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# Comparative study on the laminar flame speed enhancement of Ammonia with Hydrogen and Methane addition

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## Introduction

To strengthen fundamental analysis of multi-component ammonia-based blends, an outwardly propagating spherical flame was employed to measure the flame speeds and Markstein lengths of pure NH<sub>3</sub>, H<sub>2</sub> and CH<sub>4</sub>, alongside precisely mixed blends of NH<sub>3</sub>/H<sub>2</sub> and NH<sub>3</sub>/CH<sub>4</sub>. Theoretical relationships between the Markstein length and Lewis number were explored alongside effective Lewis number formulations. Across all conditions, an exponential and linear increase in laminar burning velocity upon H<sub>2</sub> and CH<sub>4</sub> addition, respectively, was measured; in good agreement with appraised chemical reaction mechanisms. The Stagni et al. [1] mechanism yielded best agreement for NH<sub>3</sub>/H<sub>2</sub> mixtures, whilst the Okafor et al. [2] reaction mechanism produced best agreement with NH<sub>3</sub>/CH<sub>4</sub> mixtures. For NH<sub>3</sub>/H<sub>2</sub> blends under lean and stoichiometric conditions, a diffusional based Lewis number formulation best captured the non-linear stretch-related behaviour measured, whilst a heat-release model resulted in better agreement for richer conditions. On the other hand, for NH<sub>3</sub>/CH<sub>4</sub> blends, a volume-based Lewis number displayed best agreement across all tested conditions. Furthermore, a systematic analysis of the flame speed enhancement effects (thermal, kinetic, diffusive) of H<sub>2</sub> and CH<sub>4</sub> addition to NH<sub>3</sub> was undertaken. Augmented flame propagation was demonstrated to be principally an Arrhenius effect, predominantly through the reduction of associated activation temperature. Finally, flame temperature had a stronger effect than the diffusive pathway, both for H<sub>2</sub> and CH<sub>4</sub> addition to NH<sub>3</sub> flames.

## Materials and Methods

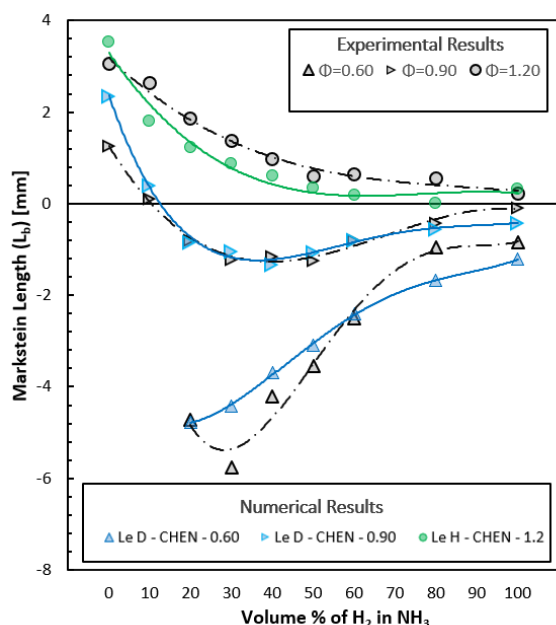
Laminar flame speed measurements were performed using a constant-volume spherical vessel. Details of the apparatus and post-processing techniques can be found in [3], updated for NH<sub>3</sub> specifications in [4]. Measurements were performed at initial conditions of 298 K ( $\pm 3$  K) and 0.1 MPa ( $\pm 1 \times 10^{-3}$  MPa), employing high-purity fuel components of NH<sub>3</sub> (99.95%), CH<sub>4</sub> (>99.995%) and H<sub>2</sub> (99.999%) and dry-zero compressed air (AirLiquide, 20.9% O<sub>2</sub>). To investigate the influence of CH<sub>4</sub> and H<sub>2</sub> on NH<sub>3</sub> flame speed and stretch-related behaviour, molar ratios were varied (0 – 100% CH<sub>4</sub>; 0 – 100% H<sub>2</sub>), in incremental steps across a wide range of equivalence ratios ( $\Phi = 0.7 - 1.2$  CH<sub>4</sub>;  $0.6 - 1.4$  H<sub>2</sub>). Limits were set on the range of radii utilised to minimise the influence of spark energy, buoyancy or cellularity, and confinement during flame growth, ensuring measurements were restricted within the quasi-steady regime. Due to flame motion and its intrinsic curvature, the outwardly propagating flame is subjected to a temporal change of the flame surface element, known as stretch at a given rate. For this work, unstretched flames speeds were extrapolated employing the recommendations of Chen [5]. The adiabatic expansion ratio at constant pressure (defined as  $\sigma = \rho_b / \rho_u$ , where  $\rho_u$  and  $\rho_b$  are the unburnt and burnt gas densities, respectively), was accounted in order to obtain representative values of laminar flame speed.

Theoretical relationships linking the Markstein length as proposed by Chen [5], [6], Law and Sung [7], and Matalon and Bechtold [8] were explored. These theoretical correlations require the calculations of various fundamental flame parameters, namely the Zel'dovich number ( $Ze$ ), the laminar flame thickness ( $\delta$ ), the expansion ratio ( $\sigma$ ), with in depth detail of methodology employed available in [9]. Whilst the calculation and definition of the Lewis Number ( $Le$ ) for single-fuel mixtures is relatively straightforward, no clear consensus on the correct formulation of  $Le$  for multi-fuel mixtures seems to exist [10]; the challenge arising from the fact that the diffusivity of each fuel must be considered. This is particularly applicable to mixtures of H<sub>2</sub>, NH<sub>3</sub>, and n-alkanes which exhibit different transport diffusion mechanisms and flame characteristics. Bouvet et al. [10] identified three 'effective'  $Le$  formulations ( $Le_{eff}$ ); a heat release formulation, a diffusion weighted formulation, and a volume weighted formulation, defined respectively in this work as  $Le_H$ ,  $Le_D$  and  $Le_V$ , which were appraised.

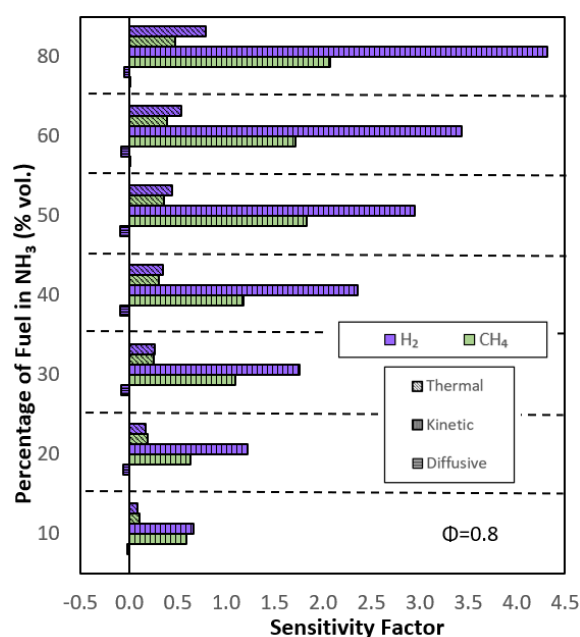
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## Results and Discussions



**Fig. 1** Comparison of measured  $L_b$  with numerical  $L_b$  evaluated using the Chen model and  $Le_D$  formulation for  $NH_3/H_2$  blends



**Fig. 2** Sensitivity Analysis of laminar burning velocity for  $NH_3/H_2$  and  $NH_3/CH_4$  blends,  $\Phi = 0.80$

The laminar burning velocity and stretch-related behaviour of  $NH_3/H_2$  and  $NH_3/CH_4$  was measured experimentally as well as evaluated numerically. With respect to the laminar burning velocity, a linear increase was measured upon  $CH_4$  addition whilst an exponential increase was observed upon  $H_2$  addition, with the Okafor and Stagni reaction mechanisms yielded best agreement with recorded results. With respect to the Markstein length behaviour, a decrease in Markstein length was measured upon  $CH_4$  addition, with the magnitude of reduction decreasing as the equivalence ratio decreased, with nominal changes observed at leanest conditions ( $\Phi=0.7-0.8$ ). The Chen formulation coupled with a volume-based Lewis number formulation ( $Le_V$ ) demonstrated good quantitative and qualitative agreement. The flame stretch sensitivity varies non-monotonically with the  $H_2$  ratio, see Fig. 1, with an initial substantial decrease in  $L_b$  with increasing  $H_2$ , prior to a minor increase in  $L_b$  upon further  $H_2$  addition, with minimal variation in recorded  $L_b$  of  $NH_3$  flames upon  $H_2$  enrichment. Data illustrated in Fig. 1 fulfils the scarce  $L_b$  data available in peer-published literature ([11],  $\Phi = 1.0$ ). Furthermore, it was observed that a diffusion-based Lewis number ( $Le_D$ ) best captured this non-linear behaviour, under lean and stoichiometric conditions. Given that the  $Le_D$  formulation was derived from modelling of lean turbulent  $CH_4/H_2$  flames, using the assumption that flame curvature is dominant, hence local enrichment of the most diffusive fuel at the flames leading edge is predicted. Since for ultra-lean conditions  $H_2$  and  $NH_3$  have higher mass diffusivities than  $O_2$ , this concept appears valid. Under rich conditions, a heat release based-formulation ( $Le_H$ ) appears better suited as pictured in Fig. 1. Once a suitable  $Le$  was appraised, a sensitivity analysis related to the contribution of the major flame enhancing pathways (thermal, diffusive, kinetic) was undertaken, for an  $\Phi = 0.80, 1.0, 1.20$ ). Fig. 2 illustrates the sensitivity analysis of the laminar burning velocity for  $NH_3/H_2$  and  $NH_3/CH_4$  under lean conditions ( $\Phi = 0.80$ ). For all evaluated blends, under lean and stoichiometric conditions, enhanced flame propagation is principally an Arrhenius effect (kinetic), predominantly through the reduction in activation temperature and thus activation energy. The thermal pathway is comparable for both  $CH_4$  and  $H_2$  addition, and much greater than the diffusive pathway, which is negligible in comparison to the other evaluated pathways.

## Conclusions

Addition of  $CH_4$  and  $H_2$  addition results in a linear and exponential increase in laminar burning velocity of  $NH_3$  based fuels, respectively. Reaction mechanisms show good agreement with experimental results.  $NH_3$  displays very different stretch related behaviour to that of pure  $CH_4$  and  $H_2$ , with a non-linear relationship measured upon  $H_2$  addition. With respect to effective Lewis number formulations,  $Le_V$  displayed best agreement with  $NH_3/CH_4$  blends, whilst  $Le_D$  resulted in best agreement for lean and stoichiometric  $NH_3/H_2$  blends, with a  $Le_H$  to be preferred under rich conditions. Finally, enhanced flame propagation of  $NH_3/H_2$  and  $NH_3/CH_4$  blends was principally demonstrated to be a kinetic effect, predominantly through the reduction of the activation energy.

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