shown to be satisfactory with the PCA flames investigated.

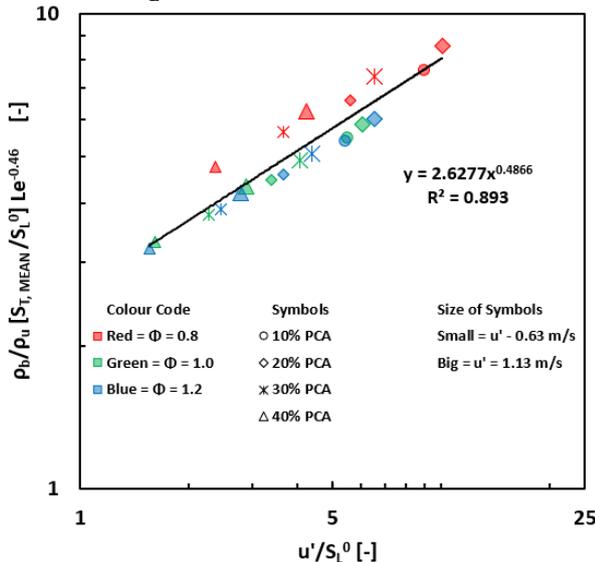


Fig. 5 Correlation of Le -corrected S_T/S_L^0 ratio against u'/S_L^0

4. Concluding Remarks

The partial dissociation (‘cracking’) of the NH_3 molecule to enhance combustion has been investigated under turbulent conditions using the spherical flame configuration. Fuel lean, stoichiometric, and rich conditions, with dissociation ratios up to 40% have been considered. In general, lean flames exhibited a higher

velocity ratio for the same turbulent intensities than richer fuel flames. This behavior can potentially be explained by the opposite stretch-related behavior (Markstein Length) and preferential-diffusional effects (Lewis Number), enhancing the overall burning intensity of the leanest flames. Present experimental data appears to correlate well with literature proposed correlation considering preferential-diffusional effects.

Acknowledgments

This project has received funding from the European Union’s Horizon 2020 Research and Innovation Program agreement No. 884157. Also, this research has received funding from the French Government’s ‘‘Investissement d’avenir’’ program: ‘Laboratoire d’excellence CAPRYSES’ (Grant N. ANR-11-LABX-0006-01).

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