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## **Influence of Hydrogen and Methane Addition in Laminar Ammonia Premixed Flame on Burning Velocity, Lewis Number and Markstein Length**

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### **Abstract:**

The use of Ammonia ( $\text{NH}_3$ ) and blends with either Methane ( $\text{CH}_4$ ) or Hydrogen ( $\text{H}_2$ ) obtained by in-situ  $\text{NH}_3$  cracking, seem to be promising solutions to partially or fully decarbonise our energy systems. To strengthen understanding of fundamental combustion characteristics of these  $\text{NH}_3$  blends, the outwardly propagating spherical flame configuration was employed to determine the flame speeds and Markstein lengths. The air/fuel mixtures were varied across a large range of compositions and equivalence ratios. In general addition of  $\text{CH}_4$  or  $\text{H}_2$  results in a linear and exponential increase in measured laminar burning velocity, respectively. Of the appraised mechanisms, Stagni and Okafor kinetics mechanisms yielded best agreement with  $\text{NH}_3/\text{H}_2$  and  $\text{NH}_3/\text{CH}_4$  flame speed measurements. With respect to measured Markstein length, for a fixed equivalence ratio, addition of  $\text{CH}_4$  to  $\text{NH}_3$  resulted in a linear reduction in stretch sensitivity for the tested conditions. For lean  $\text{NH}_3/\text{H}_2$  flames, an initial decrease in Markstein length is observed up to 30 – 40%  $\text{H}_2$  addition, at which point any further addition of  $\text{H}_2$  results in an increase in Markstein Length, with a non-linear behaviour accentuated as conditions get leaner. Above stoichiometry similar stretch behaviour is observed to that of  $\text{NH}_3/\text{CH}_4$ . Different theoretical relationships between the Markstein length and Lewis Number were explored alongside effective Lewis Number formulations. For lean  $\text{NH}_3/\text{H}_2$  mixtures, a diffusional based Lewis Number formulation yielded a favourable correlation, whilst a heat release model resulted in better agreement at richer conditions. For  $\text{NH}_3/\text{CH}_4$  mixtures, a volumetric based Lewis Number formulation displayed best agreement for all evaluated equivalence ratios. For  $\text{NH}_3/\text{H}_2$ , changes in measured Markstein Length were demonstrated to potentially be the result of competing hydrodynamic and thermo-diffusive instabilities, with the influence of the thermo-diffusional instabilities reducing as the equivalence ratio increases. On the other hand, the addition of  $\text{CH}_4$  to  $\text{NH}_3$  results in the propensity of moderating hydrodynamic instabilities, resulting in a stabilising influence on the flame, reflected by increasing positive Markstein number values. Finally, a systematic analysis of the flame speed enhancements effects (kinetic, thermal, diffusive) of  $\text{CH}_4$  and  $\text{H}_2$  addition to  $\text{NH}_3$  was undertaken. Augmented flame propagation of  $\text{NH}_3/\text{CH}_4$  and  $\text{NH}_3/\text{H}_2$  was demonstrated to be principally an Arrhenius effect, predominantly through the reduction of the associated activation energy.

**Keywords:** Ammonia-hydrogen, ammonia-methane, Laminar flame Speed, Lewis Number, Markstein Length

## 1. Introduction

The historical prevalence of hydrocarbon fuel usage to sustain our power and transport needs, and the associated greenhouse gas emissions produced, have resulted in important environmental and ecological adversities [1]. As such, in order to attain zero-carbon targets, the large-scale employment of renewable and carbon-free fuels within our energy systems is required to maintain a balanced trajectory between human development, progress and cohesion with the environment. In light of this context, Ammonia ( $\text{NH}_3$ ) has emerged in recent years as an efficient zero-carbon hydrogen ( $\text{H}_2$ ) carrier. Liquid  $\text{NH}_3$  offers higher  $\text{H}_2$  content than for example, ethanol, methanol and gasoline, in conjunction with exhibiting a higher volumetric energy density than that of liquid  $\text{H}_2$  [2]. Due to  $\text{NH}_3$  prevalent use in the agricultural industry, considerable storage and distribution infrastructure is already established [2]. Although  $\text{NH}_3$  offers several advantages, there remains several practical combustion challenges, notably the control and reduction of pollutant emissions ( $\text{NO}_x$  and  $\text{N}_2\text{O}$ ). Moreover,  $\text{NH}_3$  exhibits slow burning velocities, often associated to low burning efficiency in engines, a narrow flammable range and high ignition energy, potentially yielding poor flame stabilisation and extinction characteristics resulting in local or global extinctions. To improve  $\text{NH}_3$ 's combustion properties, blending  $\text{NH}_3$  with methane ( $\text{CH}_4$ ) (for a partial decarbonisation) or  $\text{H}_2$  (from the possible 'in situ' cracking of ammonia) has been proposed, and has gained considerable recent attention, with comprehensive reviews of  $\text{NH}_3$  related work undertaken [2], [3]. Successful demonstrations in both gas turbines [4]–[6] and internal combustion engines [7], [8] have been achieved at high temperatures and pressures. Nevertheless, studies remain limited, as such there seems to be a practical necessity to develop and strengthen understanding of fundamental combustion characteristics of blends containing  $\text{NH}_3$ , ultimately leading to the development of combustors offering greater flame stability and reduced pollutant emissions.

The unstretched laminar burning velocity ( $S_L^0$ ), is one main fundamental physio-chemical property of any premixed air-fuel mixture, reflecting both the combustion process and mixture reactivity. As such,  $S_L^0$  is a key parameter helping understand premixed operational instabilities, notably flashback, blow-off or extinction, and a central step in turbulent flame modelling [9]. Variations in fuel composition inherently introduce changes in transport and chemical properties, in turn influencing witnessed burning and reactivity characteristics of the fuel mixture. The Lewis number ( $Le$ ), defined as the ratio of thermal to mass diffusivity of the deficient reactant, details the transport mechanisms of various species across the flame front [9]. Early experimental investigations [10], [11], supported by the development of asymptotic theories [12], [13], underline that preferential diffusion (i.e.  $Le$  deviating from unity), can strongly influence the burning rates of stretched flames – which undergo the combined effects of strain, curvature, and flame motion. Flames with  $Le > 1$  exhibit greater relative thermal diffusivity, displaying a reduction in burning rate with increased stretch, due to heat loss to the unburned reactant. Conversely, flames with  $Le < 1$  show a relative acceleration with increasing stretch [9]. The burnt gas Markstein length ( $L_b$ ) is a measurable parameter which characterises the influence of  $Le$  on the flame response to the stretch rate. The Markstein number ( $Ma$ ), defined as  $L_b$  divided by the laminar flame thickness ( $\delta_L$ ) – is an indicator of the propensity of a combustion system to be or not influenced by thermo-acoustic instability, and thus of interest to study [14].

Recent experimental studies have investigated  $S_L^0$  and  $L_b$  characteristics of  $\text{NH}_3$ /air flames, notably by Hayakawa et al. [15], at atmospheric and 0.5 MPa of initial ambient pressure, and Kanoshima et al. [16], expanded on that work to include the influence of initial ambient temperature (400-500 K). Results from these studies underline that  $S_L^0$  peaks at an equivalence ratio ( $\phi$ ) of  $\approx 1.1$ , with an increase in pressure and temperature ensuing a decrease and increase

1 in  $S_L^0$ , respectively. With respect to  $L_b$ ,  $NH_3$ /air flames display an increasing  $L_b$  with increasing  $\phi$ , a  
2 similar trend to that of  $CH_4$ /air and  $H_2$ /air flames. It is noted that at normal temperature and  
3 pressure conditions ( $T=298K$ ,  $P=0.1MPa$ ) lean  $NH_3$  flames exhibit negative  $L_b$ , with positive values  
4 recorded under rich conditions. Furthermore,  $L_b$  is observed to decrease with a rise in pressure  
5 and temperature, analogous behaviour to that of the flame thickness.

6  
7 Okafor et al. [17], [18], investigated the influence of  $NH_3$  on  $CH_4$  based flames (up to  $\approx 52\%$   $NH_3$   
8 by vol.%) across a wide range of  $\phi$  and pressures (0.1 – 0.5 MPa), highlighting that  $S_L^0$  decreases  
9 with increasing  $NH_3$  fraction and pressure, developing a detailed and reduced kinetic mechanism.  
10 Experimental results of Shu et al. [19] on  $NH_3/CH_4$  flames (298 K, 0.1 MPa), demonstrated similar  
11 tendency but with a uniform decrease in the flame flammability limits with  $NH_3$  increase. They also  
12 highlighted the important role played by the H and OH radicals in  $NH_3/CH_4$  flame propagation. In  
13 relation to flame stretch sensitivity of  $CH_4/NH_3$  flames, Okafor et al. [17] emphasize the shift from  
14 a linear to a non-linear flame speed-stretch rate relationship exhibited with increasing  $\phi$  and  $NH_3$   
15 fraction. It should be noted that this is unusual for fuels displaying Le values close to 1 (as is the  
16 case for pure  $CH_4$  and  $NH_3$ ), with this behaviour mainly attributed to an increase in the preheating  
17 zone thickness.

18  
19 Lee et al. [20], [21] and more recently, Ichikawa et al. [22] and Lhuillier et al. [23] investigated  
20 the influence of  $H_2$  upon  $NH_3$  based flames. Ichikawa et al., demonstrated that at stoichiometric  
21 conditions ( $\phi=1$ ),  $S_L^0$  increases non-linearly with increasing  $H_2$  fraction, and decreases with  
22 increasing pressure. Lhuillier et al. reported an exponential increase in  $S_L^0$  upon addition of  $H_2$  at  
23 various initial conditions (298-473K,  $\phi = 0.8 - 1.4$ ,  $H_2 = 60\%$  vol. max). With respect to the flame  
24 stretch sensitivity, Ichikawa et al.[22] reported a non-monotonic variation, with an initial  
25 substantial decrease in  $L_b$  with increasing  $H_2$ , prior to a minor increase in  $L_b$  upon further  $H_2$   
26 addition. Interestingly, this stretch behaviour dampens at higher pressures, with minimal variation  
27 in recorded  $L_b$  of  $NH_3$  flames upon  $H_2$  enrichment. Noteworthy, similar stretch-related non-  
28 monotonic trends have been observed for lean  $CH_4/H_2$  flames [24].

29  
30 The importance of flame stretch sensitivity and Le goes clearly beyond the laminar flame  
31 regime. Lipatnikov and Chomiak [25], in their extensive review of molecular transport effects on  
32 flame propagation, highlighted that preferential diffusional instabilities affect both weak and  
33 strong turbulent combustion. The influence of Le on turbulent flames has been reported in the  
34 course of experimental studies [26]–[28] as well as in direct numerical simulations [29], [30].  
35 Although limited in scale, emerging studies focusing on turbulence-flame interaction for  $NH_3$  and  
36 its blends with either  $H_2$  and  $CH_4$  underlined the potential role of preferential-diffusion and flame-  
37 stretch interaction upon turbulent flame characteristics. For example, Ichimura et al. [31]  
38 investigated  $NH_3$ /air flames at various turbulent intensities, underlining that although  $S_L^0$  of  
39  $NH_3$ /air is greatest at  $\phi \approx 1.1$ , lean mixtures exhibited better resistance to turbulence induced  
40 extinction than richer conditions, due to the potential thermo-diffusive accelerating effects of lean  
41  $NH_3$ /air mixtures, displaying  $Le < 1$ . Similarly, Lhuillier et al. [8] investigated  $NH_3/H_2$  and  $NH_3/CH_4$   
42 (15% vol. of  $H_2$  or  $CH_4$ ) turbulent flame propagation under engine related operating conditions  
43 (445K, 0.54 MPa). They reported a decreasing and increasing turbulent to laminar flame speed  
44 ratio upon  $CH_4$  and  $H_2$  addition, respectively, induced by the different thermo-diffusive properties  
45 and stretch-related behaviour of these ammonia blends.

46  
47 Clearly, although emerging, the experimental study on the addition of  $H_2$  or  $CH_4$  to  $NH_3$ -based  
48 flames remains scarce. Furthermore, recent turbulent combustion experiments underlined the  
49 potential influence of preferential-diffusional instabilities upon  $NH_3$ -based flames [8], [31], [32],  
50 hence, the aim of this work is to investigate in detail the influence of Le change on flame behaviour.  
51  $NH_3/CH_4$  and  $NH_3/H_2$  mixtures were varied across a large range of blend composition and  
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equivalence ratio, representative of the prospective demands of fuel-flexible combustors widely employed for power generation. The addition of either CH<sub>4</sub> or H<sub>2</sub> to a given NH<sub>3</sub>/air mixture increases flame temperature, reactivity, mixture flame speed but changes the thermo-diffusive behaviour, which is studied in-detail throughout this work.

## 2. Experimental set-up and specifications

Laminar flame speed measurements were performed using a constant-volume spherical vessel. Details of the apparatus and post-processing techniques can be found in [33], updated for NH<sub>3</sub> specifications in [23], and thus only a brief summary is presented herein. The spherical vessel is equipped with four orthogonal 70 mm quartz viewing windows and has a nominal internal volume of 4.2 L. Thermal mass flow controllers (Brooks 5850S ( $\pm 1\%$ )) were employed to introduce the reactants into the vessel. Mole fractions of all species were determined as a function of temperature (T), initial pressure (P) and fuel-air equivalence ratio. A piezo-electric pressure transducer and a type-K thermocouple were employed to check respectively the pressure and temperature prior to ignition. The maximum deviation between the effective initial pressure inside the chamber and the required initial pressure was no more than 1%. A vacuum-pump was used to empty the combustion chamber twice between tests ensuring a residual pressure of no more than 0.009 bar, with the remaining air compensated within the equivalence ratio calculation. Pre-mixing was achieved using an internal fan. A capacitor-discharge ignition was achieved via fine tungsten electrodes mounted at 90° to the measurement plane. After quiescence is attained, simultaneous TTL signal to the data-acquisition and ignition systems trigger the experiments. High speed Schlieren imaging of flame propagation was accomplished using a CMOS high speed camera (Phantom V1210) set to a suitable frame capture rate (3000 – 12000 fps), facilitating a spatial resolution of  $\sim 0.10$  mm per pixel. Edge-detection algorithms written in a bespoke MATLAB script were employed to calculate flame propagation rates. A minimum of 3 to 5 repeats were conducted per experimental condition.

## 3. Experimental specifications and theory

Measurements were performed at initial conditions of 298 K ( $\pm 3$  K) and 0.1 MPa ( $\pm 1 \times 10^{-3}$  MPa), with high-purity fuels (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 from 0 – 100% for CH<sub>4</sub>; and 0 – 80% for H<sub>2</sub>, in incremental steps across a wide range of equivalence ratios ( $\phi = 0.7 - 1.2$  and  $0.6 - 1.4$  respectively), with Table 1 summarising the experimental conditions.

**Table 1:** Experimental conditions ; T<sub>u</sub> = 298 K ( $\pm 3$  K), P<sub>u</sub> = 0.1 MPa ( $\pm 1 \times 10^{-3}$  MPa).

Equivalence Ratio ( $\phi$ )	Percentage of Fuel in NH <sub>3</sub> (vol.%)	
	CH <sub>4</sub>	H <sub>2</sub>
0.6	/	20,30,40,50,60,80
0.7	20,30,40,50,60,80,100	/
0.8	0,10,20,30,40,50,60,80,100	0,10,20,30,40,50,60,80
0.9	0,10,20,30,40,50,60,80,100	0,10,20,30,40,50,60,80
1.0	0,10,20,30,40,50,60,80,100	0,10,20,30,40,50,60,80
1.1	0,10,20,30,40,50,60,80,100	0,10,20,30,40,50,60,80

1.2	0,10,20,30,40,50,60,80,100	0,10,20,30,40,50,60,80
1.4	/	20,30,40,50,60,80

Schlieren images were undertaken as in [17], [23], [34], with the shadowed edge considered as the burnt gas isotherm, which as discussed by Giannakopoulos et al. [35], is critical for characterising the influence of flame stretch. The laminar burning velocity and  $L_b$  relative to the burnt side were experimentally determined employing the same procedure as in previous studies [34], [36]. For an outwardly spherically propagating flame, the stretched flame speed ( $S_b$ ) is expressed as the temporal derivative of the Schlieren flame radius ( $r_{sch}$ ) as in Equation 1:

$$S_b = \frac{dr_{sch}}{dt} \quad (1)$$

The flame stretch rate ( $K$ ) is defined as the change in flame area ( $A$ ) gradient and calculated for a propagating spherical flame as shown in Equation 2:

$$K = \frac{1}{A} \cdot \frac{dA}{dt} = \frac{2}{r_{sch}} \cdot \frac{dr_{sch}}{dt} \quad (2)$$

Various correlations between  $S_b$  and  $K$  have been proposed, allowing the estimation of the unstretched flame speed ( $S_b^0$ ). Two methodologies are employed in this study. The first model is based upon the assumption of large flame radii, considering both the effects of thermal expansion and  $Le$ , as in Equation 3 [37], which illustrates that the flame curvature ( $\kappa_{curv}=2/r_f$ ) and  $S_b$  vary linearly, hence allowing the evaluation of  $S_b^0$  and  $L_b$  from the linear extrapolation of  $S_b$  and  $K$  [38], [39]:

$$S_b = S_b^0 - L_b \cdot K = S_b^0 - S_b^0 \cdot L_b \cdot \frac{2}{r_f} \quad (3)$$

This methodology will be referenced herein as Linear Model based on Curvature (LMC). The second extrapolation method, attributed to Kelley and Law [40], is a non-linear model that allows for arbitrary  $Le$  and takes into account the deviations in adiabatic and planar assumptions, prominent in flames which are heavily influenced by stretch such as lean  $H_2$ -based flames. This non-linear model is expressed as in Equation 4:

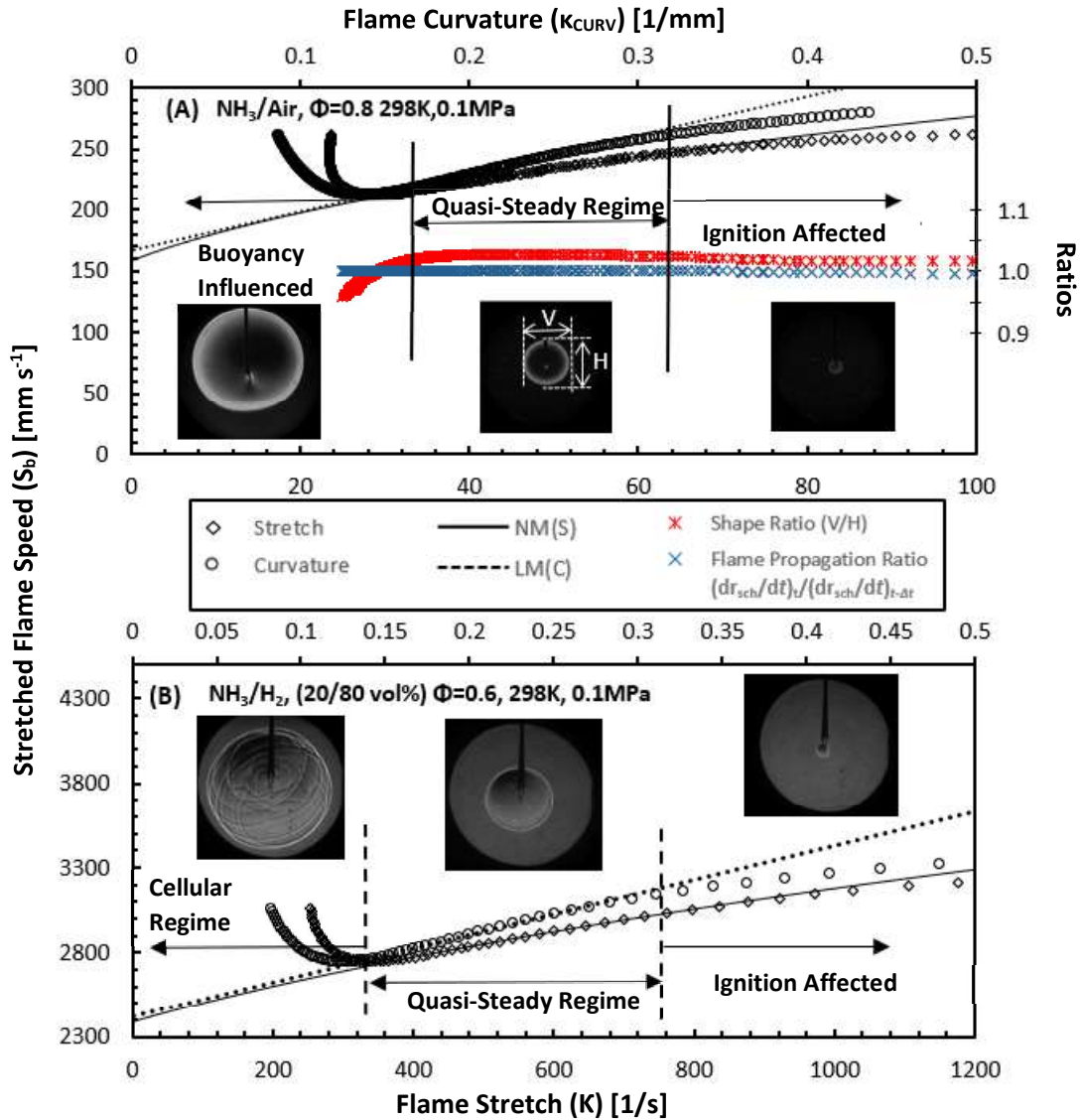
$$\left(\frac{S_b}{S_b^0}\right) \cdot \ln\left(\frac{S_b}{S_b^0}\right)^2 = -\frac{2 \cdot L_b \cdot K}{S_b^0} \quad (4)$$

This model has been used frequently over the last decade, improving accuracy [39], [41], and will be referenced here as the Non-Linear Model based on Stretch (NMS).

Chen [38] underlined that the accuracy of different extrapolation techniques is related to the  $Le$  of the fuel-air mixture. Chen [38] demonstrated that it is preferable to employ LMC for mixtures exhibiting  $Le > 1$  (i.e. positive  $L_b$ ) and NMS for  $Le < 1$  (i.e. negative  $L_b$ ), due to the non-linear relationship between  $S_b$  and  $K$ ; with these recommendations adopted in this study. Moreover, Wu et al. [39], quantified the uncertainty in extrapolation through the limitation of exploitable data range in relation to Markstein and Karlovitz numbers ( $Ma_{lin}Ka_{mid}$ ); all data presented in this work fall within the recommended values of -0.05 – 0.15 range.

Irrespective of the extrapolation methodology employed, to obtain representative values of laminar flame speed, the burned gas expansion factor has to be used as  $S_L^0 = S_b^0 \cdot (\rho_b/\rho_u)$  with equilibrium densities calculated using CHEMKIN-Pro, using Stagni et al. [42] and Okafor et al. [18]

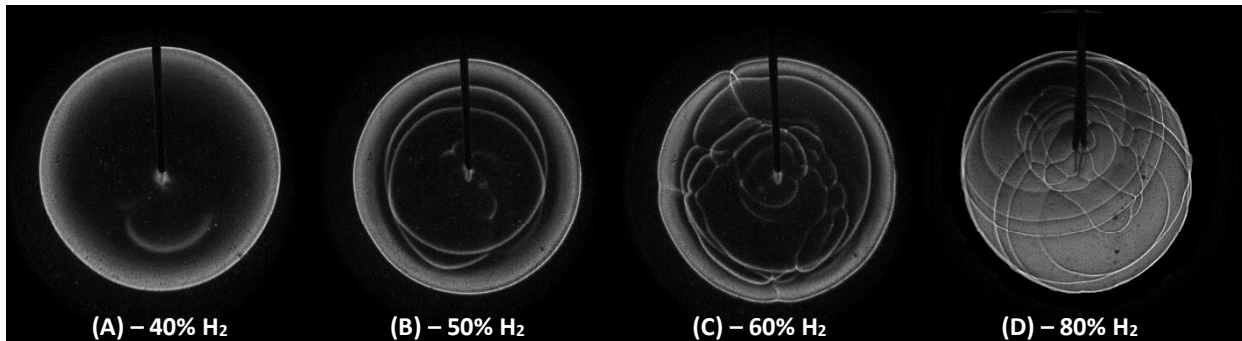
kinetics reaction mechanisms, for  $\text{NH}_3/\text{H}_2$  and  $\text{NH}_3/\text{CH}_4$ , respectively. The selection of these mechanisms is discussed later in section 5.2.



**Fig. 1** – Stretched flame speed vs stretch rate (K) and curvature ( $K_{\text{CURV}}$ ) for (a) pure  $\text{NH}_3/\text{air}$  and (b)  $\text{NH}_3/\text{H}_2$  (20/80 vol.%) ( $T_u = 298$  K,  $P = 0.1$  MPa)

Limits were set on the range of exploitable radii to minimise the influence of the spark, the buoyancy or the cellularity, and the confinement during the flame growth, ensuring measurements were restricted within the quasi-steady regime. Bradley et al. [43] suggest a spark affected radius up to 6 mm for  $\text{CH}_4/\text{air}$  flames, however Chen et al. [44] demonstrate this critical radius value to be dependent of  $L_e$ . For all data presented here, 9 mm was chosen as the minimum radius, with preliminary investigation demonstrating minimal variation in results derived from data above 7 mm. To limit pressure effects a maximum radius of 25 mm was considered, within the 30% of chamber radius as proposed by Burke et al. [45] and satisfying  $r_{\text{sch}}/(3V/4\pi)^{1/3} < 25\%$  as recommended by Chen [46]. Extrapolation methods used to yield flame speed and the corresponding  $L_b$  rely on a sufficiently large stable quasi-steady flame propagation regime. In the present study, pure  $\text{NH}_3/\text{air}$  flames, or blends containing less than 10% of  $\text{CH}_4$  or  $\text{H}_2$  (vol.%) at leanest and richest conditions were observed to be heavily influenced by the buoyancy, a consequence of their very low burning rate. As a result these flames were observed to lose sphericity, morphing in an ellipsoidal expanding flame, as noted

by Hayakawa et al. [15] and Chen et al. [47] for identical initial conditions (298 K, 0.1 MPa). For such flames, the methodology proposed by Hayakawa et al. [15] in delimiting the transition between ignition influenced, quasi-steady and buoyancy influenced propagation regimes was followed. The aforementioned regimes are determined based upon the flame shape and propagation ratio, defined as the vertical and horizontal radius of the flame ( $r_{sch,V}/r_{sch,H}$ ) and  $(dr_{sch}/dt)_t/(dr_{sch}/dt)_{t-\Delta t}$  (where  $dr_{sch}/dt$  denoting the flame propagation speed at time t), respectively. Figure 1.a illustrates the change in flame shape ratio and moving average of the flame propagation ratio against stretch for a lean  $NH_3$ /air flame ( $\phi=0.80$ ); with the relationship of stretched flame speed with stretch and curvature superimposed. As can be seen in Fig 1.a, a quasi-steady propagation regime is clearly identifiable, as such the point at which the flame shape ratio considerably changed was taken to represent the maximum flame radius limit. It should be noted that the upward motion of the growing flame kernel does not yield a significant influence upon the propagation speed, since change in the stretched flame speed still maintained proportionality to both flame-stretch and curvature until the transition point was attained. Under other conditions, minor modifications in useable flame radius selection were also required due to known instability issues associated with lean combustion of  $H_2$ -containing fuels. Lean  $H_2$ -based flames are particularly unstable with regard to diffusive effects, a consequence of their low  $Le$  ( $Le \ll 1$ ), resulting in flame acceleration at low stretch and curvature rates [48], as illustrated in Figure 1.b, with an example case of a lean  $NH_3/H_2$  (20/80 vol.%,  $\phi=0.6$ ) flame. Under the tested experimental conditions, it was noted that no flames developed a cellular surface composed of cells of comparable size. However, large cracks of a permanent nature appeared at leanest conditions ( $\phi=0.60$ ) for flames containing  $\geq 40\%$   $H_2$ , with further  $H_2$  enrichment enhancing surface cracking, as illustrated in Fig. 2. As underlined by Jomaas et al. [49], these large-scale cracks are most probably the result of large-amplitude initial disturbances, most probably triggered by the ignition event, and not a consequence of preferential diffusion. Nevertheless, using a suitably fast frame capture rate, a minimum of 30 acquired radii was obtained even for the fastest flames, from which flame speed data were estimated.



**Figure 2** – Schlieren images illustrating the development of flame surface cracking as a function of  $H_2$  fraction for  $NH_3/H_2$  flames ( $T_u = 298$  K,  $P = 0.1$  MPa,  $\phi=0.60$ )

The measurements of laminar flame speed are an essential step in order to improve the accuracy of reaction mechanisms [46]. Therefore, the quantification of the measurement uncertainties is required. For this study, uncertainty quantification relies upon the methods outlined by Moffat [50], employing a combination of the experimental facility specifications and accuracy of the processing techniques employed. It should be noted that the uncertainty is quantified for the unstretched flame speed ( $S_b^0$ ), and not for  $S_L^0$ , since this is the parameter measured, here named as  $U_{S_b^0}$ . The total uncertainty estimate is given by Equation 5, where  $B_{S_b^0}$  represents the total bias uncertainty,  $t_{M-1,95}$  the student's value at 95% confidence interval and M-1 degrees of freedom,  $\sigma_{S_b^0}$  the standard deviation of the repeated experiments, and M the number of experimental repeats at each condition;



$$U_{S_b^0} = \sqrt{B_{S_b^0}^2 + \left(\frac{t_{M-1,95}\sigma_{S_b^0}}{\sqrt{M}}\right)^2} \quad (5)$$

The total bias uncertainty, given by Equation 6, relating changes in  $S_b^0$  with respect to an independent influential variable, ( $v_i$ , i.e. temperature, ambient pressure,  $\phi$ , optical system, gas mixture quality) and the fixed error linked to that variable,  $y_i$ ,

$$B_{S_b^0} = \sqrt{\sum_{i=1}^n \left(\frac{\partial S_b^0(v_i)}{\partial v_i} y_i\right)^2} \quad (6)$$

In order to determine  $B_{S_b^0}$  by Equation 6, the relationships between  $S_b^0$  and each independent variable must be established. As applied in [7], the potential changes in  $S_b^0$  from several parameters are calculated as a function of  $\phi$ ; such as temperature ( $\pm 3$  K) and pressure ( $\pm 1 \times 10^{-3}$  MPa) by using data modelling with CHEMKIN-PRO. Uncertainty resulting from the optical system was evaluated from the summated fractional error of both the spatial resolution of the system ( $\pm 0.05/25\text{mm}$ ) and camera ( $\pm 1.5\text{-}7.5/3000\text{-}15000$  fps). Losses due to radiation influence measured flame burning speed, through the combined effect on the flame propagation itself and the calculated density ratio, with radiation-induced uncertainty particularly significant for slow propagating flames ( $< 12 \text{ cm s}^{-1}$ ) [51]. Lhuillier et al. [7] investigated the dependence of errors resulting from radiation for  $\text{NH}_3/\text{air}$  flames, concluding that the correlation proposed by Yu et al. [51] was applicable, with this recommendation adopted for this study. Accordingly, error bars on all subsequent plots illustrating laminar flame speed measurements ( $S_L^0$ ) are derived from Equation 5 and 6, with the error for  $U_{S_b^0}$  scaled with respect to the density ratio.

#### 4. Evaluation of Fundamental Parameters

Chen and Ju [38], [44] and Matalon and Bechtold [52], have proposed theoretical relationships relating the Markstein length ( $L_b$ ) and Lewis Number ( $Le$ ), requiring the evaluation of various fundamental flame parameters. The Zel'dovich number, was evaluated using the expression  $Ze = (E_a/R_u) \cdot [(T_{ad} - T_u)/(T_{ad}^2)]$  with  $R_u$  the universal gas constant,  $T_u$  and  $T_{ad}$ , the temperature of the unburnt mixture and the adiabatic flame temperature, respectively. The activation energy,  $E_a$ , is defined as the slope of the mass burning flux ( $m^0$ ) and the inverse adiabatic flame temperature at constant  $\phi$  and pressure, empirically determined using the expression  $E_a = -2R\partial[(m^0)]/[1/T_{ad}]$ , where the mass burning flux can be replaced by  $m^0 = (\rho_u \cdot S_L^0)$ , as recommended by Egolfopoulos and Law [53]. It should be noted that this method is only valid for sufficiently off-stoichiometric conditions, with interpolation required for  $E_a$  values for mixtures near stoichiometry [54]. For the flame thickness, two definitions can be considered [9]. The first, commonly termed as the kinetic (or diffusion) flame thickness ( $\delta_K$ ), is defined as  $\delta_K = \lambda/(\rho_u \cdot c_p \cdot S_L^0)$ , where  $\lambda$  represents the thermal conductivity and  $c_p$  the specific heat at constant pressure. The second, referenced as the 'gradient' flame thickness ( $\delta_G$ ) can be expressed as  $\delta_G = (T_{ad} - T_u)/(dT/dx)_{\max}$ . The 'kinetic' flame thickness is consistent with the approach detailed by Chen [38], [44] whilst the 'gradient' flame thickness is consistent with the method detailed by Bechtold and Matalon [52] and employed accordingly in the derivations  $Le$  and  $L_b$  as defined by the given authors.

##### 4.1 Relationships of $Le$ and $L_b$

For the purpose of this work, the relationships relating  $Le$  to  $L_b$ , proposed by Chen [38], [44] and Matalon and Bechtold [52] are considered. The first formulation based on spherically expanding flames is derived from the analytical developments done by Chen and Ju, and then used by Bouvet et al. [55], Lapalme et al. [56] and Zitouni et al. [34] in their studies on preferential-diffusion effects upon

multi-component fuels. This estimate of  $Le$  is referenced herein as  $Le_{CHEN}$  and can be expressed per Equation 7:

$$Le_{CHEN} = \left[ \frac{L_b}{\sigma \cdot \delta_K} - \frac{Ze}{2} \right]^{-1} \left[ 1 - \frac{Ze}{2} \right] \quad (7)$$

With  $\sigma = \rho_b/\rho_u$ , the expansion ratio. From Equation 7, the retrieval of  $L_b$  is possible as in Equation (8).

$$L_{b-CHEN} = \left[ \frac{1}{Le} - \left( \frac{Ze}{2} \right) \left( \frac{1}{Le} - 1 \right) \right] \sigma \cdot \delta_L \quad (8)$$

A second formulation by Bechtold and Matalon, was derived from theoretical analysis on the dependence of  $L_b$  on stoichiometry. This formulation was considered by Jomaas et al. [49] in the case of acetylene ( $C_2H_2$ ), Lapalme et al. [56] for  $H_2/CO$  and Zitouni et al. [34], for  $CH_4$  blended with  $H_2$  or  $C_3H_8$ . This estimate is denoted in following as  $Le_{BM}$ , and is expressed per Equation 9:

$$Le_{BM} = 1 + \left[ \frac{L_b}{\delta_G} - \frac{2}{\sqrt{\sigma} + 1} \right] \left[ \frac{2 \cdot Ze}{\sigma - 1} \left\{ \sqrt{\sigma} - 1 - \ln \left( \frac{1}{2} (\sqrt{\sigma} + 1) \right) \right\} \right]^{-1} \quad (9)$$

Which provides  $L_{b-BM}$  as per Equation 10:

$$L_{b-BM} = \delta_G \left[ \frac{\gamma_1}{\sigma} - \left\{ \frac{Ze}{2} (Le - 1) \gamma_2 \right\} \right] \quad (10)$$

where  $\gamma_1$  and  $\gamma_2$  are functions of the expansion ratio given in Equation 11:

$$\gamma_1 = \frac{2 \cdot \sigma}{(\sqrt{\sigma} + 1)} ; \quad \gamma_2 = \left[ \frac{4}{\sigma - 1} \right] \left[ \sqrt{\sigma} - 1 - \ln \left( \frac{\sqrt{\sigma} + 1}{2} \right) \right] \quad (11)$$

#### 4.2 Lewis Number evaluation of multi-component fuels

Whilst the definition of the Lewis Number for single-fuel mixtures is relatively straightforward, no clear consensus on the correct formulation of  $Le$  for multi-fuel mixtures seems to exist [55]; the challenge arising from the fact that the diffusivity of each fuel must be considered. This is particularly applicable when the transport diffusion mechanisms are different as is the case for  $H_2$ ,  $NH_3$  or any alkanes. Bouvet et al. [55] identified three 'effective'  $Le$  formulations. The first formulation is based upon a volumetric fraction weighted average, resulting from Muppala et al. [26] computational study of turbulent  $CH_4 - H_2/C_3H_8$  flames. At low-turbulence, this formulation results in reasonable agreement between modelled and experimental burning velocities; whilst at higher turbulent intensity modelled burning rates significantly underpredicted measurements. This volume weighted formulation will be referenced in this work as  $Le_V$ , and is expressed per Equation 12:

$$Le_V = \sum_{i=1}^f x_i \cdot Le_i \quad (12)$$

where  $x_i$ , is the fuel volumetric or mol fraction of the species  $i$ .

The second  $Le$  formulation is derived by Law et al. [57] from the asymptotic analysis of high pressure  $H_2/C_3H_8$  laminar spherical flames. This formulation has been widely employed to discuss the thermo-diffusive behaviour of mostly binary and tertiary blends of hydrocarbons and hydrogen [27], [58]. This formulation is based upon the weighted average of the fuels' nondimensional heat release ( $q_i$ ), referenced in this work as  $Le_H$ , and expressed as per Equation 13:

$$Le_H = 1 + \frac{\sum_{i=1}^f q_i (Le_i - 1)}{\sum_{i=1}^f q_i} \quad (13a)$$

where

$$q_i = \frac{Q \cdot Y_{i,unburnt}}{c_p \cdot T_u} \quad (13b)$$

with Q representing the overall heat of reaction,  $Y_i$ , the mass fraction of species i.

The third one is related to the work conducted by Dinkelacker et al. [27] on lean  $H_2/CH_4$  flames. It is assumed that if the flame curvature is dominant, then the local enrichment of the most diffusive fuel at the flames leading edge can be expected. This overall reaction-rate enhancement is translated into a volumetric-weighted average of the fuel diffusivities. This diffusion weighted formulation will be referenced in this work as  $Le_D$ , and expressed per Equation 14:

$$Le_D = \frac{D_T}{\sum_{i=1}^F x_i \cdot D_{ij}} \quad (14)$$

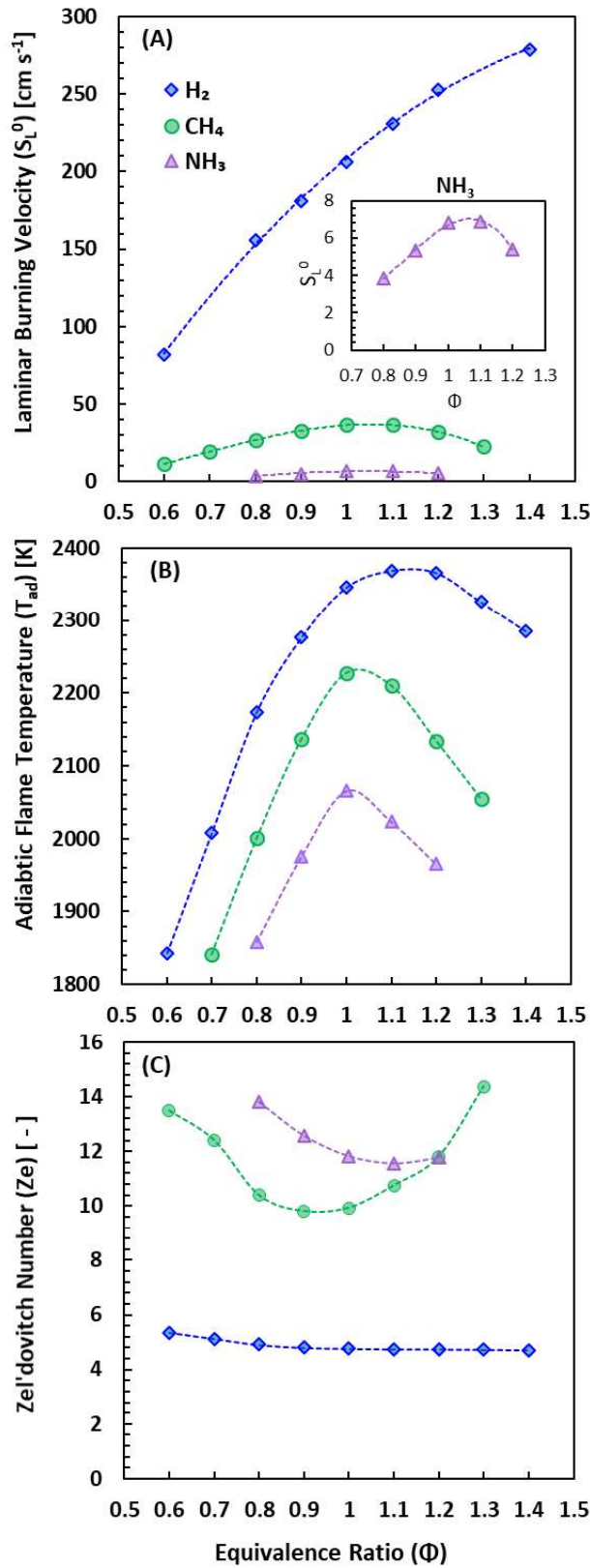
where  $D_T$  is the mixture's thermal diffusivity and  $D_{ij}$  are the binary mass diffusion coefficients. Several methods have been proposed to estimate the binary mass diffusion coefficients at moderate ambient pressure (<10 bar), with empirical constants based upon experimental data [59]. The method of Wilke as well as that of Hirschfelder, Bird and Spot, detailed in [59], is used in this study. Once the binary coefficients for the combinations of gases are estimated, an effective formulation of the deficient species in the mixture must be designated. For lean fuel-air mixtures, the deficient reactant is scarce compared to the surrounding  $N_2$  [9]. For that reason,  $D_{ij}$  is taken as the fuel, 'i', diffusing into  $N_2$  (denoted with the subscript j). This may hold true for hydrocarbons due to their high molar fuel-air ratio, but not for fuels that have low molar fuel-air ratio such as  $H_2$ , as underlined by Lapalme et al. [56]. Thus, as proposed by Wilke [60], the mixture-averaged coefficient of mass diffusion ( $D_{i,mix}$ ) into the mixture was employed as defined in Equation 15:

$$D_{i,mix} = (1 - Y_{i,mix}) \left( \sum_{\substack{s=1 \\ s \neq i}}^N \frac{X_s}{D_{is}} \right)^{-1} \quad (15)$$

where Y is the mass fraction of the species 'i' and 'X' the molar fraction of each species 's' in the mixture; with details of the method available in [59]. In order to ensure the correct application of the method, the binary diffusion coefficients calculated in this work were compared with values generated employing the STANJAN transport calculator [61]. Differences were no greater than  $\pm 3\%$  for binary blends containing  $CH_4$ ,  $NH_3$ ,  $O_2$  and  $N_2$ , and up to 10% in the presence of  $H_2$ , in agreement with expected deviations [59], and thus the derived coefficients are deemed suitable for the purpose of this study.

## 5. Results and Discussion

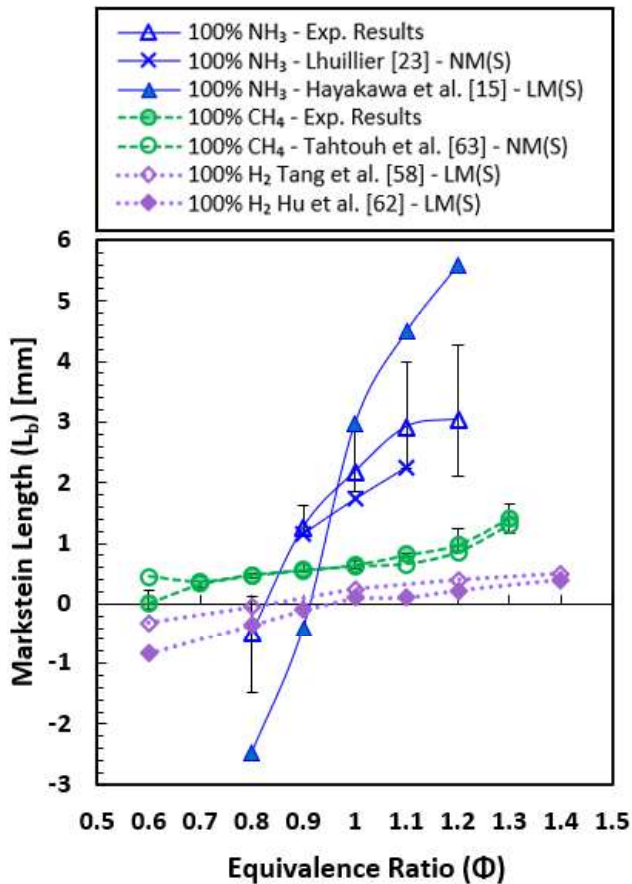
### 5.1 Pure Fuels



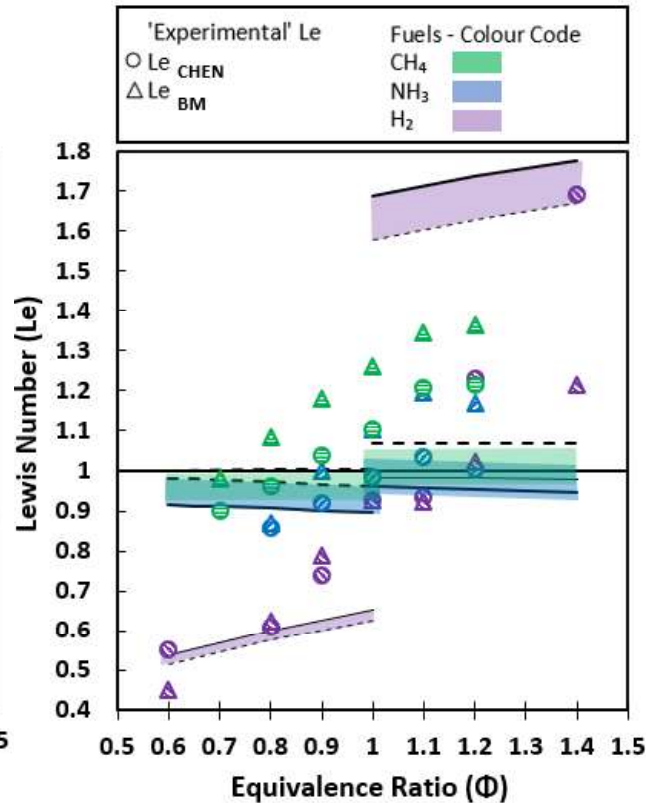
**Figure 3** – Comparison of (a) laminar burning velocity, (b) Adiabatic flame temperature and (c) Zel'dovich number as a function of equivalence ratio for pure  $\text{NH}_3$ ,  $\text{CH}_4$ , and  $\text{H}_2$ /air flames at 298 K & 0.1 MPa.  $S_L^0$  data for  $\text{H}_2$ /air flames from [62].

1 The measured  $S_L^0$  for the pure  $NH_3$ ,  $CH_4$  and  $H_2$  /air flames are compared in Figure 3.a.  $NH_3$ /air  
2 flames display the slowest flame propagation rates, five to six times slower than those of  $CH_4$ /air  
3 flames; with a similar difference in flame speed magnitude between  $H_2$ /air and  $CH_4$ /air flames at  
4 stoichiometric conditions. It should be noted that the thermal diffusivity of these fuels decreases in  
5 the order of  $H_2$ ,  $CH_4$  and  $NH_3$ , analogous to the decreasing  $S_L^0$  values. The adiabatic flame temperature  
6 and activation energy (represented by  $Ze$ ) with respect to  $\phi$  for the aforementioned pure fuels is  
7 illustrated in Fig. 3 (b) and (c), respectively. For  $CH_4$  (and in general  $C_{1-4}$  alkanes),  $S_L^0$  and  $T_{ad}$  peak at  
8 conditions slightly richer than stoichiometric conditions ( $\phi \sim 1.05 - 1.10$ ), underlining the sensitivity of  
9 the flame propagation to the flame temperature. The fact that the minimum activation energy is  
10 located at similar conditions ( $\phi \sim 0.9$ ), underlines the dictating influence of the flame temperature on  
11 the global activation energy. Due to flames temperatures peaking at around stoichiometric conditions,  
12 temperature-sensitive branching reactions are facilitated, thereby leading to overall faster reactions  
13 and reduced global activation energies, as highlighted by Jomaas et al. [49]. With respect to  $H_2$ , a  
14 similar trend in  $Ze$  is observed when plotted upon a much larger range of  $\phi$  than that illustrated in Fig.  
15 3 (c). Viewed across the total flammability range of  $H_2$  a similar parabolic relationship analogous to  
16 that exhibited by  $CH_4$  and  $NH_3$  is apparent. Although  $H_2$  flame temperature peaks at similar conditions  
17 to that of  $CH_4$  ( $\phi \sim 1.1 - 1.2$ ), both the maximum flame speed and minimum values of  $Ze$  are located at  
18 much richer conditions ( $S_{L^0, max}$  for  $\phi \sim 1.6-1.8$ ,  $Ze_{min}$  for  $\phi \sim 1.4 - 1.6$ ). This shift in the flame speed to  
19 richer conditions (and by extension the reduced influence of flame temperature on  $S_L^0$ ) has been  
20 attributed to the much larger value of the Lewis Number ( $Le \gg 1$  for  $\phi > 1.6$ ), with flame acceleration,  
21 a consequence of preferential diffusion [49]. As a result, the minimum  $Ze$  witnesses a corresponding  
22 shift to richer conditions, since  $Ze$  is directly extracted from the flame speed (see Section 4). Thus, a  
23 transport mechanism (i.e. the thermo-diffusive response of the fuel for  $Le \gg 1$ ) generates a change in  
24 response in the flame speed, which subsequently impacts the flame property, highlighting the  
25 influence of transport on a supposedly chemical property [49]. This is of importance when attempting  
26 to understand behaviour of fuel blends which possess different transport properties (as it is the case  
27 here with  $H_2$ ,  $CH_4$  and  $NH_3$ ) and the subsequent consequence on flame behaviour. On the other hand,  
28 for  $NH_3$ ,  $S_L^0$  and  $T_{ad}$  peak at approximately at the same equivalence ratio ranges ( $\phi \sim 1.0 - 1.10$ ). The fact  
29 that the maximum flame speed, adiabatic flame temperature and minimum  $Ze$  all arise at nominally  
30 identical  $\phi$  conditions underlines the equi-diffusive nature of  $NH_3$ , with  $Le$  close to unity, comparable  
31 to the preferential-diffusional properties of pure  $CH_4$ .

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40 In premixed flames, instabilities can result from both preferential-diffusional and  
41 hydrodynamic (Darrieus-Landau) instabilities. It should be highlighted that the Marshtein length ( $L_b$ )  
42 indicates the response of the flame to the stretch, it is also an indicator of the flame's propensity to  
43 instability and not the cause of the instability. Fig. 4 presents measured  $L_b$  for  $NH_3$ ,  $CH_4$  and  $H_2$  / air  
44 flames from lean to rich conditions, from the present study and some other measurements available  
45 in literature at similar initial temperature ( $\pm 5$  K) and pressure conditions. To facilitate fair comparison,  
46 it is also indicated in the legend what methodology was used to extrapolate  $L_b$  (Linear or Non-Linear  
47 Model by Stretch (LMS) or (NMS); Linear Model based on Curvature, (LMC)). First, it should be  
48 highlighted that the values for  $CH_4$  and  $H_2$  are in a good agreement with previous data but for  $NH_3$ /air  
49 flame, the discrepancies are noticeable and can be partially attributed to the extrapolation  
50 methodology employed. All three fuels exhibit an increasing  $L_b$  as a function of  $\phi$  increase from lean to  
51 rich conditions with the greatest change exhibited by  $NH_3$ , with negative value of  $L_b$  under lean  
52 conditions (comparable to that of  $H_2$ ), and larger positive value than that of  $CH_4$  and  $H_2$  under rich  
53 conditions.  
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**Figure 4** – Experimental values of  $L_b$  for pure  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{H}_2$  as a function of  $\phi$  (298 K, 0.1MPa). Data for  $\text{NH}_3$  from [15] [23],  $\text{CH}_4$  [63],  $\text{H}_2$  [58] [62]



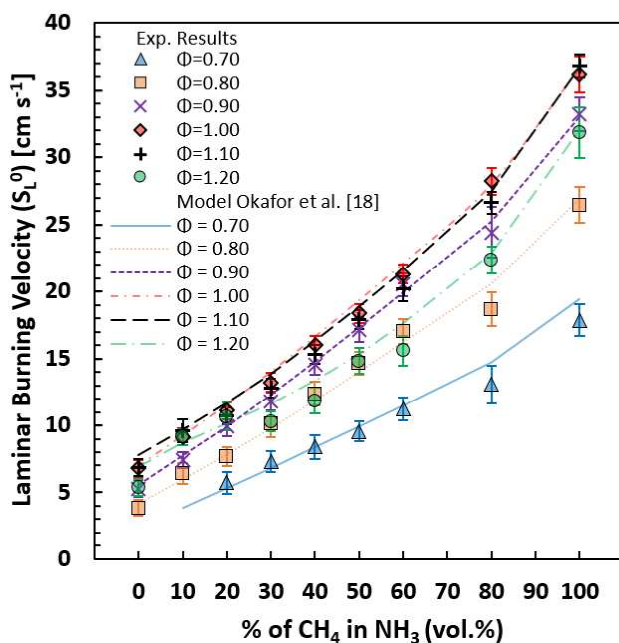
**Figure 5** – Theoretical and experimental  $Le$  for  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{H}_2$  as a function of  $\phi$  (data for  $\text{H}_2$  [75]). Full and dotted lines respectively reflect Hirschfelder and Wilke methods to evaluate  $D_{ij}$  (298 K, 0.1MPa)

To better understand the changes in the stretch response of pure fuels/air flames, the evolution of the corresponding  $Le$  is presented in Fig. 5, from lean to rich mixtures. ‘Theoretical’ Lewis numbers, estimated using the free-stream properties of the mixtures, are illustrated as colour bands with the upper and lower limits (represented by full and dashed lines) denoting the differences between either the Hirschfelder or Wilke method to evaluate the mass diffusion coefficient. While the correct  $Le$  is evaluated ( $Le \sim 1$  for  $\text{NH}_3$  and  $\text{CH}_4$ ;  $Le \ll 1$  at  $\phi < 1$  and  $Le \gg 1$  at  $\phi > 1$  for  $\text{H}_2$ ), little variation is observable across the considered  $\phi$ , aside from the transition from lean to rich conditions. Furthermore, it should be highlighted that minimum  $Le$  for  $\text{NH}_3$  is just prior to stoichiometric conditions in agreement with [15], whilst for  $\text{CH}_4$  and  $\text{H}_2$ , minimum  $Le$  is obtained at leanest conditions. Since  $Le$  was simply evaluated as a function of the mixture’s thermal and mass diffusivity, variations in fundamental flame parameters such as the flame thickness, the activation energy and the expansion ratio [52] were not considered. As such,  $Le$  can be evaluated from the experimental  $L_b$  and these other properties affecting the flame, as recommended by Jomaas et al. [49], with the use of theoretical relationships established in literature (denoted as  $Le_{\text{CHEN}}$  and  $Le_{\text{BM}}$ , Eqn. 7 and 9, accordingly). Therefore, as it can be seen when comparing Figure 4 and 5, analogous  $L_b$  and  $Le$  evolution as a function of the fuel and the equivalence ratio is observable, regardless of the theoretical relationship relating  $L_b$  to  $Le$ . However, it is interesting to note that the greatest change in  $L_b$  magnitude is observed for  $\text{NH}_3$ , whilst exhibiting least change in  $Le$ , as noted by [8], potentially alluding that  $Le$  may not be the main driving factor behind the measured changes in stretch sensitivity for  $\text{NH}_3$ -based flames. Furthermore,

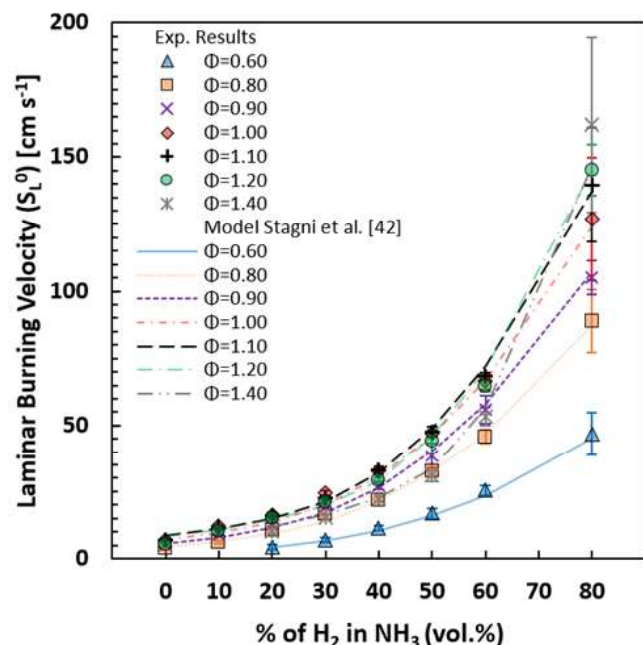
the transition from a negative to positive  $L_b$  for  $\text{NH}_3$  obtained for  $\phi \sim 0.8 - 1.0$  is at comparable  $\phi$  with the transition from  $Le < 1$  to  $Le > 1$  occurred.

## 5.2 Binary Fuel Mixtures

The influence of increasing fraction of either  $\text{CH}_4$  or  $\text{H}_2$  in  $\text{NH}_3/\text{air}$  mixture on  $S_L^0$ , across a wide range of  $\phi$  is depicted in Figures 6 and 7 respectively. With respect to  $\text{NH}_3/\text{H}_2$  blends, Otomo et al. [64], Shrestha et al. [65], Gotama et al. [66], Okafor et al., [18] and Stagni et al. [42] reaction mechanisms were all appraised by simulating a premixed 1-D adiabatic planar flame with the CHEMKIN-Pro package. A simulation of 10 cm was considered, with a total of 3000 grid points used with grid parameters GRID (0.025) and CURV (0.1), including multi-component diffusion and an assumed air composition of 79%  $\text{N}_2 - 21\% \text{O}_2$ . However only the two latter mechanism are shown since they consistently gave best agreement with, respectively, all  $\text{NH}_3/\text{CH}_4$  and  $\text{NH}_3/\text{H}_2$  blends evaluated in this study.



**Figure 6** –  $S_L^0$  for binary  $\text{NH}_3/\text{CH}_4$  mixtures, comparison with simulated values with Okafor et al. kinetics model [18] (298 K, 0.1MPa)



**Figure 7** –  $S_L^0$  for binary  $\text{NH}_3/\text{H}_2$  mixtures, comparison with simulated values with Stagni et al. kinetics mechanism [42] (298 K, 0.1MPa)

As can be seen in Figure 6, irrespective of the  $\phi$ , a quite linear increase in  $\text{NH}_3$  laminar flame speed is observable upon  $\text{CH}_4$  addition, with a very good prediction by Okafor et al. [18] mechanism. On the other hand, as illustrated in Figure 7, an increase in  $\text{H}_2$  fraction results in an exponential increase in  $S_L^0$ , across the entire tested  $\phi$  range, with also a very good prediction by Stagni et al. [42] mechanism, across all tested conditions. It is worth highlighting that  $\sim 10\text{-}20\%$  addition (vol.%) of either  $\text{CH}_4$  or  $\text{H}_2$  results in a similar increase in  $\text{NH}_3$  flame speed, with further increases resulting in very different flame speed behaviour. This increased reactivity of  $\text{NH}_3$  based blends upon  $\text{CH}_4$  and  $\text{H}_2$  addition has been previously suitably reported [19] [67], with modelling work and sensitivity analysis suggesting that the flame speed, burning intensity ( $Q'$ ) and production of radicals, particularly O and H appear to be strongly correlated.

To investigate the stretch-related behaviour of  $\text{NH}_3/\text{CH}_4$  and  $\text{NH}_3/\text{H}_2$  flames,  $L_b$  is plotted as a function of either  $\text{CH}_4$  or  $\text{H}_2$  addition to  $\text{NH}_3$  across a wide range of  $\phi$  in Figure 8 and 9, respectively. Note that the evolutions of  $L_b$  as a function of  $\phi$  are in SM3 and 4. For a  $\phi \geq 0.9$ , a linear decrease in  $L_b$  is observed with increasing  $\text{CH}_4$  fraction. At  $\phi = 0.80$ , a negative value  $L_b$  is obtained for pure ammonia while 10%  $\text{CH}_4$  addition results in  $L_b$  sign inversion (from negative to positive). As pure  $\text{NH}_3/\text{air}$  mixtures could not be ignited for  $\phi < 0.8$ , with this experimental apparatus, this tendency cannot be verified. Under rich conditions ( $\phi \geq 1.1$ ), a decreasing stretch sensitivity is measured upon increasing  $\text{H}_2$  fraction, similar in trend and magnitude to that observed for  $\text{NH}_3/\text{CH}_4$  flames but for  $\phi \geq 0.9$ . However, interestingly for  $\phi \leq 1.0$ , an initial decrease in  $L_b$  is observed up to 30 – 40%  $\text{H}_2$  addition, at which point any further addition of  $\text{H}_2$  results in an increase in  $L_b$ , with non-linear behaviour accentuated as conditions get leaner. Similar non-monotonical variation in stretch-related behaviour was measured by Lhuillier [68] as well as by Ichikawa et al. [22], for  $\text{NH}_3/\text{H}_2$  flames, at  $\phi = 1.0$  and ostensibly identical experimental conditions ( $T_u = 298 \text{ K}$ ,  $P_u = 0.1 \text{ MPa}$ ), also plotted in Figure 9 for comparison purposes. As such, under lean conditions,  $\text{NH}_3/\text{H}_2$  mixtures exhibit a greater negative  $L_b$  than that of pure  $\text{H}_2$  flames. It should be highlighted that similar non-linear  $L_b$  behaviour was measured by Okafor et al. [24] for  $\text{CH}_4/\text{H}_2$  flames, with an inflection point occurring upon  $\sim 70\%$   $\text{H}_2$  addition. Similarly, Huang et al. [69] also reported similar behaviour for natural gas – hydrogen – air blends. As such, it may seem that this maybe a phenomenon attributable to the  $\text{H}_2$  contribution, at least for  $\text{NH}_3$  or  $\text{CH}_4$  based flames, due to the strong and fast diffusivity of  $\text{H}_2$  in the reactants. This stretch-sensitivity behaviour is of importance since the flames exhibiting negative  $L_b$  will be accelerated in highly stretched turbulent environments, whilst flames displaying a positive  $L_b$  will be weakened. This stretch-sensitivity response inevitably impacts the operation of practical combustion systems.

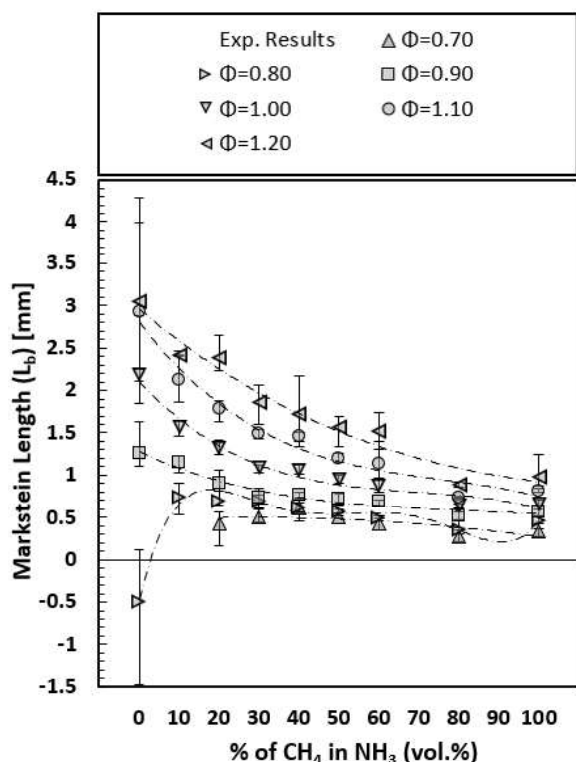


Figure 8 –  $L_b$  values of  $\text{NH}_3/\text{CH}_4$  mixtures (298 K, 0.1 MPa)

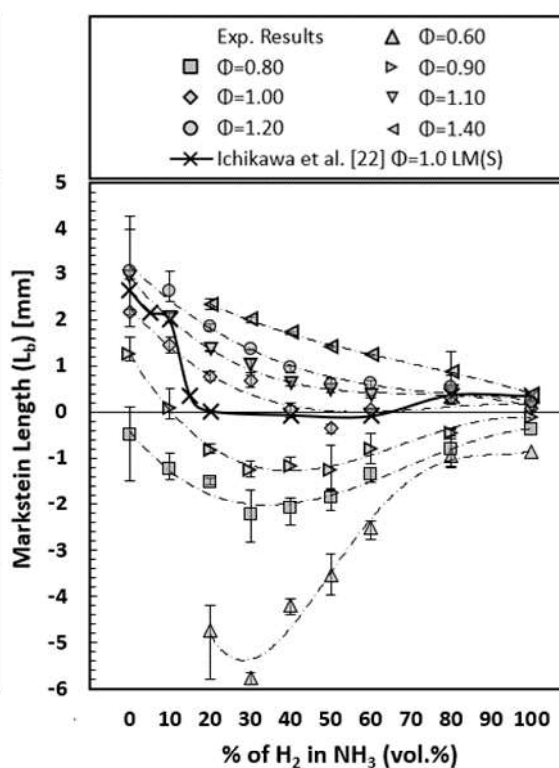
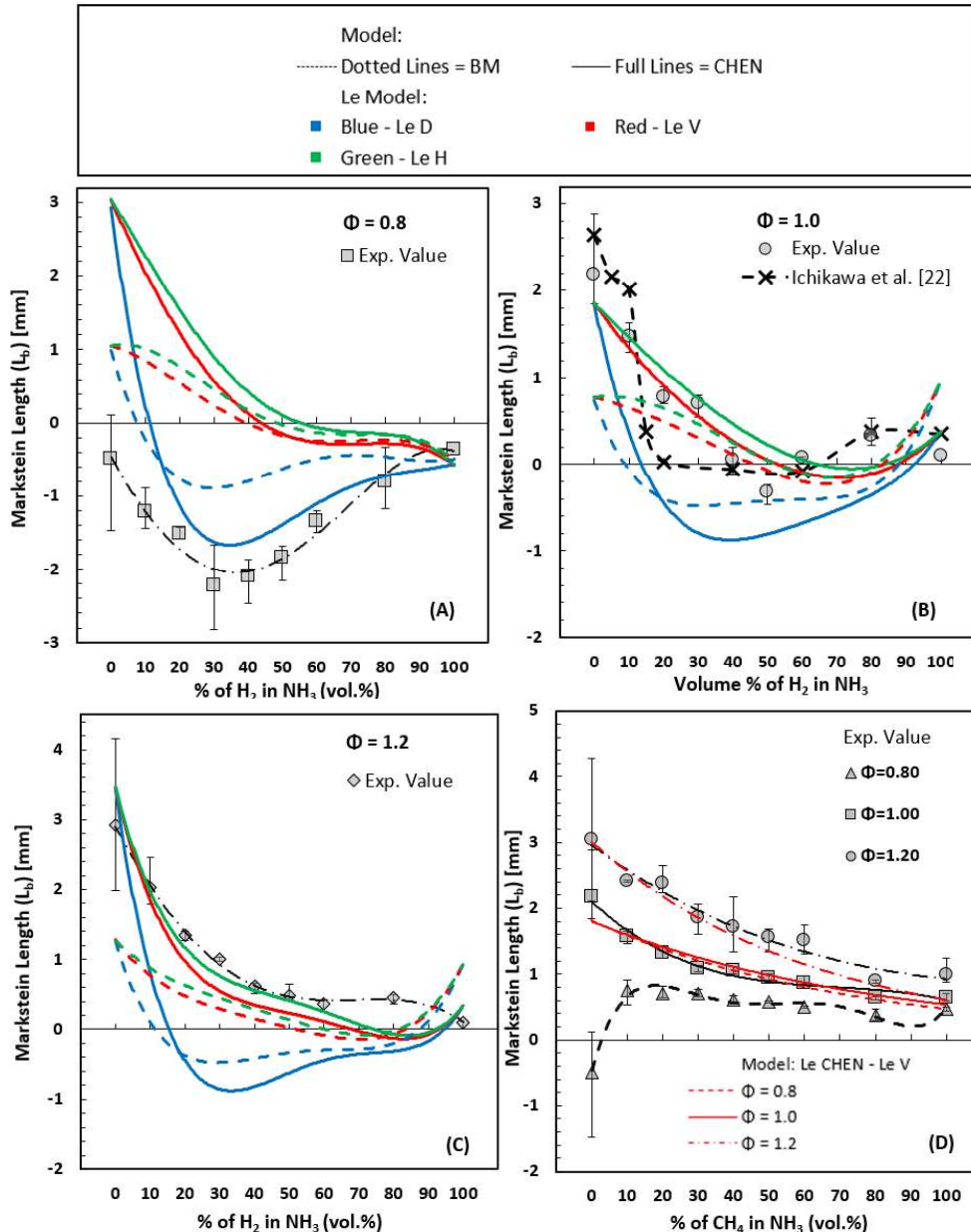


Figure 9 –  $L_b$  values of  $\text{NH}_3/\text{H}_2$  mixtures (298 K, 0.1 MPa) 100%  $\text{H}_2$   $L_b$  values from [62]



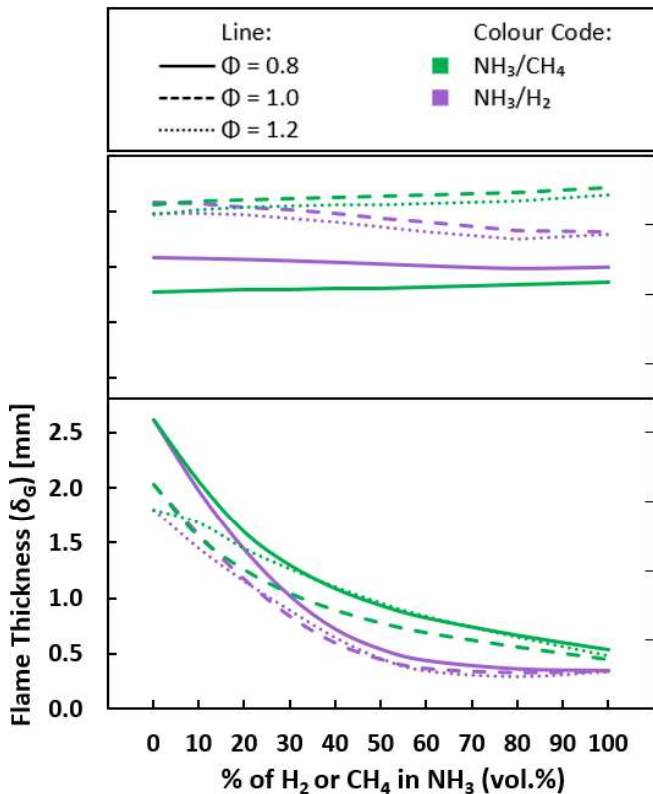
For a better understanding of this change, a sensitivity analysis related to the contribution of major flame enhancing pathways (diffusive, thermal, kinetic) was undertaken. However, to correctly quantify the diffusive pathway, the most suitable  $Le$  formulation has to be considered. As such, the different  $Le_{eff}$  models (i.e.  $Le_V$ ,  $Le_H$ ,  $Le_D$  from Equations 12, 13 and 14 respectively) are used to yield to an estimate of  $L_b$ , by using the relationships proposed by Chen or Matalon and Bechtold, referred as  $L_b$ -Chen and  $L_b$ -BM, respectively. It should be noted that the purpose of such analysis is more qualitative than quantitative to validate which  $Le_{eff}$  model best captures the measured  $L_b$  behaviour of the tested blends.



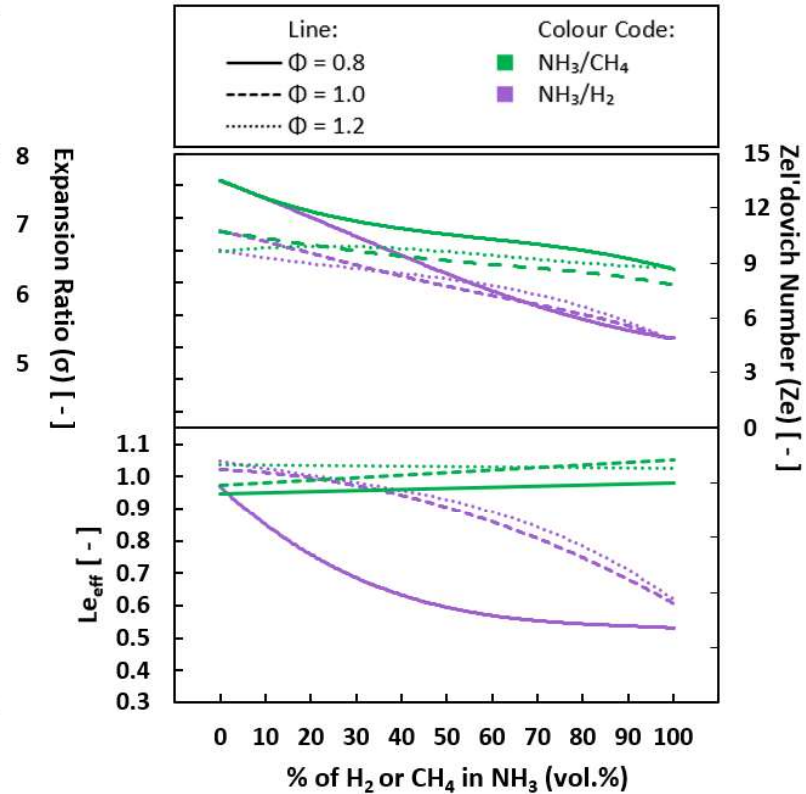
**Figure 10** – Comparison of  $L_b$ -CHEN and  $L_b$ -BM estimates to the measured  $L_b$  for NH<sub>3</sub>/H<sub>2</sub> flames (a)  $\phi = 0.8$  (b)  $\phi = 1.0$  (c)  $\phi = 1.2$  and for (d) NH<sub>3</sub>/CH<sub>4</sub> flames

Figure 10 illustrates  $L_b$ -CHEN and  $L_b$ -BM for NH<sub>3</sub>/H<sub>2</sub> blends, alongside experimentally measured  $L_b$  values. With respect to the CHEN formulation under lean H<sub>2</sub> condition ( $\phi = 0.8$ , Fig. 10.a),

quantitative and qualitative agreements are observed with  $Le_D$  formulation, with the non-linear stretch behaviour well captured. Under  $H_2$  richer condition ( $\phi = 1.2$ , Fig.11.c),  $Le_D$  overpredicts the influence of  $H_2$  on  $NH_3$  with better agreement observed with a  $Le_V$  or  $Le_H$  model better reflecting the measured trend. Poor agreement is observed with the BM formulation, with again a  $Le_D$  best reflecting expected stretch behaviour under lean conditions, and  $Le_H$  exhibiting better agreement at richer conditions. Considering that the  $Le_D$  model was derived from the modelling of lean turbulent  $CH_4/H_2$  flames [27], as well as that lean  $CH_4/H_2$  appear to display similar non-linear stretch behaviour [24] to that of lean  $NH_3/H_2$  flames, a better agreement was expected. Furthermore, this influence is due to the assumption that the flame curvature is dominant, hence the local enrichment of the most diffusive fuel at the flames leading edge is predicted. This concept appears to be valid under lean conditions, since  $H_2$  and  $NH_3$  have higher mass diffusivities than  $O_2$ . For richer conditions ( $\phi \geq 1.0$ ), a model based on either volume or non-dimensional heat release appears to be more appropriate. With respect to  $NH_3/CH_4$  flames, measured  $L_b$  and  $L_b$ -CHEN are compared in Fig. 10.d for  $\phi = 0.8 - 1.2$ . It should be noted that since  $NH_3$  and  $CH_4$  display very similar preferential-diffusional behaviour ( $Le \sim 0.9 - 1.1$ ), the application of either  $Le_{eff}$  models results in very similar values. Consequently, only the  $Le_V$  model is plotted on Figure 10.d. For the conditions greater than stoichiometry, a good quantitative and qualitative agreement is observed with the CHEN model, but under lean conditions, the CHEN model does not allow to verify the change from negative to positive  $L_b$  measured experimentally obtained upon 10%  $CH_4$  addition to  $NH_3$  (for only one equivalence ratio). In summary, for lean and rich  $NH_3/H_2$  flames, the  $Le_D$  and  $Le_H$  formulation respectively, best captured changes in thermo-diffusive behaviour. With respect to  $NH_3/CH_4$  flames,  $Le_V$  demonstrated the best agreement for all considered  $\phi$ , with these conclusions maintained for the remainder of the analysis.



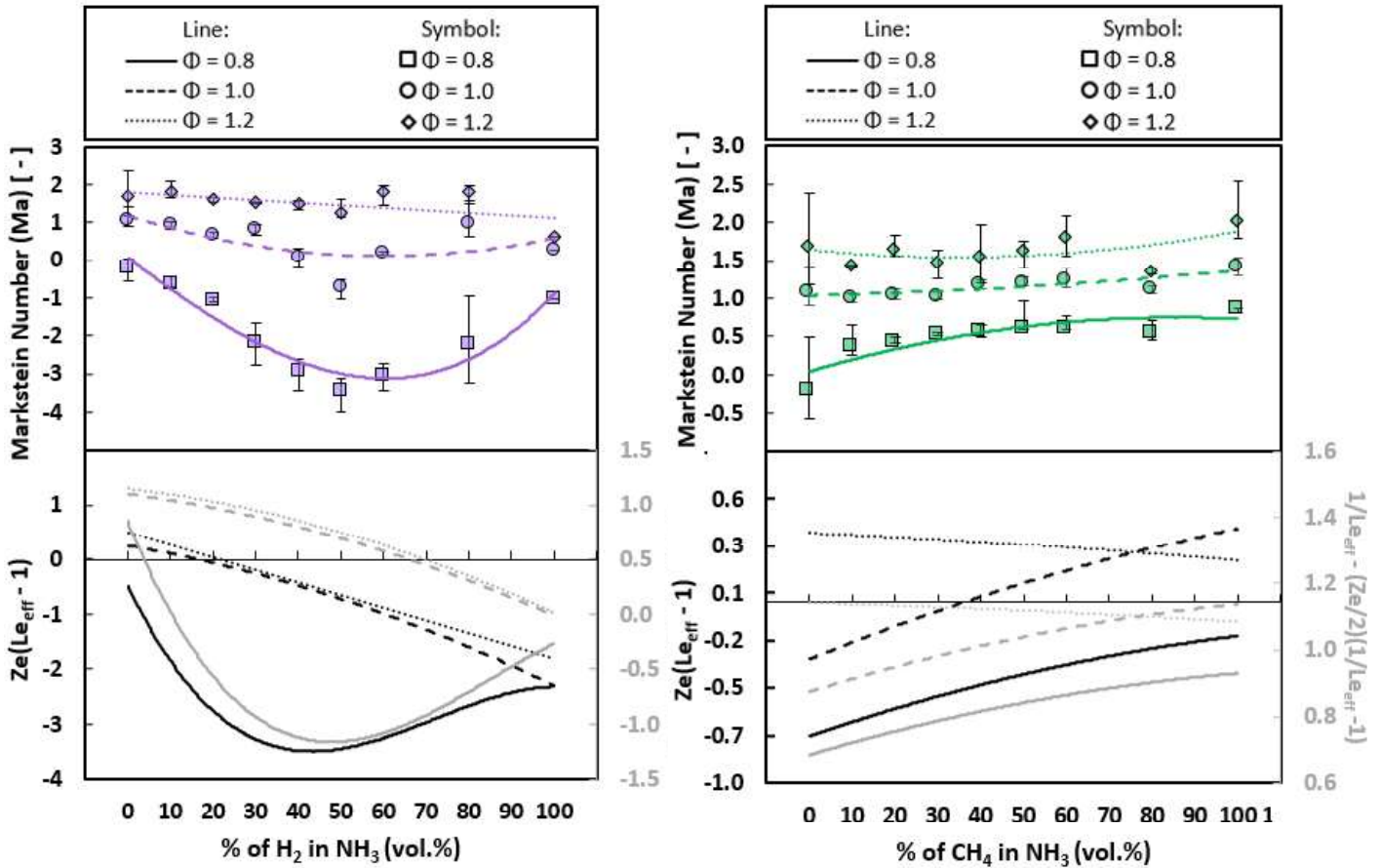
**Figure 11** – Variation in  $\delta_G$  and  $\sigma$  with addition of either  $CH_4$  or  $H_2$  to  $NH_3$ ,  $\phi = 0.8, 1.0, 1.2$



**Figure 12** – Variation in  $Le_{eff}$  and  $Ze$  with addition of either  $CH_4$  or  $H_2$  to  $NH_3$ ,  $\phi = 0.8, 1.0, 1.2$

1 As emphasised by Kwon et al. [70] and reviewed in [71], the fundamental parameters that  
2 induce hydrodynamic and diffusional-thermal instabilities are the thermal expansion, the flame  
3 thickness, the non-unity  $Le$  and the global activation energy (or equivalently  $Ze$ ). Consistent with the  
4 hydrodynamic theory of Darrieus and Landau [9], the hydrodynamic instabilities arise from the thermal  
5 expansion of gases, with the density jump across the flame front proportional to the growth rate of  
6 hydrodynamic instability. In the case of an outwardly propagating spherical flame, the flame tends to  
7 be stabilised due to curvature induced positive stretch, consequently the flame thickness plays a  
8 significant role, since the thinner the flame the weaker the influence of curvature. Hence the risk of  
9 destabilisation is enhanced for thinner flames. It is interesting to note that addition of either  $CH_4$  or  $H_2$   
10 to  $NH_3$  does not really affect the thermal expansion, irrespective of  $\phi$ , as shown in Figure 11. On the  
11 other hand, the flame thickness decreases strongly with increasing  $CH_4$  or  $H_2$  fractions, in effect  
12 promoting hydrodynamic instabilities to a similar extent. Nevertheless, the addition of either  $CH_4$  or  
13  $H_2$  to  $NH_3$  results in similar stretch-related behaviour under rich conditions, whilst exhibiting very  
14 different stretch-behaviour as conditions get leaner. The development of preferential-diffusional  
15 instabilities, characterised by  $Le$ , is the result of non-equi-diffusion. With respect to the  $NH_3/H_2$  flames,  
16 the effects of preferential diffusion are a consequence of the higher mass diffusivity of  $H_2$  and  $NH_3$   
17 compared to the  $O_2$  molecule. As illustrated in Figure 12,  $Le$  decreases significantly with increasing  $H_2$   
18 fraction thereby promoting diffusional-thermal instabilities at  $\phi = 0.8$ . Furthermore, as could be  
19 expected, the change in  $Le$  increases as the conditions get leaner, a consequence of each of the fuel's  
20 individual  $Le$  response. As underlined by Kwon et al. [70], considering that the development of  
21 preferential diffusional instabilities requires a modification of the flame front, it is thus reasonable to  
22 expect the global activation energy should also affect the development of diffusional-thermal  
23 instabilities. Accordingly, a lower  $E_a$  (illustrated as  $Ze$  in Figure 12) will tend to enhance instability of a  
24 diffusionaly unstable flame such as lean  $NH_3/H_2$  flame, with both  $Le$  and  $Ze$  decreasing with increasing  
25  $H_2$  concentration for all  $\phi$ . The decrease in  $Ze$  is largely due to a decrease in the inner-layer temperature  
26 coupled with an increase in adiabatic flame temperature with increasing  $H_2$  concentration for  $\phi$ . For  
27  $NH_3/H_2$ , the changes in measured  $L_b$  are thus potentially the result of competing hydrodynamic and  
28 thermo-diffusive instabilities, with the influence of the thermo-diffusional instabilities reducing as the  
29  $\phi$  increases. On the other hand, for  $NH_3/CH_4$  flames, the addition of  $CH_4$  to  $NH_3$  results in little  
30 diffusional-thermal effects ( $Le \sim 1$ ) across the entire considered  $\phi$  range.  
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**Figure 13** – Comparison of variation of  $Ze(L_{eff} - 1)$  and  $1/Le_{eff} - (Ze/2)(1/Le_{eff} - 1)$  to measured Marsktein number as a function of (a)  $H_2$  mole fraction, and (b)  $CH_4$  mole fraction

From the analytical expression developed by Chen [38], [44], the equation 8 can be re-arranged to yield the Marsktein Number ( $Ma = L_b/\delta$ ), resulting in  $Ma = [1/Le_{eff} - (Ze/2)(1/Le - 1)]\sigma$ , where  $1/Le_{eff} - (Ze/2)(1/Le_{eff} - 1)$  represents the thermo-diffusive effect. Similarly, the relationship linking  $L_b$  to  $Le$  developed by Matalon and Bechtold (Equation 9) can be re-arranged to evaluate  $Ma$ , in which the term  $Ze(L_{eff} - 1)$  reflects the thermo-diffusive influence as underlined by Okafor et al. [24]. Figures 14.a and 14.b compare the experimental  $Ma$  to the trends in  $1/Le_{eff} - (Ze/2)(1/Le - 1)$  and  $Ze(L_{eff} - 1)$ , for  $NH_3/H_2$  and  $NH_3/CH_4$  mixtures, respectively, at  $\phi = 0.8 - 1.0 - 1.2$ . First, as expected both  $Ze(L_{eff} - 1)$  and  $1/Le_{eff} - (Ze/2)(1/Le - 1)$  exhibit the same trends. For the lean  $NH_3/H_2$  mixtures, the changes in measured  $Ma$  appear to be to a great extent the result, of changes in the thermo-diffusive properties,  $Le$  and  $Ze$ . At richer condition, slightly different trends are displayed between the experimental  $Ma$  and  $Ze(L_{eff} - 1)$  and  $1/Le_{eff} - (Ze/2)(1/Le - 1)$ , potentially due to a greater change in the expansion ratio (see Figures 12) than under lean conditions. In relation to the  $NH_3/CH_4$  mixtures (Figure 13.b), the measured  $Ma$  under lean and stoichiometric conditions yield matching trends to  $Ze(L_{eff} - 1)$  and  $1/Le_{eff} - (Ze/2)(1/Le - 1)$ , potentially alluding that the  $Le$  and  $Ze$  are the driving forces behind the changes in stretch-related behaviour. At  $\phi = 1.2$ , a less good agreement is observed, potentially the consequence of nominal changes in  $Le$  and  $Ze$ , combined with an increasing expansion ratio. For lean  $NH_3/H_2$  flames it seems that the changes in measured  $L_b$  are to a large extent the consequence of thermo-diffusive effects, with this influence reducing as conditions get richer. For the  $NH_3/CH_4$  mixtures, the competition between thermo-diffusional and hydrodynamic instabilities yields to increasingly positive  $Ma$  values, resulting in propensity of flame stabilisation.

### 5.3 Flame Sensitivity Analysis

The enhancement of the flame propagation due to the addition of CH<sub>4</sub> or H<sub>2</sub> to NH<sub>3</sub> can be characterised as a combination of diffusive, thermal and kinetic effects [72], [73]. The individual pathway can be modelled as:

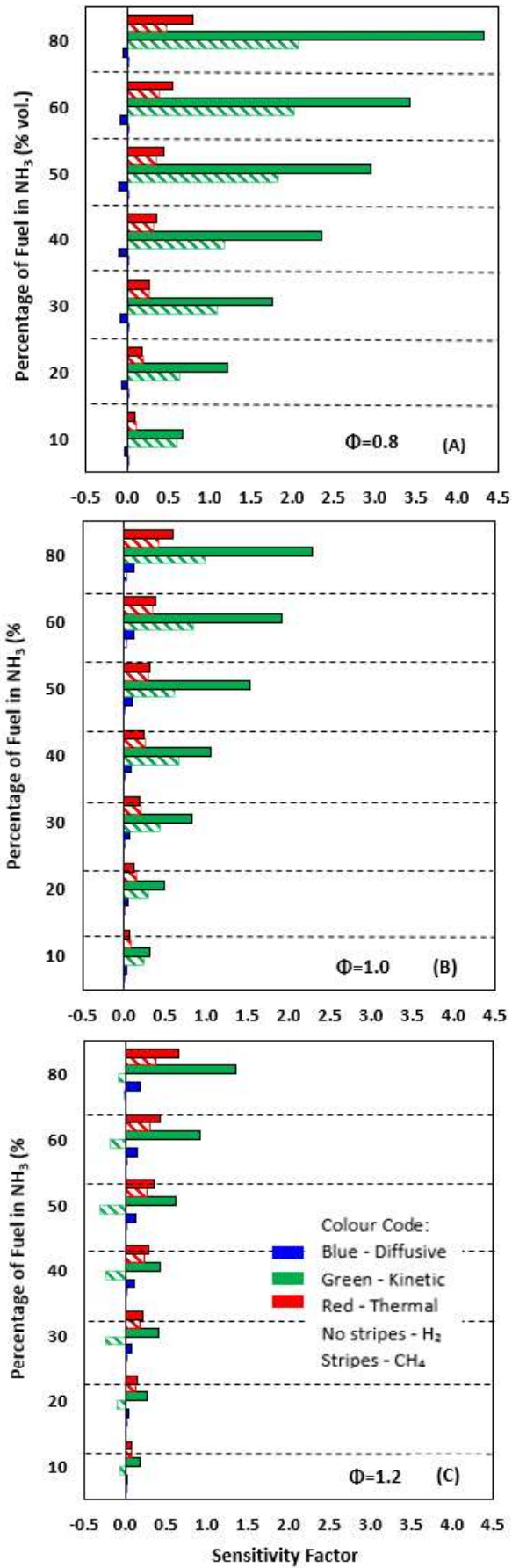
$$S_L^0 \sim (D_T \cdot Le_{eff})^{1/2} \exp(-T_a/2T_{ad}) \quad (16)$$

The first term on the right-hand side ( $D_T \cdot Le_{eff}$ ) reflects the diffusive influence. The Arrhenius factor, which combines the relative influence of the global activation energy through the activation temperature ( $T_a = E_a/R_u$ ), and the adiabatic flame temperature are represented in the second term [ $\exp(-T_a/2T_{ad})$ ]. These individually represent the thermal ( $T_{ad}$ ) and kinetic ( $T_a$ ) influences on the flame speed. Concerning the Le formulation, it was previously determined from Figure 11 that for lean and rich NH<sub>3</sub>/H<sub>2</sub> flames, the Le<sub>D</sub> and Le<sub>H</sub> formulation respectively, best captured changes in thermo-diffusive behaviour. With respect to NH<sub>3</sub>/CH<sub>4</sub> flames, Le<sub>V</sub> demonstrated the best agreement for all considered  $\phi$ . These conclusions are maintained regardless of the theoretical relationship relating L<sub>b</sub> to Le, and hence applied for the following analysis. Equation 16 may be differentiated to determine the sensitivity of each individual pathway on the overall influence of the flame speed. Accordingly, the overall sensitivity coefficient can be expressed as per Equation 17 [72]:

$$\frac{1}{S_L^0} \cdot \frac{dS_L^0}{dx} = \frac{1}{2 \cdot D_T \cdot Le} \cdot \frac{d(D_T \cdot Le)}{dx} - \frac{1}{2 \cdot T_{ad}} \cdot \frac{2 \cdot T_a}{dx} + \frac{T_a}{2 \cdot T_{ad}^2} \frac{2 \cdot T_{ad}}{dx} \quad (17)$$

where  $x$ , the volume fraction of either CH<sub>4</sub> or H<sub>2</sub>. Note that the three terms on the right-hand side denote the influence of the diffusive, kinetic, and thermal pathways, correspondingly. Sensitivity analysis is illustrated in Figure 14 for the blends and  $\phi$  considered, with a positive and negative sensitivity factor representing flame speed enhancement and inhibition, respectively.

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**Figure 14** – Sensitivity Analysis of  $S_L^0$  for NH<sub>3</sub>/H<sub>2</sub> and NH<sub>3</sub>/CH<sub>4</sub> blends, (a)  $\phi = 0.8$  (b)  $\phi = 1.0$  (c)  $\phi = 1.2$



1 As illustrated in Figure 14, the enhancement in flame speed of NH<sub>3</sub> based blends upon addition of  
2 either CH<sub>4</sub> or H<sub>2</sub> is predominantly an Arrhenius effect (kinetic), principally through the reduction of the  
3 overall activation energy and thus the activation temperature. For identical volumetric additions of up  
4 to 10% CH<sub>4</sub> or H<sub>2</sub> results in a similar reduction in E<sub>a</sub>, leading to similar flame speeds, a trend well  
5 captured both experimentally and numerically. Any further addition of H<sub>2</sub> results in a significantly  
6 greater reduction in E<sub>a</sub> than in the case of CH<sub>4</sub> addition, resulting in greater flame speeds. It should be  
7 noted that although remaining predominant for lean and stoichiometric conditions, the influence of  
8 the kinetic pathway reduces at richest conditions, particularly for CH<sub>4</sub> addition to NH<sub>3</sub>, with a negative  
9 sensitivity at  $\phi = 1.2$ . This agrees with the minor increase in E<sub>a</sub> (represented by Z<sub>e</sub>, see Figure 12) at  
10 that condition, the consequence of the shifted minimum E<sub>a</sub> to slightly richer conditions ( $\phi = 1.1-1.2$ ) of  
11 NH<sub>3</sub>, as in Figure 3. The thermal pathway impact is lower than the kinetic effect, with the influence of  
12 the thermal pathway correlating well with modelled changes in adiabatic flame temperature. The  
13 addition of up to 60% of either CH<sub>4</sub> or H<sub>2</sub> results in changes of < 45 K, regardless of  $\phi$ . With respect to  
14 the diffusive influence, it assumes negative sensitivity (or inhibiting effect) for lean NH<sub>3</sub>/H<sub>2</sub> mixtures,  
15 and is negligible in comparison to other pathways. This is particularly the case for NH<sub>3</sub>/CH<sub>4</sub>, a  
16 consequence of the nominal changes in Le (Fig. 12) coupled with the limited change in thermal  
17 diffusivity of the mixture upon CH<sub>4</sub> addition, irrespective of the  $\phi$ . It should be noted that even if the  
18 use of different kinetics mechanisms can induce different Arrhenius coefficients, the qualitative trends  
19 should remain valid, and thus performing such sensitivity analysis from first principles remains relevant  
20 providing useful insights.

## 25 6. Conclusions

27 The spherically expanding flame configuration was used to measure the unstretched laminar flame  
28 speeds and corresponding Markstein lengths in NH<sub>3</sub>/H<sub>2</sub> and NH<sub>3</sub>/CH<sub>4</sub> premixed flame across a wide  
29 range of compositions and equivalence ratio. A special attention was given to the estimate of Lewis  
30 number to analyse its influence on flame behaviour of NH<sub>3</sub>, H<sub>2</sub> and CH<sub>4</sub> as well as for the blends. From  
31 this study, the following main outcomes can be made:

- 34 • Increasing H<sub>2</sub> and CH<sub>4</sub> fraction to NH<sub>3</sub>-air laminar premixed flames results in an exponential  
35 and linear increase in flame speed, respectively. The greatest relative change in flame  
36 speed upon H<sub>2</sub> addition occurs under leanest and richest conditions while upon CH<sub>4</sub>  
37 addition, only under lean conditions. Stagni et al. and Okafor et al. mechanisms displayed  
38 the best agreement with experimental NH<sub>3</sub>/H<sub>2</sub> and NH<sub>3</sub>/CH<sub>4</sub> results, respectively.
- 39 • With respect to the stretch related behaviour, the addition of CH<sub>4</sub> to NH<sub>3</sub> results in a linear  
40 reduction in the stretch sensitivity for a fixed equivalence ratio. The volumetric based  
41 Lewis number yielded the best correlation with the measured Markstein lengths, for CH<sub>4</sub>  
42 addition to NH<sub>3</sub> resulting in nominal diffusional-thermal effects. For the stoichiometric and  
43 lean NH<sub>3</sub>/H<sub>2</sub> flames, a non-monotonical variation in measured Markstein length was  
44 obtained, with a less and less linear behaviour as conditions get leaner. For NH<sub>3</sub>/H<sub>2</sub>, the  
45 changes in measured L<sub>b</sub> were demonstrated to mainly be the result of thermo-diffusive  
46 effects (through the modelled changes in Le<sub>eff</sub> and global activation energy) with the  
47 influence of the thermo-diffusional instabilities reducing as the equivalence ratio  
48 increases. For lean NH<sub>3</sub>/H<sub>2</sub> mixtures, the diffusional-based Lewis number well captured the  
49 non-linear stretch behaviour as function of H<sub>2</sub> addition, whilst the heat release-based  
50 Lewis number resulted in better agreement at richer conditions.
- 51 • A sensitivity analysis related to the major flame enhancing pathways (diffusive, kinetic,  
52 thermal) has demonstrated that the enhanced flame propagation of NH<sub>3</sub>/H<sub>2</sub> and NH<sub>3</sub>/CH<sub>4</sub>,  
53 is mainly due to the kinetic change, especially through the reduction of the activation  
54 temperature. The influence of the kinetic pathway reduces as conditions get richer,  
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1 particularly for CH<sub>4</sub> addition. The thermal pathway holds less influence in comparison to  
2 the kinetic pathway, with its influence showing good correlation with limited changes in  
3 adiabatic flame temperature of the considered blends. The diffusive pathway was  
4 negligible for all investigated mixtures, with a negative sensitivity for the lean NH<sub>3</sub>/H<sub>2</sub>  
5 mixtures.

## 6 **Declaration of Competing Interest**

7  
8 The authors declare that they have no known competing financial interest or personal  
9 relationships that could have appeared to influence the work reported in this paper.

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## **Influence of Hydrogen and Methane Addition in Laminar Ammonia Premixed Flame on Burning Velocity, Lewis Number and Markstein Length**

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### **Abstract:**

The use of Ammonia (NH<sub>3</sub>) and blends with either Methane (CH<sub>4</sub>) or Hydrogen (H<sub>2</sub>) obtained by in-situ NH<sub>3</sub> cracking, seem to be promising solutions to partially or fully decarbonise our energy systems. To strengthen understanding of fundamental combustion characteristics of these NH<sub>3</sub> blends, the outwardly propagating spherical flame configuration was employed to determine the flame speeds and Markstein lengths. The air/fuel mixtures were varied across a large range of compositions and equivalence ratios. In general addition of CH<sub>4</sub> or H<sub>2</sub> results in a linear and exponential increase in measured laminar burning velocity, respectively. Of the appraised mechanisms, Stagni and Okafor kinetics mechanisms yielded best agreement with NH<sub>3</sub>/H<sub>2</sub> and NH<sub>3</sub>/CH<sub>4</sub> flame speed measurements. With respect to measured Markstein length, for a fixed equivalence ratio, addition of CH<sub>4</sub> to NH<sub>3</sub> resulted in a linear reduction in stretch sensitivity for the tested conditions. For lean NH<sub>3</sub>/H<sub>2</sub> flames, an initial decrease in Markstein length is observed up to 30 – 40% H<sub>2</sub> addition, at which point any further addition of H<sub>2</sub> results in an increase in Markstein Length, with a non-linear behaviour accentuated as conditions get leaner. Above stoichiometry similar stretch behaviour is observed to that of NH<sub>3</sub>/CH<sub>4</sub>. Different theoretical relationships between the Markstein length and Lewis Number were explored alongside effective Lewis Number formulations. For lean NH<sub>3</sub>/H<sub>2</sub> mixtures, a diffusional based Lewis Number formulation yielded a favourable correlation, whilst a heat release model resulted in better agreement at richer conditions. For NH<sub>3</sub>/CH<sub>4</sub> mixtures, a volumetric based Lewis Number formulation displayed best agreement for all evaluated equivalence ratios. For NH<sub>3</sub>/H<sub>2</sub>, changes in measured Markstein Length were demonstrated to potentially be the result of competing hydrodynamic and thermo-diffusive instabilities, with the influence of the thermo-diffusional instabilities reducing as the equivalence ratio increases. On the other hand, the addition of CH<sub>4</sub> to NH<sub>3</sub> results in the propensity of moderating hydrodynamic instabilities, resulting in a stabilising influence on the flame, reflected by increasing positive Markstein number values. Finally, a systematic analysis of the flame speed enhancements effects (kinetic, thermal, diffusive) of CH<sub>4</sub> and H<sub>2</sub> addition to NH<sub>3</sub> was undertaken. Augmented flame propagation of NH<sub>3</sub>/CH<sub>4</sub> and NH<sub>3</sub>/H<sub>2</sub> was demonstrated to be principally an Arrhenius effect, predominantly through the reduction of the associated activation energy.

**Keywords:** Ammonia-hydrogen, ammonia-methane, Laminar flame Speed, Lewis Number, Markstein Length

## 1. Introduction

The historical prevalence of hydrocarbon fuel usage to sustain our power and transport needs, and the associated greenhouse gas emissions produced, have resulted in important environmental and ecological adversities [1]. As such, in order to attain zero-carbon targets, the large-scale employment of renewable and carbon-free fuels within our energy systems is required to maintain a balanced trajectory between human development, progress and cohesion with the environment. In light of this context, Ammonia ( $\text{NH}_3$ ) has emerged in recent years as an efficient zero-carbon hydrogen ( $\text{H}_2$ ) carrier. Liquid  $\text{NH}_3$  offers higher  $\text{H}_2$  content than for example, ethanol, methanol and gasoline, in conjunction with exhibiting a higher volumetric energy density than that of liquid  $\text{H}_2$  [2]. Due to  $\text{NH}_3$  prevalent use in the agricultural industry, considerable storage and distribution infrastructure is already established [2]. Although  $\text{NH}_3$  offers several advantages, there remains several practical combustion challenges, notably the control and reduction of pollutant emissions ( $\text{NO}_x$  and  $\text{N}_2\text{O}$ ). Moreover,  $\text{NH}_3$  exhibits slow burning velocities, often associated to low burning efficiency in engines, a narrow flammable range and high ignition energy, potentially yielding poor flame stabilisation and extinction characteristics resulting in local or global extinctions. To improve  $\text{NH}_3$ 's combustion properties, blending  $\text{NH}_3$  with methane ( $\text{CH}_4$ ) (for a partial decarbonisation) or  $\text{H}_2$  (from the possible 'in situ' cracking of ammonia) has been proposed, and has gained considerable recent attention, with comprehensive reviews of  $\text{NH}_3$  related work undertaken [2], [3]. Successful demonstrations in both gas turbines [4]–[6] and internal combustion engines [7], [8] have been achieved at high temperatures and pressures. Nevertheless, studies remain limited, as such there seems to be a practical necessity to develop and strengthen understanding of fundamental combustion characteristics of blends containing  $\text{NH}_3$ , ultimately leading to the development of combustors offering greater flame stability and reduced pollutant emissions.

The unstretched laminar burning velocity ( $S_L^0$ ), is one main fundamental physico-chemical property of any premixed air-fuel mixture, reflecting both the combustion process and mixture reactivity. As such,  $S_L^0$  is a key parameter helping understand premixed operational instabilities, notably flashback, blow-off or extinction, and a central step in turbulent flame modelling [9]. Variations in fuel composition inherently introduce changes in transport and chemical properties, in turn influencing witnessed burning and reactivity characteristics of the fuel mixture. The Lewis number ( $Le$ ), defined as the ratio of thermal to mass diffusivity of the deficient reactant, details the transport mechanisms of various species across the flame front [9]. Early experimental investigations [10],[11], supported by the development of asymptotic theories [12], [13], underline that preferential diffusion (i.e.  $Le$  deviating from unity), can strongly influence the burning rates of stretched flames – which undergo the combined effects of strain, curvature, and flame motion. Flames with  $Le > 1$  exhibit greater relative thermal diffusivity, displaying a reduction in burning rate with increased stretch, due to heat loss to the unburned reactant. Conversely, flames with  $Le < 1$  show a relative acceleration with increasing stretch [9]. The burnt gas Markstein length ( $L_b$ ) is a measurable parameter which characterises the influence of  $Le$  on the flame response to the stretch rate. The Markstein number ( $Ma$ ), defined as  $L_b$  divided by the laminar flame thickness ( $\delta_L$ ) – is an indicator of the propensity of a combustion system to be or not influenced by thermo-acoustic instability, and thus of interest to study [14].

Recent experimental studies have investigated  $S_L^0$  and  $L_b$  characteristics of  $\text{NH}_3$ /air flames, notably by Hayakawa et al. [15], at atmospheric and 0.5 MPa of initial ambient pressure, and Kanoshima et al. [16], expanded on that work to include the influence of initial ambient temperature (400-500 K). Results from these studies underline that  $S_L^0$  peaks at an equivalence ratio ( $\phi$ ) of  $\approx 1.1$ , with an increase in pressure and temperature ensuing a decrease and increase in  $S_L^0$ , respectively. With respect to  $L_b$ ,  $\text{NH}_3$ /air flames display an increasing  $L_b$  with increasing  $\phi$ , a

similar trend to that of CH<sub>4</sub>/air and H<sub>2</sub>/air flames. It is noted that at normal temperature and pressure conditions (T=298K, P=0.1MPa) lean NH<sub>3</sub> flames exhibit negative L<sub>b</sub>, with positive values recorded under rich conditions. Furthermore, L<sub>b</sub> is observed to decrease with a rise in pressure and temperature, analogous behaviour to that of the flame thickness.

Okafor et al. [17], [18], investigated the influence of NH<sub>3</sub> on CH<sub>4</sub> based flames (up to ≈ 52% NH<sub>3</sub> by vol.%) across a wide range of  $\phi$  and pressures (0.1 – 0.5 MPa), highlighting that S<sub>L</sub><sup>0</sup> decreases with increasing NH<sub>3</sub> fraction and pressure, developing a detailed and reduced kinetic mechanism. Experimental results of Shu et al. [19] on NH<sub>3</sub>/CH<sub>4</sub> flames (298 K, 0.1 MPa), demonstrated similar tendency but with a uniform decrease in the flame flammability limits with NH<sub>3</sub> increase. They also highlighted the important role played by the H and OH radicals in NH<sub>3</sub>/CH<sub>4</sub> flame propagation. In relation to flame stretch sensitivity of CH<sub>4</sub>/NH<sub>3</sub> flames, Okafor et al. [17] emphasize the shift from a linear to a non-linear flame speed-stretch rate relationship exhibited with increasing  $\phi$  and NH<sub>3</sub> fraction. It should be noted that this is unusual for fuels displaying Le values close to 1 (as is the case for pure CH<sub>4</sub> and NH<sub>3</sub>), with this behaviour mainly attributed to an increase in the preheating zone thickness.

Lee et al. [20], [21] and more recently, Ichikawa et al. [22] and Lhuillier et al. [23] investigated the influence of H<sub>2</sub> upon NH<sub>3</sub> based flames. Ichikawa et al., demonstrated that at stoichiometric conditions ( $\phi=1$ ), S<sub>L</sub><sup>0</sup> increases non-linearly with increasing H<sub>2</sub> fraction, and decreases with increasing pressure. Lhuillier et al. reported an exponential increase in S<sub>L</sub><sup>0</sup> upon addition of H<sub>2</sub> at various initial conditions (298-473K,  $\phi = 0.8 - 1.4$ , H<sub>2</sub> = 60% vol. max). With respect to the flame stretch sensitivity, Ichikawa et al.[22] reported a non-monotonic variation, with an initial substantial decrease in L<sub>b</sub> with increasing H<sub>2</sub>, prior to a minor increase in L<sub>b</sub> upon further H<sub>2</sub> addition. Interestingly, this stretch behaviour dampens at higher pressures, with minimal variation in recorded L<sub>b</sub> of NH<sub>3</sub> flames upon H<sub>2</sub> enrichment. Noteworthy, similar stretch-related non-monotonic trends have been observed for lean CH<sub>4</sub>/H<sub>2</sub> flames [24].

**Table 1: Summary of Literature Review**

All references below employed the spherically expanding flame configuration

Fuel Mixture (vol.%)	Equivalence Ratio ( $\phi$ )	T <sub>u</sub> (K)	P <sub>u</sub> (MPa)	Radiation Corrected	Ref
100% NH <sub>3</sub>	0.7 – 1.3	298	0.1 – 0.3 – 0.5	No	[15]
100% NH <sub>3</sub>	0.8 – 1.2	400 - 500	0.1 – 0.3 – 0.5	Yes	[16]
CH <sub>4</sub> /NH <sub>3</sub> (up to 52% NH <sub>3</sub> )	0.8 – 1.3	298	0.1	Yes	[17]
CH <sub>4</sub> /NH <sub>3</sub> (up to 52% NH <sub>3</sub> )	0.8 – 1.3	298	0.3 – 0.5	Yes	[18]
CH <sub>4</sub> /NH <sub>3</sub> (NH <sub>3</sub> ; 10, 30, 50,70, 90%)	0.6 – 1.4	298	0.1 – 0.5	No	[19]
H <sub>2</sub> /NH <sub>3</sub> (up to 30% H <sub>2</sub> )	0.8, 1.0, 1.67	298	0.1	No	[20]
H <sub>2</sub> /NH <sub>3</sub> (H <sub>2</sub> ; 10, 30,50%)	0.6, 0.8, 1.0, 1.25, 1.67	298	0.1	No	[21]
H <sub>2</sub> /NH <sub>3</sub> (H <sub>2</sub> ; 0,5,10,15,20,40,60,80,100%)	1.0	298	0.1 – 0.3 – 0.5	No	[22]
H <sub>2</sub> /NH <sub>3</sub> (H <sub>2</sub> ; 0,5,30,40,50,60%)	0.8 – 1.4	298 – 473	0.1	Yes	[23]

The importance of flame stretch sensitivity and Le goes clearly beyond the laminar flame regime. Lipatnikov and Chomiak [25], in their extensive review of molecular transport effects on flame propagation, highlighted that preferential diffusional instabilities affect both weak and strong



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turbulent combustion. The influence of  $Le$  on turbulent flames has been reported in the course of experimental studies [26]–[28] as well as in direct numerical simulations [29], [30]. Although limited in scale, emerging studies focusing on turbulence-flame interaction for  $NH_3$  and its blends with either  $H_2$  and  $CH_4$  underlined the potential role of preferential-diffusion and flame-stretch interaction upon turbulent flame characteristics. For example, Ichimura et al. [31] investigated  $NH_3$ /air flames at various turbulent intensities, underlining that although  $S_L^0$  of  $NH_3$ /air is greatest at  $\phi \approx 1.1$ , lean mixtures exhibited better resistance to turbulence induced extinction than richer conditions, due to the potential thermo-diffusive accelerating effects of lean  $NH_3$ /air mixtures, displaying  $Le < 1$ . Similarly, Lhuillier et al. [8] investigated  $NH_3/H_2$  and  $NH_3/CH_4$  (15% vol. of  $H_2$  or  $CH_4$ ) turbulent flame propagation under engine related operating conditions (445K, 0.54 MPa). They reported a decreasing and increasing turbulent to laminar flame speed ratio upon  $CH_4$  and  $H_2$  addition, respectively, induced by the different thermo-diffusive properties and stretch-related behaviour of these ammonia blends.

Clearly, although emerging, the experimental study on the addition of  $H_2$  or  $CH_4$  to  $NH_3$ -based flames remains scarce. Furthermore, recent turbulent combustion experiments underlined the potential influence of preferential-diffusional instabilities upon  $NH_3$ -based flames [8], [31], [32], hence, the aim of this work is to investigate in detail the influence of  $Le$  change on flame behaviour.  $NH_3/CH_4$  and  $NH_3/H_2$  mixtures were varied across a large range of blend composition and equivalence ratio, representative of the prospective demands of fuel-flexible combustors widely employed for power generation. The addition of either  $CH_4$  or  $H_2$  to a given  $NH_3$ /air mixture increases flame temperature, reactivity, mixture flame speed but changes the thermo-diffusive behaviour, which is studied in-detail throughout this work.

## 2. Experimental set-up and specifications

Laminar flame speed measurements were performed using a constant-volume spherical vessel. Details of the apparatus and post-processing techniques can be found in [33], updated for  $NH_3$  specifications in [23], and thus only a brief summary is presented herein. The spherical vessel is equipped with four orthogonal 70 mm quartz viewing windows and has a nominal internal volume of 4.2 L. Thermal mass flow controllers (Brooks 5850S ( $\pm 1\%$ )) were employed to introduce the reactants into the vessel. Mole fractions of all species were determined as a function of temperature ( $T$ ), initial pressure ( $P$ ) and fuel-air equivalence ratio. A piezo-electric pressure transducer and a type-K thermocouple were employed to check respectively the pressure and temperature prior to ignition. The maximum deviation between the effective initial pressure inside the chamber and the required initial pressure was no more than 1%. A vacuum-pump was used to empty the combustion chamber twice between tests ensuring a residual pressure of no more than 0.009 bar, with the remaining air compensated within the equivalence ratio calculation. Pre-mixing was achieved using an internal fan. A capacitor-discharge ignition was achieved via fine tungsten electrodes mounted at  $90^\circ$  to the measurement plane. After quiescence is attained, simultaneous TTL signal to the data-acquisition and ignition systems trigger the experiments. High speed Schlieren imaging of flame propagation was accomplished using a CMOS high speed camera (Phantom V1210) set to a suitable frame capture rate (3000 – 12000 fps), facilitating a spatial resolution of  $\sim 0.10$  mm per pixel. Edge-detection algorithms written in a bespoke MATLAB script were employed to calculate flame propagation rates. A minimum of 3 to 5 repeats were conducted per experimental condition.

## 3. Experimental specifications and theory

Measurements were performed at initial conditions of 298 K ( $\pm 3$  K) and 0.1 MPa ( $\pm 1 \times 10^{-3}$  MPa), with high-purity fuels ( $NH_3$  (99.95%),  $CH_4$  (>99.995%) and  $H_2$  (99.999%)) and dry-zero compressed air (AirLiquide, 20.9%  $O_2$ ). To investigate the influence of  $CH_4$  and  $H_2$  on  $NH_3$  flame speed and stretch-related behaviour, molar ratios were varied from 0 – 100% for  $CH_4$ ; and 0 – 80% for  $H_2$ , in incremental

steps across a wide range of equivalence ratios ( $\phi = 0.7 - 1.2$  and  $0.6 - 1.4$  respectively), with Table 2 summarising the experimental conditions.

**Table 2:** Experimental conditions ;  $T_u = 298 \text{ K} (\pm 3 \text{ K})$ ,  $P_u = 0.1 \text{ MPa} (\pm 1 \times 10^{-3} \text{ MPa})$ .

Equivalence Ratio ( $\phi$ )	Percentage of Fuel in $\text{NH}_3$ (vol.%)	
	$\text{CH}_4$	$\text{H}_2$
0.6	/	20,30,40,50,60,80
0.7	20,30,40,50,60,80,100	/
0.8	0,10,20,30,40,50,60,80,100	0,10,20,30,40,50,60,80
0.9	0,10,20,30,40,50,60,80,100	0,10,20,30,40,50,60,80
1.0	0,10,20,30,40,50,60,80,100	0,10,20,30,40,50,60,80
1.1	0,10,20,30,40,50,60,80,100	0,10,20,30,40,50,60,80
1.2	0,10,20,30,40,50,60,80,100	0,10,20,30,40,50,60,80
1.4	/	20,30,40,50,60,80

Schlieren images were undertaken as in [17], [23], [34], with the shadowed edge considered as the burnt gas isotherm, which as discussed by Giannakopoulos et al. [35], is critical for characterising the influence of flame stretch. The laminar burning velocity and  $L_b$  relative to the burnt side were experimentally determined employing the same procedure as in previous studies [34], [36]. For an outwardly spherically propagating flame, the stretched flame speed ( $S_b$ ) is expressed as the temporal derivative of the Schlieren flame radius ( $r_{sch}$ ) as in Equation 1:

$$S_b = \frac{dr_{sch}}{dt} \quad (1)$$

The flame stretch rate ( $K$ ) is defined as the change in flame area ( $A$ ) gradient and calculated for a propagating spherical flame as shown in Equation 2:

$$K = \frac{1}{A} \cdot \frac{dA}{dt} = \frac{2}{r_{sch}} \cdot \frac{dr_{sch}}{dt} \quad (2)$$

Various correlations between  $S_b$  and  $K$  have been proposed, allowing the estimation of the unstretched flame speed ( $S_b^0$ ). Wu et al [10], proposed a linear relationship, based upon the assumption the flame is weakly stretched and that thermal and mass diffusion are near equal ( $Le \approx 1$ ) and suggest that the flame speed and  $K$  are related as per Equation 3:

$$S_b = S_b^0 - L_b \cdot K \quad (3)$$

Hence, according to the theoretical model given by Equation 3,  $S_b^0$  can be subsequently derived by extrapolation of the relationship to a corresponding intercept value ( $K = 0$ ), equivalent to a flame radius of infinite radius. It may also be noted that  $L_b$  characterises the influence of stretch upon flame propagation, with the magnitude and sign of  $L_b$  related to  $Le$ . This linear model has been the most commonly employed for flame speed measurements using expanding spherical flames, however, as highlighted by Wu et al. [37], it is a first order correction of the stretch effect and hence some degree of uncertainty in the flame speed extrapolation is to be expected. In this work, this methodology will be referenced as LMS (i.e. Linear Model based on flame Stretch).

The second model is attributed to Frankel and Sivashinsky [38], first proposed by Markstein [39], is based upon the assumption of large flame radii. Frankel and Sivashinsky analysed spherically expanding flames considering the effects of thermal expansion and  $Le$ , obtaining the following relationship in Equation 4:

$$S_b = S_b^0 - S_b^0 \cdot L_b \cdot \frac{2}{r_{fsch}} \quad (4)$$

Equation 4 shows that the flame curvature ( $\kappa_{curv}=2/r_{fsch}$ ) and  $S_b$  vary linearly, hence allowing the evaluation of  $S_b^0$  and  $L_b$  from the linear extrapolation of  $S_b$  and  $2/r_{fsch}$  [37], [40]. This method has not received widespread use [19], [34], [40], and here is referenced as LMC (i.e. Linear Model based on Curvature).

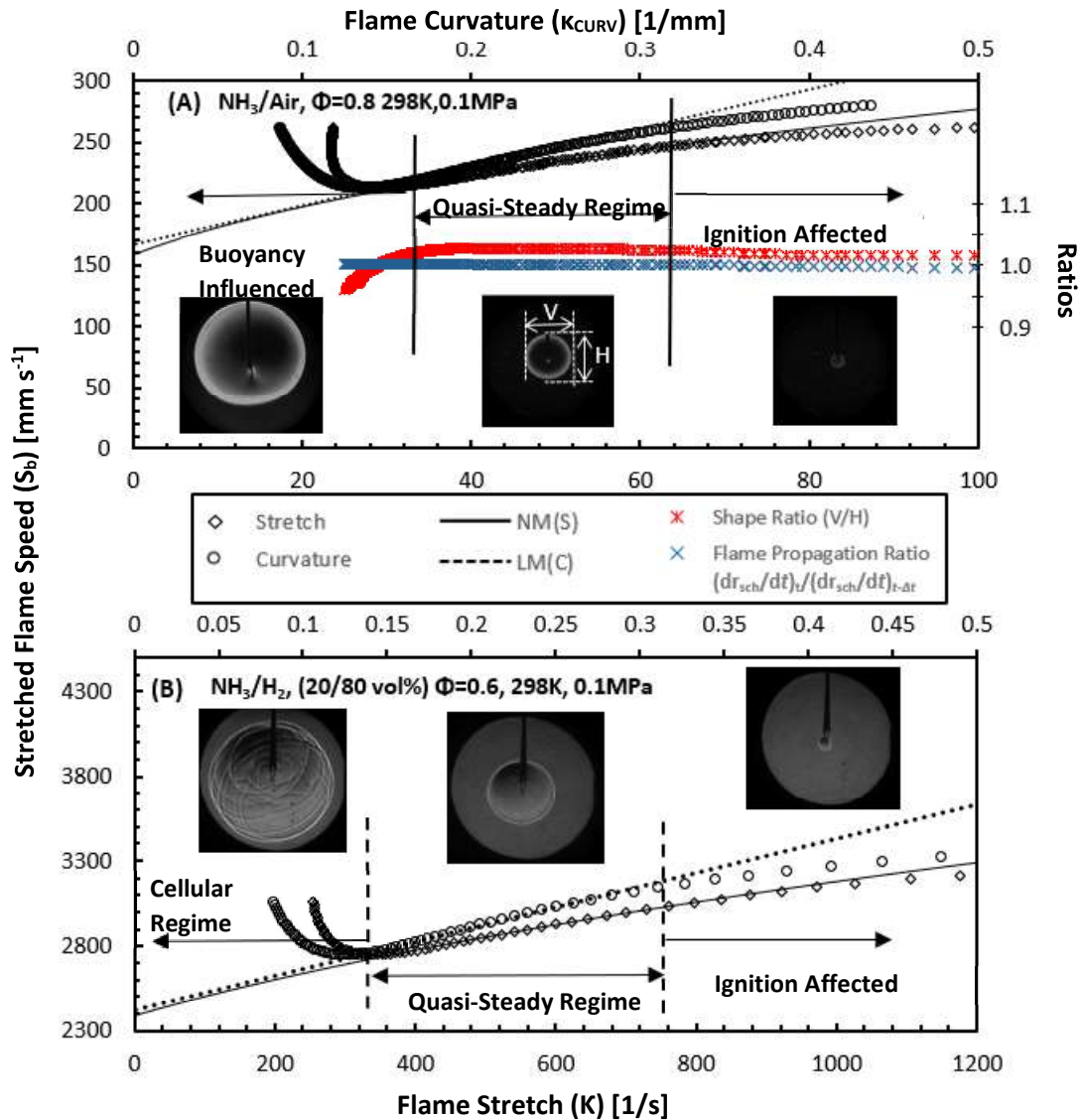
The third extrapolation method, attributed to Kelley and Law [41], is a non-linear model that allows for arbitrary  $Le$  and takes into account the deviations in adiabatic and planar assumptions, prominent in flames which are heavily influenced by stretch such as lean  $H_2$ -based flames. This non-linear model is expressed as in Equation 5:

$$\left(\frac{S_b}{S_b^0}\right) \cdot \ln\left(\frac{S_b}{S_b^0}\right)^2 = -\frac{2 \cdot L_b \cdot K}{S_b^0} \quad (5)$$

A quasi-steady nonlinear association between  $S_b$  and  $K$  is employed – rearranged with the error used for least squares regression – to obtain an extrapolated unstretched flame speed. This model has been used frequently over the last decade, improving accuracy [37], [42], and will be referenced here as the NMS (i.e. Non-Linear Model based on Stretch).

Chen [40] and Wu et al. [37] underline that the accuracy of different extrapolation techniques is related to the  $Le$  of the fuel-air mixture. Chen [40] demonstrated that LMS is only suitable for fuel/air mixtures that exhibit weak stretch and  $Le$  close to unity. Chen [40] showed that it is preferable to employ LMC for mixtures exhibiting positive  $L_b$  and NMS for negative  $L_b$ , due to the non-linear relationship between  $S_b$  and  $K$ ; with these recommendations adopted in this study. Moreover, Wu et al. [37], quantified the uncertainty in extrapolation through the limitation of exploitable data range in relation to Markstein and Karlovitz numbers ( $Ma_{lin}Ka_{mid}$ ); all data presented in this work fall within the recommended values of -0.05 – 0.15 range.

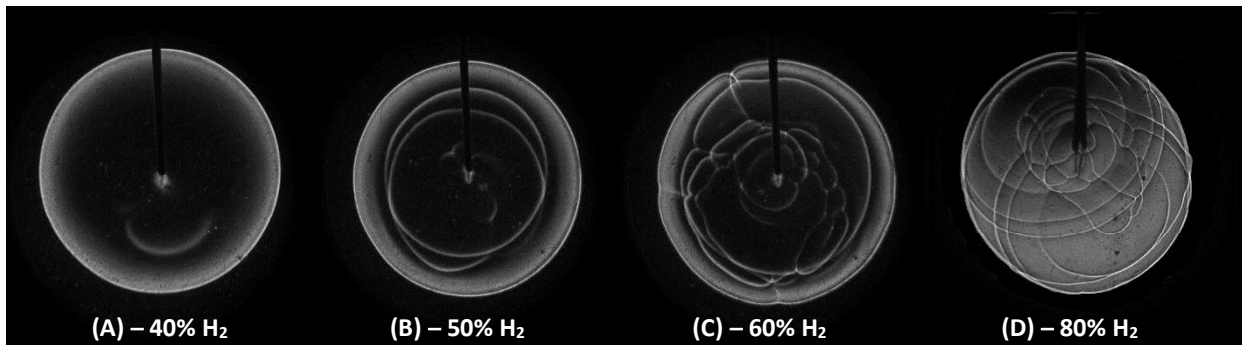
Irrespective of the extrapolation methodology employed, to obtain representative values of laminar flame speed, the burned gas expansion factor has to be used as  $S_L^0 = S_b^0 \cdot (\rho_b/\rho_u)$  with adiabatic equilibrium densities calculated using CHEMKIN-Pro, employing the PREMIX software and using Stagni et al. [43] and Okafor et al. [18] kinetics reaction mechanisms, for  $NH_3/H_2$  and  $NH_3/CH_4$ , respectively. The selection of these mechanisms is discussed later in section 5.2.



**Figure. 1** – Stretched flame speed vs stretch rate ( $K$ ) and curvature ( $\kappa_{CURV}$ ) for (a) pure  $\text{NH}_3/\text{air}$  and (b)  $\text{NH}_3/\text{H}_2$  (20/80 vol.%) ( $T_u = 298 \text{ K}$ ,  $P = 0.1 \text{ MPa}$ )

Limits were set on the range of exploitable radii to minimise the influence of the spark, the buoyancy or the cellularity, and the confinement during the flame growth, ensuring measurements were restricted within the quasi-steady regime. Bradley et al. [44] suggest a spark affected radius up to 6 mm for  $\text{CH}_4/\text{air}$  flames, however Chen et al. [45] demonstrate this critical radius value to be dependent of  $L_e$ . The capacitor-discharge ignition energy was varied in order to minimise the influence of the spark upon flame propagation. Preliminary investigation related to the influence of ignition energy demonstrated minimal variation in results derived from data above 7 mm. Consequently, for all data presented here, 8 mm was chosen as the minimum radius. To limit pressure effects a maximum radius of 25 mm was considered, within the 30% of chamber radius as proposed by Burke et al. [46]. Extrapolation methods used to yield flame speed and the corresponding  $L_b$  rely on a sufficiently large stable quasi-steady flame propagation regime. In the present study, pure  $\text{NH}_3/\text{air}$  flames, or blends containing less than 10% of  $\text{CH}_4$  or  $\text{H}_2$  (vol.%) at leanest and richest conditions were observed to be heavily influenced by the buoyancy, a consequence of their very low burning rate. As a result these flames were observed to lose sphericity, morphing in an ellipsoidal expanding flame, as noted by Hayakawa et al. [15] and Chen et al. [47] for identical initial conditions (298 K, 0.1 MPa). For such flames, the methodology proposed by Hayakawa et al. [15] in delimiting the transition between

ignition influenced, quasi-steady and buoyancy influenced propagation regimes was followed. The aforementioned regimes are determined based upon the flame shape and propagation ratio, defined as the vertical and horizontal radius of the flame ( $r_{sch,V}/r_{sch,H}$ ) and  $(dr_{sch}/dt)_t/(dr_{sch}/dt)_{t-\Delta t}$  (where  $dr_{sch}/dt$  denoting the flame propagation speed at time  $t$ ), respectively. Figure 1.a illustrates the change in flame shape ratio and moving average of the flame propagation ratio against stretch for a lean  $NH_3$ /air flame ( $\phi=0.80$ ); with the relationship of stretched flame speed with stretch and curvature superimposed. As can be seen in Figure 1.a, a quasi-steady propagation regime is clearly identifiable, as such the point at which the flame shape ratio considerably changed ( $\pm 3\%$ ) was taken to represent the maximum flame radius limit. It should be noted that the upward motion of the growing flame kernel does not yield a significant influence upon the propagation speed, since change in the stretched flame speed still maintained proportionality to both flame-stretch and curvature until the transition point was attained. Under other conditions, minor modifications in useable flame radius selection were also required due to known instability issues associated with lean combustion of  $H_2$ -containing fuels. Lean  $H_2$ -based flames are particularly unstable with regard to diffusive effects, a consequence of their low  $Le$  ( $Le \ll 1$ ), resulting in flame acceleration at low stretch and curvature rates [48], as illustrated in Figure 1.b, with an example case of a lean  $NH_3/H_2$  (20/80 vol.%,  $\phi=0.6$ ) flame. Under the tested experimental conditions, it was noted that no flames developed a cellular surface composed of cells of comparable size. However, large cracks of a permanent nature appeared at leanest conditions ( $\phi=0.60$ ) for flames containing  $\geq 40\%$   $H_2$ , with further  $H_2$  enrichment enhancing surface cracking, as illustrated in Figure 2. As underlined by Jomaas et al. [49], these large-scale cracks are most probably the result of large-amplitude initial disturbances, most probably triggered by the ignition event, and not a consequence of preferential diffusion. Nevertheless, using a suitably fast frame capture rate, a minimum of 30 acquired radii was obtained even for the fastest flames, from which flame speed data were estimated.



**Figure 2** – Schlieren images illustrating the development of flame surface cracking as a function of  $H_2$  fraction for  $NH_3/H_2$  flames ( $T_u = 298$  K,  $P = 0.1$  MPa,  $\phi=0.60$ )

The measurements of laminar flame speed are an essential step in order to improve the accuracy of reaction mechanisms [50]. Therefore, the quantification of the measurement uncertainties is required. For this study, uncertainty quantification relies upon the methods outlined by Moffat [51], employing a combination of the experimental facility specifications and accuracy of the processing techniques employed. It should be noted that the uncertainty is quantified for the unstretched flame speed ( $S_b^0$ ), and not for  $S_L^0$ , since this is the parameter measured, here named as  $U_{S_b^0}$ . The total uncertainty estimate is given by Equation 6, where  $B_{S_b^0}$  represents the total bias uncertainty,  $t_{M-1,95}$  the student's value at 95% confidence interval and  $M-1$  degrees of freedom,  $\sigma_{S_b^0}$  the standard deviation of the repeated experiments, and  $M$  the number of experimental repeats at each condition;

$$U_{S_b^0} = \sqrt{B_{S_b^0}^2 + \left(\frac{t_{M-1,95}\sigma_{S_b^0}}{\sqrt{M}}\right)^2} \quad (6)$$

The total bias uncertainty, given by Equation 7, relating changes in  $S_b^0$  with respect to an independent influential variable, ( $v_i$ , i.e. temperature, ambient pressure,  $\phi$ , optical system, gas mixture quality) and the fixed error linked to that variable,  $y_i$ ,

$$B_{S_b^0} = \sqrt{\sum_{i=1}^n \left(\frac{\partial S_b^0(v_i)}{\partial v_i} y_i\right)^2} \quad (7)$$

In order to determine  $B_{S_b^0}$  by Equation 7, the relationships between  $S_b^0$  and each independent variable must be established. As applied in [23], the potential changes in  $S_b^0$  from several parameters are calculated as a function of  $\phi$ ; such as temperature ( $\pm 3$  K) and pressure ( $\pm 1 \times 10^{-3}$  MPa) by using data modelling with CHEMKIN-PRO. Uncertainty resulting from the mixture preparation was estimated to be  $\pm 0.01\%$ , that of the optical system was evaluated from the summated fractional error of both the spatial resolution of the system ( $\pm 0.05/25\text{mm}$ ) and camera ( $\pm 1.5-7.5/3000-15000$  fps). Losses due to radiation influence measured flame burning speed, through the combined effect on the flame propagation itself and the calculated density ratio, with radiation-induced uncertainty particularly significant for slow propagating flames ( $< 12 \text{ cm s}^{-1}$ ) [52]. Lhuillier et al. [23] investigated the dependence of errors resulting from radiation for  $\text{NH}_3/\text{air}$  flames, concluding that the correlation proposed by Yu et al. [52] was applicable, with this recommendation applied for this study. For the experimental results in this study, the greatest radiation-induced error ( $\sim 23\%$ ) was related to leanest  $\text{NH}_3/\text{air}$  flame measured ( $\phi = 0.80$ ), indicating that the laminar flame speed was underestimated by  $\sim 0.56 \text{ cm/s}$ . Finally, error bars on all subsequent plots illustrating laminar flame speed measurements ( $S_L^0$ ) are derived from Equation 6 and 7, with the error for  $U_{S_b^0}$  scaled with respect to the density ratio.

#### 4. Evaluation of Fundamental Parameters

Chen and Ju [40], [45] and Matalon and Bechtold [53], have proposed theoretical relationships relating the Markstein length ( $L_b$ ) and Lewis Number ( $Le$ ), requiring the evaluation of various fundamental flame parameters. The Zel'dovich number, was evaluated using the expression  $Ze = (E_a/R_u) \cdot [(T_{ad} - T_u)/(T_{ad}^2)]$  with  $R_u$  the universal gas constant,  $T_u$  and  $T_{ad}$ , the temperature of the unburnt mixture and the adiabatic flame temperature, respectively. The activation energy,  $E_a$ , is defined as the slope of the mass burning flux ( $m^0$ ) and the inverse adiabatic flame temperature at constant  $\phi$  and pressure, empirically determined using the expression  $E_a = -2R_u \{ \partial[\ln(m^0)] / \partial[1/T_{ad}] \}$ , where the mass burning flux can be replaced by  $m^0 = (\rho_u \cdot S_L^0)$ , as recommended by Egolfopoulos and Law [54]. It should be noted that this method is only valid for sufficiently off-stoichiometric conditions, with interpolation required for  $E_a$  values for mixtures near stoichiometry [55]. For the flame thickness, two definitions can be considered [9]. The first, commonly termed as the kinetic (or diffusion) flame thickness ( $\delta_K$ ), is defined as  $\delta_K = \lambda / (\rho_u \cdot c_p \cdot S_L^0)$ , where  $\lambda$  represents the thermal conductivity and  $c_p$  the specific heat at constant pressure. The second, referenced as the 'gradient' flame thickness ( $\delta_G$ ) can be expressed as  $\delta_G = (T_{ad} - T_u) / (dT/dx)_{max}$ .

##### 4.1 Relationships of $Le$ and $L_b$

For the purpose of this work, the relationships relating  $Le$  to  $L_b$ , proposed by Chen [40], [45] and Matalon and Bechtold [53] are considered. The first formulation based on spherically expanding flames is derived from the analytical developments done by Chen and Ju, and then used by Bouvet et al. [56], Lapalme et al. [57] and Zitouni et al. [34] in their studies on preferential-diffusion effects upon



multi-component fuels. It should be noted that the 'kinetic' flame thickness is consistent with the approach detailed by Chen [40], [45]. This estimate of  $Le$  is referenced herein as  $Le_{CHEN}$  and can be expressed per Equation 8:

$$Le_{CHEN} = \left[ \frac{L_b}{\sigma \cdot \delta_K} - \frac{Ze}{2} \right]^{-1} \left[ 1 - \frac{Ze}{2} \right] \quad (8)$$

With  $\sigma = \rho_b / \rho_u$ , the expansion ratio. From Equation 8, the retrieval of  $L_b$  is possible as in Equation 9.

$$L_{b-CHEN} = \left[ \frac{1}{Le} - \left( \frac{Ze}{2} \right) \left( \frac{1}{Le} - 1 \right) \right] \sigma \cdot \delta_K \quad (9)$$

A second formulation by Bechtold and Matalon, was derived from theoretical analysis on the dependence of  $L_b$  on stoichiometry. This formulation was considered by Jomaas et al. [49] in the case of acetylene ( $C_2H_2$ ), Lapalme et al. [57] for  $H_2/CO$  and Zitouni et al. [34], for  $CH_4$  blended with  $H_2$  or  $C_3H_8$ . Lapalme et al. [57], on their assessment of the method of calculating  $Le$  and comparison with experimental results, demonstrate that employing the kinetic flame thickness definition with the Bechtold and Matalon relationship results in much higher values of  $Le$  than plausible. Similar conclusions are drawn by Zitouni [58], hence the 'gradient' flame thickness is employed. This estimate of  $Le$  is denoted in following as  $Le_{BM}$ , and is expressed per Equation 10:

$$Le_{BM} = 1 + \left[ \frac{L_b}{\delta_G} - \frac{2}{\sqrt{\sigma} + 1} \right] \left[ \frac{2 \cdot Ze}{\sigma - 1} \left\{ \sqrt{\sigma} - 1 - \ln \left( \frac{1}{2} (\sqrt{\sigma} + 1) \right) \right\} \right]^{-1} \quad (10)$$

Which provides  $L_{b-BM}$  as per Equation 11:

$$L_{b-BM} = \delta_G \left[ \frac{\gamma_1}{\sigma} - \left\{ \frac{Ze}{2} (Le - 1) \gamma_2 \right\} \right] \quad (11)$$

where  $\gamma_1$  and  $\gamma_2$  are functions of the expansion ratio given in Equation 12:

$$\gamma_1 = \frac{2 \cdot \sigma}{(\sqrt{\sigma} + 1)} ; \quad \gamma_2 = \left[ \frac{4}{\sigma - 1} \right] \left[ \sqrt{\sigma} - 1 - \ln \left( \frac{\sqrt{\sigma} + 1}{2} \right) \right] \quad (12)$$

#### 4.2 Lewis Number evaluation of multi-component fuels

Whilst the definition of the Lewis Number for single-fuel mixtures is relatively straightforward, no clear consensus on the correct formulation of  $Le$  for multi-fuel mixtures seems to exist [56]. The challenge arising from the fact that the diffusivity of each fuel must be considered. This is particularly applicable when the transport diffusion mechanisms are different as is the case for  $H_2$ ,  $NH_3$  or any alkanes. Bouvet et al. [56] identified three 'effective'  $Le$  formulations. The first formulation is based upon a volumetric fraction weighted average, resulting from Muppala et al. [26] computational study of turbulent  $CH_4 - H_2 / C_3H_8$  flames. At low-turbulence, this formulation results in reasonable agreement between modelled and experimental burning velocities; whilst at higher turbulent intensity modelled burning rates significantly underpredicted measurements. This volume weighted formulation will be referenced in this work as  $Le_V$ , and is expressed per Equation 13:

$$Le_V = \sum_{i=1}^f x_i \cdot Le_i \quad (13)$$

where  $x_i$ , is the fuel volumetric or mol fraction of the species  $i$ .

The second  $Le$  formulation is derived by Law et al. [59] from the asymptotic analysis of high pressure  $H_2/C_3H_8$  laminar spherical flames. This formulation has been widely employed to discuss the thermo-

diffusive behaviour of mostly binary and tertiary blends of hydrocarbons and hydrogen [27], [60]. This formulation is based upon the weighted average of the fuels' nondimensional heat release ( $q_i$ ), referenced in this work as  $Le_H$ , and expressed as per Equation 14:

$$Le_H = 1 + \frac{\sum_{i=1}^f q_i (Le_i - 1)}{\sum_{i=1}^f q_i} \quad (14a)$$

where

$$q_i = \frac{Q \cdot Y_{i,unburnt}}{c_p \cdot T_u} \quad (14b)$$

with  $Q$  representing the overall heat of reaction,  $Y_i$ , the mass fraction of species  $i$ .

The third one is related to the work conducted by Dinkelacker et al. [27] on lean  $H_2/CH_4$  flames. It is assumed that if the flame curvature is dominant, then the local enrichment of the most diffusive fuel at the flames leading edge can be expected. This overall reaction-rate enhancement is translated into a volumetric-weighted average of the fuel diffusivities. This diffusion weighted formulation will be referenced in this work as  $Le_D$ , and expressed per Equation 15:

$$Le_D = \frac{D_T}{\sum_{i=1}^F x_i \cdot D_{ij}} \quad (15)$$

where  $D_T$  is the mixture's thermal diffusivity and  $D_{ij}$  are the binary mass diffusion coefficients. Several methods have been proposed to estimate the binary mass diffusion coefficients at moderate ambient pressure (<10 bar), with empirical constants based upon experimental data [61]. The method of Wilke as well as that of Hirschfelder, Bird and Spot, detailed in [61], is used in this study. Once the binary coefficients for the combinations of gases are estimated, an effective formulation of the deficient species in the mixture must be designated. For lean fuel-air mixtures, the deficient reactant is scarce compared to the surrounding  $N_2$  [9]. For that reason,  $D_{ij}$  is taken as the fuel, ' $i$ ', diffusing into  $N_2$  (denoted with the subscript  $j$ ). This may hold true for hydrocarbons due to their high molar fuel-air ratio, but not for fuels that have low molar fuel-air ratio such as  $H_2$ , as underlined by Lapalme et al. [57]. Thus, as proposed by Wilke [62], the mixture-averaged coefficient of mass diffusion ( $D_{i,mix}$ ) into the mixture was employed as defined in Equation 16:

$$D_{i,mix} = (1 - Y_{i,mix}) \left( \sum_{\substack{s=1 \\ s \neq i}}^N \frac{X_s}{D_{is}} \right)^{-1} \quad (16)$$

where  $Y$  is the mass fraction of the species ' $i$ ' and ' $X$ ' the molar fraction of each species ' $s$ ' in the mixture; with details of the method available in [61]. In order to ensure the correct application of the method, the binary diffusion coefficients calculated in this work were compared with values generated employing the STANJAN transport calculator [63]. Differences were no greater than  $\pm 3\%$  for binary blends containing  $CH_4$ ,  $NH_3$ ,  $O_2$  and  $N_2$ , and up to 10% in the presence of  $H_2$ , in agreement with expected deviations [61]. This would translate to a maximum difference of < 3% upon the theoretical  $Le$  for  $H_2$  air/flames, and < 1% for blends containing  $CH_4$  and  $NH_3$ , and thus the derived coefficients are deemed suitable for the purpose of this study.

Irrespective of the Lewis Number formulation employed, the thermal diffusivity  $D_T = \lambda / (\rho_u \cdot c_p)$  has to be evaluated. The calculation of  $\rho_u$  and  $c_p$  (specific heat capacity at constant pressure) were



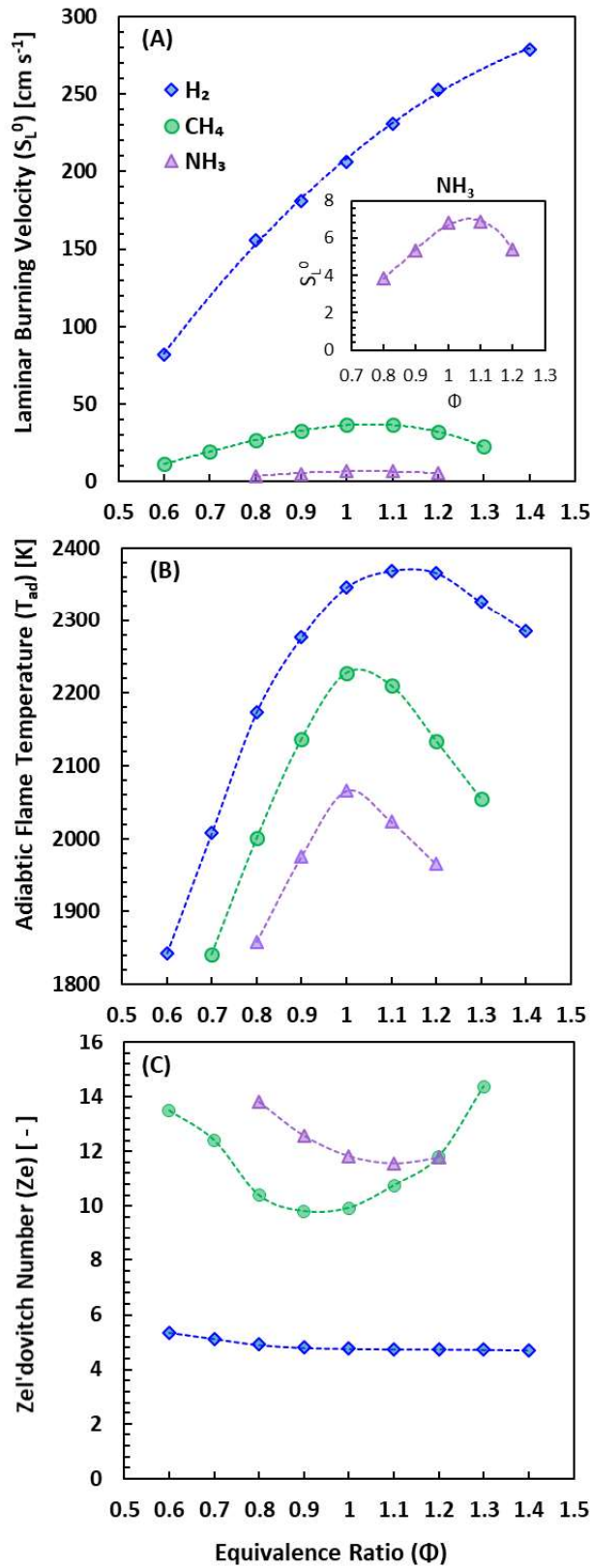
1 based on the ideal gas theory and are relatively straightforward. The evaluation of the thermal  
2 conductivity for each individual species ( $\lambda_i$ ) was calculated based upon the Chung et al. [64] method  
3 and outlined by Poling et al. [61]. This calculation procedure uses a predictive method to estimate  $\lambda_i$ ,  
4 and requires only the critical temperature ( $T_c$ ), volume ( $V_c$ ) and pressure ( $P_c$ ) as inputs, available in  
5 [61]. This correlation has been compared to extensive testing with experimental data and  
6 demonstrated to be robust, with deviations of expected  $\lambda_i < 6\%$  [65]. For multi-component fuels, the  
7 mixed average thermal conductivities ( $\lambda_{mix}$ ) were calculated using Mathur et al.'s [66] suggestion:  
8

$$\lambda_{mix} = \frac{1}{2} \left( \sum_{i=1}^N x_i \lambda_i + \frac{1}{\sum_{k=1}^N \frac{x_i}{\lambda_i}} \right) \quad (17)$$

9  
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14 Where ( $x_i$ ) and ( $\lambda_i$ ) are the mole fraction and thermal conductivity of the 'i<sup>th</sup>' species, respectively. This  
15 method has previously been employed by Bouvet et al. [56], in their study of Le for multi-component  
16 fuel mixtures. To ensure the validity and correct application of the methodologies employed to  
17 calculate the thermal diffusivity, evaluated values were compared to values calculated using the  
18 STANJAN transport calculator [63] for single and binary mixtures. Differences are less than  $\pm 3\%$ ,  
19 irrespective of the number of fuels composing the blend, thereby validating the robustness of the  
20 methodologies selected, and thus deemed suitable for the purpose of this work.  
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## 5. Results and Discussion

### 5.1 Pure Fuels



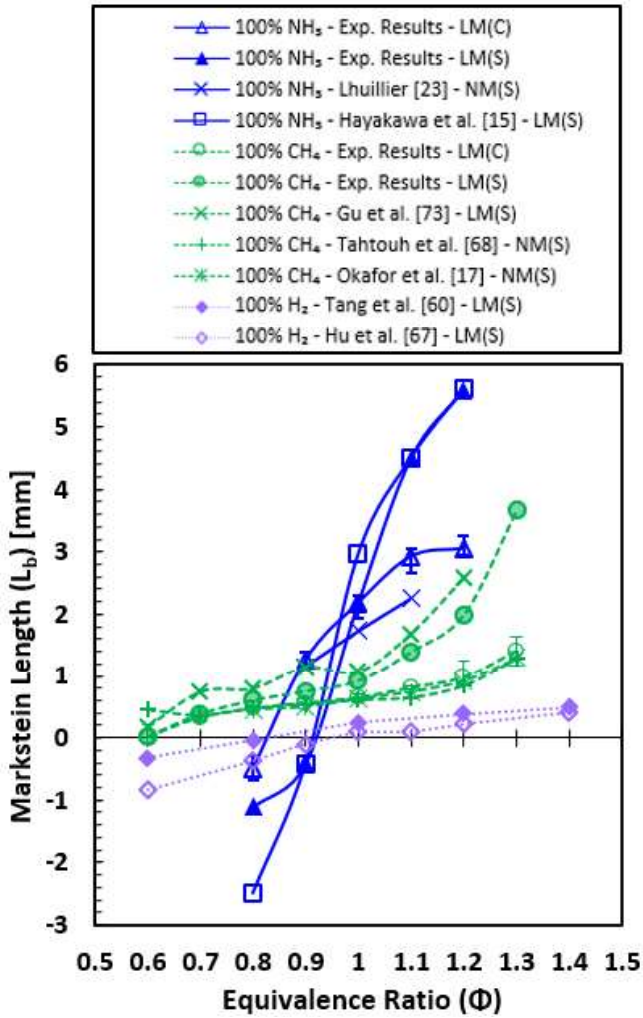
**Figure 3** – Comparison of (a) laminar burning velocity, (b) Adiabatic flame temperature and (c) Zel'dovich number as a function of equivalence ratio for pure  $\text{NH}_3$ ,  $\text{CH}_4$ , and  $\text{H}_2$ /air flames at 298 K & 0.1 MPa.  $S_L^0$  data for  $\text{H}_2$ /air flames from [67].

1 The measured  $S_L^0$  for the pure  $\text{NH}_3$ ,  $\text{CH}_4$  and  $\text{H}_2$  /air flames are compared in Figure 3.a.  $\text{NH}_3$ /air  
2 flames display the slowest flame propagation rates, five to six times slower than those of  $\text{CH}_4$ /air  
3 flames; with a similar difference in flame speed magnitude between  $\text{H}_2$ /air and  $\text{CH}_4$ /air flames at  
4 stoichiometric conditions. It should be noted that the thermal diffusivity of these fuels decreases in  
5 the order of  $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{NH}_3$ , analogous to the decreasing  $S_L^0$  values. Comparison of the measured  
6 pure fuel flame speeds for  $\text{CH}_4$ /air and  $\text{NH}_3$ /air with other peer-reviewed datasets [17], [68]–[73],  
7 alongside values attained numerically, are located in the supplementary materials (SM). With respect  
8 to  $\text{CH}_4$ /air (SM.1), excellent agreement is displayed with selected literature [17], [68],[69], particularly  
9 with datasets from [17], [68], both employing the NM(S), with the Okafor et al. [18] reaction  
10 mechanism exhibiting excellent agreement with measured results in this study. With respect to  $\text{NH}_3$ /air  
11 (SM.2), measurements of  $S_L^0$  remain limited. Good agreement is observed with Hayakawa et al. [15]  
12 and Lhuillier et al. [23], who both employed the spherically expanding flame method. Very good  
13 agreement is also observed with the dataset of Han et al. [71], who employed the Heat Flux Method.  
14 However, overall relatively large scatter is observable between the various datasets, with relative  
15 differences close to  $\sim 30\%$  and  $25\%$  under rich ( $\phi=1.2$ ) and lean conditions ( $\phi=0.9$ ). These differences  
16 may potentially be attributable in part to the different experimental methods employed, as well as the  
17 fact that not all the datasets compared have taken into account losses due to radiation, with radiation-  
18 induced uncertainty particularly significant for slow propagating flames ( $< 12 \text{ cm s}^{-1}$ ) [52]. With respect  
19 to the appraised reaction mechanisms, all reaction mechanisms greatly over-predict  $\text{NH}_3$ /air  $S_L^0$  at  
20 leanest conditions ( $\phi=0.8$ ) and under rich conditions ( $\phi>1.1$ ). Overall, good agreement is observed only  
21 at  $\phi=0.9 - 1.0$  with Okafor et al. [18] and Stagni et al. [43] reaction mechanisms, with best agreement  
22 overall with Okafor et al. [18].  
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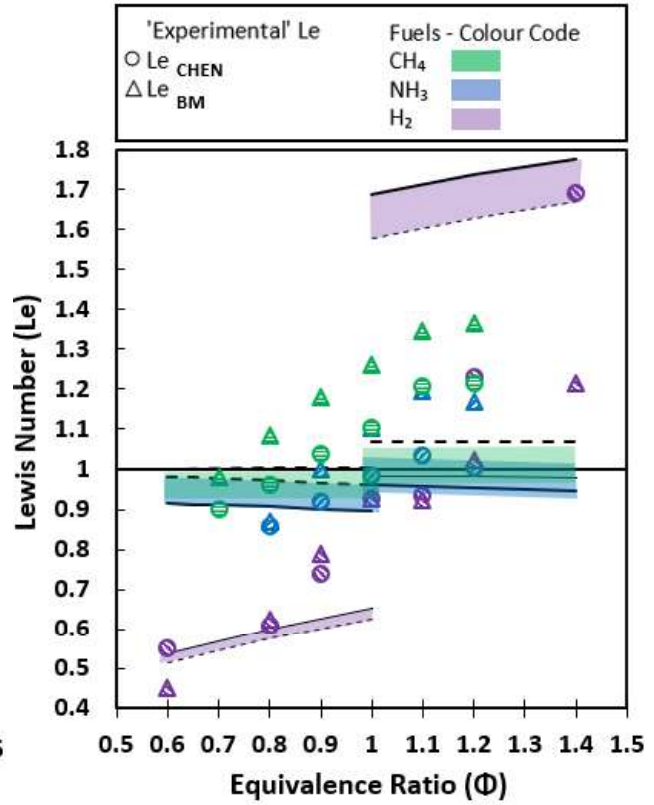
28 The adiabatic flame temperature and activation energy (represented by  $Z_e$ ) with respect to  $\phi$   
29 for the aforementioned pure fuels is illustrated in Figure 3 (b) and (c), respectively. For  $\text{CH}_4$  (and in  
30 general  $\text{C}_{1-4}$  alkanes),  $S_L^0$  and  $T_{ad}$  peak at conditions slightly richer than stoichiometric conditions  
31 ( $\phi \sim 1.05 - 1.10$ ), underlining the sensitivity of the flame propagation to the flame temperature. The  
32 fact that the minimum activation energy is located at similar conditions ( $\phi \sim 0.9$ ), underlines the  
33 dictating influence of the flame temperature on the global activation energy. Due to flames  
34 temperatures peaking at around stoichiometric conditions, temperature-sensitive branching reactions  
35 are facilitated, thereby leading to overall faster reactions and reduced global activation energies, as  
36 highlighted by Jomaas et al. [49]. With respect to  $\text{H}_2$ , a similar trend in  $Z_e$  is observed when plotted  
37 upon a much larger range of  $\phi$  than that illustrated in Figure 3 (c). Viewed across the total flammability  
38 range of  $\text{H}_2$  a similar parabolic relationship analogous to that exhibited by  $\text{CH}_4$  and  $\text{NH}_3$  is apparent.  
39 Although  $\text{H}_2$  flame temperature peaks at similar conditions to that of  $\text{CH}_4$  ( $\phi \sim 1.1 - 1.2$ ), both the  
40 maximum flame speed and minimum values of  $Z_e$  are located at much richer conditions ( $S_{L,max}^0$  for  $\phi$   
41  $\sim 1.6-1.8$  [74],  $Z_{e,min}$  for  $\phi \sim 1.4 - 1.6$ ). This shift in the flame speed to richer conditions (and by extension  
42 the reduced influence of flame temperature on  $S_L^0$ ) has been attributed to the much larger value of  
43 the Lewis Number ( $Le \gg 1$  for  $\phi > 1.6$ ), with flame acceleration, a consequence of preferential diffusion  
44 [49]. As a result, the minimum  $Z_e$  witnesses a corresponding shift to richer conditions, since  $Z_e$  is  
45 directly extracted from the flame speed (see Section 4). Thus, a transport mechanism (i.e. the thermo-  
46 diffusive response of the fuel for  $Le \gg 1$ ) generates a change in response in the flame speed, which  
47 subsequently impacts the flame property, highlighting the influence of transport on a supposedly  
48 chemical property [49]. This is of importance when attempting to understand behaviour of fuel blends  
49 which possess different transport properties (as it is the case here with  $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{NH}_3$ ) and the  
50 subsequent consequence on flame behaviour. On the other hand, for  $\text{NH}_3$ ,  $S_L^0$  and  $T_{ad}$  peak at  
51 approximately at the same equivalence ratio ranges ( $\phi \sim 1.0 - 1.10$ ). The fact that the maximum flame  
52 speed, adiabatic flame temperature and minimum  $Z_e$  all arise at nominally identical  $\phi$  conditions  
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1 underlines the equi-diffusive nature of  $\text{NH}_3$ , with  $Le$  close to unity, comparable to the preferential-  
2 diffusional properties of pure  $\text{CH}_4$ .

3 In premixed flames, instabilities can result from both preferential-diffusional and  
4 hydrodynamic (Darrieus-Landau) instabilities. It should be highlighted that the Markstein length ( $L_b$ )  
5 indicates the response of the flame to the stretch, it is also an indicator of the flame's propensity to  
6 instability and not the cause of the instability. Figure 4 presents measured  $L_b$  from the present study  
7 as well as some other measurements available in literature, at similar initial temperature ( $\pm 5$  K) and  
8 pressure conditions, for  $\text{NH}_3$  [15], [70],  $\text{CH}_4$  [17], [68], [75] and  $\text{H}_2$  [60], [67] flames from lean to rich  
9 conditions. To facilitate fair comparison, it is also indicated in the legend what methodology was used  
10 to extrapolate  $L_b$  (Linear or Non-Linear Model by Stretch (LMS) or (NMS); Linear Model based on  
11 Curvature, (LMC)). First, it should be noted that there exist very limited experimental  $L_b$  datasets for  
12  $\text{NH}_3$ . At first there appears to be relatively large scatter between the various datasets, particularly for  
13  $\text{NH}_3$  and rich  $\text{CH}_4$  flames. However, good agreement is observed between datasets when the same or  
14 a similar extrapolation method are compared, irrespective of the fuel evaluated. For example, good  
15 agreement is observed between our measured  $L_b$  values for  $\text{NH}_3$  and  $\text{CH}_4$  when employing LM(S) and  
16 those of Hayakawa et al. [15] and Gu et al. [17] respectively, who also employed LM(S). Similarly, when  
17 employing LM(C) and comparing results to research groups that employed NM(S), excellent agreement  
18 is also observed, irrespective of the fuel, with results from both extrapolation models expected to be  
19 similar, as highlighted by Chen [40]. The above highlights the influence that the extrapolation models  
20 have on the Markstein Length. All three fuels exhibit an increasing  $L_b$  as a function of  $\phi$  increase from  
21 lean to rich conditions with the greatest change exhibited by  $\text{NH}_3$ , with negative value of  $L_b$  under lean  
22 conditions (comparable to that of  $\text{H}_2$ ), and larger positive value than that of  $\text{CH}_4$  and  $\text{H}_2$  under rich  
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**Figure 4** – Experimental values of  $L_b$  for pure  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{H}_2$  as a function of  $\phi$  (298 K, 0.1MPa).



**Figure 5** – Theoretical and experimental  $Le$  for  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{H}_2$  as a function of  $\phi$  (data for  $\text{H}_2$  [67]). Full and dotted lines respectively reflect Hirschfelder and Wilke methods to evaluate  $D_{ij}$  (298 K, 0.1MPa)

To better understand the changes in the stretch response of pure fuels/air flames, the evolution of the corresponding  $Le$  is presented in Figure 5, from lean to rich mixtures. ‘Theoretical’ Lewis numbers, estimated using the free-stream properties of the mixtures, are illustrated as colour bands with the upper and lower limits (represented by full and dashed lines) denoting the differences between either the Hirschfelder or Wilke method to evaluate the mass diffusion coefficient. While the correct  $Le$  is evaluated ( $Le \sim 1$  for  $\text{NH}_3$  and  $\text{CH}_4$ ;  $Le \ll 1$  at  $\phi < 1$  and  $Le \gg 1$  at  $\phi > 1$  for  $\text{H}_2$ ), little variation is observable across the considered  $\phi$ , aside from the transition from lean to rich conditions. Furthermore, it should be highlighted that minimum  $Le$  for  $\text{NH}_3$  is just prior to stoichiometric conditions in agreement with [15], whilst for  $\text{CH}_4$  and  $\text{H}_2$ , minimum  $Le$  is obtained at leanest conditions. Since  $Le$  was simply evaluated as a function of the mixture’s thermal and mass diffusivity, variations in fundamental flame parameters such as the flame thickness, the activation energy and the expansion ratio [53] were not considered. As such,  $Le$  can be evaluated from the experimental  $L_b$  and these other properties affecting the flame, as recommended by Jomaas et al. [49], with the use of theoretical relationships established in literature (denoted as  $Le_{\text{CHEN}}$  and  $Le_{\text{BM}}$ , Eqn. 8 and 10, accordingly). Therefore, as it can be seen when comparing Figure 4 and 5, analogous  $L_b$  and  $Le$  evolution as a function

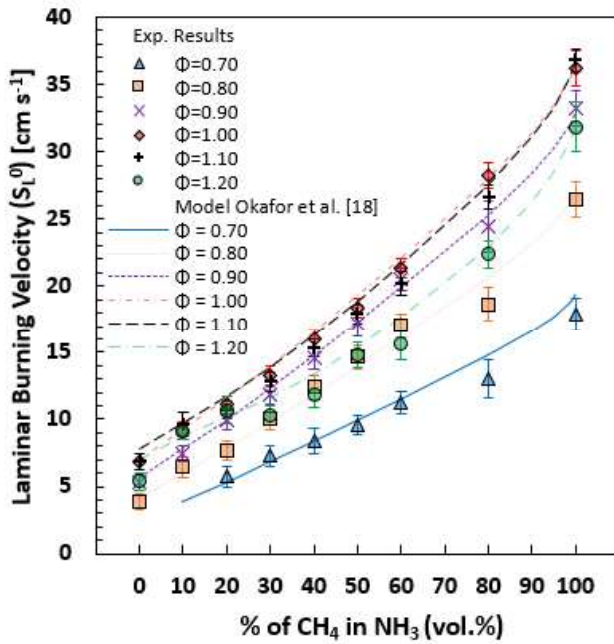
of the fuel and the equivalence ratio is observable, regardless of the theoretical relationship relating  $L_b$  to  $Le$ . However, it is interesting to note that the greatest change in  $L_b$  magnitude is observed for  $NH_3$ , whilst exhibiting least change in  $Le$ , as noted by [8], potentially alluding that  $Le$  may not be the main driving factor behind the measured changes in stretch sensitivity for  $NH_3$ -based flames. Furthermore, the transition from a negative to positive  $L_b$  for  $NH_3$  obtained for  $\phi \sim 0.8 - 1.0$  is at comparable  $\phi$  with the transition from  $Le < 1$  to  $Le > 1$  occurred.

In order to assess how well the considered formulations captured  $Le$  behaviour the lean and rich limits of  $Le$  for each fuel was evaluated. The  $Le$  limits bound the minimum (lean) and maximum (rich) plausible  $Le$  values for ultra-lean and ultra-rich mixtures. To estimate those limits the upper and lower flammability limits of the fuels were utilised. With respect to  $CH_4$ , lean and rich limits were evaluated to be 0.93 and 1.07, respectively, marginally smaller than those reported previously, namely 0.955 [27] and 1.10 [57], underlining the equi-diffusive nature of  $CH_4$ . As can be seen from Figure 5,  $Le_{CHEN}$  best respects these limits, particularly at richest conditions, in agreement with similar conducted by Lapalme et al. [57] and Zitouni et al. [34]. For  $H_2$ ,  $Le$  lean and rich limits were estimated to be 0.34 and 2.02, respectively. On the lean side, this is in good agreement with literature, 0.29 [57], whilst on the rich side,  $Le$  limits evaluated in this work (2.02) are smaller than other reported values, 2.32 [76] and 2.58 [57], potentially due to the underestimation of the  $H_2$  binary mass diffusion coefficients, as underlined previously (Section 4.2). Nevertheless, good agreement is attained by all formulations for  $H_2$ . With respect to  $NH_3$ , with lean and rich limits of 0.89 and 1.08, respectively, similar in scale to those of  $CH_4$ . Although no sources were found to compare the  $Le$  limits of  $NH_3$ , Hayakawa et al. [15] evaluated an  $Le$  of 0.95 and 1.09, for  $NH_3$ /air mixtures under lean ( $\Phi = 0.7$ ) and rich ( $\Phi = 1.3$ ) conditions, respectively (flammability limits of  $NH_3$ ;  $\Phi_{min} \sim 0.63$  and  $\Phi_{max} \sim 1.4$ ). Overall,  $Le_{CHEN}$  best captures expected thermo-diffusive behaviour of  $NH_3$ .

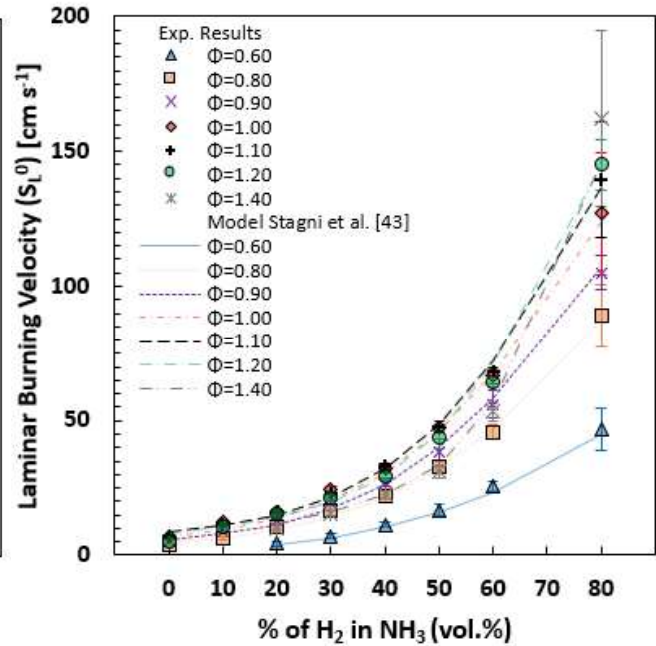
## 5.2 Binary Fuel Mixtures

The influence of increasing fraction of either  $CH_4$  or  $H_2$  on  $NH_3$ /air  $S_L^0$ , across a wide range of  $\Phi$  is depicted in Figure 6 and 7 respectively, alongside values attained numerically. With respect to  $NH_3$ / $H_2$  blends, the Tian et al. [77], Shrestha et al. [78], Gotama et al. [79], Okafor et al., [18] and Stagni et al. [43] reaction mechanisms were all appraised, however only the latter is illustrated since it consistently gave best agreement with all  $NH_3$ / $H_2$  blends evaluated in this study. Similarly, with respect to  $NH_3$ / $CH_4$  blends, only the Okafor et al. [18] is depicted since it consistently yielded best agreement with the evaluated blends.





**Figure 6** –  $S_L^0$  for binary  $\text{NH}_3/\text{CH}_4$  mixtures, comparison with simulated values with Okafor et al. kinetics model [18] (298 K, 0.1MPa)

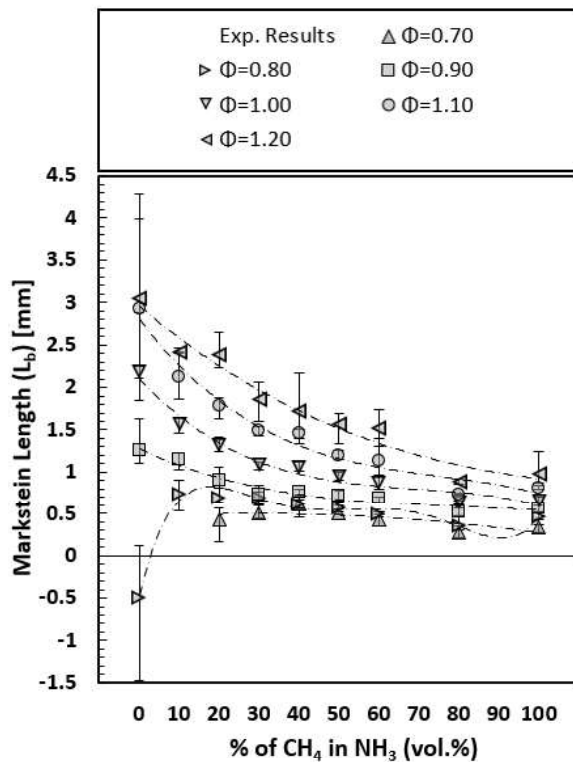


**Figure 7** –  $S_L^0$  for binary  $\text{NH}_3/\text{H}_2$  mixtures, comparison with simulated values with Stagni et al. kinetics mechanism [42] (298 K, 0.1MPa)

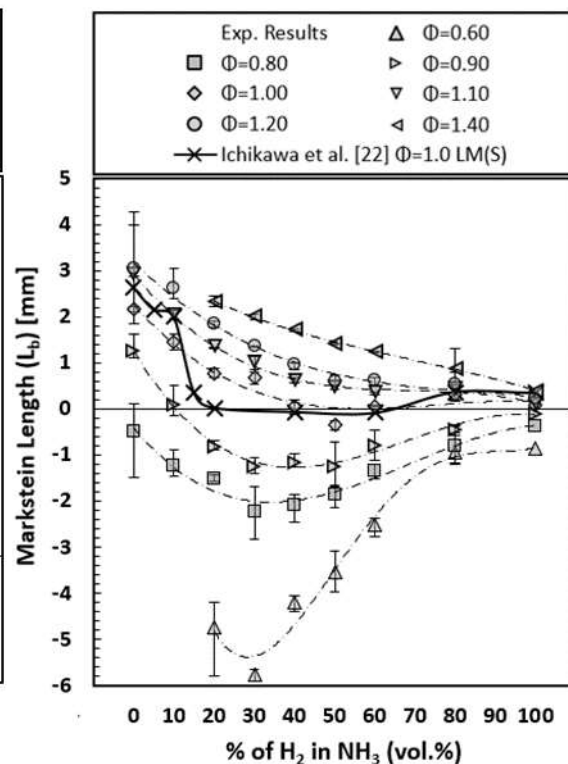
As can be seen in Figure 6, irrespective of the  $\Phi$ , a fairly linear increase in  $\text{NH}_3$  flame speed is observable upon  $\text{CH}_4$  addition, with the Okafor et al. [18] mechanism exhibiting very good agreement with measured results. On the other hand, as illustrated in Figure 7, an increase in  $\text{H}_2$  addition results in an exponential increase in  $S_L^0$  of  $\text{NH}_3$  based flames, across the entire tested  $\phi$  range. The Stagni et al. [43] mechanism best captured this exponential increase in flame speed, showing excellent agreement with experimental values from this study, across all tested conditions. It is worth highlighting that  $\sim 10\text{-}20\%$  addition (vol.%) of either  $\text{CH}_4$  or  $\text{H}_2$  results in a similar increase in  $\text{NH}_3$  flame speed, with further increases resulting in very different flame speed behaviour. This increased reactivity of  $\text{NH}_3$  based blends upon  $\text{CH}_4$  and  $\text{H}_2$  addition has been previously suitably reported [19] [80], with modelling work and sensitivity analysis suggesting that the flame speed, burning intensity ( $Q'$ ) and production of radicals, particularly O and H appear to be strongly correlated.

To investigate the stretch-related behaviour of  $\text{NH}_3/\text{CH}_4$  and  $\text{NH}_3/\text{H}_2$  flames,  $L_b$  is plotted as a function of either  $\text{CH}_4$  or  $\text{H}_2$  addition to  $\text{NH}_3$  across a wide range of  $\phi$  in Figure 8 and 9, respectively. Note that the evolutions of  $L_b$  as a function of  $\phi$  are in SM3 and 4. For a  $\phi \geq 0.9$ , a linear decrease in  $L_b$  is observed with increasing  $\text{CH}_4$  fraction. At  $\phi = 0.80$ , a negative value  $L_b$  is obtained for pure ammonia while 10%  $\text{CH}_4$  addition results in  $L_b$  sign inversion (from negative to positive). As pure  $\text{NH}_3/\text{air}$  mixtures could not be ignited for  $\phi < 0.8$ , with this experimental apparatus, this tendency cannot be verified. Under rich conditions ( $\phi \geq 1.1$ ), a decreasing stretch sensitivity is measured upon increasing  $\text{H}_2$  fraction, similar in trend and magnitude to that observed for  $\text{NH}_3/\text{CH}_4$  flames but for  $\phi \geq 0.9$ . However, interestingly for  $\phi \leq 1.0$ , an initial decrease in  $L_b$  is observed up to 30 – 40%  $\text{H}_2$  addition, at which point any further addition of  $\text{H}_2$  results in an increase in  $L_b$ , with non-linear behaviour accentuated as conditions get leaner. Similar non-monotonical variation in stretch-related behaviour was measured by Lhuillier [70] as well as by Ichikawa et al. [22], for  $\text{NH}_3/\text{H}_2$  flames, at  $\phi = 1.0$  and ostensibly identical experimental conditions ( $T_u = 298 \text{ K}$ ,  $P_u = 0.1 \text{ MPa}$ ), also plotted in Figure 9 for comparison purposes. As such, under lean conditions,  $\text{NH}_3/\text{H}_2$  mixtures exhibit a greater negative  $L_b$  than that of pure  $\text{H}_2$

flames. It should be highlighted that similar non-linear  $L_b$  behaviour was measured by Okafor et al. [24] for  $\text{CH}_4/\text{H}_2$  flames, with an inflection point occurring upon  $\sim 70\%$   $\text{H}_2$  addition. Similarly, Huang et al. [81] also reported similar behaviour for natural gas – hydrogen – air blends. As such, it may seem that this maybe a phenomenon attributable to the  $\text{H}_2$  contribution, at least for  $\text{NH}_3$  or  $\text{CH}_4$  based flames, due to the strong and fast diffusivity of  $\text{H}_2$  in the reactants. This stretch-sensitivity behaviour is of importance since the flames exhibiting negative  $L_b$  will be accelerated in highly stretched turbulent environments, whilst flames displaying a positive  $L_b$  will be weakened. This stretch-sensitivity response inevitably impacts the operation of practical combustion systems.



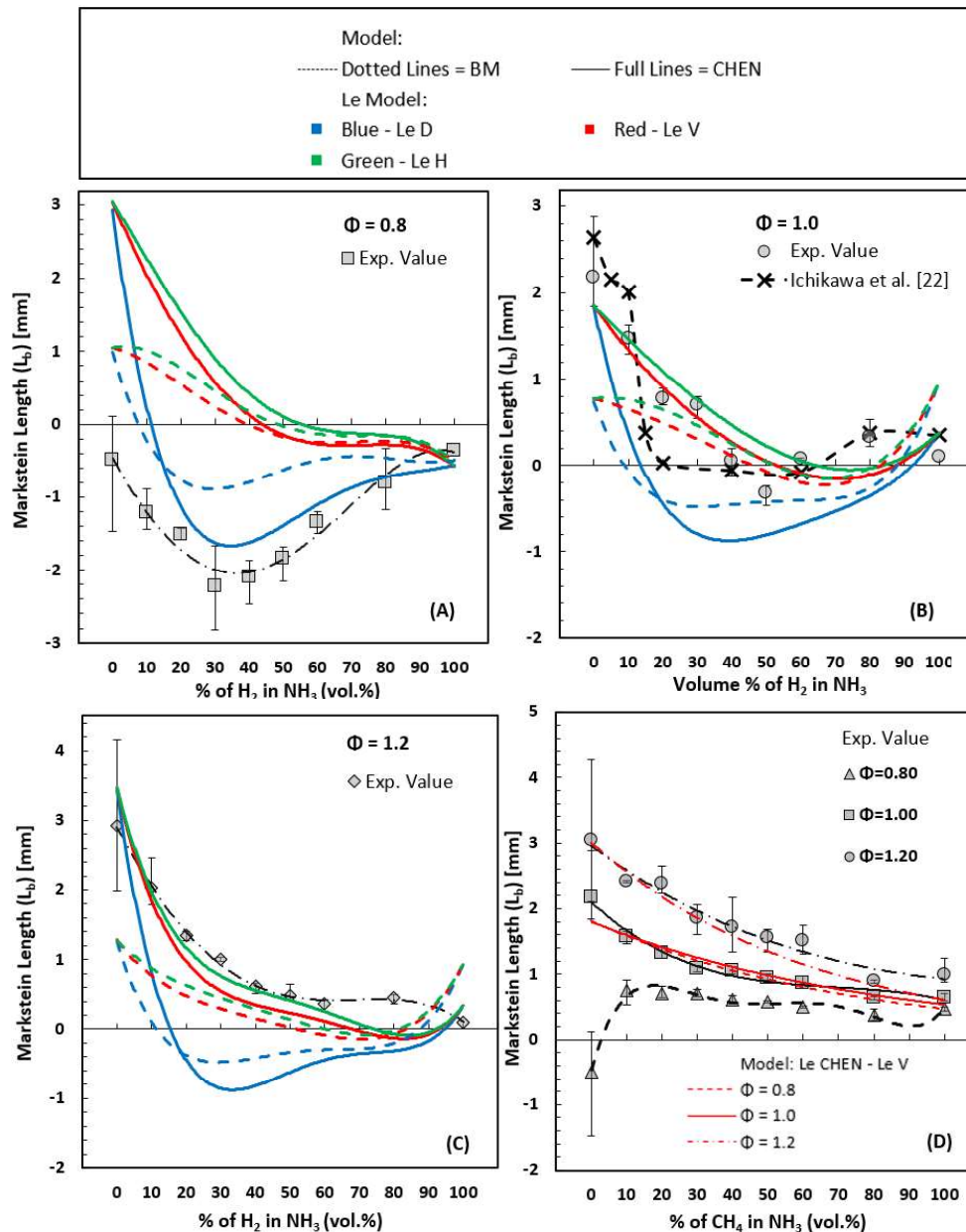
**Figure 8** –  $L_b$  values of  $\text{NH}_3/\text{CH}_4$  mixtures (298 K, 0.1 MPa)



**Figure 9** -  $L_b$  values of  $\text{NH}_3/\text{H}_2$  mixtures (298 K, 0.1 MPa) 100%  $\text{H}_2$   $L_b$  values from [62]

For a better understanding of this change, a sensitivity analysis related to the contribution of major flame enhancing pathways (diffusive, thermal, kinetic) was undertaken. However, to correctly quantify the diffusive pathway, the most suitable  $L_e$  formulation has to be considered. As such, the different  $L_{e\text{eff}}$  models (i.e.  $L_{eV}$ ,  $L_{eH}$ ,  $L_{eD}$  from Equations 12, 13 and 14 respectively) are used to yield to an estimate of  $L_b$ , by using the relationships proposed by Chen or Matalon and Bechtold, referred as  $L_b$ -Chen and  $L_b$ -BM, respectively. It should be noted that the purpose of such analysis is more qualitative than quantitative to validate which  $L_{e\text{eff}}$  model best captures the measured  $L_b$  behaviour of the tested blends.

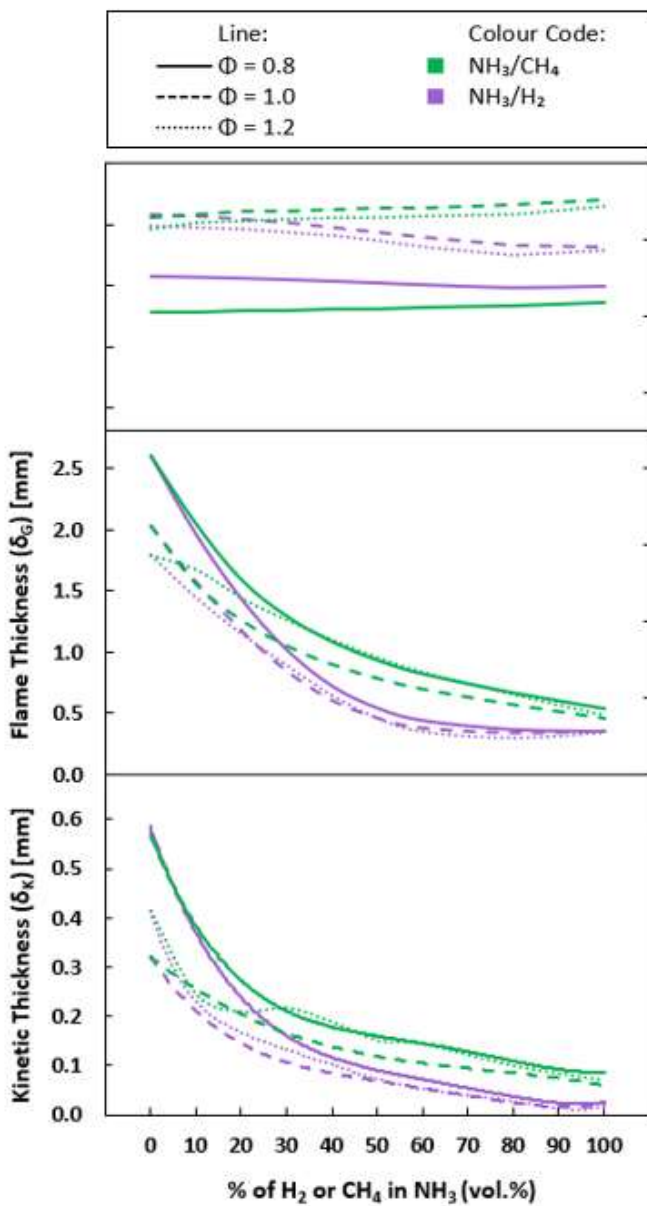




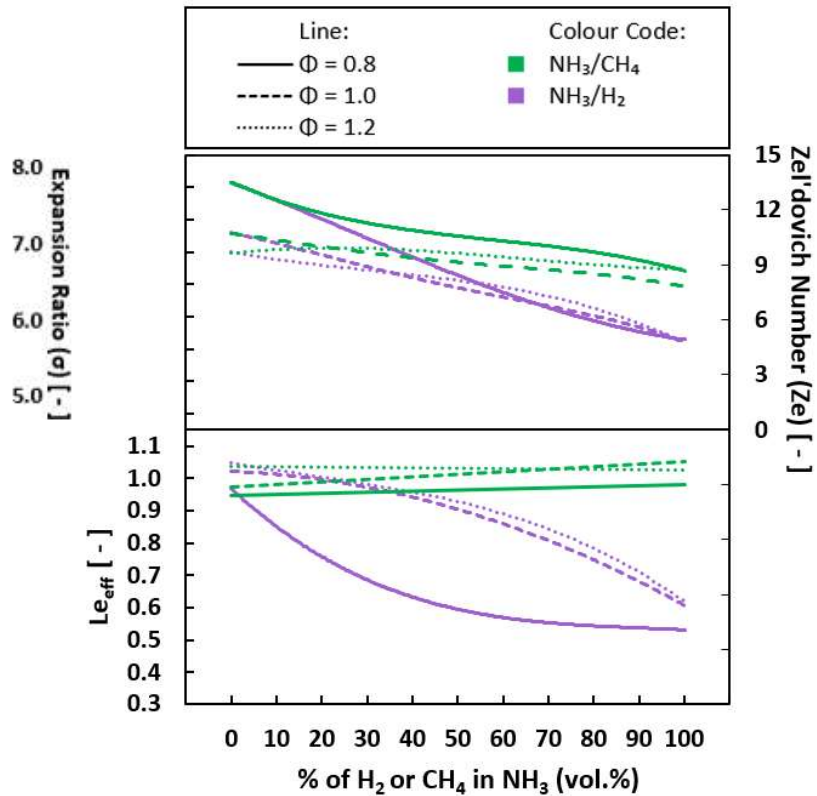
**Figure 10** – Comparison of  $L_b$ -CHEN and  $L_b$ -BM estimates to the measured  $L_b$  for NH<sub>3</sub>/H<sub>2</sub> flames (a)  $\phi = 0.8$  (b)  $\phi = 1.0$  (c)  $\phi = 1.2$  and for (d) NH<sub>3</sub>/CH<sub>4</sub> flames

Figure 10 illustrates  $L_b$ -CHEN and  $L_b$ -BM for NH<sub>3</sub>/H<sub>2</sub> blends, alongside experimentally measured  $L_b$  values. With respect to the CHEN formulation under lean H<sub>2</sub> condition ( $\phi = 0.8$ , Figure 10.a), quantitative and qualitative agreements are observed with Le<sub>D</sub> formulation, with the non-linear stretch behaviour well captured. Under H<sub>2</sub> richer condition ( $\phi = 1.2$ , Figure 11.c), Le<sub>D</sub> overpredicts the influence of H<sub>2</sub> on NH<sub>3</sub> with better agreement observed with a Le<sub>V</sub> or Le<sub>H</sub> model better reflecting the measured trend. Poor agreement is observed with the BM formulation, with again a Le<sub>D</sub> best reflecting expected stretch behaviour under lean conditions, and Le<sub>H</sub> exhibiting better agreement at richer conditions. Considering that the Le<sub>D</sub> model was derived from the modelling of lean turbulent CH<sub>4</sub>/H<sub>2</sub> flames [27], as well as that lean CH<sub>4</sub>/H<sub>2</sub> appear to display similar non-linear stretch behaviour [24] to that of lean NH<sub>3</sub>/H<sub>2</sub> flames, a better agreement was expected. Furthermore, this influence is due to the assumption that the flame curvature is dominant, hence the local enrichment of the most diffusive fuel at the flames leading edge is predicted. This concept appears to be valid under lean conditions, since H<sub>2</sub> and

NH<sub>3</sub> have higher mass diffusivities than O<sub>2</sub>. For richer conditions ( $\phi \geq 1.0$ ), a model based on either volume or non-dimensional heat release appears to be more appropriate. With respect to NH<sub>3</sub>/CH<sub>4</sub> flames, measured  $L_b$  and  $L_b$ -CHEN are compared in Figure 10.d for  $\phi = 0.8 - 1.2$ . It should be noted that since NH<sub>3</sub> and CH<sub>4</sub> display very similar preferential-diffusional behaviour ( $Le \sim 0.9 - 1.1$ ), the application of either  $Le_{eff}$  models results in very similar values. Consequently, only the  $Le_V$  model is plotted on Figure 10.d. For the conditions greater than stoichiometry, a good quantitative and qualitative agreement is observed with the CHEN model, but under lean conditions, the CHEN model does not allow to verify the change from negative to positive  $L_b$  measured experimentally obtained upon 10% CH<sub>4</sub> addition to NH<sub>3</sub> (for only one equivalence ratio). In summary, for lean and rich NH<sub>3</sub>/H<sub>2</sub> flames, the  $Le_D$  and  $Le_H$  formulation respectively, best captured changes in thermo-diffusive behaviour. With respect to NH<sub>3</sub>/CH<sub>4</sub> flames,  $Le_V$  demonstrated the best agreement for all considered  $\phi$ , with these conclusions maintained for the remainder of the analysis.



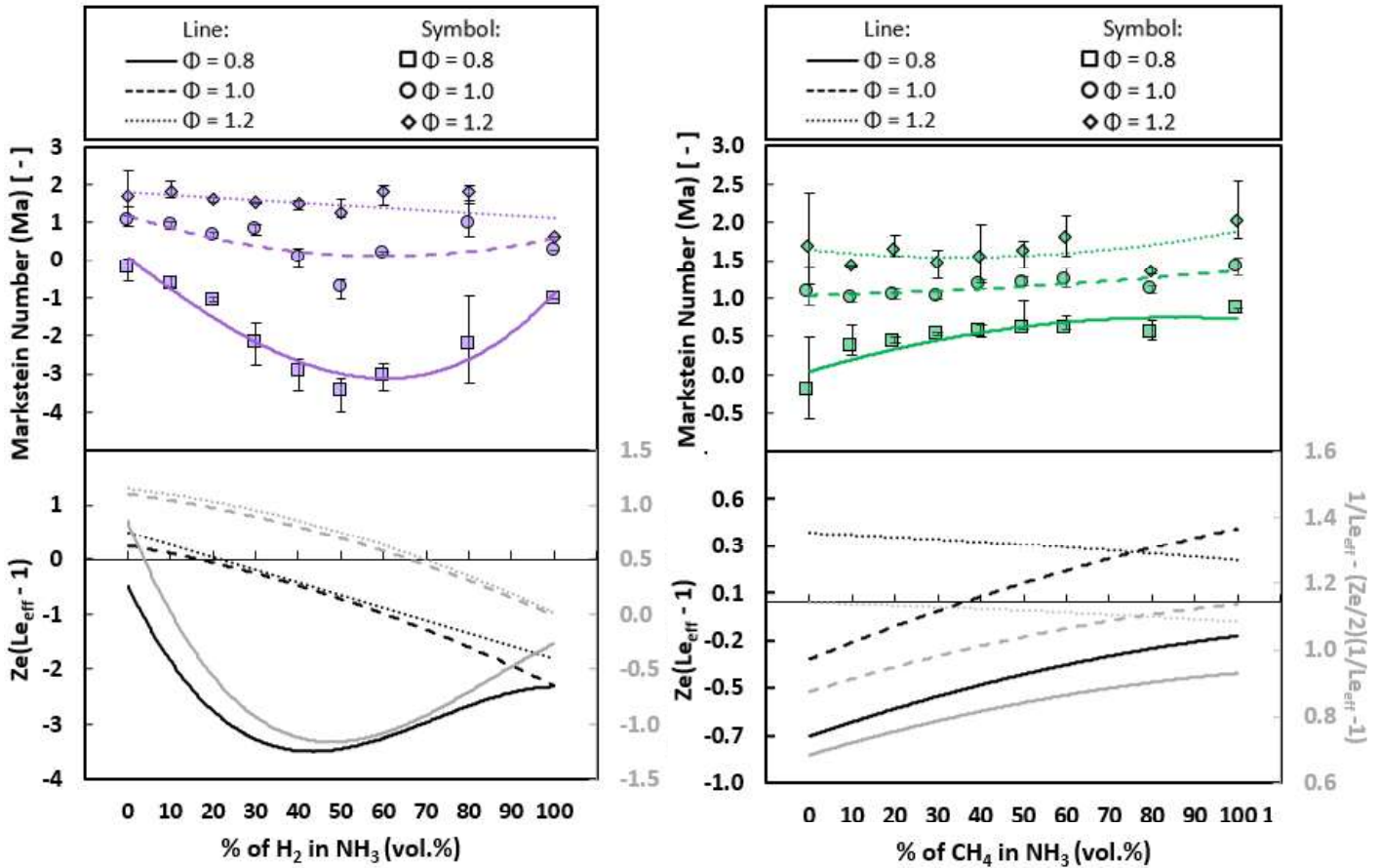
**Figure 11** – Variation in  $\delta_K$ ,  $\delta_G$  and  $\sigma$  with addition of either CH<sub>4</sub> or H<sub>2</sub> to NH<sub>3</sub>,  $\phi = 0.8, 1.0, 1.2$



**Figure 12** – Variation in  $Le_{eff}$  and  $Ze$  with addition of either CH<sub>4</sub> or H<sub>2</sub> to NH<sub>3</sub>,  $\phi = 0.8, 1.0, 1.2$

1 As emphasised by Kwon et al. [82] and reviewed in [83], the fundamental parameters that  
2 induce hydrodynamic and diffusional-thermal instabilities are the thermal expansion, the flame  
3 thickness, the non-unity  $Le$  and the global activation energy (or equivalently  $Ze$ ). Consistent with the  
4 hydrodynamic theory of Darrieus and Landau [9], the hydrodynamic instabilities arise from the thermal  
5 expansion of gases, with the density jump across the flame front proportional to the growth rate of  
6 hydrodynamic instability. In the case of an outwardly propagating spherical flame, the flame tends to  
7 be stabilised due to curvature induced positive stretch, consequently the flame thickness plays a  
8 significant role, since the thinner the flame the weaker the influence of curvature. Hence the risk of  
9 destabilisation is enhanced for thinner flames. It is interesting to note that addition of either  $CH_4$  or  $H_2$   
10 to  $NH_3$  does not really affect the thermal expansion, irrespective of  $\phi$ , as shown in Figure 11. On the  
11 other hand, the flame thickness decreases strongly with increasing  $CH_4$  or  $H_2$  fractions, in effect  
12 promoting hydrodynamic instabilities to a similar extent. Nevertheless, the addition of either  $CH_4$  or  
13  $H_2$  to  $NH_3$  results in similar stretch-related behaviour under rich conditions, whilst exhibiting very  
14 different stretch-behaviour as conditions get leaner. The development of preferential-diffusional  
15 instabilities, characterised by  $Le$ , is the result of non-equi-diffusion. With respect to the  $NH_3/H_2$  flames,  
16 the effects of preferential diffusion are a consequence of the higher mass diffusivity of  $H_2$  and  $NH_3$   
17 compared to the  $O_2$  molecule. As illustrated in Figure 12,  $Le$  decreases significantly with increasing  $H_2$   
18 fraction thereby promoting diffusional-thermal instabilities at  $\phi = 0.8$ . Furthermore, as could be  
19 expected, the change in  $Le$  increases as the conditions get leaner, a consequence of each of the fuel's  
20 individual  $Le$  response. As underlined by Kwon et al. [82], considering that the development of  
21 preferential diffusional instabilities requires a modification of the flame front, it is thus reasonable to  
22 expect the global activation energy should also affect the development of diffusional-thermal  
23 instabilities. Accordingly, a lower  $E_a$  (illustrated as  $Ze$  in Figure 12) will tend to enhance instability of a  
24 diffusionaly unstable flame such as lean  $NH_3/H_2$  flame, with both  $Le$  and  $Ze$  decreasing with increasing  
25  $H_2$  concentration for all  $\phi$ . The decrease in  $Ze$  is largely due to a decrease in the inner-layer temperature  
26 coupled with an increase in adiabatic flame temperature with increasing  $H_2$  concentration for  $\phi$ . For  
27  $NH_3/H_2$ , the changes in measured  $L_b$  are thus potentially the result of competing hydrodynamic and  
28 thermo-diffusive instabilities, with the influence of the thermo-diffusional instabilities reducing as the  
29  $\phi$  increases. On the other hand, for  $NH_3/CH_4$  flames, the addition of  $CH_4$  to  $NH_3$  results in little  
30 diffusional-thermal effects ( $Le \sim 1$ ) across the entire considered  $\phi$  range.  
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**Figure 13** – Comparison of variation of  $Ze(L_{eff} - 1)$  and  $1/Le_{eff} - (Ze/2)(1/Le_{eff} - 1)$  to measured Marsktein number as a function of (a)  $H_2$  mole fraction, and (b)  $CH_4$  mole fraction

From the analytical expression developed by Chen [40], [45], the equation 9 can be re-arranged to yield the Marsktein Number ( $Ma = L_b/\delta$ ), resulting in  $Ma = [1/Le_{eff} - (Ze/2)(1/Le - 1)]\sigma$ , where  $1/Le_{eff} - (Ze/2)(1/Le_{eff} - 1)$  represents the thermo-diffusive effect. Similarly, the relationship linking  $L_b$  to  $Le$  developed by Matalon and Bechtold (Equation 10) can be re-arranged to evaluate  $Ma$ , in which the term  $Ze(L_{eff} - 1)$  reflects the thermo-diffusive influence as underlined by Okafor et al. [24]. **Figures 13.a and 13.b** compare the experimental  $Ma$  to the trends in  $1/Le_{eff} - (Ze/2)(1/Le - 1)$  and  $Ze(L_{eff} - 1)$ , for  $NH_3/H_2$  and  $NH_3/CH_4$  mixtures, respectively, at  $\phi = 0.8 - 1.0 - 1.2$ . First, as expected both  $Ze(L_{eff} - 1)$  and  $1/Le_{eff} - (Ze/2)(1/Le - 1)$  exhibit the same trends. For the lean  $NH_3/H_2$  mixtures, the changes in measured  $Ma$  appear to be to a great extent the result, of changes in the thermo-diffusive properties,  $Le$  and  $Ze$ . At richer condition, slightly different trends are displayed between the experimental  $Ma$  and  $Ze(L_{eff} - 1)$  and  $1/Le_{eff} - (Ze/2)(1/Le - 1)$ , potentially due to a greater change in the expansion ratio (see Figures 12) than under lean conditions. In relation to the  $NH_3/CH_4$  mixtures (Figure 13.b), the measured  $Ma$  under lean and stoichiometric conditions yield matching trends to  $Ze(L_{eff} - 1)$  and  $1/Le_{eff} - (Ze/2)(1/Le - 1)$ , potentially alluding that the  $Le$  and  $Ze$  are the driving forces behind the changes in stretch-related behaviour. At  $\phi = 1.2$ , a less good agreement is observed, potentially the consequence of nominal changes in  $Le$  and  $Ze$ , combined with an increasing expansion ratio. For lean  $NH_3/H_2$  flames it seems that the changes in measured  $L_b$  are to a large extent the consequence of thermo-diffusive effects, with this influence reducing as conditions get richer. For the  $NH_3/CH_4$  mixtures, the competition between thermo-diffusional and hydrodynamic instabilities yields to increasingly positive  $Ma$  values, resulting in propensity of flame stabilisation.

### 5.3 Flame Sensitivity Analysis

The enhancement of the flame propagation due to the addition of CH<sub>4</sub> or H<sub>2</sub> to NH<sub>3</sub> can be characterised as a combination of diffusive, thermal and kinetic effects [84], [85]. The individual pathway can be modelled as:

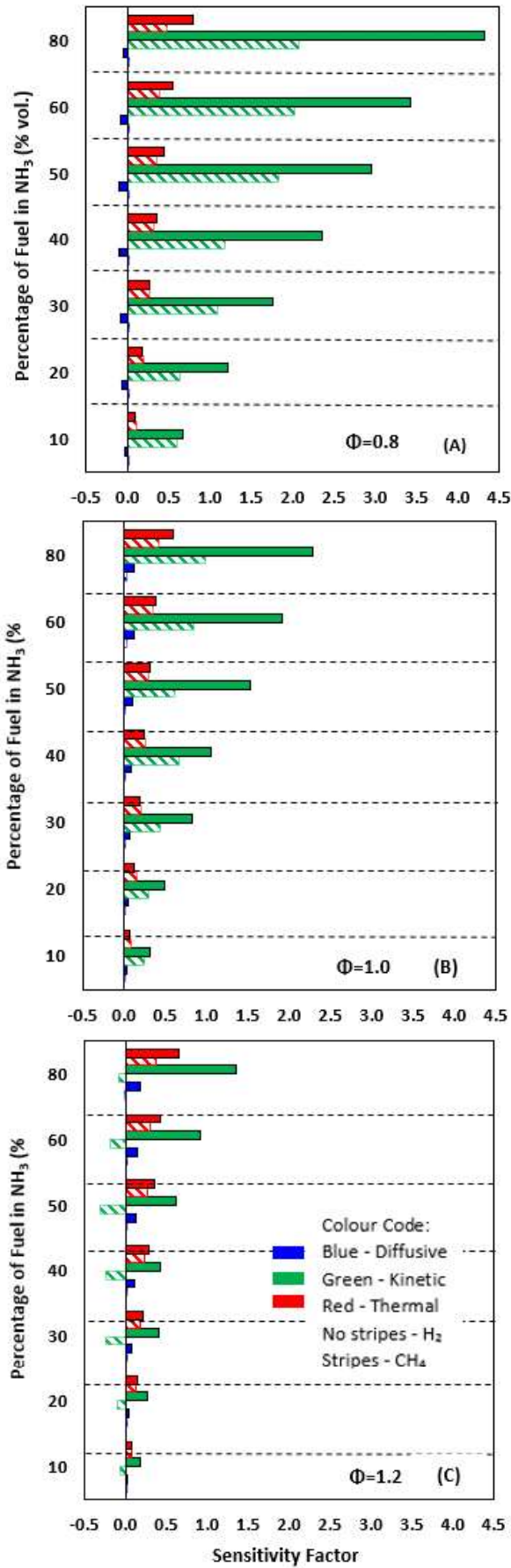
$$S_L^0 \sim (D_T \cdot Le_{eff})^{1/2} \exp(-T_a/2T_{ad}) \quad (18)$$

The first term on the right-hand side ( $D_T \cdot Le_{eff}$ ) reflects the diffusive influence. The Arrhenius factor, which combines the relative influence of the global activation energy through the activation temperature ( $T_a = E_a/R_u$ ), and the adiabatic flame temperature are represented in the second term [ $\exp(-T_a/2T_{ad})$ ]. These individually represent the thermal ( $T_{ad}$ ) and kinetic ( $T_a$ ) influences on the flame speed. Concerning the Le formulation, it was previously determined from Figure 10 that for lean and rich NH<sub>3</sub>/H<sub>2</sub> flames, the Le<sub>D</sub> and Le<sub>H</sub> formulation respectively, best captured changes in thermo-diffusive behaviour. With respect to NH<sub>3</sub>/CH<sub>4</sub> flames, Le<sub>V</sub> demonstrated the best agreement for all considered  $\phi$ . These conclusions are maintained regardless of the theoretical relationship relating L<sub>b</sub> to Le, and hence applied for the following analysis. Equation 18 may be differentiated to determine the sensitivity of each individual pathway on the overall influence of the flame speed. Accordingly, the overall sensitivity coefficient can be expressed as per Equation 19 [84]:

$$\frac{1}{S_L^0} \cdot \frac{dS_L^0}{dx} = \frac{1}{2 \cdot D_T \cdot Le} \cdot \frac{d(D_T \cdot Le)}{dx} - \frac{1}{2 \cdot T_{ad}} \cdot \frac{2 \cdot T_a}{dx} + \frac{T_a}{2 \cdot T_{ad}^2} \frac{2 \cdot T_{ad}}{dx} \quad (19)$$

where  $x$ , the volume fraction of either CH<sub>4</sub> or H<sub>2</sub>. Note that the three terms on the right-hand side denote the influence of the diffusive, kinetic, and thermal pathways, correspondingly. Sensitivity analysis is illustrated in Figure 14 for the blends and  $\phi$  considered, with a positive and negative sensitivity factor representing flame speed enhancement and inhibition, respectively.

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**Figure 14** – Sensitivity Analysis of  $S_L^0$  for  $\text{NH}_3/\text{H}_2$  and  $\text{NH}_3/\text{CH}_4$  blends, (a)  $\phi = 0.8$  (b)  $\phi = 1.0$  (c)  $\phi = 1.2$



1 As illustrated in Figure 14, the enhancement in flame speed of NH<sub>3</sub> based blends upon addition of  
2 either CH<sub>4</sub> or H<sub>2</sub> is predominantly an Arrhenius effect (kinetic), principally through the reduction of the  
3 overall activation energy and thus the activation temperature. For identical volumetric additions of up  
4 to 10% CH<sub>4</sub> or H<sub>2</sub> results in a similar reduction in E<sub>a</sub>, leading to similar flame speeds, a trend well  
5 captured both experimentally and numerically. Any further addition of H<sub>2</sub> results in a significantly  
6 greater reduction in E<sub>a</sub> than in the case of CH<sub>4</sub> addition, resulting in greater flame speeds. It should be  
7 noted that although remaining predominant for lean and stoichiometric conditions, the influence of  
8 the kinetic pathway reduces at richest conditions, particularly for CH<sub>4</sub> addition to NH<sub>3</sub>, with a negative  
9 sensitivity at  $\phi = 1.2$ . This agrees with the minor increase in E<sub>a</sub> (represented by Z<sub>e</sub>, see Figure 12) at  
10 that condition, the consequence of the shifted minimum E<sub>a</sub> to slightly richer conditions ( $\phi = 1.1-1.2$ ) of  
11 NH<sub>3</sub>, as in Figure 3. The thermal pathway impact is lower than the kinetic effect, with the influence of  
12 the thermal pathway correlating well with modelled changes in adiabatic flame temperature. The  
13 addition of up to 60% of either CH<sub>4</sub> or H<sub>2</sub> results in changes of < 45 K, regardless of  $\phi$ . With respect to  
14 the diffusive influence, it assumes negative sensitivity (or inhibiting effect) for lean NH<sub>3</sub>/H<sub>2</sub> mixtures,  
15 and is negligible in comparison to other pathways. This is particularly the case for NH<sub>3</sub>/CH<sub>4</sub>, a  
16 consequence of the nominal changes in Le (Fig. 12) coupled with the limited change in thermal  
17 diffusivity of the mixture upon CH<sub>4</sub> addition, irrespective of the  $\phi$ . It should be noted that even if the  
18 use of different kinetics mechanisms can induce different Arrhenius coefficients, the qualitative trends  
19 should remain valid, and thus performing such sensitivity analysis from first principles remains relevant  
20 providing useful insights.

## 25 6. Conclusions

27 The spherically expanding flame configuration was used to measure the unstretched laminar flame  
28 speeds and corresponding Markstein lengths in NH<sub>3</sub>/H<sub>2</sub> and NH<sub>3</sub>/CH<sub>4</sub> premixed flame across a wide  
29 range of compositions and equivalence ratio. A special attention was given to the estimate of Lewis  
30 number to analyse its influence on flame behaviour of NH<sub>3</sub>, H<sub>2</sub> and CH<sub>4</sub> as well as for the blends. From  
31 this study, the following main outcomes can be made:

- 34 • Increasing H<sub>2</sub> and CH<sub>4</sub> fraction to NH<sub>3</sub>-air laminar premixed flames results in an exponential  
35 and linear increase in flame speed, respectively. The greatest relative change in flame  
36 speed upon H<sub>2</sub> addition occurs under leanest and richest conditions while upon CH<sub>4</sub>  
37 addition, only under lean conditions. Stagni et al. and Okafor et al. mechanisms displayed  
38 the best agreement with experimental NH<sub>3</sub>/H<sub>2</sub> and NH<sub>3</sub>/CH<sub>4</sub> results, respectively.
- 39 • With respect to the stretch related behaviour, the addition of CH<sub>4</sub> to NH<sub>3</sub> results in a linear  
40 reduction in the stretch sensitivity for a fixed equivalence ratio. The volumetric based  
41 Lewis number yielded the best correlation with the measured Markstein lengths, for CH<sub>4</sub>  
42 addition to NH<sub>3</sub> resulting in nominal diffusional-thermal effects. For the stoichiometric and  
43 lean NH<sub>3</sub>/H<sub>2</sub> flames, a non-monotonical variation in measured Markstein length was  
44 obtained, with a less and less linear behaviour as conditions get leaner. For NH<sub>3</sub>/H<sub>2</sub>, the  
45 changes in measured L<sub>b</sub> were demonstrated to mainly be the result of thermo-diffusive  
46 effects (through the modelled changes in Le<sub>eff</sub> and global activation energy) with the  
47 influence of the thermo-diffusional instabilities reducing as the equivalence ratio  
48 increases. For lean NH<sub>3</sub>/H<sub>2</sub> mixtures, the diffusional-based Lewis number well captured the  
49 non-linear stretch behaviour as function of H<sub>2</sub> addition, whilst the heat release-based  
50 Lewis number resulted in better agreement at richer conditions.
- 51 • A sensitivity analysis related to the major flame enhancing pathways (diffusive, kinetic,  
52 thermal) has demonstrated that the enhanced flame propagation of NH<sub>3</sub>/H<sub>2</sub> and NH<sub>3</sub>/CH<sub>4</sub>,  
53 is mainly due to the kinetic change, especially through the reduction of the activation  
54 temperature. The influence of the kinetic pathway reduces as conditions get richer,  
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1 particularly for CH<sub>4</sub> addition. The thermal pathway holds less influence in comparison to  
2 the kinetic pathway, with its influence showing good correlation with limited changes in  
3 adiabatic flame temperature of the considered blends. The diffusive pathway was  
4 negligible for all investigated mixtures, with a negative sensitivity for the lean NH<sub>3</sub>/H<sub>2</sub>  
5 mixtures.

## 6 **Declaration of Competing Interest**

7  
8 The authors declare that they have no known competing financial interest or personal  
9 relationships that could have appeared to influence the work reported in this paper.

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