

# **Influence of hydrogen and methane addition in laminar ammonia premixed flame on burning velocity, Lewis number and Markstein length**

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# Manuscript

# <u>Influence of Hydrogen and Methane Addition in Laminar Ammonia Premixed Flame on Burning<br>Velocity, Lewis Number and Markstein Length<br>Authors: Zitouni, S. (\*), Brequigny P., Mounaïm-Rousselle C.,</u> **1** Superior Velocity, Lewis Number and Markstein Length **Example 2018**

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# **Abstract: Abstract:**

15 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  $\frac{17}{10}$  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  $^{21}$  equivalence ratios. In general addition of CH<sub>4</sub> or H<sub>2</sub> results in a linear and exponential increase in  $\frac{22}{23}$  measured laminar burning velocity, respectively. Of the appraised mechanisms, Stagni and Okafor 24 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> 26 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 an initial decrease in Markstein length is observed up to  $30 - 40\%$  H<sub>2</sub> addition, at which point any 29 **I** 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  $\frac{31}{32}$  that of NH<sub>3</sub>/CH<sub>4</sub>. Different theoretical relationships between the Markstein length and Lewis Number 33 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  $\frac{35}{26}$  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 37 measured Markstein Length were demonstrated to potentially be the result of competing hydrodynamic and thermo-diffusive instabilities, with the influence of the thermo-diffusional  $\frac{1}{40}$  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 <sup>44</sup> 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  $NH_3/CH_4$  and  $NH_3/H_2$  was demonstrated to be  $46$ principally an Arrhenius effect, predominantly through the reduction of the associated activation 48 energy. 18 Strengthen anderstanding of the **Theasured Tannifer During Veloc**  an initial decrease in iviarkstein and of Nii<sub>3</sub>, Ch<sub>4</sub>. Diretent theore **TOrmulation displayed best agree** 41 motabilities reducing as the equiv was undertaken. Augmented na 

**Keywords:** Ammonia-hydrogen, ammonia-methane, Laminar flame Speed, Lewis Number, Markstein  $\frac{53}{2}$  Length **Exercise 18** 

# $2$  **1.** Introduction  $1$  and  $\mathbf{1}$  and  $\mathbf{$

 $\frac{3}{4}$  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 5  $6$  and ecological adversities [1]. As such, in order to attain zero-carbon targets, the large-scale  $\frac{7}{8}$  employment of renewable and carbon-free fuels within our energy systems is required to maintain  $\frac{3}{9}$  a balanced trajectory between human development, progress and cohesion with the environment. 10 **In light of this context, Ammonia (NH**<sub>3</sub>) has emerged in recent years as an efficient zero-carbon 11 hydrogen (H<sub>2</sub>) carrier. Liquid NH<sub>3</sub> offers higher H<sub>2</sub> content than for example, ethanol, methanol http://www.  $\frac{12}{12}$  and gasoline, in conjunction with exhibiting a higher volumetric energy density than that of liquid  $\frac{13}{14}$  H<sub>2</sub> [2]. Due to NH<sub>3</sub> prevalent use in the agricultural industry, considerable storage and distribution 15 **infrastructure is already established** [2]. Although NH<sub>3</sub> offers several advantages, there remains several practical combustion challenges, notably the control and reduction of pollutant emissions 16 17 (NO<sub>x</sub> and N<sub>2</sub>O). Moreover, NH<sub>3</sub> exhibits slow burning velocities, often associated to low burning efficiency in engines, a narrow flammable range and high ignition energy, potentially yielding poor 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 20 21 MH<sub>3</sub>'s combustion properties, blending NH<sub>3</sub> with methane (CH<sub>4</sub>) (for a partial decarbonisation) or  $\frac{22}{22}$  H<sub>2</sub> (from the possible 'in situ' cracking of ammonia) has been proposed, and has gained  $\frac{23}{24}$  considerable recent attention, with comprehensive reviews of NH<sub>3</sub> related work undertaken [2], 25 [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, 26  $\frac{27}{20}$  as such there seems to be a practical necessity to develop and strengthen understanding of  $\frac{28}{29}$  fundamental combustion characteristics of blends containing NH<sub>3</sub>, ultimately leading to the development of combustors offering greater flame stability and reduced pollutant emissions. 30  $4$  The historical prevalence of 8 component of renewable and  $14$   $\blacksquare$   $\blacksquare$ 19 **ETTCHETCY IT ETIGLES, a TIATTOV** 24 Considerable recent attention 29 **IUILLA LUILLE CONTINUESTION** 

The unstretched laminar burning velocity ( $S<sub>L</sub>$ <sup>0</sup>), is one main fundamental physio-chemical property of any premixed air-fuel mixture, reflecting both the combustion process and mixture 33  $34$  reactivity. As such, S<sub>L</sub><sup>0</sup> is a key parameter helping understand premixed operational instabilities,  $\frac{35}{36}$  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, 37 in turn influencing witnessed burning and reactivity characteristics of the fuel mixture. The Lewis 38  $39$  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], 42 underline that preferential diffusion (i.e. Le deviating from unity), can strongly influence the 43  $\frac{44}{10}$  burning rates of stretched flames – which undergo the combined effects of strain, curvature, and 45 flame motion. Flames with Le > 1 exhibit greater relative thermal diffusivity, displaying a reduction  $\frac{17}{47}$  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 48  $49$  length (L<sub>b</sub>) 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<sub>b</sub> divided by the laminar  $51$ <br>52 **finition** 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]. 53 31 32 **The unstretched laminar**  $36$  mutally hashback, blow-on  $\alpha$ 41 and the computer mechanisms of 46 manic motion. Frames with Le  $\frac{50}{24}$  response to the stretch rate. The Markstein number (Ma), defined as L<sub>b</sub> divided by the laminar  $52$  lidine thickness  $(0_L) - 15$  different

Recent experimental studies have investigated  $S_L^0$  and  $L_b$  characteristics of NH<sub>3</sub>/air flames, notably by Hayakawa et al. [15], at atmospheric and 0.5 MPa of initial ambient pressure, and 56  $57$  Kanoshima et al. [16], expanded on that work to include the influence of initial ambient  $\frac{58}{58}$  temperature (400-500 K). Results from these studies underline that  $S_L^0$  peaks at an equivalence 60 ratio ( $\phi$ ) of  $\approx$  1.1, with an incress 54 55 Recent experimental stu  $59$  cemperature (400-300 K). Ne

in S<sub>L</sub><sup>0</sup>, respectively. With respect to L<sub>b</sub>, NH<sub>3</sub>/air flames display an increasing L<sub>b</sub> with increasing  $\phi$ , a 1 5 1 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 <sup>2</sup> pressure conditions (T=298K, P=0.1MPa) lean NH<sub>3</sub> flames exhibit negative L<sub>b</sub>, with positive values  $r_{\text{recoched}}$  and rich conditions. Furthermore,  $L_{\text{b}}$  is observed to decrease with a rise in pressure recorded under rich conditions. Furthermore,  $L_{\text{b}}$  is observed to decrease with a rise in pressure and temperature, analogous behaviour to that of the flame thickness. 5  $\frac{4}{4}$  recorded under field condition

 $\frac{6}{7}$  Okafor et al. [17], [18], investigated the influence of NH<sub>3</sub> on CH<sub>4</sub> based flames (up to  $\approx$  52% NH<sub>3</sub> 8 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 NH3/CH4 flames (298 K, 0.1 MPa), demonstrated similar 10 12 tendency but with a uniform decrease in the flame flammability limits with NH<sub>3</sub> increase. They also 13 highlighted the important role played by the H and OH radicals in NH<sub>3</sub>/CH<sub>4</sub> flame propagation. In <sup>14</sup> relation to flame stretch sensitivity of CH<sub>4</sub>/NH<sub>3</sub> flames, Okafor et al. [17] emphasize the shift from 15<br>16 **and 12** a linear to a non-linear flame speed-stretch rate relationship exhibited with increasing  $\phi$  and NH<sub>3</sub> 17 **fraction. It should be noted that this is unusual for fuels displaying Le values close to 1 (as is the** 18 case for pure CH<sub>4</sub> and NH<sub>3</sub>), with this behaviour mainly attributed to an increase in the preheating 19 **zone thickness**.  $7$  Okafor et al. [17], [18], inve 11 Experimental results of situation  $16$  a mear to a non-mear name 20

21 Lee et al. [20], [21] and more recently, Ichikawa et al. [22] and Lhuillier et al. [23] investigated 22<br>23 the influence of H<sub>2</sub> upon NH<sub>3</sub> based flames. Ichikawa et al., demonstrated that at stoichiometric  $\frac{23}{24}$  conditions ( $\phi$ =1), S<sub>L</sub><sup>0</sup> increases non-linearly with increasing H<sub>2</sub> fraction, and decreases with 25 **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 and the same states and the states and the states are states and the states are states and the states are stat**  $^{26}$  various initial conditions (298-473K, φ = 0.8 – 1.4, H<sub>2</sub> = 60% vol. max). With respect to the flame  $\frac{27}{28}$  stretch sensitivity, Ichikawa et al.[22] reported a non-monotonic variation, with an initial 29 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 30  $31$  in recorded L<sub>b</sub> of NH<sub>3</sub> flames upon H<sub>2</sub> enrichment. Noteworthily, similar stretch-related non- $\frac{32}{22}$  monotonic trends have been observed for lean CH<sub>4</sub>/H<sub>2</sub> flames [24].  $24$  conditions ( $\phi$ =1), S<sub>L</sub>° increas 28 Sucture School of Turnawa 33 monotonic denus nuve been

 $\frac{34}{25}$  The importance of flame stretch sensitivity and Le goes clearly beyond the laminar flame  $\frac{1}{36}$  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 37 38 strong turbulent combustion. The influence of Le on turbulent flames has been reported in the  $\frac{39}{40}$  course of experimental studies [26]–[28] as well as in direct numerical simulations [29], [30].  $\frac{40}{41}$  Although limited in scale, emerging studies focusing on turbulence-flame interaction for NH<sub>3</sub> and 42 its blends with either H<sub>2</sub> and CH<sub>4</sub> underlined the potential role of preferential-diffusion and flame-43 stretch interaction upon turbulent flame characteristics. For example, Ichimura et al. [31] <sup>44</sup> investigated NH<sub>3</sub>/air flames at various turbulent intensities, underlining that although S<sub>L</sub><sup>0</sup> of  $^{45}$  MH<sub>3</sub>/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 47 <sup>48</sup> NH<sub>3</sub>/air mixtures, displaying Le < 1. Similarly, Lhuillier et al. [8] investigated NH<sub>3</sub>/H<sub>2</sub> and NH<sub>3</sub>/CH<sub>4</sub>  $^{49}_{50}$  (15% vol. of H<sub>2</sub> or CH<sub>4</sub>) turbulent flame propagation under engine related operating conditions (1976 Vol. 61.17 of Chapter and Propagation and Profession Chatter Operating conditions<br>
51 (445K, 0.54 MPa). They reported a decreasing and increasing turbulent to laminar flame speed 52 ratio upon CH<sub>4</sub> and H<sub>2</sub> addition, respectively, induced by the different thermo-diffusive properties and stretch-related behaviour of these ammonia blends. 53 35 and the importance of hame 41 **ARTIOUSH INTILED IN SCALE, ETH**  $46$  **NH<sub>3</sub>/air is greatest at**  $\varphi \approx 1$ **.**  $51$  (445K, 0.54 MPa). They repo 54

55 Clearly, although emerging, the experimental study on the addition of  $H_2$  or CH<sub>4</sub> to NH<sub>3</sub>-based flames remains scarce. Furthermore, recent turbulent combustion experiments underlined the 56  $\frac{57}{58}$  potential influence of preferential-diffusional instabilities upon NH<sub>3</sub>-based flames [8], [31], [32], hence, the aim of this work is to investigate in detail the influence of Le change on flame behaviour. 59  $60$  NH<sub>3</sub>/CH<sub>4</sub> and NH<sub>3</sub>/H<sub>2</sub> mixtures were varied across a large range of blend composition and 58 potential importance of preference

65

equivalence ratio, representative of the prospective demands of fuel-flexible combustors widely 1 1 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  $\frac{2}{3}$  increases flame temperature, reactivity, mixture flame speed but changes the thermo-diffusive  $\frac{3}{4}$  behaviour, which is studied in-detail throughout this work.  $4$  Denaviour, writer is statical in-

# $\frac{5}{6}$  2. Experimental set-up and specifications  $6$  **E.** Experimental set up and speci-

 $\frac{7}{8}$  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  $\frac{8}{9}$ 10 **NH<sub>3</sub>** specifications in [23], and thus only a brief summary is presented herein. The spherical vessel <sup>11</sup> is equipped with four orthogonal 70 mm quartz viewing windows and has a nominal internal  $\frac{12}{12}$  volume of 4.2 L. Thermal mass flow controllers (Brooks 5850S ( $\pm$  1%)) were employed to introduce  $t_{14}$  the reactants into the vessel. Mole fractions of all species were determined as a function of  $t_{14}$ temperature (T), initial pressure (P) and fuel-air equivalence ratio. A piezo-electric pressure 15 transducer and a type-K thermocouple were employed to check respectively the pressure and 16  $\frac{17}{10}$  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 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 20 0.009 bar, with the remaining air compensated within the equivalence ratio calculation. Pre-mixing 21  $\frac{22}{20}$  was achieved using an internal fan. A capacitor-discharge ignition was achieved via fine tungsten  $\frac{23}{24}$  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 25 26 Schlieren imaging of flame propagation was accomplished using a CMOS high speed camera <sup>27</sup> (Phantom V1210) set to a suitable frame capture rate (3000 – 12000 fps), facilitating a spatial 28 **a** resolution of ~0.10 mm per pixel. Edge-detection algorithms written in a bespoke MATLAB script  $\frac{28}{29}$ were employed to calculate flame propagation rates. A minimum of 3 to 5 repeats were conducted 30 per experimental condition. 31  $9$  vessel. Details of the apparatus  $14$  and the reactants into the vesse 19 **The Chamber and the required**  $24$  electrones mounted at 50 to 29 resolution of 0.10 min per p

# 3. Experimental specifications and theory 33

35 Measurements were performed at initial conditions of 298 K ( $\pm$  3 K) and 0.1 MPa ( $\pm$  1 x 10<sup>-3</sup>  $36$  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  $\frac{37}{20}$  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 form  $0 - 100\%$  for CH<sub>4</sub>; and  $0 - 80\%$  speed and stretch-related behaviour, molar ratios were varied form  $0 - 100\%$  for CH<sub>4</sub>; and  $0 - 80\%$ 40 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 41 respectively), with Table 1 summarising the experimental conditions. 39 Speed and stretch-related ber



<sup>43</sup> Table 1: Experimental conditions ; T<sub>u</sub> = 298 K ( $\pm$  3 K), P<sub>u</sub> = 0.1 MPa ( $\pm$  1 x 10<sup>-3</sup> MPa).



5 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  $L<sub>b</sub>$  relative to the burnt side were experimentally determined employing the same procedure as in previous studies [34], [36]. For an  $\frac{9}{5}$ 10 outwardly spherically propagating flame, the stretched flame speed  $(S_b)$  is expressed as the temporal 12 derivative of the Schlieren flame radius ( $r_{sch}$ ) as in Equation 1: Schliefen linges were und **Cutwaruly spiretically propagatifie** 

$$
S_b = \frac{dr_{sch}}{dt} \tag{1}
$$

16 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: The name stretch rate (K) is defi

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

23 Various correlations between S<sub>b</sub> and K have been proposed, allowing the estimation of the unstretched  $^{24}_{27}$  flame speed (S<sub>b</sub><sup>0</sup>). Two methodologies are employed in this study. The first model is based upon the  $\frac{25}{26}$  assumption of large flame radii, considering both the effects of thermal expansion and Le, as in 27 **Equation 3 [37], which illustrates that the flame curvature (K<sub>curv</sub>=2/rf) and S<sub>b</sub> vary linearly, hence** 28 allowing the evaluation of  $S_b{}^0$  and  $L_b$  from the linear extrapolation of  $S_b$  and K [38], [39]: assumption of large name radii,

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

 $\frac{33}{2}$  This methodology will be referenced herein as Linear Model based on Curvature (LMC). The second  $\frac{34}{35}$  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 37 which are heavily influenced by stretch such as lean H<sub>2</sub>-based flames. This non-linear model is expressed as in Equation 4: 35 CAUGOROM Method, attributed 

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

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  $^{48}_{40}$  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<sub>b</sub>) and NMS for Le < 1 (i.e. negative L<sub>b</sub>), due to the non-linear relationship between S<sub>b</sub> 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 53 to Markstein and Karlovitz numbers (Ma<sub>lin</sub>Ka<sub>mid</sub>); all data presented in this work fall within the recommended values of  $-0.05 - 0.15$  range. eximplifigually  $\frac{1}{2}$  (i.e. positive  $L_b$ ) d recommended values of -0.05  $-$  0

**Interspective of the extrapolation methodology employed, to obtain representative values of solutions** 58 laminar flame speed, the burned gas expansion factor has to be used as  $S_L^0 = S_D^0$  ( $\rho_D/\rho_u$ ) with equilibrium densities calculated using CHEMKIN-Pro, using Stagni et al. [42] and Okafor et al. [18] **Systems Systems Systems Systems Systems** 

1 mechanisms is discussed later in section 5.2.



42 **Fig. 1** – Stretched flame speed vs stretch rate (K) and curvature ( $\kappa_{\text{CURV}}$ ) for (a) pure NH<sub>3</sub>/air and (b) 43 NH<sub>3</sub>/H<sub>2</sub> (20/80 vol.%) (T<sub>u</sub> - 298 K, P - 0.1 MPa)

**Prefilminary investigation demonstrating minimal variation in results derived from data above 7 mm.**<br> **Prefilminary in the sum of th** 3300<br> **Example 1200**<br> **Exampl Example 1. Example 1. Considering**<br> **Example 1. Considering the Consideration of the consideration of the consideration of the same stretch (K) [1/s]**<br> **Example 5tretch (K) [1/s]**<br> **Example 5tretch (K) [1/s]**<br> **Exa** 54 radius as proposed by Burke et al. [45] and satisfying  $r_{sch}/(3V/4\pi)^{1/3}$  < 25% as recommended by Chen **Example 19.1.** Extrapolation methods used to yield flame speed and the corresponding L<sub>a</sub>pher Dental (the corresponding Lappe) between the corresponding to the methods used to yield flame speed to the range of exploitabl large stable quasi-steady flame propagation regime. In the present study, pure NH3/air flames, or **Consistendy Regime**<br>
2000 **Fiame Streetch (K) [1/56]**<br> **Eig. 1** – Stretched flame speed vs stretch rate (K) and curvature (Kc<sub>CMN</sub>) for (a) pure NH<sub>3</sub>/air and (b)<br>
NH<sub>3</sub>/H<sub>1</sub> (20/80 vol.%) (T<sub>u</sub> – 298 K, P – 0.1 MPa)<br>
Li to be heavily influenced by the buoyancy, a consequence of their very low burning rate. As a result **Fig. 1** – Stretched flame speed vs stretch (K) [1/s]<br> **Fig. 1** – Stretched flame speed vs stretch rate (K) and curvature (<sub>KcJW</sub>) for (a) pure NH<sub>3</sub>/air and (b)<br>
NH<sub>3</sub>/H<sub>2</sub> (20/80 vol.96) (T<sub>i</sub> – 298 K, P – 0.1 MPa)<br>
Lim 45 Limits were set on the range of exploitable radii to minimise the influence of the spark, the 46<br>buoyancy or the cellularity, and the confinement during the flame growth, ensuring measurements **Subjuily of the centrality, and Were restricted within the quasi-s** 49 to 6 mm for CH<sub>4</sub>/air flames, however Chen et al. [44] demonstrate this critical radius value to be 50 dependent of Le. For all data presented here, 9 mm was chosen as the minimum radius, with  $\frac{51}{2}$  preliminary investigation demonstrating minimal variation in results derived from data above 7 mm. **10 IIIIII** pressure errects a maxim 55 [46]. Extrapolation methods used to yield flame speed and the corresponding  $L_b$  rely on a sufficiently **Example Statistic quadricional continuity** name of 58 DIENUS CONTRAINING IESS LIMIT 10% 60 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<br>flames, the methodology proposed by Hayakawa et al. [15] in delimiting the transition between<br>ignition influenced, q flames, the methodology proposed by Hayakawa et al. [15] in delimiting the transition between 1  $\frac{2}{3}$  ignition influenced, quasi-steady and buoyancy influenced propagation regimes was followed. The  $\frac{3}{4}$  aforementioned regimes are determined based upon the flame shape and propagation ratio, defined  $_5$  as the vertical and horizontal radius of the flame (rsch,v/rsch, H) and (drsch/dt)t/(drsch/dt)t-4t (where drsch/dt denoting the flame propagation speed at time t), respectively. Figure 1.a illustrates the change in flame 6  $\frac{7}{2}$  shape ratio and moving average of the flame propagation ratio against stretch for a lean NH<sub>3</sub>/air flame  $\frac{8}{9}$  ( $\phi$ =0.80); with the relationship of stretched flame speed with stretch and curvature superimposed. As  $_{10}$  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 11  $12$  limit. It should be noted that the upward motion of the growing flame kernel does not yield a  $\frac{13}{14}$  significant influence upon the propagation speed, since change in the stretched flame speed still  $_{15}\,$  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 16 17 to known instability issues associated with lean combustion of H<sub>2</sub>-containing fuels. Lean H<sub>2</sub>-based  $\frac{18}{10}$  flames are particularly unstable with regard to diffusive effects, a consequence of their low Le (Le <<  $20$  1), resulting in flame acceleration at low stretch and curvature rates [48], as illustrated in Figure 1.b, 21 with an example case of a lean NH<sub>3</sub>/H<sub>2</sub> (20/80 vol.%,  $\phi$ =0.6) flame. Under the tested experimental  $22$  conditions, it was noted that no flames developed a cellular surface composed of cells of comparable 23 size. However, large cracks of a permanent nature appeared at leanest conditions ( $\phi$ =0.60) for flames 25 containing ≥ 40% H<sub>2</sub>, with further H<sub>2</sub> 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-26  $27$  amplitude initial disturbances, most probably triggered by the ignition event, and not a consequence  $\frac{28}{20}$  of preferential diffusion. Nevertheless, using a suitably fast frame capture rate, a minimum of 30  $\frac{29}{30}$  acquired radii was obtained even for the fastest flames, from which flame speed data were estimated.  $4$  and emergency regnites are deter  $9$  ( $\psi$ -0.00), with the relationship or s 14 Significant inflation upon the p 19 maines are particularly answered  $24$  Size. However, large cracks of a p 30 acquired radii was obtained even



<sup>43</sup> **Figure 2** – Schlieren images illustrating the development of flame surface cracking as a function of H<sub>2</sub> Figure 2 Connection mages massivaling the development of hand satisfied or<br>  $\mu_5$  fraction for NH<sub>3</sub>/H<sub>2</sub> flames (T<sub>u</sub> - 298 K, P - 0.1 MPa,  $\phi$ =0.60)  $45$  reaction for NH<sub>3</sub>/H<sub>2</sub> flames (T<sub>u</sub> – 2)

 $\frac{46}{47}$  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. 48 <sup>49</sup> For this study, uncertainty quantification relies upon the methods outlined by Moffat [50], employing 50 a combination of the experimental facility specifications and accuracy of the processing techniques  $\frac{51}{52}$  employed. It should be noted that the uncertainty is quantified for the unstretched flame speed ( $S_b^0$ ),  $\mathbf{0}$ ), 53 and not for S<sub>L</sub><sup>0</sup>, since this is the parameter measured, here named as  $U_{S_{\mathcal{E}}^0}$ . The total uncertainty <sup>54</sup> estimate is given by Equation 5, where  $B_{S_1^0}$  represents the total bias uncertainty, t<sub>M-1.95</sub> the student's 56 value at 95% confidence interval and M-1 degrees of freedom,  $\sigma_{S_R^0}$  the standard deviation of the  $\frac{57}{20}$  repeated experiments, and M the number of experimental repeats at each condition; 47 The measurements of laminar ria  $52$  employed. It should be noted that  $55$  countries to given by Equation by  $\frac{1}{2}$ 58

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

4 The total bias uncertainty, given by Equation 6, relating changes in  $S_b^0$  with respect to an independent <sup>5</sup> influential variable, ( $v_i$ , i.e. temperature, ambient pressure,  $\phi$ , optical system, gas mixture quality) and  $\frac{6}{7}$  the fixed error linked to that variable,  $y_i$ , 7 CHE TIXED ETTOT ITTINED TO THE VATION

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

In order to determine  $B_{S_v^0}$  by Equation 6, the relationships between  $S_b^0$  and each independent variable <sup>15</sup> 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 (±3 K) and pressure (±1 x 10<sup>-3</sup> MPa) by using data that the calculated as a function of  $\phi$ ; such as temperature (±3 K) and pressure (±1 x 10<sup>-3</sup> MPa) by using data modelling with CHEMKIN-PRO. Uncertainty resulting from the optical system was evaluated from the 18 summated fractional error of both the spatial resolution of the system (±0.05/25mm) and camera (± 19 <sup>20</sup> 1.5-7.5/3000-15000 fps). Losses due to radiation influence measured flame burning speed, through 21<br>
the combined effect on the flame propagation itself and the calculated density ratio, with radiation-23 induced uncertainty particularly significant for slow propagating flames (< 12 cm s<sup>-1</sup>) [51]. Lhuillier et 24 al. [7] investigated the dependence of errors resulting from radiation for NH<sub>3</sub>/air flames, concluding 25 that the correlation proposed by Yu et al. [51] was applicable, with this recommendation adopted for  $\frac{25}{100}$ 26 this study. Accordingly, error bars on all subsequent plots illustrating laminar flame speed  $\frac{27}{28}$  measurements (S<sub>L</sub><sup>0</sup>) are derived from Equation 5 and 6, with the error for  $U_{\rm g0}$  scaled with respect to 29 the density ratio.  $_{14}$  In order to determine  $B_{S^0_B}$  by Equa  $17$  calculated as a furiction of  $\psi$ , such 22 The combined effect on the name  $28$  measurements (SL°) are derived f

# 4. Evaluation of Fundamental Parameters 31

Chen and Ju [38], [44] and Matalon and Bechtold [52], have proposed theoretical relationships 33  $\frac{34}{25}$  relating the Markstein length (L<sub>b</sub>) and Lewis Number (Le), requiring the evaluation of various  $\frac{35}{36}$  fundamental flame parameters. The Zel'dovich number, was evaluated using the expression Ze = 37  $(E_a/R_u) \cdot [(T_{ad}-T_u)/(T_{ad}^2)]$  with  $R_u$  the universal gas constant,  $T_u$  and  $T_{ad}$ , the temperature of the unburnt  $38$  mixture and the adiabatic flame temperature, respectively. The activation energy,  $E_a$ , is defined as the  $\frac{39}{40}$  slope of the mass burning flux (m<sup>0</sup>) and the inverse adiabatic flame temperature at constant  $\phi$  and  $p_{10}$  and the mass burning that  $p_{11}$  and the inverse databatic hand temperature at constant  $\phi$  and  $q_{11}$  and the mass burning  $p_{21}$  and the expression  $E_a = -2R\delta[(m^0)]/[1/T_{ad}]$ , where the mass burning 42 flux can be replaced by  $m^0 = (\rho_u \cdot S_L^0)$ , as recommended by Egolfopoulos and Law [53]. It should be noted 43 that this method is only valid for sufficiently off-stoichiometric conditions, with interpolation required  $\frac{44}{15}$  for E<sub>a</sub> values for mixtures near stoichiometry [54]. For the flame thickness, two definitions can be  $\frac{45}{46}$  considered [9]. The first, commonly termed as the kinetic (or diffusion) flame thickness ( $\delta_{\rm k}$ ), 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 <sup>48</sup> pressure. The second, referenced as the 'gradient' flame thickness (δ<sub>G</sub>) can be expressed as δ<sub>G</sub> = (T<sub>ad</sub> –  $T_{\text{u}}$   $T_{\text{u}}$ /(dT/dx)<sub>max</sub>. The 'kinetic' flame thickness is consistent with the approach detailed by Chen [38], [44]  $\frac{50}{51}$  whilst the 'gradient' flame thickness is consistent with the method detailed by Bechtold and Matalon  $52$  [52] and employed accordingly in the derivations Le and L<sub>b</sub> as defined by the given authors. 36 Tundamental hame parameters.  $41$  pressure, empirically determined  $46$  considered [5]. The first, common 51 WILD LITE BLACKER HATTE LITERTY

# $\frac{53}{54}$  4.1 Relationships of Le and L<sub>b</sub>  $54$  4.1 Relationships of Le and L<sub>b</sub>

**For the purpose of this work, the relationships relating Le to L<sub>b</sub>, proposed by Chen [38], [44] For the purpose of this work, the relationships relating Le to L<sub>b</sub>, proposed by Chen [38], [44]** and Matalon and Bechtold [52] are considered. The first formulation based on spherically expanding 57 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 59 **For the purpose of this w** and  $[35]$ , Lapanne et and  $[30]$  and  $2\pi$ 

multi-component fuels. This estimate of Le is referenced herein as Le<sub>CHEN</sub> and can be expressed per<br>Equation 7:<br> $Le_{CHEN} = \left[\frac{L_b}{\sigma \cdot \delta_K} - \frac{Ze}{2}\right]^{-1} \left[1 - \frac{Ze}{2}\right]$  (7) **Equation 7:** Provide the Contract of the Equation 7:

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

 $\sigma^6$  With  $\sigma = \rho_b / \rho_u$ , the expansion ratio. From Equation 7, the retrieval of L<sub>b</sub> is possible as in Equation (8).  $\gamma$  with  $\sigma = p_b/p_u$ , the expansion ra (8).

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

A second formulation by Bechtold and Matalon, was derived from theoretical analysis on the 14 dependence of  $L_b$  on stoichiometry. This formulation was considered by Jomaas et al. [49] in the case <sup>15</sup> of acetylene (C<sub>2</sub>H<sub>2</sub>), Lapalme et al. [56] for H<sub>2</sub>/CO and Zitouni et al. [34], for CH<sub>4</sub> blended with H<sub>2</sub> or  $C_3H_8$ . This estimate is denoted in following as Le<sub>BM</sub>, and is expressed per Equation 9: 13 A second formulation by Becht 17 Canadian Community Service in the 17

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

 $\frac{22}{22}$  Which provides L<sub>b-BM</sub> as per Equation 10: **CONTRACTES** CONTROL CONTRACTED POINT 23

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

27 **body on the expansion ratio given in Equation 11:**<br>28 **body on the expansion ratio given in Equation 11:** Wriefe  $\gamma_1$  and  $\gamma_2$  are functions of the

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

### 4.2 Lewis Number evaluation of multi-component fuels 4.2 Lewis Number evaluation of  $\mu$

Whilst the definition of the Lewis Number for single-fuel mixtures is relatively straightforward,  $\frac{37}{2}$  no clear consensus on the correct formulation of Le for multi-fuel mixtures seems to exist [55]; the 38 challenge arising from the fact that the diffusivity of each fuel must be considered. This is particularly  $_{40}$  applicable when the transport diffusion mechanisms are different as is the case for H<sub>2</sub>, NH<sub>3</sub> or any alkanes. Bouvet et al. [55]  $\frac{42}{12}$  upon a volumetric fraction weighted average, resulting from Muppala et al. [26] computational study  $\frac{43}{44}$  of turbulent CH<sub>4</sub> – H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> 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 <sup>47</sup> referenced in this work as Le<sub>V</sub>, and is expressed per Equation 12: 39 Chancing ansing non-the ract the or canonic change  $1/2$  c<sub>3</sub> is names. 

$$
Le_V = \sum_{i=1}^{f} x_i \cdot Le_i \tag{12}
$$

52 where x<sub>i</sub>, 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 thermodiffusive behaviour of mostly binary and tertiary blends of hydrocarbons and hydrogen [27], [58]. This 58 formulation is based upon the weighted average of the fuels' nondimensional heat release  $(q_i)$ , referenced in this work as Le<sub>H</sub>, and expressed as per Equation 13:  $\overline{27}$   $\overline{378}$  iditional spilerical fidities. 

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

4 where where

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

 $\frac{10}{11}$  with Q representing the overall heat of reaction, Y<sub>i</sub>, the mass fraction of species i. 11 man & representing the overall in

 $\frac{12}{12}$  The third one is related to the work conducted by Dinkelacker et al. [27] on lean H<sub>2</sub>/CH<sub>4</sub> flames. It is  $\frac{13}{14}$  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  $\frac{17}{10}$  referenced in this work as Le<sub>D</sub>, and expressed per Equation 14: assumed that if the name curvature 

$$
Le_D = \frac{D_T}{\sum_{I=1}^F x_i \cdot D_{ij}}\tag{14}
$$

 $\frac{22}{23}$  where D<sub>T</sub> is the mixture's thermal diffusivity and D<sub>ij</sub> 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 26 as well as that of Hirschfelder, Bird and Spot, detailed in [59], is used in this study. Once the binary  $\frac{27}{28}$  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 30 compared to the surrounding N<sub>2</sub> [9]. For that reason, D<sub>ij</sub> is taken as the fuel, 'i', diffusing into N<sub>2</sub>  $\frac{31}{2}$  (denoted with the subscript j). This may hold true for hydrocarbons due to their high molar fuel-air  $\frac{32}{22}$  ratio, but not for fuels that have low molar fuel-air ratio such as H<sub>2</sub>, as underlined by Lapalme et al.  $_{34}$  [56]. Thus, as proposed by Wilke [60], the mixture-averaged coefficient of mass diffusion (D<sub>i,mix</sub>) into the mixture was employed as defined in Equation 15: where  $\nu_{\text{I}}$  is the initial extreminal **COUNTER TOT THE COMMITMENT** and, but not for facts that have

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

 $\frac{44}{45}$  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 <sup>48</sup> 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 52 this study. 45 Where Y is the mass fraction of Dienus containing CH<sub>4</sub>, NH<sub>3</sub>, O<sub>2</sub>

**5.1 Pure Fuels** 



 **Figure 3** – Comparison of (a) laminar burning velocity, (b) Adiabatic flame temperature and (c)  $^{58}_{59}$  Zel'dovich number as a function of equivalence ratio for pure NH<sub>3</sub>, CH<sub>4</sub>, and H<sub>2</sub>/air flames at 298 K & 0.1 MPa. S<sub>L</sub><sup>0</sup> data for H<sub>2</sub>/air flames from [62]. **Let do view hannel as a failed** of the

The measured  $S_L^0$  for the pure NH<sub>3</sub>, CH<sub>4</sub> and H<sub>2</sub> /air flames are compared in Figure 3.a. NH<sub>3</sub>/air for the pure NH<sub>3</sub>, CH<sub>4</sub> and H<sub>2</sub> /air flames are compared in Figure 3.a. NH<sub>3</sub>/air<br>st flame propagation rates, five to six times slower than those of CH<sub>4</sub>/air<br>ference in flame speed magnitude between H<sub>2</sub>/air and CH<sub>4</sub> 1 flames display the slowest flame propagation rates, five to six times slower than those of CH<sub>4</sub>/air  $\frac{2}{3}$  flames; with a similar difference in flame speed magnitude between H<sub>2</sub>/air and CH<sub>4</sub>/air flames at  $\frac{3}{4}$  stoichiometric conditions. It should be noted that the thermal diffusivity of these fuels decreases in  $\frac{1}{5}$  the order of H<sub>2</sub>, CH<sub>4</sub> and NH<sub>3</sub>, analogous to the decreasing S<sub>L</sub><sup>0</sup> values. The adiabatic flame temperature 6 and activation energy (represented by Ze) with respect to  $\phi$  for the aforementioned pure fuels is and activation energy (represented by Ze) with respect to  $\phi$  for the aforementioned pure fuels is Illustrated in Fig. 3 (b) and (c), respectively. For CH<sub>4</sub> (and in general C<sub>1-4</sub> alkanes), S<sub>L</sub><sup>0</sup> and T<sub>ad</sub> peak at  $\frac{8}{9}$  conditions slightly richer than stoichiometric conditions ( $\phi \sim 1.05 - 1.10$ ), underlining the sensitivity of the flame propagation to the flame temperature. The fact that the minimum activation energy is 10 11 located at similar conditions ( $\phi \sim 0.9$ ), underlines the dictating influence of the flame temperature on  $\frac{12}{12}$  the global activation energy. Due to flames temperatures peaking at around stoichiometric conditions, temperature-sensitive branching reactions are facilitated, thereby leading to overall faster reactions temperature-sensitive branching reactions are facilitated, thereby leading to overall faster reactions 15 and reduced global activation energies, as highlighted by Jomaas et al. [49]. With respect to H<sub>2</sub>, a 16 Similar trend in Ze is observed when plotted upon a much larger range of  $\phi$  than that illustrated in Fig.  $\frac{17}{10}$  3 (c). Viewed across the total flammability range of H<sub>2</sub> a similar parabolic relationship analogous to  $t_{19}$  that exhibited by CH<sub>4</sub> and NH<sub>3</sub> is apparent. Although H<sub>2</sub> flame temperature peaks at similar conditions that exhibited by CH<sub>4</sub> and NH<sub>3</sub> is apparent. Although H<sub>2</sub> flame temperature peaks at similar conditions 20 to that of CH<sub>4</sub> ( $\phi$  $\sim$ 1.1 – 1.2), both the maximum flame speed and minimum values of Ze are located at 21 much richer conditions (S<sub>L</sub><sup>0</sup>,<sub>max</sub> for  $\phi$  ~1.6-1.8, Ze,<sub>min</sub> for  $\phi$  ~1.4 – 1.6). This shift in the flame speed to  $\frac{22}{22}$  richer conditions (and by extension the reduced influence of flame temperature on SL<sup>0</sup>) has been  $\frac{23}{24}$  attributed to the much larger value of the Lewis Number (Le >> 1 for  $\phi$  >1.6), with flame acceleration, a consequence of preferential diffusion [49]. As a result, the minimum Ze witnesses a corresponding 25 26  $\,$  shift to richer conditions, since Ze is directly extracted from the flame speed (see Section 4). Thus, a 27 transport mechanism (i.e. the thermo-diffusive response of the fuel for Le  $\gg$  1) generates a change in  $\frac{28}{29}$  response in the flame speed, which subsequently impacts the flame property, highlighting the influence of transport on a supposedly chemical property [49]. This is of importance when attempting 30 to understand behaviour of fuel blends which possess different transport properties (as it is the case 31  $\frac{32}{22}$  here with H<sub>2</sub>, CH<sub>4</sub> and NH<sub>3</sub>) and the subsequent consequence on flame behaviour. On the other hand, for NH<sub>3</sub>, S<sub>L</sub><sup>0</sup> and T<sub>ad</sub> peak at approximately at the same equivalence ratio ranges ( $\phi \sim 1.0 - 1.10$ ). The fact that the maximum flame speed, adiabatic flame temperature and minimum Ze all arise at nominally 35  $\frac{36}{2}$  identical  $\phi$  conditions underlines the equi-diffusive nature of NH<sub>3</sub>, with Le close to unity, comparable  $\frac{37}{28}$  to the preferential-diffusional properties of pure CH<sub>4</sub>.  $\frac{39}{40}$  ln premixed flames, instabilities can result from both preferential-diffusional and 4 SUCHIDITIER'S CONDITIONS IT SHOWS  $9$  conditions signify neiter than store  $14$  comperatore-sensitive branding  $19$  and eximpled by Cri4 and Nri3 is a  $24$  attributed to the much larger value 29 response in the name speed, v  $34$  TOF NH<sub>3</sub>, S<sub>L</sub> and T<sub>ad</sub> peak at approx 38 **CONTROLLER CONTROL** 

hydrodynamic (Darrieus-Landeau) instabilities. It should be highlighted that the Marsktein length (L<sub>b</sub>) hydrodynamic (Darrieus-Landeau) instabilities. It should be highlighted that the Marsktein length (L<sub>b</sub>) 42 indicates the response of the flame to the stretch, it is also an indicator of the flame's propensity to <sup>43</sup> instability and not the cause of the instability. Fig. 4 presents measured L<sub>b</sub> for NH<sub>3</sub>, CH<sub>4</sub> and H<sub>2</sub> / air  $\frac{44}{15}$  flames from lean to rich conditions, from the present study and some other measurements available in literature at similar initial temperature (±5 K) and pressure conditions. To facilitate fair comparison, and  $\frac{45}{46}$  $47$  it is also indicated in the legend what methodology what used to extrapolate L<sub>b</sub> (Linear or Non-Linear  $47$ 48 Model by Stretch (LMS) or (NMS); Linear Model based on Curvature, (LMC)). First, it should be <sup>49</sup> highlighted that the values for CH<sub>4</sub> and H<sub>2</sub> are in a good agreement with previous data but for NH<sub>3</sub>/air  $\frac{50}{51}$  flame, the discrepancies are noticeable and can be partially attributed to the extrapolation  $52$  methodology employed. All three fuels exhibit an increasing L<sub>b</sub> as a function of  $\phi$  increase from lean to 53 comportions with the greatest change exhibited by NH<sub>3</sub>, with negative value of L<sub>b</sub> under lean 53  $^{54}$  conditions (comparable to that of H<sub>2</sub>), and larger positive value than that of CH<sub>4</sub> and H<sub>2</sub> under rich conditions.  $41$  rivariouynamic (Darrieus-Landeau  $46$  in interature at similar initial temp  $51$  Halle, the discrepancies are in 55 conditions  $56$  conditions.

65



31  $pure NH_3$ , CH<sub>4</sub>, H<sub>2</sub> as a function of  $\phi$  (298 K, for N 0.1MPa). Data for NH3 from [15] [23], CH4 [63], H2 [58] [62]  $\frac{33}{1621 \text{ H}}$   $\frac{1}{1621}$ [ $34$ ],  $12$  [ $30$ ]  $102$ ]

for NH<sub>3</sub>, CH<sub>4</sub>, H<sub>2</sub> as a function of  $\phi$  (data for H<sub>2</sub> [75]). Full and dotted lines respectively reflect Hirschfelder and Wilke methods to evaluate D<sub>ij</sub> (298 K, 0.1MPa)

To better understand the changes in the stretch response of pure fuels/air flames, the<br>
37<br>
32  $\frac{38}{39}$  evolution of the corresponding Le is presented in Fig. 5, from lean to rich mixtures. 'Theoretical' Lev numbers, estimated using the free-stream properties of the mixtures, are illustrated as colour bands 41 with the upper and lower limits (represented by full and dashed lines) denoting the differences  $\frac{42}{10}$  between either the Hirschfelder or Wilke method to evaluate the mass diffusion coefficient. While the correct Le is evaluated (Le  $\sim$  1 for NH<sub>3</sub> and CH<sub>4</sub>; Le << 1 at  $\phi$  < 1 and Le >> 1 at  $\phi$  > 1 for H<sub>2</sub>), little variation is observable across the considered  $\phi$ , aside from the transition from lean to rich conditions. <sup>46</sup> Furthermore, it should be highlighted that minimum Le for NH<sub>3</sub> is just prior to stoichiometric conditions <sup>47</sup> in agreement with [15], whilst for CH<sub>4</sub> and H<sub>2</sub>, minimum Le is obtained at leanest conditions. Since Le  $\frac{48}{49}$  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 51 ratio [52] were not considered. As such, Le can be evaluated from the experimental L<sub>b</sub> and these other  $\frac{1}{2}$  properties affecting the flame, as recommended by Jomaas et al. [49], with the use of theoretical relationships established in literature (denoted as Le<sub>CHEN</sub> and Le<sub>BM</sub>, Eqn. 7 and 9, accordingly). 55 Therefore, as it can be seen when comparing Figure 4 and 5, analogous L<sub>b</sub> 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<sub>b</sub> magnitude is observed for NH<sub>3</sub>,  $58$  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 NH3-based flames. Furthermore, **EVOILLIOIT OF LITE COFFESPOTIOITIS**  correct Le is evaluated (Le  $\frac{1}{2}$  T for f was simply evaluated as a function 54 relationships established in liter  $L_b$  to Le. However, it is interesting to note that the greatest change in  $L_b$  magnitude is observed for NH<sub>3</sub>, 59 WILDSL EXHIDITING ICAST CHAIRSCHILL

the transition from a negative to positive L<sub>b</sub> for NH<sub>3</sub> obtained for  $\phi \sim 0.8 - 1.0$  is at comparable  $\phi$  with 1 the transition from Le < 1 to Le > 1 occurred.

# $\frac{3}{4}$  5.2 Binary Fuel Mixtures J. Dinary Fuer Mixtures

 $\frac{5}{6}$  The influence of increasing fraction of either CH<sub>4</sub> or H<sub>2</sub> in NH<sub>3</sub>/air mixture on S<sub>L</sub><sup>0</sup>, across a wide  $\tau$  range of  $\phi$  is depicted in Figures 6 and 7 respectively. With respect to NH<sub>3</sub>/H<sub>2</sub> 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 10<br>
package. A simulation of 10 cm was considered, with a total of 3000 grid points used with grid 12 parameters GRID (0.025) and CURV (0.1), including multi-component diffusion and an assumed air 13 composition of 79%  $N_2$  – 21%  $O_2$ . However only the two latter mechanism are shown since they  $^{14}$  consistently gave best agreement with, respectively, all NH<sub>3</sub>/CH<sub>4</sub> and NH<sub>3</sub>/H<sub>2</sub> blends evaluated in this study. **6 111 111 1111 1111 1111 1111 1111 1111 1111 1111 1111 1111**  package. A simulation of 10 cm  $\frac{15}{\frac{15}{\frac{1}{2}}}}$ study.



<sup>39</sup> **Figure 6** - S<sub>L</sub><sup>0</sup> for binary NH<sub>3</sub>/CH<sub>4</sub> mixtures, **Figure 7** - S<sub>L</sub><sup>0</sup><br>41 **comparison with simulated values with comparison v** Okafor et al. kinetics model [18] (298 K, 0.1MPa) rigule  $\sigma$   $\rightarrow$  101 binary 19113/  $\frac{1}{41}$  comparison with simulated values with 

**Figure 7** –  $S_L^0$  for binary NH<sub>3</sub>/H<sub>2</sub> 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 NH<sub>3</sub> laminar flame 47 speed is observable upon CH<sub>4</sub> addition, with a very good prediction by Okafor et al. [18] mechanism. <sup>48</sup> On the other hand, as illustrated in Figure 7, an increase in H<sub>2</sub> fraction results in an exponential increase  $\frac{49}{50}$  in S<sub>L</sub><sup>0</sup>, across the entire tested  $\phi$  range, with also a very good prediction by Stagni et al. [42] mechanism,  $_{51}$  across all tested conditions. It is worth highlighting that  $\sim$  10-20% addition (vol.%) of either CH<sub>4</sub> or H<sub>2</sub> results in a similar increase in NH3 flame speed, with further increases resulting in very different flame 53 speed behaviour. This increased reactivity of NH<sub>3</sub> based blends upon CH<sub>4</sub> and H<sub>2</sub> addition has been previously suitably reported [19] [67], with modelling work and sensitivity analysis suggesting that the 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 57 strongly correlated.  $\cdots$   $\cdots$ previously suitably reported  $\begin{bmatrix} 1 & 5 \end{bmatrix}$ 

 $\frac{1}{2}$  To investigate the stretch-related behaviour of NH<sub>3</sub>/CH<sub>4</sub> and NH<sub>3</sub>/H<sub>2</sub> flames, L<sub>b</sub> is plotted as a 3 function of either CH<sub>4</sub> or H<sub>2</sub> addition to NH<sub>3</sub> across a wide range of  $\phi$  in Figure 8 and 9, respectively. Note that the evolutions of L<sub>b</sub> as a function of  $\phi$  are in SM3 and 4. For a  $\phi \ge 0.9$ , a linear decrease in L<sub>b</sub> is observed with increasing CH<sub>4</sub> fraction. At  $\phi = 0.80$ , a negative value L<sub>b</sub> is obtained for pure ammonia  $\gamma$  while 10% CH<sub>4</sub> addition results in L<sub>b</sub> sign inversion (from negative to positive). As pure NH<sub>3</sub>/air mixtures <sup>8</sup> could not be ignited for  $\phi$  < 0.8, with this experimental apparatus, this tendency cannot be verified. 9<br>10 Under rich conditions ( $\phi \ge 1.1$ ), a decreasing stretch sensitivity is measured upon increasing H<sub>2</sub> fraction,  $\frac{10}{11}$  similar in trend and magnitude to that observed for NH<sub>3</sub>/CH<sub>4</sub> flames but for  $\phi \ge 0.9$ . Howe 12 interestingly for  $\phi \le 1.0$ , an initial decrease in L<sub>b</sub> 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 L<sub>b</sub>, with non-linear behaviour accentuated as  $\frac{14}{15}$  conditions get leaner. Similar non-monotonical variation in stretch-related behaviour was measured 16 by Lhuillier [68] as well as by Ichikawa et al. [22], for NH<sub>3</sub>/H<sub>2</sub> flames, at  $\phi$  = 1.0 and ostensibly identical 17 experimental conditions (T<sub>u</sub> = 298 K, P<sub>u</sub> = 0.1 MPa), also plotted in Figure 9 for comparison purposes. 18 As such, under lean conditions, NH<sub>3</sub>/H<sub>2</sub> mixtures exhibit a greater negative L<sub>b</sub> than that of pure H<sub>2</sub>  $\frac{19}{20}$  flames. It should be highlighted that similar non-linear L<sub>b</sub> behaviour was measured by Okafor et al. [24] 21 for CH<sub>4</sub>/H<sub>2</sub> flames, with an inflection point occurring upon  $\sim$  70% H<sub>2</sub> addition. Similarly, Huang et al. 22 [69] also reported similar behaviour for natural gas – hydrogen – air blends. As such, it may seem that 23 this maybe a phenomenon attributable to the H<sub>2</sub> contribution, at least for NH<sub>3</sub> or CH<sub>4</sub> based flames,  $\frac{24}{25}$  due to the strong and fast diffusivity of H<sub>2</sub> in the reactants. This stretch-sensitivity behaviour is of 26 importance since the flames exhibiting negative L<sub>b</sub> will be accelerated in highly stretched turbulent 27 environments, whilst flames displaying a positive L<sub>b</sub> will be weakened. This stretch-sensitivity response inevitably impacts the operation of practical combustion systems. **10 Investigate the stretch-** is observed with increasing CH4 ira similar in trend and magnitude conditions get realier. Jurillar flor 20 marries. It should be highlighted the 25 auch der Strong and Tast amat



 $\frac{57}{58}$  (298 K, 0.1 MPa) (298 K, 0.1 IVIPa)

/CH<sub>4</sub> mixtures **Figure 9 -** L<sub>b</sub> values of NH<sub>3</sub>/H<sub>2</sub> mixtures (298 K, 0.1 MPa) 100%  $H_2$  L<sub>b</sub> values from [62]

 $\frac{1}{2}$  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 <sup>4</sup> the diffusive pathway, the most suitable Le formulation has to be considered. As such, the different For a better understanding of this change, a sensitivity analysis related to the contribution of major<br>flame enhancing pathways (diffusive, thermal, kinetic) was undertaken. However, to correctly quantify<br>the diffusive pa estimate of L<sub>b</sub>, by using the relationships proposed by Chen or Matalon and Bechtold, referred as L<sub>b</sub>- $8 \text{ Chen}$  and  $L_b$ -BM, respectively. It should be noted that the purpose of such analysis is more qualitative <sup>9</sup> than quantitative to validate which Le<sub>eff</sub> model best captures the measured L<sub>b</sub> behaviour of the tested the tested  $\frac{10}{11}$  blends. For a better understanding of this  $\frac{5}{5}$  Lempedole (i.e. Lempedole 1.1 and 1.0 from  $\epsilon$  EC<sub>ell</sub> moders (i.e. EC<sub>V</sub>, EC<sub>H</sub>, EC<sub>D</sub> HO signals.



 $\frac{1}{5}$  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  $\frac{54}{12}$  Figure 10 – Comparison of L<sub>b</sub>-CHEN and L<sub>b</sub>-BM estimates to the measured L<sub>b</sub> for NH<sub>3</sub>/H<sub>2</sub> and  $\pi$  indities (d)  $\psi$  = 0.8 (d)  $\psi$  =

58<br>Figure 10 illustrates L<sub>b</sub>-CHEN and L<sub>b</sub>-BM for NH<sub>3</sub>/H<sub>2</sub> blends, alongside experimentally measured L<sub>b</sub> values. With respect to the

quantitative and qualitative agreements are observed with Le<sub>D</sub> formulation, with the non-linear stretch<br>behaviour well captured. Under H<sub>2</sub> richer condition ( $\phi = 1.2$ , Fig.11.c), Le<sub>D</sub> overpredicts the influence<br>of H<sub>2</sub> quantitative and qualitative agreements are observed with Le<sub>D</sub> formulation, with the non-linear stretch<br>behaviour well captured. Under H<sub>2</sub> richer condition ( $\phi = 1.2$ , Fig.11.c), Le<sub>D</sub> overpredicts the influence<br>of H<sub>2</sub>  $\frac{2}{3}$  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  $\frac{3}{4}$  trend. Poor agreement is observed with the BM formulation, with again a Le<sub>D</sub> best reflecting expected quantitative and qualitative agreements are observed with Le<sub>p</sub> formulation, with the non-linear stretch<br>behaviour well captured. Under  $H_2$  richer condition ( $\phi = 1.2$ , Fig.11.c), Le<sub>p</sub> overpredicts the influence<br>of H<sub>2</sub> 6 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], quantitative and qualitative agreements are observed with Le<sub>p</sub> formulation, with the non-linear stretch<br>behaviour well captured. Under  $H_2$  inter condition ( $\oint_0 = 1.2$ ,  $F_0 = 1.41.c$ ), Le<sub>p</sub> overpredicts the influence<br>t quantitative and qualitative agreements are observed with Le<sub>p</sub> formulation, with the non-linear stretch<br>behaviour well captured. Under  $H_2$  richer condition ( $\phi = 1.2$ , Fig.11.c), Le<sub>p</sub> overpredicts the influence<br>of  $H_$  $_{10}$  that the flame curvature is dominant, hence the local enrichment of the most diffusive fuel at the 11 flames leading edge is predicted. This concept appears to be valid under lean conditions, since H<sub>2</sub> and quantitative and qualitative agreements are observed with Le<sub>p</sub> formulation, with the non-linear stretch<br>behaviour well captured. Under H<sub>2</sub> richer condition ( $\phi = 1.2$ , Fig.11.c), Le<sub>p</sub> overpredicts the influence<br>of H<sub>3</sub>  $\frac{13}{14}$  volume or non-dimensional heat release appears to be more appropriate. With respect to NH<sub>3</sub>/CH<sub>4</sub> 15 flames, measured L<sub>b</sub> and L<sub>b</sub>-CHEN are compared in Fig. 10.d for  $\phi$  = 0.8 – 1.2. It should be noted that 16 since NH<sub>3</sub> and CH<sub>4</sub> display very similar preferential-diffusional behaviour (Le ~ 0.9 – 1.1), the application quantitative and qualitative agreements are observed with Les formulation, with the non-linear stretch<br>behaviour well captured. Under H<sub>2</sub> richer condition ( $\delta = 1.2$ , Fig.11.c), Les overpredicts the influence<br>of H<sub>2</sub> on 18<br>
Figure 10.d. For the conditions greater than stoichiometry, a good quantitative and qualitative quantitative and qualitative agreements are observed with Le., formulation, with the non-linear stretch<br>behaviour well captured. Under H<sub>2</sub> richer condition ( $\phi = 1.2$ , Fig.11.c), Le<sub>1</sub> overpredicts the influence<br>of H<sub>2</sub> o 21 allow to verify the change from negative to positive  $L_b$  measured experimentally obtained upon 10% emention of the condition to the state of the matching the that the matching the that and the measured of H<sub>3</sub> on NH<sub>3</sub> with better agreement bisevered with a Le<sub>v</sub> or Le<sub>u</sub> model better reflecting the measured trend. Poor  $\frac{23}{24}$  Le<sub>D</sub> and Le<sub>H</sub> formulation respectively, best captured changes in thermo-diffusive behaviour. With 25 respect to NH<sub>3</sub>/CH<sub>4</sub> flames, Le<sub>v</sub> demonstrated the best agreement for all considered  $\phi$ , with these conclusions maintained for the remainder of the analysis. 26 1 behaviour well captured. Under H<sub>2</sub> richer condition ( $\phi$  = 1.2, Fig.11.c), Le<sub>D</sub> overpredicts the influence  $4$  and  $4$  and  $4$  are  $4$  and  $4$  and  $4$  and  $4$  and  $4$  and  $4$  and  $4$  a  $5$  stretch behaviour under lean conditions, and Le<sub>H</sub> exhibiting better agreement at richer conditions. 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  $8$  NII /II flames a botter agreement  $9$   $^{113}$   $^{112}$   $^{116}$   $^{116}$ ,  $^{116}$   $^{116}$   $^{116}$   $^{116}$   $^{116}$   $^{116}$ <sup>12</sup> NH<sub>3</sub> have higher mass diffusivities than O<sub>2</sub>. For richer conditions ( $\phi$  and 1.0), a model based on either 14 volume of non-unnensional near <sup>17</sup> of either Le<sub>eff</sub> models results in very similar values. Consequently, only the Le<sub>v</sub> model is plotted on 19 right 10.0. For the conditions  $\frac{1}{20}$  agreement is observed with the CHEN model, but under lean conditions, the CHEN model does not 22 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 24 ECD and ECH TOMMUNION TESPECT



 $^{57}_{50}$  either CH<sub>4</sub> or H<sub>2</sub> to NH<sub>3</sub>,  $\phi$  = 0.8, 1.0, 1.2 of either CH<sub>1</sub> c <sup>56</sup> **Figure 11** – Variation in δ<sub>6</sub> and σ with addition of  $58$  canceled  $\frac{1}{4}$  of  $\frac{1}{2}$  to  $\frac{1}{3}$ ,  $\frac{1}{4}$  - 0.0, 1.0, 1.

of either CH<sub>4</sub> or H<sub>2</sub> to NH<sub>3</sub>,  $\phi = 0.8, 1.0, 1.2$ 

As emphasised by Kwon et al. [70] and reviewed in [71], the fundamental parameters that<br>hydrodynamic and diffusional-thermal instabilities are the thermal expansion, the flame<br>is, the non-unity Le and the global activation induce hydrodynamic and diffusional-thermal instabilities are the thermal expansion, the flame <sup>2</sup> thickness, the non-unity Le and the global activation energy (or equivalently Ze). Consistent with the  $\frac{3}{4}$  hydrodynamic theory of Darrieus and Landau [9], the hydrodynamic instabilities arise from the thermal expansion of gases, with the density jump across the flame front proportional to the growth rate of hydrodynamic instability. In the case of an outwardly propagating spherical flame, the flame tends to  $\frac{7}{1}$  be stabilised due to curvature induced positive stretch, consequently the flame thickness plays a  $\frac{8}{\circ}$  significant role, since the thinner the flame the weaker the influence of curvature. Hence the risk of destabilisation is enhanced for thinner flames. It is interesting to note that addition of either CH<sub>4</sub> or H<sub>2</sub> destabilisation is enhanced for thinner flames. It is interesting to note that addition of either CH<sub>4</sub> or H<sub></sub> 11 to NH<sub>3</sub> does not really affect the thermal expansion, irrespective of  $\phi$ , as shown in Figure 11. On the 12 other hand, the flame thickness decreases strongly with increasing CH<sub>4</sub> or H<sub>2</sub> fractions, in effect 13 promoting hydrodynamic instabilities to a similar extent. Nevertheless, the addition of either CH<sub>4</sub> or  $_{15}$  H<sub>2</sub> to NH<sub>3</sub> results in similar stretch-related behaviour under rich conditions, whilst exhibiting very different stretch-behaviour as conditions get leaner. The development of preferential-diffusional <sup>17</sup> instabilities, characterised by Le, is the result of non-equi-diffusion. With respect to the NH<sub>3</sub>/H<sub>2</sub> flames,  $\frac{18}{10}$  the effects of preferential diffusion are a consequence of the higher mass diffusivity of H<sub>2</sub> and NH<sub>3</sub>  $\frac{19}{20}$  compared to the O<sub>2</sub> molecule. As illustrated in Figure 12, Le decreases significantly with increasing H<sub>2</sub> 21 fraction thereby promoting diffusional-thermal instabilities at  $\phi = 0.8$ . Furthermore, as could be expected, the change in Le increases as the conditions get le  $\frac{23}{24}$  individual Le response. As underlined by Kwon et al. [70], considering that the development of  $\frac{1}{25}$  preferential diffusional instabilities requires a modification of the flame front, it is thus reasonable to expect the global activation energy should also affect the development of diffusional-thermal 27 **instabilities. Accordingly, a lower E**<sub>a</sub> (illustrated as Ze in Figure 12) will tend to enhance instability of a 28 diffusionally unstable flame such as lean NH<sub>3</sub>/H<sub>2</sub> flame, with both Le and Ze decreasing with increasing  $\frac{29}{30}$  H<sub>2</sub> concentration for all  $\phi$ . The decrease in Ze is largely due to a decrease in the inner-layer temperature 31 coupled with an increase in adiabatic flame temperature with increasing  $H_2$  concentration for  $\phi$ . For NH<sub>3</sub>/H<sub>2</sub>, the changes in measured L<sub>b</sub> are thus potentially the result of competing hydrodynamic and thermo-diffusive instabilities, with the influence of the thermo-diffusional instabilities reducing as the thermo-diffusional instabilities reducing as the  $35 \qquad \phi$  increases. On the other hand, for NH<sub>3</sub>/CH<sub>4</sub> flames, the addition of CH<sub>4</sub> to NH<sub>3</sub> results in little 36 diffusional-thermal effects (Le  $\sim$  1) across the entire considered  $\phi$  range. rigulou primir theory or Darrieus and  $4$  destabilisation is enhanced for the promoting nyarodynamic instability **compared to the O<sub>2</sub> molecule. As** 24 marriage Le response. As and  $\mu_2$  concentration for all  $\phi$ . The dec 34 CHEFFIND UTTUBER THEODITICS, WILL 



<sup>30</sup> Figure 13 – Comparison of variation of Ze(L<sub>eff</sub> – 1) and  $1/Le_{eff}$  – (Ze/2)( $1/Le_{eff}$  -1) to measured Marsktein number as a function of (a) H, mol manner as a function of (a) its more

arranged to yield the Marsktein Number (Ma =  $L_b/\delta$ ), resulting in Ma =  $[1/Le_{eff} - (Ze/2)(1/Le - 1)]\sigma$ , <sup>40</sup> in which the term Ze(L<sub>eff</sub> - 1) reflects the thermo-diffusive influence as underlined by Okafor et al. [24]. **Experimental Comparison of the set of the set of the experimental Ma to the trends in 1/Le<sub>eff</sub> –1 (2e/2)(1/Le –1) and**  $\frac{1}{2}$  **(a.g.**  $\frac{1}{2}$  **(a.g.**  $\frac{1}{2}$  **(a.g.**  $\frac{1}{2}$  **(a.g.**  $\frac{1}{2}$  **(b)**  $\frac{1}{2}$  **(c)**  $\frac{1}{2}$ 43 Ze(L<sub>eff</sub> - 1), for NH<sub>3</sub>/H<sub>2</sub> and NH<sub>3</sub>/CH<sub>4</sub> mixtures, respectively, at  $\phi$  = 0.8 - 1.0 - 1.2. First, as expected both  $^{44}$  Ze(L<sub>eff</sub> - 1) and 1/Le<sub>eff</sub> - (Ze/2)(1/Le - 1) exhibit the same trends. For the lean NH<sub>3</sub>/H<sub>2</sub> mixtures, the **1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.5 1.10 1.0 10. 20.** 48 experimental Ma and Ze(L<sub>eff</sub> - 1) and  $1/$ Le<sub>eff</sub> - (Ze/2)(1/Le - 1), potentially due to a greater change in **10 20 80 40 60 60 70 80 90 50 60 70 80 90 100** 10 10 70 and an 50 an 5 % of  $H_2$  in NH<sub>3</sub> (vol.%)<br>
(gure 13 – Comparison of variation of  $Ze(L_{\text{eff}} - 1)$  and  $1/(E_{\text{eff}} - [Ze/2)(1/(E_{\text{eff}} - 1))$  to measured Marsktein<br>
umber as a function of (a) H; mole fraction, and (b) CH; mole fraction<br>
from the  $\frac{51}{52}$  Ze(L<sub>eff</sub> - 1) and 1/Le<sub>eff</sub> - (Ze/2)(1/Le - 1), potentially alluding that the Le and Ze are the driving forces 53 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  $\frac{55}{25}$  ratio. For lean NH<sub>3</sub>/H<sub>2</sub> flames it seems that the changes in measured L<sub>b</sub> are to a large extent the consequence of thermo-diffusive effects, with this influence reducing as conditions get richer. For the consequence of thermo-diffusive effects, with this influence reducing as conditions get richer. For the NH3/CH4 mixtures, the competition between thermo-diffusional and hydrodynamic instabilities yields anning to itsellar and the experimental time and the diffusive effect. Similarly, the relationshis where  $1/\text{Le}_{\text{eff}} - (2e/2)1/1/\text{Le}_{\text{eff}} - 1)$  represents the thermo-diffusive effect. Similarly, the relationshis linking L<sub></sub>  $\frac{35}{26}$  From the analytical expression developed by Chen [38], [44], the equation 8 can be re- arranged to yield the Marsktein i 38 where  $1/Le_{eff} - (Ze/2)(1/Le_{eff} - 1)$  represents the thermo-diffusive effect. Similarly, the relationship <sup>39</sup> linking  $L_b$  to Le developed by Matalon and Bechtold (Equation 9) can be re-arranged to evaluate Ma,  $\ldots$   $44$   $\ldots$   $44$   $\ldots$  rigures 14.d driu 14.b compare t  $\frac{45}{16}$  changes in measured Ma appear to be to a great extent the result, of changes in the thermo-diffusive 46 Changes in measured that uppear properties, Le and Ze. At fiche <sup>49</sup> the expansion ratio (see Figures 12) than under lean conditions. In relation to the NH<sub>3</sub>/CH<sub>4</sub> mixtures  $\frac{50}{2}$  (Figure 13.b), the measured Ma under lean and stoichiometric conditions yield matching trends to **EXECU**<sub>eff</sub> - 1 and 1/Le<sub>eff</sub> - (2e/2)(1/1 **Consequence of thermo-diffusive** 59 to increasingly positive Ma values, resulting in propensity of flame stabilisation. 

### 5.3 Flame Sensitivity Analysis

 $\frac{1}{2}$  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  $\frac{4}{7}$  pathway can be modelled as: **The enhancement of the f**  $5 \qquad \qquad$ 

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

<sup>8</sup> 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 11 temperature  $(T_a = E_a/R_u)$ , and the adiabatic flame temperature are represented in the second term  $\frac{12}{12}$  [exp( $-T_a/2T_{ad}$ )]. These individually represent the thermal (T<sub>ad</sub>) and kinetic (T<sub>a</sub>) influences on the  $\frac{13}{14}$  flame speed. Concerning the Le formulation, it was previously determined from Figure 11 that for lean 15 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-16 diffusive behaviour. With respect to  $NH_3/CH_4$  flames, Le<sub>v</sub> demonstrated the best agreement for all  $\frac{17}{2}$  considered φ. 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]: and the first term on the right-14 maile speed. Concerning the Lend 19 to Le, and nence applied for the

$$
\frac{23}{24} \qquad \qquad \frac{1}{S_L^0} \cdot \frac{dS_L^0}{dx} = \frac{1}{2 \cdot D_T \cdot Le} \cdot \frac{d(D_T \cdot Le)}{dx} - \frac{1}{2 \cdot T_{ad}} \cdot \frac{2 \cdot T_a}{dx} + \frac{T_a}{2 \cdot T_{ad}^2} \frac{2 \cdot T_{ad}}{dx} \tag{17}
$$

26 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 27 denote the influence of the diffusive, kinetic, and thermal pathways, correspondingly. Sensitivity 29 analysis is illustrated in Figure 14 for the blends and  $\phi$  considered, with a positive and negative  $\frac{30}{24}$  sensitivity factor representing flame speed enhancement and inhibition, respectively. where *x*, the volume inaction of **Scholarly restor representing that** 



59<br>60 **Figure 14** – Sensitivity Analysis of S<sub>L</sub><sup>0</sup> for NH<sub>3</sub>/H<sub>2</sub> and NH<sub>3</sub>/CH<sub>4</sub> blends, (a) φ = 0.8 (b) φ = 1.0 (c) φ = 1.2 **Figure 14** – Sensitivity Analysis of

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As illustrated in Figure 14, the enhancement in flame speed of NH<sub>3</sub> based blends upon addition of<br>er CH<sub>4</sub> or H<sub>2</sub> is predominantly an Arrhenius effect (kinetic), principally through the reduction of the<br>rall activation 1  $\blacksquare$  either CH<sub>4</sub> or H<sub>2</sub> is predominantly an Arrhenius effect (kinetic), principally through the reduction of the  $\frac{2}{3}$  overall activation energy and thus the activation temperature. For identical volumetric additions of up  $\frac{3}{4}$  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  $E_a$  than in the case of CH<sub>4</sub> addition, resulting in greater flame speeds. It should be  $\frac{7}{1}$  noted that although remaining predominant for lean and stoichiometric conditions, the influence of  $\frac{8}{\alpha}$  the kinetic pathway reduces at richest conditions, particularly for CH<sub>4</sub> addition to NH<sub>3</sub>, with a negative 10 Sensitivity at  $\phi$  = 1.2. This agrees with the minor increase in E<sub>a</sub> (represented by Ze, see Figure 12) at 11 that condition, the consequence of the shifted minimum  $E_a$  to slightly richer conditions ( $\phi$  = 1.1-1.2) of  $12$  NH<sub>3</sub>, as in Figure 3. The thermal pathway impact is lower than the kinetic effect, with the influence of  $\frac{13}{14}$  the thermal pathway correlating well with modelled changes in adiabatic flame temperature. The 15 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 16 the diffusive influence, it assumes negative sensitivity (or inhibiting effect) for lean NH<sub>3</sub>/H<sub>2</sub> mixtures,  $\frac{17}{2}$  and is negligible in comparison to other pathways. This is particularly the case for NH<sub>3</sub>/CH<sub>4</sub>, a 18<br>
19
consequence of the nominal changes in Le (Fig. 12) coupled with the limited change in thermal 20 diffusivity of the mixture upon CH<sub>4</sub> addition, irrespective of the  $\phi$ . It should be noted that even if the use of different kinetics mechanisms can induce different Arrhenius coefficients, the qualitative trends 21 22 should remain valid, and thus performing such sensitivity analysis from first principles remains relevant 23 providing useful insights.  $\frac{4}{3}$  to 10% C<sub>114</sub> or 11<sub>2</sub> results in a simple 9 14 CHE CHEFFING PACHWAY COLLEGEING 19 consequence of the nominal cha  $24$  Providing ascruitinsights.

# $\frac{25}{26}$  6. Conclusions  $26$  **b. Concressions**

 $\frac{27}{28}$  The spherically expanding flame configuration was used to measure the unstretched laminar flame 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 range of compositions and equivalence ratio. A special attention was given to the estimate of Lewis 30 31 mumber 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  $\frac{32}{22}$  this study, the following main outcomes can be made: 29 **Speeds and corresponding Marks** 33 cases and states, the following main out

- 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 <b>I** and linear increase in flame speed, respectively. The greatest relative change in flame 36 37 Speed upon H<sub>2</sub> addition occurs under leanest and richest conditions while upon CH<sub>4</sub> 38 and addition, only under lean conditions. Stagni et al. and Okafor et al. mechanisms displayed  $\frac{39}{40}$  the best agreement with experimental NH<sub>3</sub>/H<sub>2</sub> and NH<sub>3</sub>/CH<sub>4</sub> results, respectively.  $35$  and  $35$
- With respect to the stretch related behaviour, the addition of  $CH_4$  to  $NH_3$  results in a linear  $41$ reduction in the stretch sensitivity for a fixed equivalence ratio. The volumetric based 42 43 **Lewis number yielded the best correlation with the measured Markstein lengths, for CH<sub>4</sub>**  $\frac{44}{45}$  addition to NH<sub>3</sub> resulting in nominal diffusional-thermal effects. For the stoichiometric and duction to this resulting in hominal dirictional circuit enects. For the stolemometric and<br>
46 **September 16 and NH3/H<sub>2</sub> flames, a non-monotonical variation in measured Markstein length was**  $47 \,$  botained, with a less and less linear behaviour as conditions get leaner. For NH<sub>3</sub>/H<sub>2</sub>, the  $48$  changes in measured  $L_b$  were demonstrated to mainly be the result of thermo-diffusive  $^{49}$  effects (through the modelled changes in Le<sub>eff</sub> and global activation energy) with the 50<br>
51 **Influence of the thermo-diffusional instabilities reducing as the equivalence ratio** 52 **increases. For lean NH<sub>3</sub>/H<sub>2</sub> mixtures, the diffusional-based Lewis number well captured the** 53 hon-linear stretch behaviour as function of H<sub>2</sub> addition, whilst the heat release-based Lewis number resulted in better agreement at richer conditions. 54 41 **WILD PERSPECT TO THE ST**  $46$  **IEAM IVE INTERVALUATE INTERVALUATE INTERVALUATI** 51 **IIIIuence of the the**
- A sensitivity analysis related to the major flame enhancing pathways (diffusive, kinetic, 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>,<br>58 **inupy due to the kinetic change, especially through the reduction of the activation of the activation of the activation** temperature. The influence of the kinetic pathway reduces as conditions get richer, 59 56 **A SEISILIVILY dildiySiS** 58 is mainly due to the kinetic change, especially through the reduction of the activation 60 competitive m

particularly for CH<sub>4</sub> addition. The thermal pathway holds less influence in comparison to<br>the kinetic pathway, with its influence showing good correlation with limited changes in<br>adiabatic flame temperature of the consid 1 1 The kinetic pathway, with its influence showing good correlation with limited changes in 1 particularly for CH<sub>4</sub> addition. The thermal pathway holds less influence in comparison to<br>the kinetic pathway, with its influence showing good correlation with limited changes in<br>adiabatic flame temperature of the consid particularly for CH<sub>4</sub> addition. The thermal pathway holds less influence in comparison to<br>the kinetic pathway, with its influence showing good correlation with limited changes in<br>adiabatic flame temperature of the consid mixtures. 5 particularly for CH<sub>4</sub> addition. The thermal pathway holds less in<br>the kinetic pathway, with its influence showing good correlation<br>adiabatic flame temperature of the considered blends. The<br>negligible for all investigated the kinetic pathway, with its influence showing good correlation with limited changes in<br>adiabatic flame temperature of the considered blends. The diffusive pathway was<br>megligible for all investigated mixtures, with a nega adiabatic flame temperature of the considered blends. The diffusive pathway was  $\frac{3}{2}$  regligible for all investors 4 megingune for all lives

# $\frac{6}{7}$  Declaration of Competing Interest  $7$  Declaration of Competing interest

 $\frac{8}{9}$  The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper. 10 megligible for all investigated mixtures, with a negative sensitivity for the lean NH<sub>3</sub>/H<sub>2</sub><br> **Declaration of Competing Interest**<br>
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This project has received funding from the European Union's combustion, encodering methane that they have no known competing financial interest or personal<br>The authors declare that they have on known competing financial interest or personal<br>velogements<br>sproject has received funding  $9$  authors declare that

# 12 **Acknowledgements** 11



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# Influence of Hydrogen and Methane Addition in Laminar Ammonia Premixed Flame on Burning<br>Velocity, Lewis Number and Markstein Length<br>Authors: Zitouni, S. (\*), Brequigny P., Mounaïm-Rousselle C., **1** Superior Velocity, Lewis Number and Markstein Length **Example 2018** 2

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# $\frac{16}{16}$  **Abstract:**

<sup>18</sup> 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  $\frac{19}{20}$  NH<sub>3</sub> cracking, seem to be promising solutions to partially or fully decarbonise our energy systems. To  $_{21}$  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 22 23 and Markstein lengths. The air/fuel mixtures were varied across a large range of compositions and  $\frac{23}{100}$ equivalence ratios. In general addition of  $CH_4$  or  $H_2$  results in a linear and exponential increase in measured laminar burning velocity, respectively. Of the appraised mechanisms, Stagni and Okafor 26 27 kinetics mechanisms yielded best agreement with  $NH_3/H_2$  and  $NH_3/CH_4$  flame speed measurements.  $\frac{28}{20}$  With respect to measured Markstein length, for a fixed equivalence ratio, addition of CH<sub>4</sub> to NH<sub>3</sub>  $\frac{29}{30}$  resulted in a linear reduction in stretch sensitivity for the tested conditions. For lean NH<sub>3</sub>/H<sub>2</sub> flames, 31 an initial decrease in Markstein length is observed up to  $30 - 40\%$  H<sub>2</sub> addition, at which point any  $32$  further addition of H<sub>2</sub> results in an increase in Markstein Length, with a non-linear behaviour  $\frac{33}{34}$  accentuated as conditions get leaner. Above stoichiometry similar stretch behaviour is observed to that of NH3/CH4. Different theoretical relationships between the Markstein length and Lewis Number 35 36 were explored alongside effective Lewis Number formulations. For lean NH<sub>3</sub>/H<sub>2</sub> mixtures, a diffusional  $\frac{37}{20}$  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 in better agreement at richer conditions. For NH<sub>3</sub>/CH<sub>4</sub> mixtures, a volumetric based Lewis Number 40 formulation displayed best agreement for all evaluated equivalence ratios. For NH<sub>3</sub>/H<sub>2</sub>, changes in 41 measured Markstein Length were demonstrated to potentially be the result of competing  $\frac{42}{43}$  hydrodynamic and thermo-diffusive instabilities, with the influence of the thermo-diffusional  $_{44}$  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 45 <sup>46</sup> on the flame, reflected by increasing positive Markstein number values. Finally, a systematic analysis on the flame, of the flame speed enhancements effects (kinetic, thermal, diffusive) of  $CH_4$  and  $H_2$  addition to  $NH_3$ 49 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 50 energy. 20 **INTS CROWING, SCCIT to be promise**  $25$  equivalence ratios. In general ac 30 resulted in a linear reduction in s 34 accentuated as conditions get ier 39 **In better agreement at richer co** 43 *Ilyardayranne* and thermo dint 48 Of the name speed emiancement  $51$  energy  $52$  chci $5y$ .

55 Keywords: Ammonia-hydrogen, ammonia-methane, Laminar flame Speed, Lewis Number, Markstein Length 56 **Reynolds**, Annhonia Hydrogen, a  $57$  Length

**1. Introduction**<br>The historical prevalence of hydrocarbon fuel usage to sustain our pov<br>and the associated greenhouse gas emissions produced, have resulted in in<br>and ecological adversities [1]. As such, in order to attain  $\frac{1}{2}$  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 3 and ecological adversities [1]. As such, in order to attain zero-carbon targets, the large-scale  $\frac{5}{6}$  employment of renewable and carbon-free fuels within our energy systems is required to maintain  $\frac{1}{7}$  a balanced trajectory between human development, progress and cohesion with the environment. 8 In light of this context, Ammonia (NH<sub>3</sub>) has emerged in recent years as an efficient zero-carbon hydrogen (H<sub>2</sub>) carrier. Liquid NH<sub>3</sub> offers higher H<sub>2</sub> content than for example, ethanol, methanol  $\frac{10}{11}$  and gasoline, in conjunction with exhibiting a higher volumetric energy density than that of liquid  $\frac{11}{12}$  H<sub>2</sub> [2]. Due to NH<sub>3</sub> prevalent use in the agricultural industry, considerable storage and distribution 13 **infrastructure is already established [2]**. Although NH<sub>3</sub> offers several advantages, there remains  $14$  several practical combustion challenges, notably the control and reduction of pollutant emissions 15 (NO<sub>x</sub> and N<sub>2</sub>O). Moreover, NH<sub>3</sub> exhibits slow burning velocities, often associated to low burning efficiency in engines, a narrow flammable range and high ignition energy, potentially yielding poor 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 18 19 MH<sub>3</sub>'s combustion properties, blending NH<sub>3</sub> with methane (CH<sub>4</sub>) (for a partial decarbonisation) or  $\frac{20}{21}$  H<sub>2</sub> (from the possible 'in situ' cracking of ammonia) has been proposed, and has gained  $\frac{21}{22}$  considerable recent attention, with comprehensive reviews of NH<sub>3</sub> related work undertaken [2], 23 [3]. Successful demonstrations in both gas turbines [4]–[6] and internal combustion engines [7],  $24$  [8] have been achieved at high temperatures and pressures. Nevertheless, studies remain limited,  $\frac{25}{26}$  as such there seems to be a practical necessity to develop and strengthen understanding of  $\frac{26}{27}$  fundamental combustion characteristics of blends containing NH<sub>3</sub>, ultimately leading to the development of combustors offering greater flame stability and reduced pollutant emissions. 28 2 **The historical prevalence o**  6  $12$   $H_2$ [2]. Due to NH<sub>3</sub> prevalent t  $17$  entriciency in engines, a narrov 22 **CONSIDERED CONSIDERED PLANES** 27 **IUNUAMENTAL COMPUSSION** CH

The unstretched laminar burning velocity (SL<sup>0</sup>), is one main fundamental <mark>physico-chemical</mark> property of any premixed air-fuel mixture, reflecting both the combustion process and mixture 31  $\frac{32}{2}$  reactivity. As such, S<sub>L</sub><sup>0</sup> is a key parameter helping understand premixed operational instabilities,  $\frac{33}{34}$  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, 35 in turn influencing witnessed burning and reactivity characteristics of the fuel mixture. The Lewis 36  $\frac{37}{20}$  number (Le), defined as the ratio of thermal to mass diffusivity of the deficient reactant, details <sup>38</sup><br>39 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 40 that preferential diffusion (i.e. Le deviating from unity), can strongly influence the burning rates of 41  $\frac{42}{12}$  stretched flames – which undergo the combined effects of strain, curvature, and flame motion. 43 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 45 46  $\leq$  1 show a relative acceleration with increasing stretch [9]. The burnt gas Markstein length (L<sub>b</sub>) is <sup>47</sup> a measurable parameter which characterises the influence of Le on the flame response to the 48 stretch rate. The Markstein number (Ma), defined as L<sub>b</sub> divided by the laminar flame thickness (δ<sub>L</sub>)  $\frac{1}{50}$  - is an indicator of the propensity of a combustion system to be or not influenced by thermoacoustic instability, and thus of interest to study [14]. 51 29 30 The unstretched laminar 34 39 **The transport inecritainship**  $44$  ratios with Le  $\geq$  1 exhibit go 49 Succernate. The Markstein in

53 Recent experimental studies have investigated  $S_L^0$  and  $L_b$  characteristics of NH<sub>3</sub>/air flames, notably by Hayakawa et al. [15], at atmospheric and 0.5 MPa of initial ambient pressure, and 54  $55$  Kanoshima et al. [16], expanded on that work to include the influence of initial ambient  $\frac{56}{57}$  temperature (400-500 K). Results from these studies underline that  $S_L^0$  peaks at an equivalence 58 ratio ( $\phi$ ) of  $\approx$  1.1, with an incr <sup>59</sup> in S<sub>L</sub><sup>0</sup>, respectively. With respect to L<sub>b</sub>, NH<sub>3</sub>/air flames display an increasing L<sub>b</sub> with increasing φ, a  $57$  cemperature (400-500 K). Re 60

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 1 **1** pressure conditions (T=298K, P=0.1MPa) lean NH<sub>3</sub> flames exhibit negative L<sub>b</sub>, with positive values <sup>2</sup> recorded under rich conditions. Furthermore,  $L_b$  is observed to decrease with a rise in pressure  $\frac{3}{4}$  and temperature, analogous behaviour to that of the flame thickness.  $4 \qquad \qquad \text{and complete due, analogous to}$ 

5 Okafor et al. [17], [18], investigated the influence of NH<sub>3</sub> on CH<sub>4</sub> based flames (up to  $\approx$  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 8 both 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 10<br>11 tendency but with a uniform decrease in the flame flammability limits with NH<sub>3</sub> increase. They also  $_{12}$  highlighted the important role played by the H and OH radicals in NH<sub>3</sub>/CH<sub>4</sub> flame propagation. In 13 relation to flame stretch sensitivity of CH<sub>4</sub>/NH<sub>3</sub> 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<sub>3</sub>  $\frac{15}{16}$  fraction. It should be noted that this is unusual for fuels displaying Le values close to 1 (as is the 17 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. 18  $6$  CRGIOI CCGI. [17], [10], inve 11 concerny but with a unionity  $16$  matrion. It should be noted t

Lee et al. [20], [21] and more recently, Ichikawa et al. [22] and Lhuillier et al. [23] investigated 20 21 the influence of  $H_2$  upon NH<sub>3</sub> based flames. Ichikawa et al., demonstrated that at stoichiometric 22 conditions (φ=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  $S_L^0$  upon addition of H<sub>2</sub> at increasing pressure. Lhuillier et al. reported an exponential increase in  $S_L^0$  upon addition of H<sub>2</sub> at 25 various initial conditions (298-473K,  $\phi$  = 0.8 – 1.4, H<sub>2</sub> = 60% vol. max). With respect to the flame  $26$  stretch sensitivity, Ichikawa et al.[22] reported a non-monotonic variation, with an initial 27 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 29 30  $\ldots$  in recorded L<sub>b</sub> of NH<sub>3</sub> flames upon H<sub>2</sub> enrichment. Noteworthily, similar stretch-related non-31 monotonic trends have been observed for lean  $CH_4/H_2$  flames [24]. 24 **Increasing pressure.** Lnumer 28 **Substantial decrease in L<sub>0</sub> w** 32

# 33 **Table 1: Summary of Literature Review**



# 35 **All references below employed the spherically expanding flame configuration**

 $57$  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 59 propagation, highlighted that preferential diffusional instabilities affect both weak and strong 60 58 The importance of name stre

turbulent combustion. The influence of Le on turbulent flames has been reported in the course of 1 experimental studies [26]–[28] as well as in direct numerical simulations [29], [30]. Although limited in <sup>2</sup> scale, emerging studies focusing on turbulence-flame interaction for NH<sub>3</sub> and its blends with either H<sub>2</sub>  $\frac{3}{4}$  and CH<sub>4</sub> underlined the potential role of preferential-diffusion and flame-stretch interaction upon  $_{5}$  turbulent flame characteristics. For example, Ichimura et al. [31] investigated NH<sub>3</sub>/air flames at various 6 turbulent intensities, underlining that although S<sub>L</sub><sup>0</sup> of NH<sub>3</sub>/air is greatest at  $\phi \approx 1.1$ , lean m  $\frac{7}{6}$  exhibited better resistance to turbulence induced extinction than richer conditions, due to the  $\frac{8}{9}$  potential thermo-diffusive accelerating effects of lean NH<sub>3</sub>/air mixtures, displaying Le < 1. Similarly, 10 Lhuillier et al. [8] investigated NH<sub>3</sub>/H<sub>2</sub> and NH<sub>3</sub>/CH<sub>4</sub> (15% vol. of H<sub>2</sub> or CH<sub>4</sub>) turbulent flame propagation under engine related operating conditions (445K, 0.54 MPa). They reported a decreasing and 11  $^{12}$  increasing turbulent to laminar flame speed ratio upon CH<sub>4</sub> and H<sub>2</sub> addition, respectively, induced by the different thermo-diffusive properties and stretch-related behaviour of these ammonia blends.  $\frac{4}{4}$  and Crit and Criming the potential  $9$  potential thermo-diffusive acceler 14 Che unterent thermo-unrusive pro

15 Clearly, although emerging, the experimental study on the addition of H<sub>2</sub> or CH<sub>4</sub> to NH<sub>3</sub>-based 17 flames remains scarce. Furthermore, recent turbulent combustion experiments underlined the 18 potential influence of preferential-diffusional instabilities upon NH<sub>3</sub>-based flames [8], [31], [32], hence, 19 the aim of this work is to investigate in detail the influence of Le change on flame behaviour. NH<sub>3</sub>/CH<sub>4</sub> 20 and NH<sub>3</sub>/H<sub>2</sub> mixtures were varied across a large range of blend composition and equivalence ratio, 21<br>22 **Example 22** representative of the prospective demands of fuel-flexible combustors widely employed for power 23 seneration. 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,  $24$  reactivity, mixture flame speed but changes the thermo-diffusive behaviour, which is studied in-detail  $\frac{25}{26}$  throughout this work.  $16$  Cicarry, annough chiciging, 22 representative of the prospective 26 consequent this work.

# 27 **2.** Experimental set-up and specifications 28 **Experimental set up and spa**

 $\frac{29}{20}$  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 32 equipped with four orthogonal 70 mm quartz viewing windows and has a nominal internal volume of 33  $\frac{34}{25}$  4.2 L. Thermal mass flow controllers (Brooks 5850S (± 1%)) were employed to introduce the reactants  $\frac{35}{36}$  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 37 thermocouple were employed to check respectively the pressure and temperature prior to ignition. 38  $\frac{39}{2}$  The maximum deviation between the effective initial pressure inside the chamber and the required <sup>40</sup> 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 42 compensated within the equivalence ratio calculation. Pre-mixing was achieved using an internal fan. 43  $44 \over 12$  A capacitor-discharge ignition was achieved via fine tungsten electrodes mounted at 90° to the As the measurement plane. After quiescence is attained, simultaneous TTL signal to the data-acquisition and and  $\frac{1}{47}$  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 48 <sup>49</sup> (3000 – 12000 fps), facilitating a spatial resolution of  $\sim$ 0.10 mm per pixel. Edge-detection algorithms 50<br>
F<sub>1</sub> Written in a bespoke MATLAB script were employed to calculate flame propagation rates. A minimum 51 with the abspace with the script were employed to calculate hame propage<br>
52 of 3 to 5 repeats were conducted per experimental condition.  $31$  Details of the apparatus and position 36 The Gessel More Hactions of 41 million pressure was no more than 46 measurement plane. After quiese 52 OF 3 to 5 repeats were conducted

# $53$  3. Experimental specifications and theory  $54$  **5.** Experimental specifications a

55 Measurements were performed at initial conditions of 298 K ( $\pm$  3 K) and 0.1 MPa ( $\pm$  1 x 10<sup>-3</sup> MPa), 57 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 58 (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-<sup>59</sup> related behaviour, molar ratios were varied form 0 – 100% for CH<sub>4</sub>; and 0 – 80% for H<sub>2</sub>, in incremental 56 Measurements were perform 60

steps across a wide range of equivalence ratios ( $\phi$ = 0.7 – 1.2 and 0.6 – 1.4 respectively), with Table 2 1 Summarising the experimental conditions.



3 **Table 2:** Experimental conditions ;  $T_u = 298$  K ( $\pm$  3 K),  $P_u = 0.1$  MPa ( $\pm$  1 x 10<sup>-3</sup> MPa).

Schlieren images were undertaken as in [17], [23], [34], with the shadowed edge considered 19 20 as the burnt gas isotherm, which as discussed by Giannakopoulos et al. [35], is critical for characterising  $\frac{21}{22}$  the influence of flame stretch. The laminar burning velocity and  $L_b$  relative to the burnt side were  $_{23}$  experimentally determined employing the same procedure as in previous studies [34], [36]. For an 24 outwardly spherically propagating flame, the stretched flame speed  $(S_b)$  is expressed as the temporal 25 derivative of the Schlieren flame radius ( $r_{\rm sch}$ ) as in Equation 1: 22 CHE HINDERE OF Harte Stretch.

$$
S_b = \frac{dr_{sch}}{dt} \tag{1}
$$

 $30$  The flame stretch rate (K) is defined as the change in flame area (A) gradient and calculated for a  $\frac{31}{20}$  propagating spherical flame as shown in Equation 2: 32 Propagating opherical name as shi

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

 $\frac{36}{37}$  Various correlations between S<sub>b</sub> and K have been proposed, allowing the estimation of the unstretched  $38$  flame speed ( $S_b^0$ ). Wu et Law [10], proposed a linear relationship, based upon the assumption the flame 39 **is weakly stretched and that thermal and mass diffusion are near equal (Le≈1) and suggest that the**  $\frac{40}{10}$  flame speed and K are related as per Equation 3:  $\frac{9}{27}$  and  $\frac{1}{2}$  concluding between  $\frac{9}{20}$  and  $\frac{1}{2}$ 41

$$
S_b = S_b^0 - L_b \cdot K \tag{3}
$$

 $^{44}_{12}$  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 details <sub>47</sub> **of infinite radius. It may also be noted that L<sub>b</sub> characterises the influence of stretch upon flame** 48 **The propagation, with the magnitude and sign of L<sub>b</sub> related to Le. This linear model has been the most** 49 **commonly employed for flame speed measurements using expanding spherical flames, however, as**  $\frac{50}{2}$  highlighted by Wu et al. [37], it is a first order correction of the stretch effect and hence some degree 52 **of uncertainty is 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). 53 46 **Excludion of the relationship to**  $51$   $\frac{108}{3}$   $\frac{108}{3}$ 

55 **The second model is attributed to Frankel and Sivashinsky [38], first proposed by Markstein** 56 **[39]**, is based upon the assumption of large flame radii. Frankel and Sivashinsky analysed spherically 57 expanding flames considering the effects of thermal expansion and Le, obtaining the following  $\frac{58}{58}$  relationship in Equation 4: 59 relationship in Equation 4.

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

5 **Equation 4 shows that the flame curvature (** $\kappa_{\text{curv}}$ **=2/r<sub>fsch</sub>) and S<sub>b</sub> vary linearly, hence allowing 5**  $\frac{6}{5}$  the evaluation of S<sub>b</sub><sup>0</sup> and L<sub>b</sub> from the linear extrapolation of S<sub>b</sub> and 2/r<sub>fsch</sub> [37], [40]. This method has  $\frac{7}{8}$  not received widespread use [19], [34], [40], and here is referenced as LMC (i.e. Linear Model based  $\mathcal{G}$  on Curvature). HULTELEIVED WRITERS USE [15],

 $\,$  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<sub>2</sub>-based flames. This non-linear model  $\frac{14}{15}$  is expressed as in Equation 5: The third extrapolation method, is expressed as in Equation s.

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

20 **A** quasi-steady nonlinear association between S<sub>b</sub> and K is employed – rearranged with the error used and the strong with the error used  $\frac{21}{22}$  for least squares regression – to obtain an extrapolated unstretched flame speed. This model has been  $\frac{22}{23}$  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). 23 used nequently over the last deca

Chen [40] and Wu et al. [37] underline that the accuracy of different extrapolation techniques **Frank is related to the Le of the fuel-air mixture. Chen [40] demonstrated that LMS is only suitable for fuel/air and the state of the state**  $^{28}$  mixtures that exhibit weak stretch and Le close to unity. Chen [40] showed that it is preferable to  $\frac{29}{30}$  employ LMC for mixtures exhibiting positive L<sub>b</sub> and NMS for negative L<sub>b</sub>, due to the non-linear **The Study of Tandal and South These recommendations adopted in this study.** Moreover, Wu et and the study of the s al. [37], quantified the uncertainty in extrapolation through the limitation of exploitable data range in <sup>33</sup> relation to Markstein and Karlovitz numbers (Ma<sub>lin</sub>Ka<sub>mid</sub>); all data presented in this work fall within the  $\frac{34}{35}$  recommended values of -0.05 – 0.15 range. 25 and <u>the second </u> **Chen [40] and Wu et al. [3 Employ Livic Tol Tinxtures exhibi** recommended values of  $-0.03 - 0$ 

 $\frac{36}{27}$  lrrespective 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 structure values of 39 equilibrium densities calculated using CHEMKIN-Pro, **employing the PREMIX software** and using Stagni employing <sup>40</sup> et al. [43] and Okafor et al. [18] kinetics reaction mechanisms, for NH<sub>3</sub>/H<sub>2</sub> and NH<sub>3</sub>/CH<sub>4</sub>, respectively.  $\frac{41}{42}$  The selection of these mechanisms is discussed later in section 5.2. **Iaminar flame speed, the burned** 42 The selection of these incentifiants



 $39$  rigure.  $1 - 30$  etched hanne speed  $_{40}$  NH<sub>3</sub>/H<sub>2</sub> (20/80 vol.%) (T<sub>u</sub> - 298 K, P - 0.1 MPa)

48 **bubar of the spark upon flame propagation. Preliminary investigation related to the influence of ignition** associated minimal variation in results derived from data above 7 mm. Consequently, for a series of the consequently of results of the consequently of  $\frac{1}{2000}$  and  $\frac{1}{2000}$  and  $\frac{1}{2000}$  and  $\frac{1}{2000}$  and  $\$ **Example 1.1** all data presented here, 8 mm was chosen as the minimum radius. To limit pressure effects a maximum effected of the spark propagation. Prefinement dring the chosen as the minimise the influence of the spark, **Pagine 25 mm was considered** (and sisted of 25 mm was considered, within the 30% of chamber radius as proposed by Burke et al. [45].<br> **Figure 1 – Stretched flame speed vs stretch rate (K)** and curvature ( $\kappa_{\text{CUW}}$ ) f 53 Extrapolation methods used to yield flame speed and the corresponding L<sub>b</sub> rely on a sufficiently large 54 stable quasi-steady flame propagation regime. In the present study, pure NH<sub>3</sub>/air flames, or blends containing less than 10% of CH4 or H2 (vol.%) at leanest and richest conditions were observed to be **Figure.** 1 - Stretched flame speed vs strench (**K**) [**A/s**] **Figure** 1 - Stretched flame speed vs strench rate (**K**) and curvature ( $k_{\text{Cum}}$ ) for (a) pure NH<sub>V</sub>air and (b) NH<sub>3</sub>/H<sub>3</sub> (20/80 vol.%) (T<sub>0</sub> - 298 K, P - 0. **Flame Stretch (K) [1/s]**<br> **Flame** Stretch rate (K) and curvature ( $K_{\text{CdW}}$ ) for (a) pure NH<sub>a</sub>/air and (b)<br>
NH<sub>a</sub>/H<sub>3</sub> (20/80 vol.%) (T<sub>u</sub>-298 K, P-0.1 MPa)<br>
Limits were set on the range of exploitable radii to minimi **Figure. 1** – Stretched flame speed vs stretch rate (K) and curvature ( $\kappa_{\text{QW}}$ ) for (a) pure NH<sub>3</sub>/air and (b) NH<sub>3</sub>/H<sub>1</sub> (20/80 vol.%) (T<sub>u</sub> – 298 K, P – 0.1 MPa)<br>Limits were set on the range of exploitable radii to **Figure.** 1 – Stretched flame speed vs stretch rate (K) and curvature ( $\kappa_{\text{GUP}}$ ) for (a) pure NH<sub>2</sub>/air and (b) NH<sub>2</sub>/H<sub>2</sub> (20/80 vol.<sup>3</sup>N<sub>1</sub> (T<sub>1</sub> – 298 K, P – 0.1 MPa)<br>
Limits were set on the range of exploitable ra 41 42 **Limits were set on the rang** 43 buoyancy or the cellularity, and the confinement during the flame growth, ensuring measurements 44 were restricted within the quasi-steady regime. Bradley et al. [44] suggest a spark affected radius up  $45$  to  $6 \text{ mm}$  for  $CH$  /pir flamos how  $46$  to b interior chapan hannes, now  $\frac{1}{47}$  dependent of Le. The capacitor-discharge ignition energy was varied in order to minimise the influence and the senargy 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 51 an data presented nere, o mini was 52 radius of 25 mm was considered,  $\frac{55}{10}$  containing less than 10% of CH<sub>4</sub> or H<sub>2</sub> (vol.%) at leanest and richest conditions were observed to be 56 Containing resources and sextence of eng.  $57$  reavily implemed by the buoyar 58 flames were observed to lose sphericity, morphing in an ellipsoidal expanding flame, as noted by 59 Hayakawa et al. [15] and Chen et al. [47] for identical initial conditions (298 K, 0.1 MPa). For such  $60$  flames the methodology proportional 61 manners, the methodology proport

ignition influenced, quasi-steady and buoyancy influenced propagation regimes was followed. The<br>aforementioned regimes are determined based upon the flame shape and propagation ratio, defined<br>as the vertical and horizonta aforementioned regimes are determined based upon the flame shape and propagation ratio, defined 1 as the vertical and horizontal radius of the flame ( $r_{sch,V}/r_{sch,H}$ ) and (d $r_{sch}/dt$ )t/(d $r_{sch}/dt$ )t-At (where drsch/dt  $\frac{3}{4}$  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<sub>3</sub>/air flame  $\phi$  ( $\phi$ =0.80); with the relationship of stretched flame speed with stretch and curvature superimposed. As  $\frac{7}{2}$  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  $\frac{1}{2}$  ( $\frac{1}{2}$  and  $\frac{1}{2}$ ) was taken to represent the maximum  $_{10}$  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 11 12 still maintained proportionality to both flame-stretch and curvature until the transition point was  $\frac{13}{14}$  attained. Under other conditions, minor modifications in useable flame radius selection were also 15 required due to known instability issues associated with lean combustion of H<sub>2</sub>-containing fuels. Lean H2-based flames are particularly unstable with regard to diffusive effects, a consequence of their low 16 17 Le (Le << 1), resulting in flame acceleration at low stretch and curvature rates [48], as illustrated in  $\frac{18}{10}$  Figure 1.b, with an example case of a lean NH<sub>3</sub>/H<sub>2</sub> (20/80 vol.%,  $\phi$ =0.6) flame. Under the tested  $_{20}$  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 21  $($   $\phi$ =0.60) for flames containing  $\geq$  40% H<sub>2</sub>, with further H<sub>2</sub> enrichment enhancing surface cracking, as 23 illustrated in Figure 2. As underlined by Jomaas et al. [49], these large-scale cracks are most probably  $_{25}$  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 26  $27$  minimum of 30 acquired radii was obtained even for the fastest flames, from which flame speed data  $\frac{28}{28}$  were estimated.  $4$  activiting the name propagation species 9 14 attained. Onder other condition. 19 right 1.b, with an example cas  $24$  must accumulgue 2. As under m 29 were estimated.



<sup>42</sup> **Figure 2** – Schlieren images illustrating the development of flame surface cracking as a function of H<sub>2</sub>  $\frac{43}{44}$  fraction for NH<sub>3</sub>/H<sub>2</sub> flames (T<sub>u</sub> – 298 K, P – 0.1 MPa,  $\phi$ =0.60)  $44$  mathom for this grid names (i.g.  $\overline{2}$ .

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 48 <sup>49</sup> a combination of the experimental facility specifications and accuracy of the processing techniques  $\frac{50}{2}$  employed. It should be noted that the uncertainty is quantified for the unstretched flame speed (S<sub>b</sub><sup>0</sup>),  $\mathbf{0}$ ), and not for  $S_L^0$ , since this is the parameter measured, here named as  $U_{S_L^0}$ . The total uncertainty and not for  $S_L^0$ , since this is the parameter measured, here named as  $U_{S_L^0}$ . The total uncertainty 53 estimate is given by Equation 6, where  $B_{S_v^0}$  represents the total bias uncertainty, t<sub>M-1.95</sub> the student's  $\frac{54}{55}$  value at 95% confidence interval and M-1 degrees of freedom,  $\sigma_{s0}$  the standard deviation of the repeated experiments, and M the number of experimental repeats at each condition; 56 47 reaction mechanisms [50]. There is  $52$  and not for  $5\ell$ , since this is the 55 value at 95% communice interval

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

4 The total bias uncertainty, given by Equation 7, relating changes in  $S_b^0$  with respect to an independent <sup>5</sup> influential variable, ( $v_i$ , i.e. temperature, ambient pressure,  $\phi$ , optical system, gas mixture quality) and  $\frac{6}{7}$  the fixed error linked to that variable,  $y_i$ , 7 CHE TIXED ETTOT ITTINED TO THE VATION

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

In order to determine  $B_{S_v^0}$  by Equation 7, the relationships between  $S_b^0$  and each independent variable <sup>15</sup> 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  $17$ 18 **18** modelling with CHEMKIN-PRO. Uncertainty resulting from the mixture preparation was estimated to 19 **be ± 0.01%,** that of the optical system was evaluated from the summated fractional error of both the  $\frac{20}{21}$  spatial resolution of the system (±0.05/25mm) and camera (± 1.5-7.5/3000-15000 fps). Losses due to  $\frac{21}{22}$  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 23 24 significant for slow propagating flames (< 12 cm s<sup>-1</sup>) [52]. Lhuillier et al. [23] investigated the  $^{25}$  dependence of errors resulting from radiation for NH<sub>3</sub>/air flames, concluding that the correlation 26 **b** proposed by Yu et al. [52] was applicable, with this recommendation applied for this study. For the 28 **Experimental results in this study, the greatest radiation-induced error (~23%) was related to leanest** 29 MH<sub>3</sub>/air flame measured ( $\phi$  = 0.80), indicating that the laminar flame speed was underestimated by  $\sim$  $\frac{30}{2}$  0.56 cm/s. Finally, error bars on all subsequent plots illustrating laminar flame speed measurements  $(S<sub>L</sub><sup>0</sup>)$  are derived from Equation 6 and 7, with the error for  $U<sub>c</sub><sub>0</sub>$  scaled with respect to the density ratio.  $_{14}$  In order to determine  $B_{S^0_B}$  by Equa  $17$  calculated as a function of  $\psi$ , such 22 raulation importe measured in  $27$  proposed by Tu et al. [52] was ap  $32$  (3) are derived from Equation of

# $\frac{33}{34}$  4. Evaluation of Fundamental Parameters  $34$  4. Evaluation of Fundamental P

35 (Chen and Ju [40], [45] and Matalon and Bechtold [53], have proposed theoretical relationships  $\frac{35}{16}$ 37 relating the Markstein length (L<sub>b</sub>) and Lewis Number (Le), requiring the evaluation of various  $38$  fundamental flame parameters. The Zel'dovich number, was evaluated using the expression Ze =  $(10^{-39})$  (E<sub>a</sub>/R<sub>u</sub>) · [(T<sub>ad</sub> - T<sub>u</sub>)/(T<sub>ad</sub><sup>2</sup>)] with R<sub>u</sub> the universal gas constant, T<sub>u</sub> and T<sub>ad</sub>, the temperature of the unburnt  $\frac{1}{41}$  mixture and the adiabatic flame temperature, respectively. The activation energy,  $E_a$ , is defined as the mixture 42 Slope of the mass burning flux (m<sup>0</sup>) and the inverse adiabatic flame temperature at constant  $\phi$  and <sup>43</sup> pressure, empirically determined using the expression  $E_a = -2R_u\{\partial [\ln(m^0)]/\partial [1/T_{ad}]\}$ , where the mass  $\frac{44}{15}$  burning flux can be replaced by m<sup>0</sup> = ( $\rho_u \cdot S_L^0$ ), as recommended by Egolfopoulos and Law [54]. It should be noted that this method is only valid for sufficiently off-stoichiometric conditions, with interpolation be noted that this method is only valid for sufficiently off-stoichiometric conditions, with interpolation 47 required for E<sub>a</sub> values for mixtures near stoichiometry [55]. For the flame thickness, two definitions <sup>48</sup> can be considered [9]. The first, commonly termed as the kinetic (or diffusion) flame thickness ( $\delta$ <sub>K</sub>), is  $\frac{49}{20}$  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  $\frac{1}{50}$  constant pressure. The second, referenced as the 'gradient' flame thickness ( $\delta_6$ ) can be expressed as  $\frac{1}{50}$ 52  $\delta_{\mathsf{G}} = (\mathsf{T}_{\mathsf{ad}} - \mathsf{T}_{\mathsf{u}}) / (d\mathsf{T}/d\mathsf{x})_{\mathsf{max}}.$  $36$  Chen and Ju [40], [45] and M 41 46 **De noted that this method is only**  $51$  constant pressure. The second, re

### 4.1 Relationships of Le and  $L_b$  $54$  4.1 Relationships of Le and L<sub>b</sub>

For the purpose of this work, the relationships relating Le to L<sub>b</sub>, proposed by Chen [40], [45] and Matalon and Bechtold [53] are considered. The first formulation based on spherically expanding 57  $58$  flames is derived from the analytical developments done by Chen and Ju, and then used by Bouvet et 59 al. [56], Lapalme et al. [57] and Zitouni et al. [34] in their studies on preferential-diffusion effects upon 55 56 **For the purpose of this w**  $60$  and  $[50]$ , Lapanne et al.  $[57]$  and  $2\pi$ 

multi-component fuels. It should be noted that the 'kinetic' flame thickness is consistent with the 1 approach detailed by Chen [40], [45]. This estimate of Le is referenced herein as Le<sub>CHEN</sub> and can be and can be  $\frac{2}{3}$  expressed per Equation 8:  $3 \times 10^{-4}$ 

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

With  $\sigma = \rho_b/\rho_u$ , the expansion ratio. From Equation 8, the retrieval of L<sub>b</sub> is possible as in Equation 9.  $_8$  With  $\sigma = \rho_b/\rho_u$ , the expansion rat

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

A second formulation by Bechtold and Matalon, was derived from theoretical analysis on the 14 dependence of  $L_b$  on stoichiometry. This formulation was considered by Jomaas et al. [49] in the case <sup>15</sup> of acetylene (C<sub>2</sub>H<sub>2</sub>), Lapalme et al. [57] for H<sub>2</sub>/CO and Zitouni et al. [34], for CH<sub>4</sub> blended with H<sub>2</sub> or  $\frac{16}{17}$  C<sub>3</sub>H<sub>8</sub>. Lapalme et al. [57], on their assessment of the method of calculating Le and comparison with  $_{18}\,$  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**  $\frac{21}{22}$  of Le is denoted in following as Le<sub>BM</sub>, and is expressed per Equation 10: **A second formulation by Be**  exits. **Expanse of all [57]**, on the **PHLE is denoted in following as Le** 

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

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

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

 $\frac{32}{2}$  where  $\gamma_1$  and  $\gamma_2$  are functions of the expansion ratio given in Equation 12: 

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

# $\frac{39}{40}$  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 <sup>43</sup> challenge arising from the fact that the diffusivity of each fuel must be considered. This is particularly  $^{44}_{45}$  applicable when the transport diffusion mechanisms are different as is the case for H<sub>2</sub>, NH<sub>3</sub> or any alkanes. Bouvet et al. [56] identified three 'effective' Le formulations. The first formulation is based 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 <sup>48</sup> of turbulent CH<sub>4</sub> – H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> flames. At low-turbulence, this formulation results in reasonable agreement  $\frac{49}{20}$  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<sub>V</sub>, and is expressed per Equation 13: dikalies. Bouvet et al. [50] luenting 51 burning rates significantly under p

$$
Le_V = \sum_{i=1}^{f} x_i \cdot Le_i \tag{13}
$$

 $\frac{t}{56}$  where x<sub>i</sub>, is the fuel volumetric or mol fraction of the species i. where  $\mathbf{x}_i$ , is the fuel volument of

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-

 4  $5 - 5$  $6\overline{6}$  7 8 and 2010 10 11 12 13 14 24 25 and 26 an 26 41 57 61 62 63 64

diffusive behaviour of mostly binary and tertiary blends of hydrocarbons and hydrogen [27], [60]. This 1 formulation is based upon the weighted average of the fuels' nondimensional heat release  $(q_i)$ ,  $\frac{2}{3}$  referenced in this work as Le<sub>H</sub>, and expressed as per Equation 14: 3

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

9 where **where** 

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

 $\frac{15}{16}$  with Q representing the overall heat of reaction, Y<sub>i</sub>, the mass fraction of species i. 16

The third one is related to the work conducted by Dinkelacker et al. [27] on lean H<sub>2</sub>/CH<sub>4</sub> flames. It is 18<br>
19 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 20 a volumetric-weighted average of the fuel diffusivities. This diffusion weighted formulation will be 21  $^{22}$  referenced in this work as Le<sub>D</sub>, and expressed per Equation 15: 19 assumed that if the hanne curvatu 23

$$
Le_D = \frac{D_T}{\sum_{I=1}^F x_i \cdot D_{ij}}\tag{15}
$$

 $\frac{27}{28}$  where D<sub>T</sub> is the mixture's thermal diffusivity and D<sub>ij</sub> are the binary mass diffusion coefficients. Several methods have been proposed to estimate the binary mass diffusion coefficients at moderate ambient 29 pressure (<10 bar), with empirical constants based upon experimental data [61]. The method of Wilke 30 as well as that of Hirschfelder, Bird and Spot, detailed in [61], is used in this study. Once the binary 31  $\frac{32}{22}$  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 35 compared to the surrounding  $N_2$  [9]. For that reason,  $D_{ij}$  is taken as the fuel, 'i', diffusing into  $N_2$  $36$  (denoted with the subscript j). This may hold true for hydrocarbons due to their high molar fuel-air  $\frac{37}{28}$  ratio, but not for fuels that have low molar fuel-air ratio such as H<sub>2</sub>, as underlined by Lapalme et al. Figure 1. Thus, as proposed by Wilke [62], the mixture-averaged coefficient of mass diffusion (D<sub>i,mix</sub>) into  $39$  [57]. Thus, as proposed by Wilke [62], the mixture-averaged coefficient of mass diffusion (D<sub>i,mix</sub>) into the mixture was employed as defined in Equation 16: 40 28 WHELE Det is the mixture stricting 33 comments for the community. 39 [57]. Thus, as proposed by wilke

(16) 42 43 44 45 46

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 49 method, the binary diffusion coefficients calculated in this work were compared with values generated 50  $^{51}$  employing the STANJAN transport calculator [63]. Differences were no greater than  $\pm 3\%$  for binary  $\frac{52}{52}$  blends containing CH<sub>4</sub>, NH<sub>3</sub>, O<sub>2</sub> and N<sub>2</sub>, and up to 10% in the presence of H<sub>2</sub>, in agreement with  $\frac{53}{54}$  expected deviations [61]. This would translate to a maximum difference of < 3% upon the theoretical 55 **Le for H<sub>2</sub> air/flames, and < 1% for blends containing CH<sub>4</sub> and NH<sub>3</sub>, and thus the derived coefficients are** 56 **deemed suitable for the purpose of this study.** 48 WHELE I IS THE HIGSS HOLLOTTER 54 expected deviations [61]. <mark>This wo</mark>

<sup>58</sup> **Irrespective of the Lewis Number formulation employed, the thermal diffusivity D<sub>T</sub> = λ / (ρ<sub>u</sub> -<br><sub>60</sub> <b>c<sub>p</sub>) has to be evaluated. The calculation of ρ<sub>u</sub> and c<sub>p</sub> (specific heat capacity at constant pressure) were** <sup>58</sup> Irrespective of the Lewis Number formulation employed, the thermal diffusivity D<sub>T</sub> = λ / ( $ρ<sub>u</sub>$ .  $60$  C<sub>p</sub>  $\mu$  as to be evaluated. The calcular contract C<sub>p</sub>  $\mu$  and C<sub>p</sub>  $\mu$ 

65

based on the ideal gas theory and are relatively straightforward. The evaluation of the thermal 1 conductivity for each individual species (λ<sub>i</sub>) was calculated based upon the Chung et al. [64] method conductivity for each individual species (λ<sub>i</sub>) was calculated based upon the Chung et al. [64] method and outlined by Poling et al. [61]. This calculation procedure uses a predictive method to estimate  $\lambda_{i}$ <br>
3 and requires only the critical temperature (T<sub>c</sub>), volume (V<sub>c</sub>) and pressure (P<sub>c</sub>) 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 λ**<sub>i</sub> < 6% [65]. For multi-component fuels, the  $\frac{7}{1}$  mixed average thermal conductivities ( $\lambda_{\text{mix}}$ ) were calculated using Mathur et al.'s [66] suggestion: 2 and outlined by Poling et al. [61]. This calculation procedure uses a predictive method to estimate  $\lambda_i$ ,  $\frac{4}{100}$  and requires only the children temp 8 and 2010 and 2011 and 2011 and 2012 and 2012

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

 $(17)$ 

 $\frac{14}{15}$  Where (x<sub>i</sub>) and ( $\lambda_i$ ) are the mole fraction and thermal conductivity of the 'i<sup>th</sup>' species, respectively. This  $\frac{15}{16}$  method has previously been employed by Bouvet et al. [56], in their study of Le for multi-component **The Lands Extercise Consumed Consure the validity and correct application of the methodologies employed to** <sup>18</sup> calculate the thermal diffusivity, evaluated vales were compared to values calculated using the  $\frac{19}{20}$  STANJAN transport calculator [63] for single and binary mixtures. Differences are less than  $\pm$  3%,  $\frac{20}{21}$  irrespective of the number of fuels composing the blend, thereby validating the robustness of the **The methodologies selected, and thus deemed suitable for the purpose of this work.** 16 <mark>method has previously been emp</mark> **Trespective of the number of Tu** 

**5.1 Pure Fuels** 



 **Figure 3** – Comparison of (a) laminar burning velocity, (b) Adiabatic flame temperature and (c)  $^{58}_{59}$  Zel'dovich number as a function of equivalence ratio for pure NH<sub>3</sub>, CH<sub>4</sub>, and H<sub>2</sub>/air flames at 298 K & 0.1 MPa. S<sub>L</sub><sup>0</sup> data for H<sub>2</sub>/air flames from [67]. **Let do view hannel as a failed** of the

The measured  $S_L^0$  for the pure NH<sub>3</sub>, CH<sub>4</sub> and H<sub>2</sub> /air flames are compared in Figure 3.a. NH<sub>3</sub>/air for the pure NH<sub>3</sub>, CH<sub>4</sub> and H<sub>2</sub> /air flames are compared in Figure 3.a. NH<sub>3</sub>/air<br>st flame propagation rates, five to six times slower than those of CH<sub>4</sub>/air<br>ference in flame speed magnitude between H<sub>2</sub>/air and CH<sub>4</sub> 1 flames display the slowest flame propagation rates, five to six times slower than those of CH<sub>4</sub>/air  $\frac{2}{3}$  flames; with a similar difference in flame speed magnitude between H<sub>2</sub>/air and CH<sub>4</sub>/air flames at  $\frac{3}{4}$  stoichiometric conditions. It should be noted that the thermal diffusivity of these fuels decreases in the order of H<sub>2</sub>, CH<sub>4</sub> and NH<sub>3</sub>, analogous to the decreasing  $S<sub>L</sub><sup>0</sup>$  values. Comparison of the measured the order of H<sub>2</sub>, CH<sub>4</sub> and NH<sub>3</sub>, analogous to the decreasing  $S<sub>L</sub><sup>0</sup>$  values. Comparison of the 6 **bure fuel flame speeds for CH<sub>4</sub>/air and NH<sub>3</sub>/air with other peer-reviewed datasets [17], [68]–[73],**  $\overline{a}$  $\frac{7}{2}$  alongside values attained numerically, are located in the supplementary materials (SM). With respect  $\frac{8}{10}$  to CH<sub>4</sub>/air (SM.1), excellent agreement is displayed with selected literature [17], [68], [69], particularly with datasets from [17], [68], both employing the NM(S), with the Okafor et al. [18] reaction with datasets from [17], [68], both employing the NM(S), with the Okafor et al. [18] reaction 11 **In the mechanism exhibiting excellent agreement with measured results in this study. With respect to NH<sub>3</sub>/air** <sup>12</sup> (SM.2), measurements of S<sub>L</sub><sup>0</sup> remain limited. Good agreement is observed with Hayakawa et al. [15] 13 and Lhuillier et al. [23], who both employed the spherically expanding flame method. Very good agreement is also observed with the dataset of Han et al. [71], who employed the Heat Flux Method. 16 **However, overall relatively large scatter is observable between the various datasets, with relative** 17 differences close to ~30% and 25% under rich ( $\phi$ =1.2) and lean conditions ( $\phi$ =0.9). These differences  $\frac{18}{10}$  may potentially be attributable in part to the different experimental methods employed, as well as the fact that not all the datasets compared have taken into account losses due to radiation, with radiation-<br>20 21 **induced uncertainty particularly significant for slow propagating flames (< 12 cm s<sup>-1</sup>) [52]. With respect** <sup>22</sup> to the appraised reaction mechanisms, all reaction mechanisms greatly over-predict NH<sub>3</sub>/air S<sub>L</sub><sup>0</sup> at 23 **Leanest conditions (** $\phi$ **=0.8) and under rich conditions (** $\phi$ **>1.1). Overall, good agreement is observed only and the system of the sy**  $\frac{24}{\text{at } \phi=0.9-1.0 \text{ with Okafor et al. [18] and Stagni et al. [43] reaction mechanisms, with best agreement}$ overall with Okafor et al. [18]. 26  $5$  the order of H<sub>2</sub>, CH<sub>4</sub> and NH<sub>3</sub>, ana 10 15 **agreement is also observed with** 20 <mark>Tact that not all the datasets comp</mark> 25 **at 0=0.9 – 1.0 with Okafor et al. [1** 27

28 The adiabatic flame temperature and activation energy (represented by Ze) with respect to  $\phi$  $^{29}$  for the aforementioned pure fuels is illustrated in Figure 3 (b) and (c), respectively. For CH<sub>4</sub> (and in  $\frac{30}{21}$  general C<sub>1-4</sub> alkanes), S<sub>L</sub><sup>0</sup> and T<sub>ad</sub> peak at conditions slightly richer than stoichiometric conditions  $\frac{1}{32}$  ( $\phi$ ~1.05 – 1.10), underlining the sensitivity of the flame propagation to the flame temperature. The 33 fact that the minimum activation energy is located at similar conditions ( $\phi \sim 0.9$ ), underlines the  $\frac{34}{25}$  dictating influence of the flame temperature on the global activation energy. Due to flames temperatures peaking at around stoichiometric conditions, temperature-sensitive branching reactions demperatures peaking at around stoichiometric conditions, temperature-sensitive branching reactions are facilitated, thereby leading to overall faster reactions and reduced global activation energies, as 37 38 highlighted by Jomaas et al. [49]. With respect to H<sub>2</sub>, a similar trend in Ze is observed when plotted 39 upon a much larger range of  $\phi$  than that illustrated in Figure 3 (c). Viewed across the total flammability range of H<sub>2</sub> a similar parabolic relationship analogous to that exhibited by CH<sub>4</sub> and NH<sub>3</sub> is apparent. 42 Although H<sub>2</sub> flame temperature peaks at similar conditions to that of CH<sub>4</sub> ( $\phi$ ~1.1 – 1.2), both the 43 maximum flame speed and minimum values of Ze are located at much richer conditions (S<sub>L</sub><sup>0</sup>,<sub>max</sub> for  $\phi$ <sup>44</sup>  $~1.6$ -1.8 [74], Ze<sub>,min</sub> for  $\phi$  ~1.4 – 1.6). This shift in the flame speed to richer conditions (and by extension the reduced influence of flame temperature on  $S<sub>L</sub>^0$  has been attributed to the much larger value of the reduced influence of flame temperature on  $S<sub>L</sub>^0$  has been attributed to the much larger value of 47 the Lewis Number (Le  $\gg$  1 for  $\phi$  >1.6), with flame acceleration, a consequence of preferential diffusion [49]. As a result, the minimum Ze witnesses a corresponding shift to richer conditions, since Ze is 48 directly extracted from the flame speed (see Section 4). Thus, a transport mechanism (i.e. the thermodiffusive response of the fuel for Le >> 1) generates a change in response in the flame speed, which diffusive response of the fuel for Le >> 1) generates a change in response in the flame speed, which subsequently impacts the flame property, highlighting the influence of transport on a supposedly 52 chemical property [49]. This is of importance when attempting to understand behaviour of fuel blends 53  $^{54}$  which possess different transport properties (as it is the case here with H<sub>2</sub>, CH<sub>4</sub> and NH<sub>3</sub>) and the subsequent consequence on flame behaviour. On the other hand, for  $NH_3$ ,  $S_L^0$  and  $T_{ad}$  peak at subsequent consequence on flame behaviour. On the other hand, for  $NH_3$ ,  $S_L^0$  and  $T_{ad}$  peak at 57 approximately at the same equivalence ratio ranges ( $\phi \sim 1.0 - 1.10$ ). The fact that the maximum flame 58 speed, adiabatic flame temperature and minimum Ze all arise at nominally identical  $\phi$  conditions  $31$  Beneral C<sub>1-4</sub> and C<sub>3</sub>,  $5$ <sub>1</sub> and  $1$ <sub>3</sub>  $36$  competatores peaking at around  $36$  $41$  ange of its a similar parabolic re  $46$  and the reduced implement of matrix  $46$  $51$  all and  $51$  and 56 **Subsequent consequence on ha** 59

underlines the equi-diffusive nature of NH<sub>3</sub>, with Le close to unity, comparable to the preferential-1 diffusional properties of pure CH<sub>4</sub>.

 In premixed flames, instabilities can result from both preferential-diffusional and <sup>4</sup> hydrodynamic (Darrieus-Landeau) instabilities. It should be highlighted that the Marsktein length (L<sub>b</sub>) indicates the response of the flame to the stretch, it is also an indicator of the flame's propensity to  $\frac{1}{7}$  instability and not the cause of the instability<mark>. Figure 4 presents measured L<sub>b</sub> from the present study</mark> **8** as well as some other measurements available in literature, at similar initial temperature (±5 K) and **but a** <sup>9</sup> pressure conditions, for NH<sub>3</sub> [15], [70], CH<sub>4</sub> [17], [68], [75] and H<sub>2</sub> [60], [67] flames from lean to rich prich  $\frac{10}{11}$  conditions. To facilitate fair comparison, it is also indicated in the legend what methodology was used  $\frac{11}{12}$  to extrapolate L<sub>b</sub> (Linear or Non-Linear Model by Stretch (LMS) or (NMS); Linear Model based on 13 Curvature, (LMC)). First, it should be noted that there exist very limited experimental L<sub>b</sub> datasets for 14 **NH<sub>3</sub>.** At first there appears to be relatively large scatter between the various datasets, particularly for  $^{15}_{16}$  MH<sub>3</sub> and rich CH<sub>4</sub> flames. However, good agreement is observed between datasets when the same or  $\frac{16}{17}$  a similar extrapolation method are compared, irrespective of the fuel evaluated. For example, good 18 **agreement is observed between our measured L<sub>b</sub> values for NH<sub>3</sub> and CH<sub>4</sub> when employing LM(S) and 18 and** <sup>19</sup> those of Hayakawa et al. [15] and Gu et al. [17] respectively, who also employed LM(S). Similarly, when the state of the line of the line factor than the state of th  $^{20}_{21}$  employing LM(C) and comparing results to research groups that employed NM(S), excellent agreement  $\frac{21}{22}$  is also observed, irrespective of the fuel, with results from both extrapolation models expected to be **Similar, as highlighted by Chen [40]. The above highlights the influence that the extrapolation models** 24 **have on the Markstein Length. All three fuels exhibit an increasing L<sub>b</sub> as a function of**  $\phi$  **increase from**  $\alpha$  $^{25}$  lean to rich conditions with the greatest change exhibited by NH<sub>3</sub>, with negative value of L<sub>b</sub> under lean  $\frac{26}{27}$  conditions (comparable to that of H<sub>2</sub>), and larger positive value than that of CH<sub>4</sub> and H<sub>2</sub> under rich conditions. **to extrapolate L<sub>b</sub> (Linear or Non** 17 - <mark>a similar extrapolation method a</mark> **IS also observed, in espective of t** 27 Conditions (comparable to that c



 **Figure 4 –** Experimental values of L<sub>b</sub> for 36 by the NH<sub>3</sub>, CH<sub>4</sub>, H<sub>2</sub> as a function of  $\phi$  (298 K, tor N  $\frac{38}{38}$  0.1MPa). parcinity only its analogue



Figure 5 - Theoretical and experimental Le for NH<sub>3</sub>, CH<sub>4</sub>, H<sub>2</sub> as a function of  $\phi$  (data for  $H<sub>2</sub>$  [67]). Full and dotted lines respectively reflect Hirschfelder and Wilke methods to evaluate D<sub>ij</sub> (298 K, 0.1MPa)

 $\frac{42}{43}$  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. Lewis numbers, estimated using the free-stream properties of the mixtures, are illustrated as colour  $\frac{46}{17}$  bands with the upper and lower limits (represented by full and dashed lines) denoting the differences  $\frac{47}{48}$  between either the Hirschfelder or Wilke method to evaluate the mass diffusion coefficient. While the 49 correct Le is evaluated (Le  $\sim$  1 for NH<sub>3</sub> and CH<sub>4</sub>; Le << 1 at  $\phi$  < 1 and Le >> 1 at  $\phi$  > 1 for H<sub>2</sub>), little variation 50 is observable across the considered  $\phi$ , aside from the transition from lean to rich conditions.  $\frac{51}{52}$  Furthermore, it should be highlighted that minimum Le for NH<sub>3</sub> is just prior to stoichiometric conditions  $\frac{52}{53}$  in agreement with [15], whilst for CH<sub>4</sub> and H<sub>2</sub>, minimum Le is obtained at leanest conditions. Since Le fundamental flame parameters such as the flame thickness, the activation energy and the expansion  $^{56}$  ratio [53] were not considered. As such, Le can be evaluated from the experimental L<sub>b</sub> and these other  $\frac{57}{58}$  properties affecting the flame, as recommended by Jomaas et al. [49], with the use of theoretical 59 relationships established in literature (denoted as Le<sub>cHEN</sub> and Le<sub>BM</sub>, Eqn. 8 and 10, accordingly). 60 Therefore, as it can be seen when comparing Figure 4 and 5, analogous L<sub>b</sub> and Le evolution as a function  $\frac{1}{2}$ **10 Detter understand track** 48 Detween either the Hirschielder of in agreement with [15], whilst for 54 was simply evaluated as a function of the mixture's thermal and mass diffusivity, variations in properties affecting the name, a 

of the fuel and the equivalence ratio is observable, regardless of the theoretical relationship relating 1 L<sub>b</sub> to Le. However, it is interesting to note that the greatest change in L<sub>b</sub> magnitude is observed for NH<sub>3</sub>,<br><sup>2</sup> whilst exhibiting least change in Le, as noted by [8], potentially alluding that Le may not be the mai  $\frac{3}{4}$  driving factor behind the measured changes in stretch sensitivity for NH<sub>3</sub>-based flames. Furthermore, the transition from a negative to positive L<sub>b</sub> for NH<sub>3</sub> obtained for  $\phi \sim 0.8 - 1.0$  is at comparable  $\phi$  with 6 the transition from Le < 1 to Le > 1 occurred. whilst exhibiting least change in Le, as noted by [8], potentially alluding that Le may not be the main arriving ractor behind the measured

**19 In order to assess how well the considered formulations captured Le behaviour the lean and 8 August 20 Inconst**  $\frac{9}{10}$  inch limits of Le for each fuel was evaluated. The Le limits bound the minimum (lean) and maximum  $\frac{10}{11}$  (rich) plausible Le values for ultra-lean and ultra-rich mixtures. To estimate those limits the upper and  $\frac{11}{12}$  lower flammability limits of the fuels were utilised. With respect to CH<sub>4</sub>, lean and rich limits were **Evaluated to be 0.93 and 1.07, respectively, marginally smaller than those reported previously, namely** entry 0.955 [27] and 1.10 [57], underlining the equi-diffusive nature of CH<sub>4</sub>. As can be seen from Figure 5,  $\frac{15}{16}$  Le<sub>CHEN</sub> 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<sub>2</sub>, Le lean and rich limits were estimated to be 0.34 by Lapalme et al. [57] and Zitouni et al. [34]. For H<sub>2</sub>, 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 18 and 2.02, respectively. On the lean side, this is in good agreement with literature, 0.29 [57], whilst on** <sup>19</sup> **the rich side, Le limits evaluated in this work (2.02) are smaller than other reported values, 2.32 [76] the state of**  $\frac{20}{21}$  and 2.58 [57], potentially due to the underestimation of the H<sub>2</sub> binary mass diffusion coefficients, as 21<br>22 **underlined previously (Section 4.2). Nevertheless, good agreement is attained by all formulations for** 23 **H<sub>2</sub>. With respect to NH<sub>3</sub>, with lean and rich limits of 0.89 and 1.08, respectively, similar in scale to those** 24 **19 of CH<sub>4</sub>. Although no sources were found to compare the Le limits of NH<sub>3</sub>, Hayakawa et al. [15] evaluated**  $\frac{25}{26}$  an Le of 0.95 and 1.09, for NH<sub>3</sub>/air mixtures under lean ( $\Phi$  = 0.7)  $\frac{26}{27}$  respectively (flammability limits of NH<sub>3</sub>;  $\Phi_{min} \sim 0.63$  and  $\Phi_{max} \sim 1.4$ ). Overall, Le<sub>CHEN</sub> best captures 28 **expected thermo-diffusive behaviour of NH<sub>3</sub>. TOWER TRANSPORT OF THE SET OF THE SET OF THE by Lapaime et al. [57] and Zitoun underlined previously (Section 4. Expectively (Hammability limits** 

# 29<br>30 **5.2 Binary Fuel Mixtures**

 $\frac{32}{20}$  The influence of increasing fraction of either CH<sub>4</sub> or H<sub>2</sub> on NH<sub>3</sub>/air S<sub>L</sub><sup>0</sup>, across a wide range of  $\frac{33}{34}$   $\Phi$  is depicted in Figure 6 and 7 respectively, alongside values attained numerically. With respect to NH3/H2 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  $^{37}$  consistently gave best agreement with all NH<sub>3</sub>/H<sub>2</sub> blends evaluated in this study. Similarly, with respect  $\frac{38}{30}$  to NH<sub>3</sub>/CH<sub>4</sub> blends, only the Okafor et al. [18] is depicted since it consistently yielded best agreement with the evaluated blends.  $\vee$  is depicted in Figure 0 and 7 is to  $\frac{1}{10}$  only the oral of  $\frac{3}{10}$ 



**Figure 6** –  $S_L^0$  for binary NH<sub>3</sub>/CH<sub>4</sub> mixtures,<br>
comparison with simulated values with<br>
Okafor et al. kinetics model [18] (298 K,<br>
0.1MPa)<br>
As can be seen in Figure 6, irrespective of the  $\Phi$ , a fairly linear increa **Figure 6** – S<sub>L</sub><sup>0</sup> for binary NH<sub>3</sub>/CH<sub>4</sub> mixtures, **Figure 7** – S<sub>L</sub><sup>0</sup> comparison with simulated values with  $\frac{24}{25}$  Okafor et al. kinetics model [18] (298 K, Stagr  $\frac{25}{26}$  0.1MPa) 22 **Figure 6 – S**<sub>L</sub><sup>o</sup> for binary NH<sub>3</sub>  $0.1$   $u_1$ 

**Figure 7 –**  $S_L^0$  for binary NH<sub>3</sub>/H<sub>2</sub> mixtures, comparison with simulated values with Stagni et al. kinetics mechanism [42] (298 K, 0.1MPa)

29 observable upon CH<sub>4</sub> 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 H<sub>2</sub> addition results 32 in an exponential increase in S<sub>L</sub><sup>0</sup> of NH<sub>3</sub> based flames, across the entire tested  $\phi$  range. The Stagni et al. [43] mechanism best captured this exponential increase in flame speed, showing excellent  $\frac{34}{35}$  agreement with experimental values from this study, across all tested conditions. It is worth  $_{36}$  highlighting that  $\sim$  10-20% addition (vol.%) of either CH<sub>4</sub> or H<sub>2</sub> results in a similar increase in NH<sub>3</sub> flame speed, with further increases resulting in very different flame speed behaviour. This increased <sup>38</sup> reactivity of NH<sub>3</sub> based blends upon CH<sub>4</sub> and H<sub>2</sub> addition has been previously suitably reported [19] [80], with modelling work and sensitivity analysis suggesting that the flame speed, burning intensity <sup>28</sup> As can be seen in Figure 6, irrespective of the  $\Phi$ , a fairly linear increase in NH<sub>3</sub> flame speed is coscivable applied at addition, we agreement with experimental v [boj, with modelling work and set  $\frac{1}{41}$  (Q') and production of radicals, particularly O and H appear to be strongly correlated.

 $\frac{42}{43}$  To investigate the stretch-related behaviour of NH<sub>3</sub>/CH<sub>4</sub> and NH<sub>3</sub>/H<sub>2</sub> flames, L<sub>b</sub> is plotted as a 44 function of either CH<sub>4</sub> or H<sub>2</sub> addition to NH<sub>3</sub> across a wide range of  $\phi$  in Figure 8 and 9, respectively. A<sup>5</sup> Note that the evolutions of L<sub>b</sub> as a function of  $\phi$  are in SM3 and 4. For a  $\phi \ge 0.9$ , a linear decrease in L<sub>b</sub> <sup>46</sup> is observed with increasing CH<sub>4</sub> fraction. At  $\phi$  = 0.80, a negative value L<sub>b</sub> is obtained for pure ammonia  $_{48}$  while 10% CH<sub>4</sub> addition results in L<sub>b</sub> sign inversion (from negative to positive). As pure NH<sub>3</sub>/air mixtures 49 could not be ignited for  $\phi$  < 0.8, with this experimental apparatus, this tendency cannot be verified. 50 Under rich conditions ( $\phi \ge 1.1$ ), a decreasing stretch sensitivity is measured upon increasing H<sub>2</sub> fraction,  $\frac{51}{52}$  similar in trend and magnitude to that observed for NH<sub>3</sub>/CH<sub>4</sub> flames but for  $\phi \ge 0.9$ . Howe 53 interestingly for  $\phi \le 1.0$ , an initial decrease in L<sub>b</sub> 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 L<sub>b</sub>, 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  $NH_3/H_2$  flames, at  $\phi = 1.0$  and ostensibly identical by Lhuillier [70] as well as by Ichikawa et al. [22], for  $NH_3/H_2$  flames, at  $\phi = 1.0$  and ostensibly ident 58 experimental conditions ( $T_u$  = 298 K, P<sub>u</sub> = 0.1 MPa), also plotted in Figure 9 for comparison purposes. 59 As such, under lean conditions, NH<sub>3</sub>/H<sub>2</sub> mixtures exhibit a greater negative L<sub>b</sub> than that of pure H<sub>2</sub> **10 Investigate the stretch SUBSERVEY WILL THE EASING CHAIR Similar in trend and magnitude**  by Lhuillier [70] as well as by ichire 

flames. It should be highlighted that similar non-linear  $L<sub>b</sub>$  behaviour was measured by Okafor et al. [24] 1 for CH<sub>4</sub>/H<sub>2</sub> flames, with an inflection point occurring upon  $\sim$  70% H<sub>2</sub> addition. Similarly, Huang et al.  $\frac{2}{3}$  [81] also reported similar behaviour for natural gas – hydrogen – air blends. As such, it may seem that this maybe a phenomenon attributable to the H<sub>2</sub> contribution, at least for NH<sub>3</sub> or CH<sub>4</sub> based flames,  $_5$  due to the strong and fast diffusivity of  $H_2$  in the reactants. This stretch-sensitivity behaviour is of importance since the flames exhibiting negative  $L_b$  will be accelerated in highly stretched turbulent <sup>7</sup> environments, whilst flames displaying a positive L<sub>b</sub> will be weakened. This stretch-sensitivity response  $\frac{8}{9}$  inevitably impacts the operation of practical combustion systems.  $\frac{4}{4}$  and  $\frac{4}{4}$  a prendiction attributed and  $\frac{4}{4}$ 



 $\,$  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 <sup>49</sup> the diffusive pathway, the most suitable Le formulation has to be considered. As such, the different  $^{50}_{51}$  Le<sub>eff</sub> models (i.e. Le<sub>V</sub>, Le<sub>H</sub>, Le<sub>D</sub> from Equations 12, 13 and 14 respectively) are used to yield to an  $\frac{1}{2}$  estimate of L<sub>b</sub>, by using the relationships proposed by Chen or Matalon and Bechtold, referred as L<sub>b</sub>-53 Chen and L<sub>b</sub>-BM, respectively. It should be noted that the purpose of such analysis is more qualitative <sup>54</sup> than quantitative to validate which Le<sub>eff</sub> model best captures the measured L<sub>b</sub> behaviour of the tested  $\frac{55}{25}$  blends. **For a better understanding of thi**  estimate of  $L_b$ , by using the relation **Sterness** 



43 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 – Comparisor** 

51 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-Richieft and conditions, and Le-Richief and conditions, and Hersen conditions, an  $\frac{54}{55}$  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], **Example 12**<br> **as that lead CH4/H2** appear to display similar non-linear stretch behaviour [24] to that the flames leading edge is predicted. This concept appears to be valid under lean conditions, since H<sub>2</sub> and Sea Lead A<br>
Negra is a better agreement of L<sub>3</sub>-CHEN and L<sub>3</sub>-BM estimates to the measured L<sub>5</sub> for NH<sub>3</sub>/H<sub>3</sub><br>
Figure 10 – Comparison of L<sub>3</sub>-CHEN and L<sub>3</sub>-BM estimates to the measured L<sub>5</sub> for NH<sub>3</sub>/H<sub>3</sub><br>
figure 10 – Comparison that the flame curvature is dominant, hence the local enrichment of the most diffusive fuel at the  $\frac{59}{60}$  flames leading edge is predicted. This concept appears to be valid under lean conditions, since H<sub>2</sub> and 46 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), 48 quantitative and qualitative agreements are observed with Le<sub>p</sub> formulation, with the non-linear stretch 49 Maintenance and gaantative agree  $_{50}$  behaviour well captured. Under H  $\frac{53}{2}$  stretch behaviour under lean conditions, and Le<sub>H</sub> exhibiting better agreement at richer conditions. 55 **CONSIDERING CORPORATION** CONSIDERING CONTENTS OF LEG<sub>D</sub> MODEL W 56 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 and the reading edge is predicted.

NH<sub>3</sub> have higher mass diffusivities than O<sub>2</sub>. For richer conditions ( $\phi \ge 1.0$ ), 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> NH<sub>3</sub> 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<sub>3</sub>/CH<sub>4</sub> flames, meas  $\frac{3}{4}$  since NH<sub>3</sub> and CH<sub>4</sub> display very similar preferential-diffusional behaviour (Le ~ 0.9 – 1.1), the application 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, measu Figure 10.d. For the conditions greater than stoichiometry, a good quantitative and qualitative NH<sub>3</sub> 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<sub>3</sub> (Filames, measured  $\frac{8}{9}$  allow to verify the change from negative to positive L<sub>b</sub> measured experimentally obtained upon 10% NH<sub>3</sub> have higher mass diffusivities than O<sub>2</sub>. For richer conditions ( $\delta \geq 1.0$ ), 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> diames, measu Le<sub>D</sub> and Le<sub>H</sub> formulation respectively, best captured changes in thermo-diffusive behaviour. With 12 respect to NH<sub>3</sub>/CH<sub>4</sub> flames, Le<sub>V</sub> demonstrated the best agreement for all considered  $\phi$ , with these 13<br>
conclusions maintained for the remainder of the analysis. <sup>2</sup> flames, measured L<sub>b</sub> and L<sub>b</sub>-CHEN are compared in Figure 10.d for  $\phi$  = 0.8 – 1.2. It should be noted that SINCE IVE and CF4 display very similar 5 of either Le<sub>eff</sub> models results in very similar values. Consequently, only the Le<sub>v</sub> model is plotted on  $\frac{1}{2}$  agreement is observed with the CHEN model, but under lean conditions, the CHEN model does not allow to verify the change from the 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 conclusions maintained for the re



As emphasised by Kwon et al. [82] and reviewed in [83], the fundamental parameters that<br>hydrodynamic and diffusional-thermal instabilities are the thermal expansion, the flame<br>is, the non-unity Le and the global activation induce hydrodynamic and diffusional-thermal instabilities are the thermal expansion, the flame <sup>2</sup> thickness, the non-unity Le and the global activation energy (or equivalently Ze). Consistent with the  $\frac{3}{4}$  hydrodynamic theory of Darrieus and Landau [9], the hydrodynamic instabilities arise from the thermal expansion of gases, with the density jump across the flame front proportional to the growth rate of hydrodynamic instability. In the case of an outwardly propagating spherical flame, the flame tends to  $\frac{7}{1}$  be stabilised due to curvature induced positive stretch, consequently the flame thickness plays a  $\frac{8}{\circ}$  significant role, since the thinner the flame the weaker the influence of curvature. Hence the risk of destabilisation is enhanced for thinner flames. It is interesting to note that addition of either CH<sub>4</sub> or H<sub>2</sub> destabilisation is enhanced for thinner flames. It is interesting to note that addition of either CH<sub>4</sub> or H<sub></sub> 11 to NH<sub>3</sub> does not really affect the thermal expansion, irrespective of  $\phi$ , as shown in Figure 11. On the 12 other hand, the flame thickness decreases strongly with increasing CH<sub>4</sub> or H<sub>2</sub> fractions, in effect 13 promoting hydrodynamic instabilities to a similar extent. Nevertheless, the addition of either CH<sub>4</sub> or  $_{15}$  H<sub>2</sub> to NH<sub>3</sub> results in similar stretch-related behaviour under rich conditions, whilst exhibiting very different stretch-behaviour as conditions get leaner. The development of preferential-diffusional <sup>17</sup> instabilities, characterised by Le, is the result of non-equi-diffusion. With respect to the NH<sub>3</sub>/H<sub>2</sub> flames,  $\frac{18}{10}$  the effects of preferential diffusion are a consequence of the higher mass diffusivity of H<sub>2</sub> and NH<sub>3</sub>  $\frac{19}{20}$  compared to the O<sub>2</sub> molecule. As illustrated in Figure 12, Le decreases significantly with increasing H<sub>2</sub> 21 fraction thereby promoting diffusional-thermal instabilities at  $\phi = 0.8$ . Furthermore, as could be expected, the change in Le increases as the conditions get le 23 individual Le response. As underlined by Kwon et al. [82], considering that the development of  $\frac{1}{25}$  preferential diffusional instabilities requires a modification of the flame front, it is thus reasonable to expect the global activation energy should also affect the development of diffusional-thermal 27 **instabilities. Accordingly, a lower E**<sub>a</sub> (illustrated as Ze in Figure 12) will tend to enhance instability of a 28 diffusionally unstable flame such as lean NH<sub>3</sub>/H<sub>2</sub> flame, with both Le and Ze decreasing with increasing  $\frac{29}{30}$  H<sub>2</sub> concentration for all  $\phi$ . The decrease in Ze is largely due to a decrease in the inner-layer temperature 31 coupled with an increase in adiabatic flame temperature with increasing  $H_2$  concentration for  $\phi$ . For NH<sub>3</sub>/H<sub>2</sub>, the changes in measured L<sub>b</sub> are thus potentially the result of competing hydrodynamic and thermo-diffusive instabilities, with the influence of the thermo-diffusional instabilities reducing as the thermo-diffusional instabilities reducing as the  $35 \qquad \phi$  increases. On the other hand, for NH<sub>3</sub>/CH<sub>4</sub> flames, the addition of CH<sub>4</sub> to NH<sub>3</sub> results in little 36 diffusional-thermal effects (Le  $\sim$  1) across the entire considered  $\phi$  range. rigulou primir theory or Darrieus and  $4$  destabilisation is enhanced for the promoting nyarodynamic instability **compared to the O<sub>2</sub> molecule. As** 24 marriage Le response. As and  $\mu_2$  concentration for all  $\phi$ . The dec 34 CHEFFIND UTTUBER THEODITICS, WILL 



<sup>30</sup> Figure 13 – Comparison of variation of Ze(L<sub>eff</sub> – 1) and  $1/$ Le<sub>eff</sub> – (Ze/2)( $1/$ Le<sub>eff</sub> -1) to measured Marsktein number as a function of (a) H, mol manner as a function of (a) its more

arranged to yield the Marsktein Number (Ma =  $L_b/\delta$ ), resulting in Ma =  $[1/Le_{eff} - (Ze/2)(1/Le - 1)]\sigma$ , <sup>40</sup> in which the term Ze(L<sub>eff</sub> - 1) reflects the thermo-diffusive influence as underlined by Okafor et al. [24]. **Experimental Comparison of the set of the set of the experimental Ma to the trends in 1/Le<sub>eff</sub> –1 (2e/2)(1/Le –1) and**  $\frac{1}{2}$  **(a.g.**  $\frac{1}{2}$  **(a.g.**  $\frac{1}{2}$  **(a.g.**  $\frac{1}{2}$  **(a.g.**  $\frac{1}{2}$  **(b) and**  $\frac{1}{2}$  **(c) and** 43 Ze(L<sub>eff</sub> - 1), for NH<sub>3</sub>/H<sub>2</sub> and NH<sub>3</sub>/CH<sub>4</sub> mixtures, respectively, at  $\phi$  = 0.8 - 1.0 - 1.2. First, as expected both  $^{44}$  Ze(L<sub>eff</sub> - 1) and 1/Le<sub>eff</sub> - (Ze/2)(1/Le - 1) exhibit the same trends. For the lean NH<sub>3</sub>/H<sub>2</sub> mixtures, the **1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.5 1.10 1.0 1.16 1.0 1.0 1.16 10. 20.** 48 experimental Ma and Ze(L<sub>eff</sub> - 1) and  $1/$ Le<sub>eff</sub> - (Ze/2)(1/Le - 1), potentially due to a greater change in **10 20 80 40 60 60 70 80 90 50 60 70 80 90 100** 10 10 70 and an 50 an 5 % of  $H_2$  in NH<sub>3</sub> (vol.%)<br>
(gure 13 – Comparison of variation of  $Ze(L_{\text{eff}} - 1)$  and  $1/(E_{\text{eff}} - [Ze/2)(1/(E_{\text{eff}} - 1))$  to measured Marsktein<br>
umber as a function of (a) H; mole fraction, and (b) CH; mole fraction<br>
from the  $\frac{51}{52}$  Ze(L<sub>eff</sub> - 1) and 1/Le<sub>eff</sub> - (Ze/2)(1/Le - 1), potentially alluding that the Le and Ze are the driving forces 53 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  $^{55}$  ratio. For lean NH<sub>3</sub>/H<sub>2</sub> flames it seems that the changes in measured L<sub>b</sub> are to a large extent the consequence of thermo-diffusive effects, with this influence reducing as conditions get richer. For the consequence of thermo-diffusive effects, with this influence reducing as conditions get richer. For the NH3/CH4 mixtures, the competition between thermo-diffusional and hydrodynamic instabilities yields anning to it is the developed by Matalon and Bechtold (Equation 10) an be re-arranged to evaluate Ma<br>
where 1/Le<sub>nf</sub> – (Ze/2)(1/Le<sub>nf</sub> – 1) represents the thermo-diffusive effect. Similarly, the relationshi<br>
linking L<sub>5</sub>  $\frac{35}{26}$  From the analytical expression developed by Chen [40], [45], the equation 9 can be re- arranged to yield the Marsktein i 38 where  $1/Le_{eff} - (Ze/2)(1/Le_{eff} - 1)$  represents the thermo-diffusive effect. Similarly, the relationship <sup>39</sup> linking  $L<sub>b</sub>$  to Le developed by Matalon and Bechtold (Equation 10) can be re-arranged to evaluate Ma, 41  $\frac{1}{2}$   $\frac{1}{2}$   $\frac{1}{4}$   $\frac{1}{4}$   $\frac{1}{4}$   $\frac{1}{4}$   $\frac{1}{4}$   $\frac{1}{4}$   $\frac{1}{4}$ **Figures 13.4 and 13.b** compare t  $\frac{45}{16}$  changes in measured Ma appear to be to a great extent the result, of changes in the thermo-diffusive 46 Changes in measured that uppear properties, Le and Ze. At fiche <sup>49</sup> the expansion ratio (see Figures 12) than under lean conditions. In relation to the NH<sub>3</sub>/CH<sub>4</sub> mixtures  $\frac{50}{2}$  (Figure 13.b), the measured Ma under lean and stoichiometric conditions yield matching trends to **EXECU**<sub>eff</sub> - 1 and 1/Le<sub>eff</sub> - (2e/2)(1/1 **Consequence of thermo-diffusive** 59 to increasingly positive Ma values, resulting in propensity of flame stabilisation. 

### 5.3 Flame Sensitivity Analysis

 $\frac{1}{2}$  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  $\frac{4}{7}$  pathway can be modelled as: **The enhancement of the f**  $5 \qquad \qquad$ 

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

<sup>8</sup> 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 11 temperature  $(T_a = E_a/R_u)$ , and the adiabatic flame temperature are represented in the second term  $\frac{12}{12}$  [exp( $-T_a/2T_{ad}$ )]. These individually represent the thermal (T<sub>ad</sub>) and kinetic (T<sub>a</sub>) influences on the  $\frac{13}{14}$  flame speed. Concerning the Le formulation, it was previously determined from Figure 10 that for lean 15 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-16 diffusive behaviour. With respect to  $NH_3/CH_4$  flames, Le<sub>v</sub> demonstrated the best agreement for all  $\frac{17}{2}$  considered φ. 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]: and the first term on the right-14 maile speed. Concerning the Lend 19 to Le, and nence applied for the

$$
\frac{23}{24} \qquad \qquad \frac{1}{S_L^0} \cdot \frac{dS_L^0}{dx} = \frac{1}{2 \cdot D_T \cdot Le} \cdot \frac{d(D_T \cdot Le)}{dx} - \frac{1}{2 \cdot T_{ad}} \cdot \frac{2 \cdot T_a}{dx} + \frac{T_a}{2 \cdot T_{ad}^2} \frac{2 \cdot T_{ad}}{dx} \tag{19}
$$

26 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 27 denote the influence of the diffusive, kinetic, and thermal pathways, correspondingly. Sensitivity 29 analysis is illustrated in Figure 14 for the blends and  $\phi$  considered, with a positive and negative  $\frac{30}{24}$  sensitivity factor representing flame speed enhancement and inhibition, respectively. where *x*, the volume inaction of **Scholarly restor representing that** 



59<br>60 **Figure 14** – Sensitivity Analysis of S<sub>L</sub><sup>0</sup> for NH<sub>3</sub>/H<sub>2</sub> and NH<sub>3</sub>/CH<sub>4</sub> blends, (a) φ = 0.8 (b) φ = 1.0 (c) φ = 1.2 **Figure 14** – Sensitivity Analysis of

65

As illustrated in Figure 14, the enhancement in flame speed of NH<sub>3</sub> based blends upon addition of<br>er CH<sub>4</sub> or H<sub>2</sub> is predominantly an Arrhenius effect (kinetic), principally through the reduction of the<br>rall activation 1  $\blacksquare$  either CH<sub>4</sub> or H<sub>2</sub> is predominantly an Arrhenius effect (kinetic), principally through the reduction of the  $\frac{2}{3}$  overall activation energy and thus the activation temperature. For identical volumetric additions of up  $\frac{3}{4}$  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  $E_a$  than in the case of CH<sub>4</sub> addition, resulting in greater flame speeds. It should be  $\frac{7}{1}$  noted that although remaining predominant for lean and stoichiometric conditions, the influence of  $\frac{8}{\alpha}$  the kinetic pathway reduces at richest conditions, particularly for CH<sub>4</sub> addition to NH<sub>3</sub>, with a negative 10 Sensitivity at  $\phi$  = 1.2. This agrees with the minor increase in E<sub>a</sub> (represented by Ze, see Figure 12) at 11 that condition, the consequence of the shifted minimum  $E_a$  to slightly richer conditions ( $\phi$  = 1.1-1.2) of  $12$  NH<sub>3</sub>, as in Figure 3. The thermal pathway impact is lower than the kinetic effect, with the influence of  $\frac{13}{14}$  the thermal pathway correlating well with modelled changes in adiabatic flame temperature. The 15 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 16 the diffusive influence, it assumes negative sensitivity (or inhibiting effect) for lean NH<sub>3</sub>/H<sub>2</sub> mixtures,  $\frac{17}{2}$  and is negligible in comparison to other pathways. This is particularly the case for NH<sub>3</sub>/CH<sub>4</sub>, a 18<br>
19
consequence of the nominal changes in Le (Fig. 12) coupled with the limited change in thermal 20 diffusivity of the mixture upon CH<sub>4</sub> addition, irrespective of the  $\phi$ . It should be noted that even if the use of different kinetics mechanisms can induce different Arrhenius coefficients, the qualitative trends 21 22 should remain valid, and thus performing such sensitivity analysis from first principles remains relevant 23 providing useful insights.  $\frac{4}{3}$  to 10% C<sub>114</sub> or 11<sub>2</sub> results in a simple 9 14 CHE CHEFFING PACHWAY COLLEGEING 19 consequence of the nominal cha  $24$  Providing ascruitinsights.

# $\frac{25}{26}$  6. Conclusions  $26$  **b. Concressions**

 $\frac{27}{28}$  The spherically expanding flame configuration was used to measure the unstretched laminar flame 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 range of compositions and equivalence ratio. A special attention was given to the estimate of Lewis 30 31 mumber 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  $\frac{32}{22}$  this study, the following main outcomes can be made: 29 **Speeds and corresponding Marks** 33 cases and states, the following main out

- 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 <b>I** and linear increase in flame speed, respectively. The greatest relative change in flame 36 37 Speed upon H<sub>2</sub> addition occurs under leanest and richest conditions while upon CH<sub>4</sub> 38 and addition, only under lean conditions. Stagni et al. and Okafor et al. mechanisms displayed  $\frac{39}{40}$  the best agreement with experimental NH<sub>3</sub>/H<sub>2</sub> and NH<sub>3</sub>/CH<sub>4</sub> results, respectively.  $35$   $\ldots$   $\ldots$   $\ldots$
- With respect to the stretch related behaviour, the addition of  $CH_4$  to  $NH_3$  results in a linear  $41$ reduction in the stretch sensitivity for a fixed equivalence ratio. The volumetric based 42 43 **Lewis number yielded the best correlation with the measured Markstein lengths, for CH<sub>4</sub>**  $\frac{44}{45}$  addition to NH<sub>3</sub> resulting in nominal diffusional-thermal effects. For the stoichiometric and duction to this resulting in hominal dirictional circuit enects. For the stolemometric and<br>
46 **September 16 and NH3/H<sub>2</sub> flames, a non-monotonical variation in measured Markstein length was**  $47 \,$  botained, with a less and less linear behaviour as conditions get leaner. For NH<sub>3</sub>/H<sub>2</sub>, the  $48$  changes in measured  $L_b$  were demonstrated to mainly be the result of thermo-diffusive  $^{49}$  effects (through the modelled changes in Le<sub>eff</sub> and global activation energy) with the 50<br>
51 **Influence of the thermo-diffusional instabilities reducing as the equivalence ratio** 52 **increases. For lean NH<sub>3</sub>/H<sub>2</sub> mixtures, the diffusional-based Lewis number well captured the** 53 hon-linear stretch behaviour as function of H<sub>2</sub> addition, whilst the heat release-based Lewis number resulted in better agreement at richer conditions. 54 41 **WILD PERSPECT TO THE ST**  $46$  **IEAM IVE INTERVALUATE INTERVALUATE INTERVALUATI** 51 **IIIIuence of the the**
- A sensitivity analysis related to the major flame enhancing pathways (diffusive, kinetic, 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>,<br>58 **inupy due to the kinetic change, especially through the reduction of the activation of the activation of the activation** temperature. The influence of the kinetic pathway reduces as conditions get richer, 59 56 **A SEISILIVILY dildiySiS** 58 is mainly due to the kinetic change, especially through the reduction of the activation 60 competitive m

particularly for CH<sub>4</sub> addition. The thermal pathway holds less influence in comparison to<br>the kinetic pathway, with its influence showing good correlation with limited changes in<br>adiabatic flame temperature of the consid 1 1 The kinetic pathway, with its influence showing good correlation with limited changes in 1 particularly for CH<sub>4</sub> addition. The thermal pathway holds less influence in comparison to<br>the kinetic pathway, with its influence showing good correlation with limited changes in<br>adiabatic flame temperature of the consid  $\frac{3}{4}$  negligible for all investigated mixtures, with a negative sensitivity for the lean NH<sub>3</sub>/H<sub>2</sub> mixtures. 5 particularly for CH<sub>4</sub> addition. The thermal pathway holds less in<br>the kinetic pathway, with its influence showing good correlation<br>adiabatic flame temperature of the considered blends. The<br>negligible for all investigated the kinetic pathway, with its influence showing good correlation with limited changes in egligible for all investigated mixtures, with a negative sensitivity for the lean NH<sub>1</sub>/H<sub>2</sub> mixtures.<br> **Declaration of Competing Int** adiabatic flame temperature of the considered blends. The diffusive pathway was 4 megingune for all lives

# $\frac{6}{7}$  Declaration of Competing Interest  $7$  Declaration of Competing interest

 $\frac{8}{9}$  The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper. 10 megligible for all investigated mixtures, with a negative sensitivity for the lean NH<sub>3</sub>/H<sub>2</sub><br> **Declaration of Competing Interest**<br>
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rela mixtures.<br>
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ships that could have appeared to influence the work reported in this paper.<br> **Vielgements**<br>
sproject has received funding fr **Declaration of Competing Interest**<br>
The authors declare that they have no known competing financial interest or personal<br> **Acknowledgements**<br> **Acknowledgements**<br> **This project** has received funding from the European Union combustion, Branchies data they have no known competing financial interest or personal<br>The authors declare that they have no known competing financial interest or personal<br>ships that could have appeared to influence the wo  $9$  authors declare that

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