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## **Lewis Number Effects on Lean Premixed Combustion Characteristics of Multi-Component Fuel Blends**

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### **Abstract:**

Variation in natural gas composition, alongside the potential for H<sub>2</sub> enrichment, creates the potential for significant changes to premixed flame behaviour. To strengthen fundamental understanding of lean multi-component alternative fuel blends, an outwardly propagating spherical flame was employed to measure the flame speeds and Markstein lengths of C<sub>1</sub>-C<sub>4</sub> hydrocarbons, alongside precisely mixed blends of CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>, CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> and CH<sub>4</sub>/H<sub>2</sub>. Theoretical relationships between Markstein length and Lewis Number are explored alongside effective Lewis number formulations. Under lean conditions, equal volumetric additions of H<sub>2</sub> and C<sub>3</sub>H<sub>8</sub> (30% vol.) to CH<sub>4</sub> resulted in similar augmentation of burning velocity, however, opposite susceptibility to preferential diffusional instability was noted. At a fixed equivalence ratio of 0.65, limited changes in composition provide a marked change in the premixed flame response with the addition of C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> to CH<sub>4</sub>. For lean CH<sub>4</sub>/H<sub>2</sub> mixtures, a diffusional based Lewis Number formulation yielded a favourable correlation, whilst a heat-release model resulted in better agreement for lean CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> blends. Modelling work suggests that measured enhancement of lean CH<sub>4</sub> flames upon H<sub>2</sub> or C<sub>3</sub>H<sub>8</sub> is strongly correlated to changes in volumetric heat release rates and production of H radicals. Furthermore, a systematic analysis of the flame speed enhancement effects (thermal, kinetic, diffusive) of H<sub>2</sub> and C<sub>3</sub>H<sub>8</sub> addition to methane was undertaken. Augmented flame propagation of CH<sub>4</sub>/H<sub>2</sub> and CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> was demonstrated to be principally an Arrhenius effect, predominantly through reduction of associated activation energy. Finally, plausible short-term variations in composition with hydrogen-enriched multi-component natural gas flames were investigated experimentally and numerically. At the leanest conditions, small variations in CH<sub>4</sub>:C<sub>3</sub>H<sub>8</sub> content at a fixed H<sub>2</sub> fraction resulted in discernible changes in stretch related behaviour, a reflection of the thermo-diffusive behaviour of each fuel's response.

Key words: Laminar flame Speed, Lewis Number, Markstein Length, Fuel Mixtures, Hydrogen, Natural Gas

## 1.Introduction

Natural gas composition varies significantly, depending on source location, extraction, and refinement process [1]. Methane ( $\text{CH}_4$ ) levels have been shown to fluctuate between 55.8% to 98.1%, with concentrations of higher hydrocarbons ( $\text{C}_2+$ ), typically ethane ( $\text{C}_2\text{H}_6$ ) and propane ( $\text{C}_3\text{H}_8$ ), varying from 0.5% - 13.3% and 0% - 23.7%, respectively [2]. Hydrogen ( $\text{H}_2$ ) blending, sourced from various waste and sustainable processes, has also been proposed towards decarbonised gas networks. With the growing share of renewable energy sources, coupled with the demand of high-efficiency and low-emission power plants, combustor flexibility is of increasing importance in meeting the dynamic requirements of power generation systems, in terms of load and fuel variations [3]. Variations in natural gas composition and potential  $\text{H}_2$  enrichment presents significant combustion challenges to power generation gas turbines [4], particularly those running near the lean-limit, as this combustion regime tends to exacerbate any variation in flame behaviour, potentially leading to flame instability or extinction [5]. As such, there seems to be a practical necessity to develop and strengthen understanding of fundamental combustion characteristics of lean multi-component fuel blends, ultimately leading to the development of combustors tolerant of an increased share of either  $\text{H}_2$  and/or  $\text{C}_2+$  gases.

Fuel composition variation introduces changes in chemical and transport properties, which in turn alters the witnessed reactivity and burning characteristics of the fuel mixture. The Lewis number ( $Le$ ), defined as the ratio of thermal to mass diffusivity of the deficient reactant, represents a key property in premixed combustion systems, detailing the transport mechanisms of various species across the flame front. For stretched flames – undergoing the combined effects of strain, curvature, and flame motion – preferential diffusion (i.e.,  $Le$  diverging from unity) is understood to strongly influence the burning rates of premixed flames [6]. Thermo-diffusively unstable flames with  $Le < 1$  show a relative acceleration with increasing stretch rate, whereas conversely for flames exhibiting  $Le > 1$  there is greater relative thermal diffusivity, resulting in heat loss to the unburned reactants and a reduction in burning rate with increased stretch [7]. This effect is also observed at increased turbulence intensity with  $Le < 1$  mixtures exhibiting a greater increase in burning rate for an equivalent rise in turbulent velocity fluctuation [8]. A parameter often measured to characterise the influence of  $Le$  on the change in flame speed with stretch rate is the burned gas Markstein length ( $L_b$ ). Markstein number - defined as  $L_b$  divided by the flame thickness ( $\delta$ ) - is an indicator of the propensity of a combustion system to be influenced by thermo-acoustic instability [9], and is thus of interest to study.

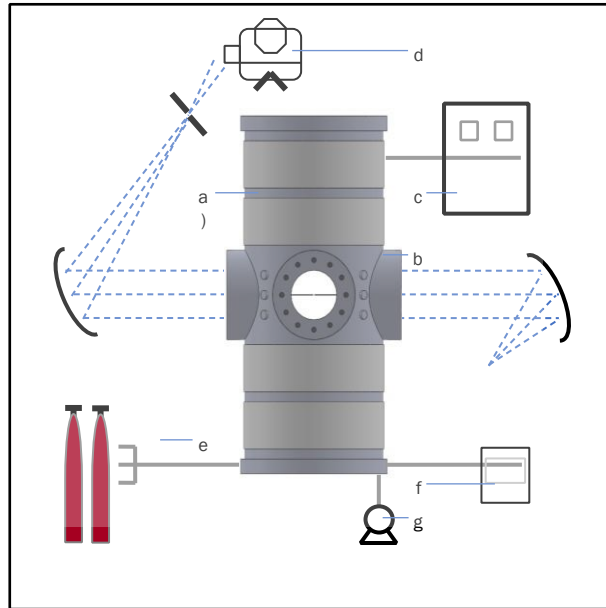
Lipatnikov and Chomiak [6], in their extensive review of molecular transport effects on flame propagation and structure, underline that weak and strong turbulent premixed combustion is affected by preferential diffusional instabilities, with increased turbulence resulting in enhanced wrinkling of the flame front, which in turn increases the turbulent burning rate [10]. However, diffusive effects in turbulent flames are often overlooked in simplified numerical simulations. Such simplification is not problematic in the case of the quasi equi-diffusive lean  $\text{CH}_4$ /air mixtures. However, issues potentially arise with increased concentrations of alternative fuels which has led to increased interest in this field [3,10–13]. Recent DNS studies characterised the influence of  $Le$  for a range of pure and blended fuels ( $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{C}_3\text{H}_8$ ) demonstrating an amplification of the diffusive effects, according to each fuels'  $Le$  behaviour [8,10,12,14]. Experimental validation of these findings is limited, with some studies investigating fixed compositions of natural gas or blends of  $\text{CH}_4$  with  $\text{C}_2+$  (generally  $\text{C}_2\text{H}_6$  and/or  $\text{C}_3\text{H}_8$ ) as surrogates of natural gas. Dagaut et al. [15] investigated the impact of  $\text{H}_2$  enrichment upon the oxidation kinetics of a  $\text{CH}_4/\text{C}_2\text{H}_6$  (10:1) mixture in a jet-stirred reactor across lean to stoichiometric conditions, concluding that enhanced reactivity was due to the augmented production of OH radicals. Similarly, other studies [16,17]

used the spherically expanding flame configuration to investigate the impact of H<sub>2</sub> on natural gas, however those compositions were mainly composed of CH<sub>4</sub> (>95% vol.), and as such outcomes are very similar to those related to CH<sub>4</sub>/H<sub>2</sub> blends. Nilsson et al. [18], employing the heat-flux (flat flame) set-up, investigated both experimentally and numerically the influence of H<sub>2</sub> (up to 50% addition by vol.) upon a natural gas composition of CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> (80/10/10 vol.%). The study similarly demonstrated an enhancement of flame speed, attributed to increases in H and OH radicals. More recently, Khan et al. [19] examined the influence of H<sub>2</sub> (25%, 50%, 75%, by vol.) to various multi-component natural gas compositions (CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub>). It was concluded that H<sub>2</sub> addition lowered Le, with flames containing the highest concentrations of CH<sub>4</sub> most affected.

Clearly, the experimental study on the addition of H<sub>2</sub> on natural gas blends containing varying quantities of C<sub>2+</sub> is scarce, hence the aim of this work was to investigate in-detail the influence of changing Le on-flame behaviour, in the context of plausible short-term variation in multi-component natural gas blends. CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> and CH<sub>4</sub>/H<sub>2</sub> blend ratios were varied across a limited range, representative of the prospective demands of fuel-flexible natural gas combustors widely employed for power generation. The use of Liquefied Natural Gas (LNG) can lead to higher hydrocarbons in the fuel mixture [15] with C<sub>3</sub>H<sub>8</sub> chosen as a surrogate in this study. It is hypothesised that the effect of this higher hydrocarbon fuel contrasts with the potential introduction of H<sub>2</sub> to the gas grid, as proposed in the power-to-X concept. Addition of either H<sub>2</sub> or C<sub>3</sub>H<sub>8</sub> to a given CH<sub>4</sub>/air mixture increases flame temperature, reactivity, and mixture flame speed and induces a change in extinction response. The change in diffusive behaviour for each of the aforementioned mixtures was studied in a fundamental laminar flame configuration, with the knowledge gained then extended to studies of tertiary blends (CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub>/H<sub>2</sub>) containing varying molar content of CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> at a fixed H<sub>2</sub> content (15% by vol.).

## **2.Experimental Facilities**

Laminar flame speed measurements were performed using a constant-volume cylindrical bomb (CVCB). Details of the rig and post-processing technique can be found in [20,21], and thus only a brief summary is presented here. A schematic overview of the experimental facility is presented in Fig. 1. The cylindrical CVCB (Fig. 1[a]) has a nominal internal volume of 34 L (260 mm ID), with four orthogonal 100 mm quartz viewing windows (Fig. 1[b]) with PID temperature control (Fig. 1[c]). High-speed Schlieren imaging of flame propagation was achieved using a CCD highspeed camera (Fig. 1[d] – Photron FASTCAM APX-RS (±0.05%)) set to capture 5,000 fps and facilitating a spatial resolution of ~0.14 mm per pixel. Flame propagation rates were calculated by edge-detection algorithms written into a bespoke MATLAB script. Reactants were introduced into the chamber using batched mass-flow control (Fig. 1[e] – Bronkhorst mini-CORI-FLOW devices (±0.5%)). Mass fractions were calculated as a function of initial pressure (P), fuel-air equivalence ratio (Φ), and temperature (T), with mixture concentrations confirmed by partial pressure (Fig. 1[f] – Edwards ASG 0–0.2 MPa transducer (±0.2%), resolution 1×10<sup>-5</sup> MPa). A diaphragm pump (Fig. 1[g]) was used to evacuate the CVCB three times between tests to reduce errors arising from imperfect vacuum (< 1%), with the remaining air compensated in the equivalence ratio calculation. Internal fans were used to pre-mix the reactants, and capacitor-discharge ignition was achieved via fine electrodes mounted at 45° to the measurement plane. Experiments were triggered by a simultaneous TTL signal to the ignition and data acquisition systems after quiescence had been attained.



**Fig. 1 – CVCB schematic (components described in text)**

### **3.Experimental Specifications and Theory**

High-purity fuel components of CH<sub>4</sub> (>99.995%), H<sub>2</sub> (>99.999%), C<sub>3</sub>H<sub>8</sub> (>99.95%) and dry zero-grade compressed air were metered using the aforementioned mass-flow controllers. Measurements were performed at initial conditions of 298 K ( $\pm$  3 K) and 0.1 MPa ( $\pm$  1x10<sup>-3</sup> MPa). To investigate the influence of elevated Le, a molar C<sub>3</sub>H<sub>8</sub>/CH<sub>4</sub> ratio of 15:85 was studied for a range of lean equivalence ratios ( $\Phi$  = 0.60 – 1.0), representative of concentrations of higher hydrocarbons found in natural gas [1,2,15]. At a fixed equivalence ratio of  $\Phi$ =0.65, the molar C<sub>3</sub>H<sub>8</sub>/CH<sub>4</sub> ratio was subsequently varied from 0-100%, to quantify the sensitivity of the lean flame response. Similarly, to investigate the influence of a decreasing Le, a H<sub>2</sub>/CH<sub>4</sub> mixture also fixed at 15:85 was studied across a range of equivalence ratios ( $\Phi$  = 0.60 – 1.0), and at a fixed equivalence ratio of 0.65 (with H<sub>2</sub> content incrementally increased; 0 – 50% by vol.%) to provide a comparison of the change in flame speed and stretch-related behaviour with each of the blends. Finally, a preliminary study of the impact of tertiary blends was undertaken; five hydrogen-enriched natural gas blends were investigated, at fuel lean conditions ( $\Phi$  = 0.60 – 8.0) with compositions presented in Table 1.

Table 1 – Composition of Selected Natural Gas Blends

Fuel Designation	Fuel Composition (Volume %)		
	CH <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	H <sub>2</sub>
NG 1	68	17	15
NG 2	73.1	11.9	15
NG 3	76.5	8.5	15
NG 4	78.2	6.8	15
NG 5	79.9	5.1	15

Schlieren measurements were undertaken using an established technique and in a similar way to many contemporary studies [2,22,23] with the shadowed edge taken to indicate the burned gas isotherm, critical for characterising the influence of flame stretch as discussed by Giannakopoulos et al. [24]. Scaled images determined the Schlieren spherical radius ( $r_{sch}$ ), with limits used to minimise spark and pressure effects. Bradley et al. [25] suggest a spark affected radius up to 6 mm for CH<sub>4</sub>/air flames; however this radius has been shown to be dependent on Le [26]. In this study 10 mm was chosen as the minimum radius employed, with preliminary investigations demonstrating minimal variation in results derived from data above 8mm (ignition energy ranged between 55–170 mJ). To limit pressure effects a maximum usable radius of 35 mm was utilised, within the 30% of chamber radius as originally proposed by Burke et al. [27], and satisfying  $r_{sch}/(3V/4\pi)^{1/3} < 25\%$  as suggested in the detailed analysis by Chen [28]. Extrapolation methods utilised to yield flame speed and corresponding  $L_b$  rely on a sufficiently large stable non-cellular flame regime. Therefore, due to known instability issues associated with lean combustion of H<sub>2</sub>-containing fuels, minor modifications in usable flame radius selection were required. H<sub>2</sub> flames are particularly unstable with regard to diffusive effects, due to the low Le ( $Le \ll 1$ ), with cellularity developing at early stages of flame propagation. This results in flame acceleration at decreased stretch rates [29]. As demonstrated by Gu et al. [30], flame acceleration related to cellular instabilities occurs at a critical radius to flame thickness ratio, defined by the Peclet number. Here, the critical radius was determined to be  $\sim 25$  mm for CH<sub>4</sub>/H<sub>2</sub> (50/50 vol%). Hence, a conservative flame limit of  $\sim 22$  mm was adopted for all CH<sub>4</sub>/H<sub>2</sub> blends, although this critical radius was shown to increase with decreasing H<sub>2</sub> fraction. It is noted that for CH<sub>4</sub>/H<sub>2</sub> flames containing  $< 25$  vol% H<sub>2</sub>, no discernible signs of flame self-acceleration were observed, with average relative differences between the initial and reduced flame radius data range (i.e., 10-35 and 10-22 mm) less than 3% and 15% for flame speed and  $L_b$ , respectively. These differences are in good agreement with previous studies which investigated the influence of flame radius range selection upon flame propagation and  $L_b$  [28,31]. Nevertheless, using a suitably fast frame capture rate, a minimum of 60 data points were obtained for even the fastest flames, from which flame speed data were derived.

For an outwardly propagating spherical flame, the stretched flame speed ( $S_n$ ) is expressed as the temporal (t) derivative of the Schlieren flame radius ( $r_{sch}$ ) as given in Eqn. (1).

$$S_n = \frac{dr_{sch}}{dt} \quad \text{Eqn. (1)}$$

The flame stretch rate ( $\alpha$ ), defined as the change in area (A) gradient as the flame stretches with growth, is calculated for a propagating spherical flame as shown in Eqn. (2):

$$\alpha = \frac{1}{A} \cdot \frac{dA}{dt} = \frac{2}{r_{sch}} \cdot \frac{dr_{sch}}{dt} \quad \text{Eqn. (2)}$$

The stretch rate defined for this method of flame speed measurement encompasses both the influence of flame curvature ( $\alpha_c$ ) and flow-field strain ( $\alpha_s$ ),  $\alpha = \alpha_c + \alpha_s$  as demonstrated by Bradley et al. [25]. Various correlations between  $S_n$  and  $\alpha$  have been previously proposed, enabling unstretched flame speed ( $S_u$ ), to be attained through extrapolation of  $S_n$  to zero stretch rate, with both  $S_u$  and  $L_b$  determined from the measured results with respect to the burned gas. Wu & Law [32], proposed a linear relationship, based upon the assumption that mass and thermal diffusion are near equal ( $Le \approx 1$ ) and that the flame is weakly stretched. Taylor [33] and Dowdy et al. [34], employing this reasoning, suggest that  $\alpha$  and flame speed are related in the following manner Eqn. (3):

$$S_u - S_n = L_b \cdot \alpha \quad \text{Eqn. (3)}$$

It may be noted that  $L_b$  characterises the effect of stretch on flame propagation, with the sign and magnitude of  $L_b$  directly related to  $Le$ .  $S_u$  is subsequently derived by extrapolation of the relationship to a corresponding intercept value ( $\alpha=0$ ), equivalent to a theoretical spherical flame of infinite radius. Here, this methodology will be referenced as LM(S) (i.e., Linear Model based on flame stretch).

The second methodology, is a model attributed to Frankel and Sivashinsky [35], originally proposed by Markstein [36], based upon the assumption of large flame radii. Frankel and Sivashinsky analysed a spherically expanding  $C_3H_8$  flame, considering the effects of thermal expansion and  $Le$ , obtaining the following relationship in Eqn. (4):

$$S_n = S_u - S_u \cdot L_b \cdot \frac{2}{r_f} \quad \text{Eqn. (4)}$$

Eqn. (4) shows that the flame curvature ( $\kappa = 2/r_f$ ) and  $S_n$  vary linearly. As such,  $S_u$  and  $L_b$  can be obtained from linear extrapolation, of  $S_n$  and  $\kappa$  [37,38]. This methodology has not received widespread use [21,39] and here is referenced as LM(C) (i.e. Linear Model based on Curvature).

Kelley and Law [40] proposed a non-linear model, based upon the theoretical work of Ronney and Sivashinsky [41]. This extrapolation technique allows for arbitrary  $Le$  and accounts for deviations in adiabatic and planar assumptions, which are more prominent for flames heavily influenced by stretch [34], such as lean  $H_2$  or  $C_3H_8$  flames. This non-linear relationship is expressed in Eqn. (5):

$$\left(\frac{S_n}{S_u}\right) \cdot \ln\left(\frac{S_n}{S_u}\right)^2 = -\frac{2 \cdot L_b \cdot \alpha}{S_u} \quad \text{Eqn. (5)}$$

A quasi-steady nonlinear association between  $S_n$  and  $\alpha$  is employed -rearranged with the error used for least squares regression- to obtain an extrapolated unstretched flame speed. This methodology has been used frequently over the last decade, improving accuracy [31,38]. Here this method will be referred to as NM(S) (i.e., Non-Linear Model based on Stretch).

The uncertainty in extrapolation was investigated by Chen [37] and Wu et al. [38], concluding that the accuracy of the different extrapolation techniques depend strongly upon  $Le$  of the fuel air mixture. Chen demonstrated that LM(S) is suitable for mixtures with  $Le$  close to unity, whilst LM(C) and NM(S) are to be preferred for mixtures with  $Le > 1$  (positive  $L_b$ ) &  $Le < 1$  (negative  $L_b$ ), respectively, because of the nonlinear trend in relationship of  $S_n$  and  $\alpha$ . These recommendations have been adopted in this work.

Irrespective of the extrapolation methodology employed, burned gas expansion must be accounted for to obtain representative values of laminar flame speed ( $U_L$ ). This adiabatic expansion at constant pressure, can be termed as the ratio of the burnt ( $\rho_b$ ) and unburnt ( $\rho_u$ ) gas densities.  $U_L$  can thus be evaluated through,  $U_L = S_u \cdot (\rho_b/\rho_u)$ , with adiabatic densities calculated using CHEMKIN-Pro, employing the Aramco 1.3 chemical reaction mechanism [42], as discussed further in section 5.2.

#### **4.1. Evaluation of Fundamental Flame Parameters**

Theoretical relationships linking  $L_b$  to  $Le$  have been proposed previously, notably by Chen [26,37] and Matalon and Bechtold [43]. These theoretical correlations require the calculations of various fundamental flame parameters. The Zel'dovich number, was evaluated using the expression  $Ze = E_a(T_{ad} - T_u)/(R^0 T_{ad}^2)$ , with  $R^0$  the universal gas constant,  $T_u$  and  $T_{ad}$ , the temperature of the unburnt mixture and the adiabatic flame temperature, respectively. The activation energy,  $E_a$ , is defined as the slope of the mass burning flux ( $m^0$ ) and the inverse adiabatic flame temperature at constant  $\Phi$  and pressure, empirically determined using the expression  $E_a = -2 \cdot R_u \cdot \partial$

$[\ln(m^0)]/\partial[1/T_{ad}]$ , where the mass burning flux is the eigenvalue of laminar flame propagation, and can be replaced by  $m^0 = (\rho_u \cdot U_L)$ , as recommended by Egolfopoulos and Law [44]. Two methods are commonly employed to vary the mass burning flux, required to evaluate the differential, the first by slightly perturbing the diluent concentration [44,45]. However, Kumar and Sung [46] note that by varying  $m^0$  and  $T_{ad}$  through different levels of  $N_2$  dilution, the reactant concentrations are also altered. As such, the second method, based upon preheating the unburnt gas, is advised. Consistent with previous studies [46,47], the second method was applied here, achieved by varying the unburnt gas temperature in CHEMKIN-Pro PREMIX. The linear variation of  $\ln(m^0)$  and  $(1/T_{ad})$  observed during this work validates this extraction method, with R-Squared values ( $R^2$ ) of at least 0.999. Note, however, that this method is only valid for sufficiently off-stoichiometric conditions, with  $E_a$  values for mixtures near stoichiometry requiring interpolation [41].

Two definitions of the laminar flame thickness have been previously proposed and deployed [7]. The first, commonly referred to as the kinetic (diffusion) thickness ( $\delta_K$ ), is given by  $\delta_K = \lambda/(\rho_u \cdot c_p \cdot U_L)$ , where ( $\lambda$ ) represents the thermal conductivity, and ( $c_p$ ) the specific heat. Jomaas et al. [48] underline the ambiguity of this definition, most notably at which temperature the ratio ( $\lambda/c_p$ ) should be assessed. As such, an expression of the flame thickness relying upon the extraction of the gradient temperature profile with axial distance through the flame is proposed [7,48]. This approximation relies upon the application of a linear gradient as the tangent of the inflection, which corresponds to  $(dT/dx)_{max}$ , which was numerically modelled using the CHEMKIN-Pro software. This flame thickness, referred to as the gradient thickness ( $\delta_G$ ), can be expressed as  $\delta_G = (T_{ad} - T_u) / (dT/dx)_{max}$ . The kinetic flame thickness definition is consistent with the approach detailed by Chen [26,27], whilst the gradient flame thickness definition is consistent with the approach detailed by Bechtold and Matalon [43], and thus each are employed accordingly in the derivations of  $Le$  and  $L_b$  as defined by the given authors. Finally, for the sake of completeness, the thermal expansion ratio ( $\sigma = \rho_u/\rho_b$ ) applied is consistent with the approach described by Matalon [43].

#### **4.2 Relationships of $Le$ and $L_b$**

In this work, two theoretical relationships linking  $L_b$  to  $Le$  have been utilized, as proposed by Chen [26,37] and Matalon and Bechtold [43]. The first method is derived from the analytical developments conducted by Chen on spherically expanding flames, since employed by Lapalme et al. [39] and Bouvet et al. [49] in their studies concerning  $Le$  effects for multi-component fuels. This method is denoted here as  $Le_{CHEN}$ , and is expressed per Eqn. (6):

$$Le_{CHEN} = \left[ \frac{L_b}{\sigma \cdot \delta} - \frac{Ze}{2} \right]^{-1} \left[ 1 - \frac{Ze}{2} \right] \quad \text{Eqn. (6)}$$

From Eqn. (6) the retrieval of  $L_b$  is possible as shown in Eqn. (7).

$$L_{b-CHEN} = \left[ \frac{1}{Le} - \left( \frac{Ze}{2} \right) \left( \frac{1}{Le} - 1 \right) \right] \sigma \cdot \delta \quad \text{Eqn. (7)}$$

A second formulation by Bechtold and Matalon [43], derived from their theoretical research on the dependence of  $L_b$  on stoichiometry, was demonstrated valid for off-stoichiometric conditions. This formulation has been employed by Jomaas et al. [48], for the determination of  $Le$  of acetylene ( $C_2H_2$ ) in air across a wide range of conditions, and employed by Lapalme et al. [39] for  $H_2/CO$  and  $H_2/CH_4$  mixtures. This relationship is denoted herein as  $Le_{BM}$ , and is expressed per Eqn. (8):



$$Le_{BM} = 1 + \left[ \frac{L_b}{\delta} - \frac{2}{\sqrt{\sigma} + 1} \right] \left[ \frac{2 \cdot Ze}{\sigma - 1} \left\{ \sqrt{\sigma} - 1 - \ln \left( \frac{1}{2} (\sqrt{\sigma} + 1) \right) \right\} \right]^{-1} \quad \text{Eqn. (8)}$$

Eqn. (8) can be re-arranged to retrieve  $L_b$ , and is defined as  $L_{b-BM}$  as per Eqn. (9):

$$L_{b-BM} = \delta \left[ \frac{\gamma_1}{\sigma} - \left\{ \frac{Ze}{2} (Le - 1) \gamma_2 \right\} \right] \quad \text{Eqn. (9)}$$

where  $\gamma_1$  and  $\gamma_2$  are functions of the expansion ratio given in Eqn. (10) and Eqn. (11):

$$\gamma_1 = \frac{2 \cdot \sigma}{(\sqrt{\sigma} + 1)} \quad \text{Eqn. (10)}$$

$$\gamma_2 = \left[ \frac{4}{\sigma - 1} \right] \left[ \sqrt{\sigma} - 1 - \ln \left( \frac{\sqrt{\sigma} + 1}{2} \right) \right] \quad \text{Eqn. (11)}$$

### **4.3 Lewis Number evaluation of multi-component mixtures**

For multi-fuel blends, the calculation of  $Le$  can become challenging since the diffusivity of each fuel must be considered. This is especially applicable to blends of  $H_2$  and hydrocarbons, which exhibit different transport diffusion mechanisms and flame characteristics. Whilst the calculation of  $Le$  for single-fuel mixtures can be considered relatively straightforward, there is little consensus on the correct formulation of  $Le$  to be employed for multi-fuel blends [49]. Bouvet et al. [49] identified three 'effective'  $Le$  formulations ( $Le_{eff}$ ). The first derived by Law et al. [23] was from the asymptotic analysis of high pressure  $H_2/C_3H_8$  laminar spherical flames. This formulation has been extensively applied to discuss the thermo-diffusive behaviour (i.e. stable,  $Le > 1$  or unstable  $Le < 1$ ) of mostly binary and tertiary blends of hydrocarbons and hydrogen [14,50–52]. Based upon the weighted average of the fuels' nondimensional heat release ( $q_i$ ), a heat release weighted formulation, referenced in this work as  $Le_H$ , can be expressed as Eqn. (12a):

$$Le_H = 1 + \frac{\sum_{i=1}^f q_i (Le_i - 1)}{\sum_{i=1}^f q_i} \quad \text{Eqn. (12a)}$$

where

$$q_i = \frac{Q \cdot Y_{i,unburnt}}{c_p \cdot T_u} \quad \text{Eqn. (12b)}$$

And ( $Q$ ) represents the overall heat of reaction,  $Y_i$ , the mass fraction of species 'i'.

The second  $Le$  formulation is based upon a volumetric fraction weighted average, stemming from the computational study of turbulent  $CH_4 - H_2/C_3H_8$  flames by Muppala et al. [8]. This formulation led to reasonable agreement with experimental burning velocities at low turbulence intensity. However, it is noted that differences between measured and modelled flame speeds increased at higher turbulent intensity, with modelled burning rates significantly underpredicting measurements. This, volume weighted, formulation will be referenced in this work as  $Le_v$ , and is expressed per Eqn. (13):

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

where  $(x_i)$ , is the fuel volumetric fraction of the component 'i'.

Finally, Dinkelacker et al. [14] using lean H<sub>2</sub>/CH<sub>4</sub> flames assumed that if flame curvature is dominant, then local enrichment of the most diffusive fuel at the flames leading edge can be expected. This overall reaction-rate enhancement is translated into a volumetric-weighted average of the fuel diffusivities. This, diffusion weighted, formulation will be referenced in this work as  $Le_D$ , and is expressed per Eqn. (14):

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

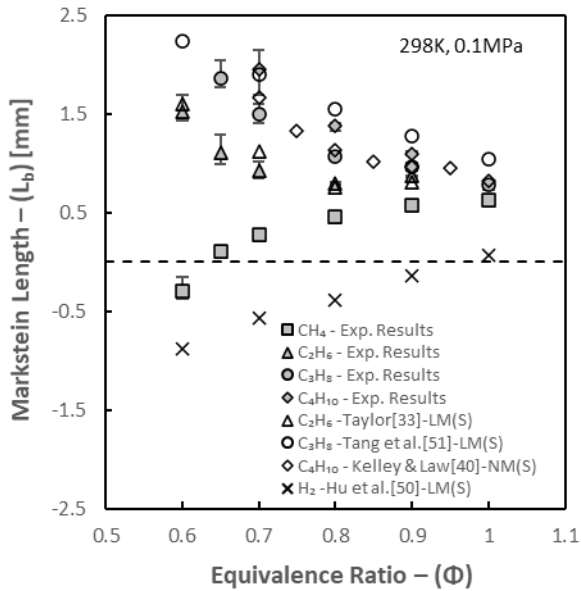
where  $D_T$  is the mixture's thermal diffusivity and  $D_{ij}$  are the binary mass diffusion coefficients. Several methods have been proposed to estimate the binary mass diffusion coefficients of moderate pressure gases (<10 bar), with empirical constants based upon experimental data [53]. The proposals of Hirschfelder, Bird and Spot, as well as that of Wilke detailed in [53], have been employed in this study. Once the binary coefficients for the combinations of gases are estimated, an effective formulation of the deficient species in the mixture must be selected. Conventionally, it is assumed that for lean fuel-air mixtures, the deficient reactant is scarce compared to the surrounding N<sub>2</sub> [7]. Consequently,  $D_{ij}$  is taken as the fuel 'i' diffusing into N<sub>2</sub> (denoted with the subscript 'j'). Thus, the binary coefficients are evaluated employing the assumption that the fuel is diffusing into N<sub>2</sub>. As highlighted by Lapalme [39], this may hold true for hydrocarbons due to their high molar fuel-air ratio, but not for fuels that have low molar fuel-air ratio such as H<sub>2</sub>. Thus, the mixture-averaged coefficient of mass diffusion into the mixture as proposed by Wilke [54] was selected here, with details of the method available in [21]. The binary diffusion coefficients attained in this study exhibit good agreement with values evaluated using the STANJAN transport calculator [55], with differences no greater than  $\pm 2\%$  for the various binary compositions composed of hydrocarbons, O<sub>2</sub> & N<sub>2</sub> and up to 10% in the presence of H<sub>2</sub>, which is in line with expected deviation [53]; hence the derived coefficients are considered suitable for the purpose of this work.

## 5. Results and Discussion

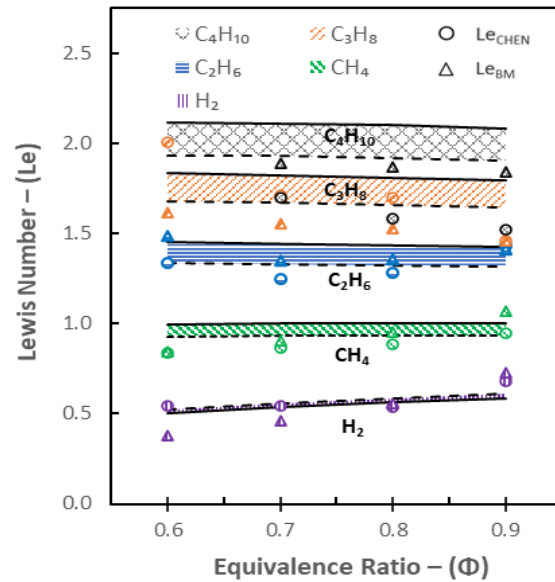
### 5.1 Pure Fuels

Prior to discussing results, it should be stressed that  $L_b$  is indicative of the influence of stretch on flame speed. In premixed flames, instabilities result from both hydrodynamic (Darrieus-Landau) and preferential-diffusional ( $Le$ ) instabilities [7,30]. Hence, in this study, experimental or theoretical  $L_b$  are utilised as a measure of a flame's susceptibility to instability and should only be viewed as indicative of the effect, not the cause. Historically, the combustion characteristics of CH<sub>4</sub> have been studied extensively using the spherically expanding flame configuration [30,31,33,56–58], however it should be noted that there remains relatively large scatter in the derived  $U_L$  and corresponding  $L_b$  values (see Supplementary Material S.1 & S.2). Large discrepancies that exist, up to 100% for  $L_b$ , have been attributed to mixture preparation (accuracy of  $\Phi$ ) as well as the correct selection of a suitable extrapolation technique for the fuel investigated, with stretch-models strongly dependent upon the  $Le$  of the mixture [37]. Furthermore, slope inversion of  $L_b$  (from positive to negative) for CH<sub>4</sub> ( $\Phi < 0.60$ ) has been reported several times [33,56,58] with opposed  $L_b$  consistently reported too [30,31], see S.2. A quantitative explanation behind these divergences has yet to be proposed, with behaviour either attributable to a physical-chemical phenomenon or uncertainty generated when extrapolating data. Published evaluations of the Lean  $Le$  Limit for CH<sub>4</sub> flames, range between  $Le = 0.955$  [14] and 1.01

[39], marginally above and below the critical value ( $Le = 1$ ). Consequently, two opposite flame behaviours are predicted for the same limit, with both measured experimentally (positive and negative  $L_b$ ). From a simple mass diffusion perspective ( $CH_4$ ,  $N_2$ ,  $O_2$  in this case), the relative diffusivities of the reactants relative to  $N_2$  gives  $CH_4$  is greater than  $O_2$ . For ultra-lean  $CH_4$ /air mixtures, increased stretch would increase local  $CH_4$  concentration within the flame front, thereby increasing burning intensity (through augmented flame temperature), influencing flame behaviour [59].



**Fig. 2** – Experimental  $L_b$  for  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ ,  $C_4H_{10}$  and  $H_2$  comparison across lean  $\Phi$



**Fig.3** – Theoretical and Experimental  $Le$  for and lean  $CH_4$ ,  $C_3H_8$  and  $H_2$  ( $H_2$  Exp. data [50]) Full & dotted lines reflect Hirschfelder & Wilke methods to evaluate  $D_{ij}$  (298K, 0.1MPa)

Fig. 2 illustrates measured  $L_b$  for the primary components of natural gas ( $C_1$ - $C_4$ ) and  $H_2$  under lean conditions. Note that all datasets presented in Fig. 2 were conducted at similar temperature ( $\pm 5K$ ) and pressure conditions, to those employed in this work. To facilitate fair comparison, the relationship relating flame speed to stretch employed to extrapolate  $L_b$  is also referenced. Flame characteristics of higher hydrocarbons ( $C_2H_6$ ,  $C_3H_8$ ,  $C_4H_{10}$ ) have been studied less than  $CH_4$ , although it is noted that there is a substantial literature of flame speed measurements for  $C_2H_6$  [1,33,60],  $C_3H_8$  [1,33,60] and  $C_4H_{10}$  [1,40], though considerably less so for measured  $L_b$ . Konnov et al. [61] recently undertook an exhaustive compilation of measured flame speeds for  $C_2$ +air flames generated using various experimental set-ups. The study highlights the scarcity of unstretched flame speed data for  $C_2H_6$  and  $C_3H_8$ , particularly in the case of spherically expanding flame configuration data, derived using contemporary nonlinear extrapolation techniques. Data illustrated in Fig. 2 fulfils this gap in knowledge under lean conditions, with corresponding  $U_L$  values provided in S.3. To highlight the influence of the extrapolation model on  $L_b$  values, average relative differences in measured  $L_b$  values for lean  $C_{1-4}$ /air mixtures, using LM(S) and NM(S) normalised to LM(C), are illustrated in S.4. Clearly, for fuels exhibiting  $Le \gg 1$  (i.e.  $C_{2-4}$ ), LM(S) overpredicts  $L_b$  values, with differences augmenting with increasing hydrocarbon number and decreasing  $\Phi$  (reflecting an increasing  $Le$ ), with significantly reduced differences recorded in relation to NM(S), in good agreement with the theoretical analysis conducted by Chen [37]. The same general trend is upheld when analysing unstretched flame speed, however, differences are substantially smaller ( $<10\%$ ), irrespective of the extrapolation model employed.

As can be seen in Fig. 2, at stoichiometric conditions, similar stretch-related behaviour (positive  $L_b$ ) are measured for  $C_{1-4}$  alkanes and  $H_2$  ( $H_2$  data sourced from Hu et al. [50], with positive  $L_b$  at  $\Phi=1.0$  also reported by [29,51]). With respect to the  $C_{1-4}$  fuels studied, increased variations in  $L_b$  occur as conditions shift leaner, with  $CH_4$  and  $C_2-C_4$  exhibiting opposing trends. It is noted that  $CH_4$  displays a behaviour characteristic to that of  $H_2$ , with  $L_b$  decreasing at leaner conditions.

Fig. 3 presents the  $Le$  behaviour of  $H_2$  and  $C_{1-4}$  alkanes under lean conditions. ‘Theoretical’ Lewis numbers, evaluated using the free stream properties of the mixtures, are illustrated as coloured bands, with the upper and lower limits (represented by full and broken lines) denoting the differences resulting from the application of either the Hirschfelder or Wilke method of mass-diffusion coefficient evaluation. Although the correct  $Le$  is evaluated ( $Le \sim 1$ ,  $Le > 1$ ,  $Le < 1$ , for  $CH_4$ ,  $C_{2-4}$ ,  $H_2$  respectively), little variation is observable across the  $\Phi$  range tested. Fundamental flame parameters such as the activation energy, flame thickness and thermal expansion, have been demonstrated to vary significantly for off-stoichiometric mixtures [43], influencing the flame’s sensitivity to stretch. Variations in those fundamental characteristics are not considered, since  $Le$  is evaluated simply as a function of the mixture’s thermal and mass diffusivity. As such,  $Le$  was evaluated from properties affecting the flame, attained experimentally (via  $L_b$ ) and numerically (via  $E_a$ ,  $\sigma$ ,  $\delta$ ), rendering  $Le$  a global parameter of the flame, as recommended by Jomaas et al. [48], through the use of theoretical relationships proposed in literature (denoted as  $Le_{CHEN}$  &  $Le_{BM}$ ). Evidently, as can be seen when comparing Fig. 2 and Fig. 3, analogous  $L_b$  and  $Le$  behaviour is apparent, irrespective of the theoretical relationship linking  $L_b$  to  $Le$ . Increasingly contrasting  $Le$  behaviour, with decreasing  $\Phi$ , is observable for  $CH_4$  and  $C_{2-4}$  alkanes (less so for  $C_2$ ), consistent with their measured stretch-related behaviour. It should be noted that for  $H_2$ , whilst exhibiting a positive measured  $L_b$  at stoichiometric conditions, all experimental  $Le$  formulations result in  $Le < 1$ .

The lean and rich limits of  $Le$  for each fuel ( $CH_4$ ,  $H_2$ ,  $C_{2-4}$ ) were evaluated to assess how well the considered formulations captured  $Le$  behaviour. The  $Le$  limits bound the minimum (lean) and maximum (rich) plausible  $Le$  values for ultra-lean and ultra-rich mixtures. Note that lean limits are largely dictated by mass-diffusion of fuel into  $N_2$  ( $\Phi < 1$ ), with rich limits dictated by mass diffusion of  $O_2$  into the fuel ( $\Phi > 1$ ). Although no experiments under rich conditions were conducted in this study, evaluations of the rich limit allow understanding of plausible variation of  $Le$  with changing  $\Phi$ . To evaluate these limits, the upper and lower flammability limits of the fuels were utilised. For  $CH_4$ , lean and rich limits were calculated to be 0.93 and 1.06, respectively, marginally smaller than those reported previously, namely 0.955 [14] and 0.98 [62] on the lean side, and 1.10 [39] on the rich side, underlining its equi-diffusive nature. Clearly, it can be seen from Fig. 3 that  $Le_{CHEN}$  better respects these limits, particularly at richer conditions, with  $Le_{BM}$  marginally above the rich limits at  $\Phi = 0.9$ , with the rising  $Le$  trends expected to increase further at richer conditions. In the case of  $C_2H_6$ , the lean limit (1.46) corresponds with Hawkes and Chen [62] value of 1.47, whilst no comparable values were found for the rich limit (0.94). It is noted that both evaluated formulations result in a similar decrease in  $Le$  between  $\Phi=0.6-0.7$ , prior to a gradual increase in  $Le$  as conditions get richer, hence not satisfactorily capturing the expected decreasing  $Le$  trend as conditions get richer. With respect to  $C_3H_8$ ,  $Le_{BM}$  shows closest agreement with the lean and rich limits, evaluated at 1.87 and 0.92, respectively. Again, these limits are in good agreement with those found in literature, with Law and Sung [59] citing 1.87 and 0.92, for rich and lean  $Le$  limits, respectively. With respect to  $C_4H_{10}$ , no sources were found to compare the  $Le$  limits for this fuel, with lean and rich limits slightly higher (2.04) and lower (0.88), respectively, than those of  $C_3H_8$ . However, the expected trend of decreasing  $Le$  with increasing  $\Phi$  is exhibited by both formulations, most pronounced upon application of  $Le_{CHEN}$ . With respect to  $H_2$ ,  $Le$  lean and rich limits were evaluated to be 0.34 and 2.02, in good agreement with literature on the lean side, 0.29 [39,62] and 0.33 [59]. The rich limit evaluated in this study (2.02) is however, smaller than other reported values, 2.32 [59] and 2.58 [39], potentially due to the underestimation of  $H_2$  binary

mass diffusion coefficients, as highlighted previously. Overall,  $Le_{CHEN}$  best captures expected thermo-diffusive behaviour for  $CH_4$ , in agreement with Lapalme [39]. Better agreement is attained by all formulations for lean  $H_2$  and  $C_{3-4}$  alkane combustion.

## 5.2 Binary Blends across Lean $\Phi$

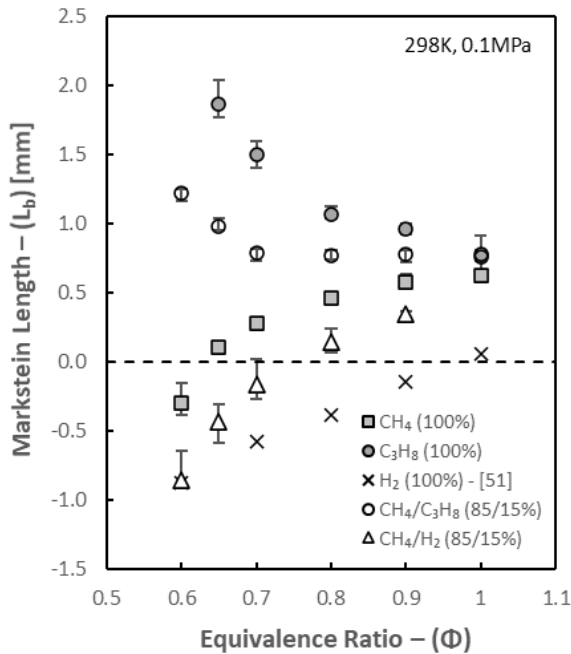


Fig. 4 –  $L_b$  vs  $\Phi$  for Selected Pure & Binary Blends

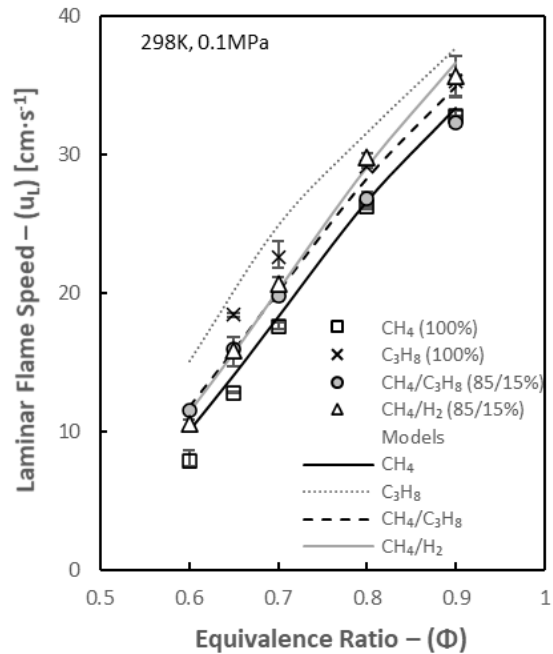
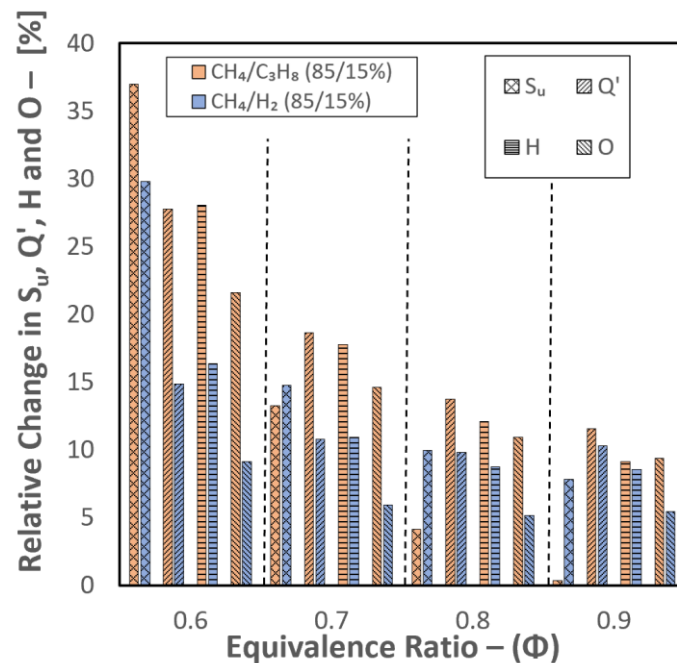


Fig. 5 –  $U_L$  for selected Pure and binary blends

Model results from Aramco 1.3

To further assess the observed opposite preferential diffusional behaviour of  $H_2$  and  $C_3H_8$ ,  $CH_4$  was subsequently blended at 15% (vol.) with  $H_2$  and  $C_3H_8$  respectively, with this blend ratio maintained across  $\Phi = 0.60 - 1.0$ , with Fig. 4 and 5 illustrating measured  $L_b$  and  $U_L$  values respectively. Note that unless otherwise stated, error bars represent maximum and minimum recorded values, around an average plotted value (minimum of 3 repeats), for graphs of experimental  $L_b$  and  $U_L$  values. Clearly, 15% (vol.) enrichment of  $CH_4$  with either  $H_2$  or  $C_3H_8$  has limited influence on  $L_b$  approaching stoichiometry ( $\Phi=0.90$ ), a consequence of each specific fuels' having similar response to stretch and  $Le$  behaviour at such conditions. However, it is evident in Fig. 4 that  $H_2$  and  $C_3H_8$  yield increasingly divergent influence on  $CH_4$  flame stability, with  $H_2$  enrichment resulting in promoting preferential diffusional instabilities, reflected by measured negative  $L_b$  values. A shift in  $L_b$  sign inversion (from positive to negative) is observable, from  $\Phi \sim 0.60 - 0.65$  for the 100%  $CH_4$  to  $\Phi \sim 0.70 - 0.80$  for the  $CH_4/H_2$  blend. It should be emphasised that near equivalent stretch behaviour was exhibited by pure  $H_2$ , as measured by Hu et al. [50], and the  $CH_4/H_2$  (85/15) mixtures at the leanest conditions. However, it is noted a linear extrapolation model [LM(S)] was utilised by Hu et al. [50], whilst a non-linear model [NM(S)] was applied in this work. As demonstrated by Chen, for mixtures exhibiting  $Le < 0.65$ , as is the case for lean ( $\Phi < 0.70$ )  $H_2$  (with 'theoretical' and experimental  $Le < 0.60$ , Fig. 3), NM(S) is preferable. It thus seems probable that  $L_b$  measurements of  $H_2$ /air flames published using LM(S), greatly overpredict  $L_b$  values with  $H_2$  displaying much lower (negative)  $L_b$  than currently reported. On the other hand, it can be seen from Fig. 4 that the  $CH_4/C_3H_8$  (85/15) exhibits very limited change in measured  $L_b$  for  $\Phi = 0.70 - 1.0$ . At leaner conditions,  $CH_4/C_3H_8$  mixtures display a stretch response like that of pure  $C_3H_8$ , with a transition point apparent at  $\Phi \sim 0.70$ ; this characteristic is investigated further in Section 5.3.

Fig. 5 presents the measured  $U_L$  values of selected pure fuels tested binary blends alongside values attained numerically. USC-II (2007) [63], GRI-Mech 3.0 (1999) [64], San Diego (2014) [65] and Aramco 1.3 (2013) [42] reaction mechanisms were all appraised, however only the latter is illustrated since it consistently gave best agreement with all blends evaluated in this study. As can be seen from Fig. 5, the addition of either  $H_2$  or  $C_3H_8$  to ultra-lean ( $\leq 0.70 \Phi$ )  $CH_4$ -based flames resulted in significant relative increases in flame speed (at  $\Phi=0.60$  relative increase in  $S_u \sim 30\%$  and  $\sim 37\%$  upon 15% vol.  $H_2$  or  $C_3H_8$  addition, respectively), with augmentation in flame propagation substantially decreasing at increasingly richer conditions, with  $C_3H_8$  addition resulting in nominal  $U_L$  enhancement at  $\Phi > 0.80$ . The CHEMKIN-Pro package employing the PREMIX module, to simulate a premixed 1-D adiabatic planar flame, was used to provide better understand reactivity trends displayed in Fig. 5. A simulation domain of 10 cm was considered, with a total of 1000 grid points used with grid parameters GRID (0.025) and CURV (0.1), including multi-component diffusion and an assumed air composition of 79%  $N_2$  – 21%  $O_2$ . The Aramco 1.3 reaction mechanism was utilised to generate numerical volumetric heat release rates ( $Q'$ ) and concentration of mole fractions of active radicals (H and O). Relative changes in measured  $S_u$  and numerically attained  $Q'$ , H and O mole fractions, normalised to that of pure  $CH_4$ , across lean conditions ( $\Phi=0.6 - 0.9$ ), are presented in Figure 6.



**Fig. 6** – Relative changes in measured  $S_u$  and modelled  $Q'$ , H and O mole fraction concentration, normalised to that of pure  $CH_4$ , for  $CH_4/H_2$  and  $CH_4/C_3H_8$  (85/15% vol.) blends at  $\Phi = 0.6 - 0.9$ .

Interestingly, volumetric additions of 15%  $C_3H_8$  or  $H_2$  to ultra-lean  $CH_4$  flames ( $\leq 0.70 \Phi$ ) produce comparable flame propagation effects. The increased reactivity of lean  $CH_4/H_2$  flames has been suitably reported [21,66], with modelling work and sensitivity analysis suggesting that the flame speed, burning intensity ( $Q'$ ), and production of radicals (notably H), appear to be strongly correlated, in agreement with measured and modelled values presented in Fig. 6. Furthermore, as evident from Fig. 6, at near stoichiometric conditions ( $\Phi = 0.9$ ),  $C_3H_8$  (15%) addition to  $CH_4$  results in practically similar relative increase in  $Q'$  as  $H_2$  addition (15%). However, when moving towards leaner conditions,  $C_3H_8$  additions yield higher relative increases in  $Q'$  than  $H_2$  addition, practically double at leanest conditions ( $\Phi=0.60$ ), in agreement with witnessed  $S_u$  augmentations. It should be emphasised that the heat of combustion per mass (kJ/mol) of  $H_2$  is 2 to 3 times greater than that of  $C_3H_8$ , however there are significant differences in terms of molecular mass between both fuels consequently suppressing the higher heat of combustion exhibited by  $H_2$ . Comparison of relative increases in

production of radical fractions (H and O) in CH<sub>4</sub> flames due to the addition of H<sub>2</sub> or C<sub>3</sub>H<sub>8</sub> (15% vol.) are plotted in Fig. 6. Modelled values predict an enhanced production of radicals related to the presence of C<sub>3</sub>H<sub>8</sub> than H<sub>2</sub>, with differences in radical production increasing with decreasing  $\Phi$ , highlighting the importance of small amounts of hydrocarbons on the oxidation mechanics of CH<sub>4</sub>. When no other fuel is present, CH<sub>4</sub> oxidation is initiated by its reaction with O<sub>2</sub> and by thermal dissociation [7,67]. For the lean CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> blends, C<sub>3</sub>H<sub>8</sub> reacts first, leading to the formation of radicals enhancing the oxidation mechanics of CH<sub>4</sub>, leading to similar increases in both burning intensity and reactivity, reflected by augmented flame speeds. Thus, both H<sub>2</sub> and C<sub>3</sub>H<sub>8</sub> promote flame propagation of ultra-lean methane-based fuels, to a similar extent for 15% volumetric enrichment levels, however, yield opposite stretch related and Le behaviour.

### 5.3 Experimental and Numerical Study of Binary Blends

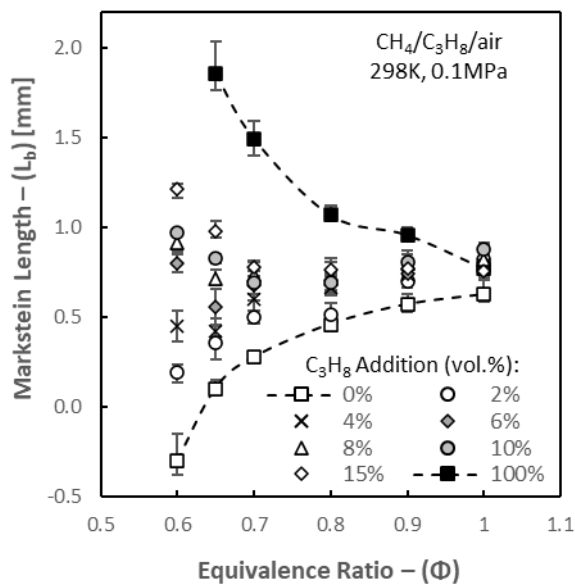


Fig. 7 –  $L_b$  vs  $\Phi$  for CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub>

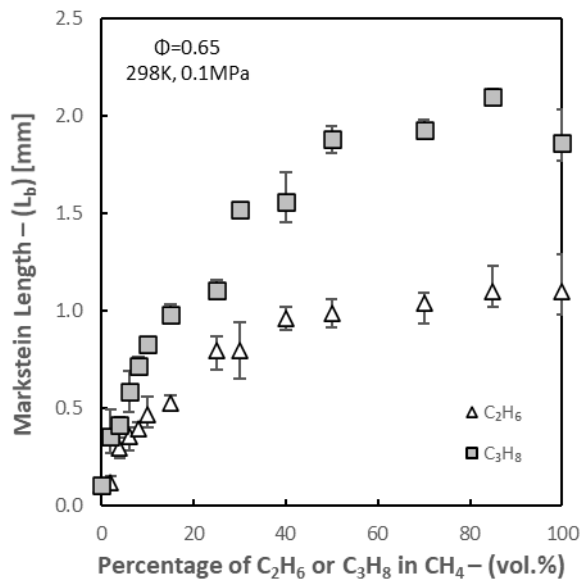
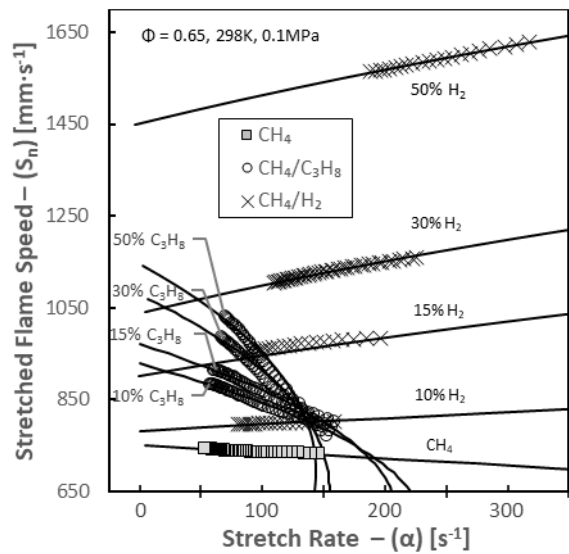


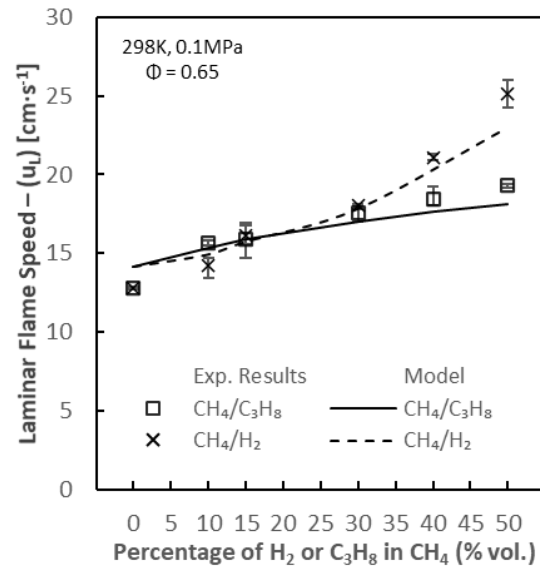
Fig. 8 – Influence of Fuel Mixtures on  $L_b$

To investigate the thermo-diffusive influence of small additions of C<sub>3</sub>H<sub>8</sub> on CH<sub>4</sub>, practically representative of natural gas variations, a study was conducted under lean combustion conditions ( $\Phi=0.60 - 1.0$ ).  $L_b$  behaviour is illustrated in Fig. 7. with all CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> blends exhibiting similar stretch-related behaviour at  $\Phi \geq 0.70$ , with minimal variation in measured  $L_b$ . At leaner conditions, the C<sub>3</sub>H<sub>8</sub> component becomes noticeable, with blends containing up to 4% C<sub>3</sub>H<sub>8</sub>, maintaining a  $L_b$  behaviour reflective of that of CH<sub>4</sub>, where  $L_b$  decreases at increasingly leaner conditions. This alludes to the fact that mass diffusion becomes increasingly more prevalent, whilst still not becoming the dominant transport mechanism. Blends containing greater than 6% C<sub>3</sub>H<sub>8</sub>, start displaying a noticeable rise in measured  $L_b$ , notwithstanding that the mixtures are still predominantly CH<sub>4</sub> (molecular weight ratio  $\sim 5.5:1$  for a 94/6% CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> blend), with relatively small concentrations of C<sub>3</sub>H<sub>8</sub> dictating the flames response to stretch. To investigate the influence of heavier hydrocarbons on stretch response of lean CH<sub>4</sub> based fuels further, a study of CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> and CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> blends at a fixed  $\Phi = 0.65$  was undertaken, with  $L_b$  measurements illustrated in Fig. 8. Clearly, relatively small additions of heavier hydrocarbons (<15%) yield a significant response on the stretch-sensitivity of CH<sub>4</sub>, naturally with this effect increasing the heavier the hydrocarbon, as a direct consequence of the blends increasing  $L_e$ . With respect to C<sub>2</sub>H<sub>6</sub> addition, it is noted that there appears to be two distinctive trends, with important incremental changes in  $L_b$  response up to 25% additions, prior to an observed plateauing in  $L_b$ , arising when the molecular weight ratio of the CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> blend is near equal ( $\sim 1:1$ , 65/35%). Little change in stretch response is reported beyond this point, with behaviour akin of pure C<sub>2</sub>H<sub>6</sub> exhibited upon any

further enrichment. A similar response is noted with the CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> blends, with important incremental increases in L<sub>b</sub> up to 30% C<sub>3</sub>H<sub>8</sub> content, although a more linear response is observable compared with the CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> blend.



**Fig. 9** – Stretch Response of CH<sub>4</sub> with H<sub>2</sub> and C<sub>3</sub>H<sub>8</sub>

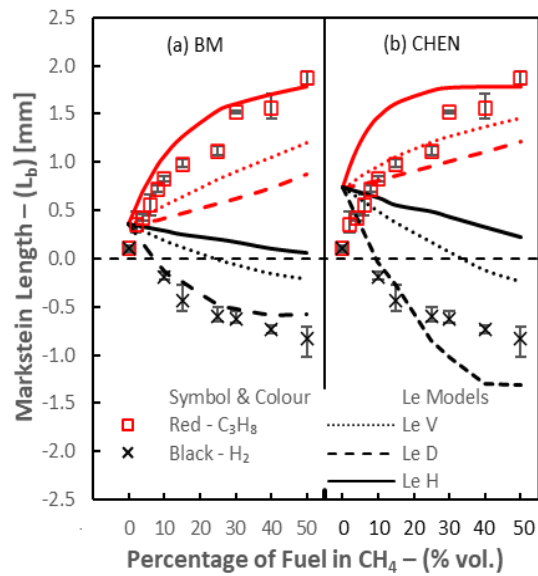


**Fig. 10** –  $u_L$  values of CH<sub>4</sub>/H<sub>2</sub> and CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> Model results from Aramco 1.3

Fig. 9 illustrates the relationship between the stretched flame speed and stretch rate for CH<sub>4</sub>, CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> and CH<sub>4</sub>/H<sub>2</sub> mixtures at an  $\Phi = 0.65$ , with a positive gradient representative of an acceleration in flame speed with increasing stretch rates, equating to a negative L<sub>b</sub>. Note that only one in three data points is plotted, to enhance readability, with NM(S) superimposed as solid lines. CH<sub>4</sub> exhibits quasi-equi-diffusion of heat and mass transport mechanisms ( $Le \sim 1$ ), with flame propagation practically independent of stretch and curvature effects, exemplified with a gradient close to zero. Significant changes are observed with the addition of H<sub>2</sub>, with an inversion in the gradient observable, and flames now experiencing acceleration with increasing stretch, with the opposite behaviour observed upon C<sub>3</sub>H<sub>8</sub> enrichment, as shown previously in Fig. 8. Hence, a CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> flame displaying  $Le > 1$  (positive L<sub>b</sub>) would be weakened in highly stretched (turbulent) environments, whilst the CH<sub>4</sub>/H<sub>2</sub> exhibiting  $Le < 1$  (negative L<sub>b</sub>) would accelerate. This thermo-diffusive flame response inevitably impacts the operation of practical combustion systems.

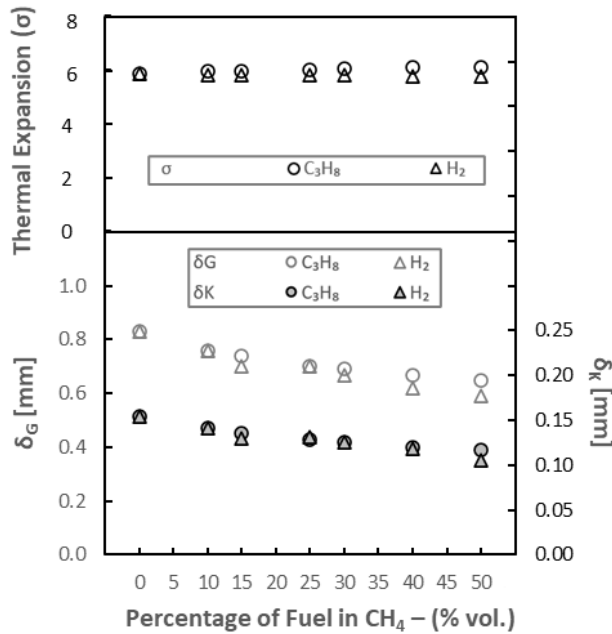
Fig. 10 presents the measured laminar burning velocities of the CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> and CH<sub>4</sub>/H<sub>2</sub> mixtures for  $\Phi = 0.65$ , with lines representing modelled values using the Aramco 1.3 mechanism. It is clearly observable that up to 30% enrichment of either H<sub>2</sub> or C<sub>3</sub>H<sub>8</sub> results in similar enhancement of flame reactivity, with this trend well captured by the Aramco 1.3 mechanism. Although displaying comparable flame propagation velocities, H<sub>2</sub> and C<sub>3</sub>H<sub>8</sub> flames exhibit opposite thermo-diffusive combustion responses with corresponding stretch-related behaviour to CH<sub>4</sub> based fuels. To better understand the nature of the augmented burning intensity of CH<sub>4</sub>/H<sub>2</sub> and CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> flames measured, a sensitivity analysis related to the contribution of major flame enhancing pathways (thermal, diffusive, kinetic) was undertaken. However, to correctly quantify the diffusive pathway, a suitable Le formulation must be validated.



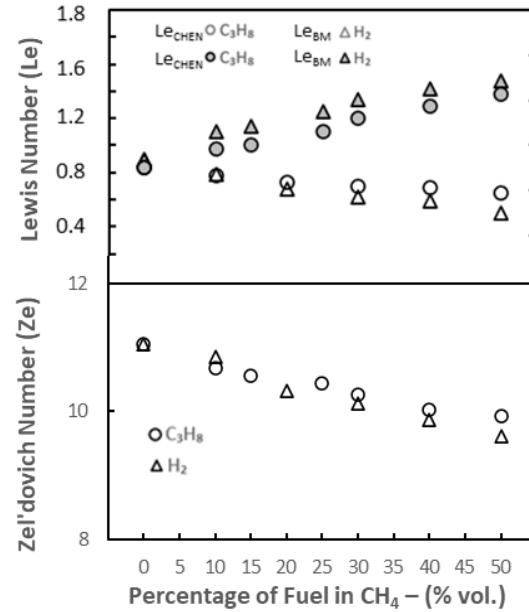


**Fig. 11** – Comparison of  $L_{b-BM}$  &  $L_{b-CHEN}$  models to measured  $L_b$

Consistent with methods presented earlier (Section 4.1 – 4.3),  $Le_{eff}$  models (i.e.  $Le_V$ ,  $Le_D$ ,  $Le_H$ ) are employed in turn to yield a numerical  $L_b$ , using the relationships  $L_b$  to  $Le$  as proposed by Chen [26,37] and Matalon & Bechtold (BM) [43], referred to in text as  $L_{b-CHEN}$  and  $L_{b-BM}$ , respectively. It should be noted that the aim of such analysis is not quantitative in nature, rather qualitative trends are sought, to validate which  $Le_{eff}$  model best captures the exhibited stretch-related behaviour of the evaluated blends.  $L_{b-CHEN}$  and  $L_{b-BM}$  for the  $CH_4/H_2$  and  $CH_4/C_3H_8$  blends are presented in Fig. 11, alongside experimentally measured  $L_b$  values. In the case of the BM formulation, both quantitative and qualitative agreement is only observed with  $Le_H$  and  $Le_D$ , for  $CH_4/C_3H_8$  and the  $CH_4/H_2$  blends, respectively. Minimal differences are noted between measured  $L_b$  and numerical  $L_{b-BM}$  across the mixture concentrations. Furthermore, the incremental changes observed in  $L_b$  upon small enrichment fractions of  $C_3H_8$  (2 – 15% vol.) is well captured. Poorer agreement is observed with the CHEN formulation, with again,  $Le_H$  and  $Le_D$  best reflecting expected stretch behaviour for  $CH_4/C_3H_8$  and the  $CH_4/H_2$  blends, respectively. The fact that an  $Le_D$  formulation displays best agreement with  $CH_4/H_2$  at very lean conditions is expected, given that the  $Le_D$  formulation was derived from modelling of lean turbulent  $CH_4/H_2$  flames [14]. This is influenced due to the assumption that flame curvature is dominant, hence local enrichment of the most diffusive fuel at the flames leading edge is predicted. Since for ultra-lean conditions  $H_2$  and  $CH_4$  have higher mass diffusivities than  $O_2$ , this concept appears valid. Bouvet et al., [49] conducted similar research, concluding that an  $Le_V$  model employing the CHEN relationship better captured changes in thermo-diffusive response of  $CH_4/H_2$ . However, Bouvet and co-workers evaluated  $CH_4/H_2$  flame behaviour at richer conditions than presented herein, ( $\Phi = 0.80$ ). It is noted that similar analysis was conducted at richer conditions ( $\Phi = 0.80 - 1.0$ ) not presented herein but available in [17], with an  $Le_V$  formulation demonstrating better agreement with measured  $L_b$ , in agreement with Bouvet et al., [49]. Consequently, it appears that for ultra-lean  $CH_4/H_2$  blends ( $\Phi < 0.70$ ),  $Le_D$  best depicts expected thermo-diffusive behaviour.



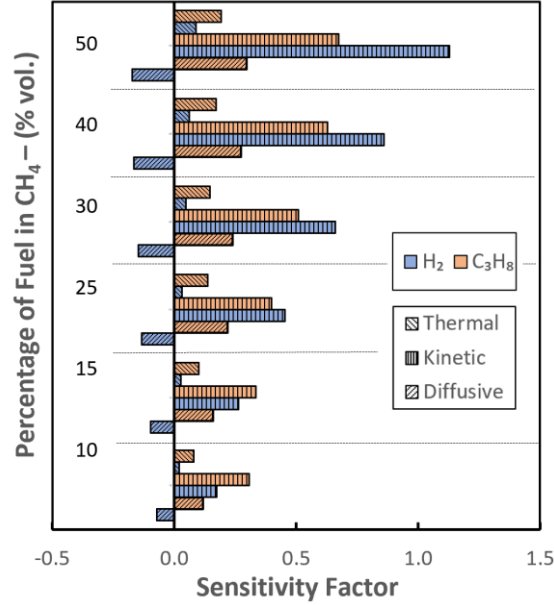
**Fig. 12** – Variations in  $\delta$  and  $\sigma$  with addition of C<sub>3</sub>H<sub>8</sub> or H<sub>2</sub> ( $\Phi=0.65$ )



**Fig. 13** – Variations in Ze and Le with addition of C<sub>3</sub>H<sub>8</sub> or H<sub>2</sub> ( $\Phi=0.65$ )

Kwon et al. [68], in their study of cellular instabilities and self-acceleration of outwardly propagating spherical flames, emphasised that the most important parameters that induce hydrodynamic and diffusional-thermal cellularities are; thermal expansion, flame thickness, non-unity Le and global activation energy (or equivalently Ze [68]). Hydrodynamic instabilities originate from the thermal expansion of gases [7], with the growth rate of hydrodynamic instability proportional to the density jump across the flame, in the limit of an infinitely thin flame propagating at a constant velocity, consistent with the hydrodynamic theory of Darrieus and Landau [7]. For outwardly propagating spherical flames, curvature induced positive stretch tends to stabilise the flame, as such the flame thickness plays a significant role, since the thinner the flame the weaker the influence of curvature, hence the risk of destabilisation is increased. It is interesting to note in Fig. 12 that in the case of the CH<sub>4</sub>/H<sub>2</sub> flames, the thermal expansion remains almost constant (relative differences < 2%), whilst the flame thickness decreases, with increasing H<sub>2</sub> fractions (up to 50% vol.), in effect promoting hydrodynamic instabilities. With respect to the CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> flames, the thermal expansion also remains almost constant (< 3%), with the flame thickness also decreasing with increasing C<sub>3</sub>H<sub>8</sub> fraction at a similar rate as with H<sub>2</sub> enrichment, thereby also promoting hydrodynamic instabilities. C<sub>3</sub>H<sub>8</sub> and H<sub>2</sub> addition to ultra-lean CH<sub>4</sub>, however, result in the opposite L<sub>b</sub> behaviour. The development of thermo-diffusional instabilities results from effect of non-equidiffusion, represented by Le. With respect to the CH<sub>4</sub>/H<sub>2</sub> flames, the effects of preferential diffusion, are a consequence of the higher mass diffusivity of H<sub>2</sub> and CH<sub>4</sub> compared to the O<sub>2</sub> molecule. Since Le decreases with increasing H<sub>2</sub> concentration (Fig. 13), diffusional-thermal instabilities are promoted. It should be noted that the front structure of the ultra-lean CH<sub>4</sub>/H<sub>2</sub> flame remained 'smooth', with some large 'cracks' appearing on the flame surface, with increasing H<sub>2</sub> fraction (>25%) and at large flame radii, although no cellular growth was observed. Since the development of preferential diffusional instabilities requires a modification of the flame structure, Kwon et al. [68] emphasised that it is reasonable to expect that the global activation energy (illustrated as Ze in Fig. 13), should also impact on the development of cellularity. As such, a lower E<sub>a</sub> will tend to enhance instability of a diffusionaly unstable flame, such as the CH<sub>4</sub>/H<sub>2</sub> flame, with both Le and Ze decreasing with increasing H<sub>2</sub> content, as illustrated in Fig.

13. For lean CH<sub>4</sub>/H<sub>2</sub>, changes in measured L<sub>b</sub> are thus potentially the result of the competing hydrodynamic and thermo-diffusive instabilities. However, with respect to the CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> flames, since the mass diffusivity of C<sub>3</sub>H<sub>8</sub> is lower than that of air, diffusional-thermal effects (Le > 1, see Fig. 13) seem to have the propensity of moderating hydrodynamic instabilities, yielding a stabilising influence on the flame, reflected in augmented L<sub>b</sub>.



**Fig. 14** – Sensitivity Analysis of U<sub>L</sub> for CH<sub>4</sub>/H<sub>2</sub> and CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> blends, Φ=0.65

Enhancement in flame speed due to enrichment of H<sub>2</sub> or C<sub>3</sub>H<sub>8</sub> to CH<sub>4</sub> can be categorised as a combination of thermal, kinetic, and diffusive effects [47,69]. The individual impact of each pathway can be modelled as per Eqn. 15:

$$U_L \sim (D_T \cdot Le_{eff})^{1/2} \exp(-T_a/2T_{ad}) \quad \text{Eqn. (15)}$$

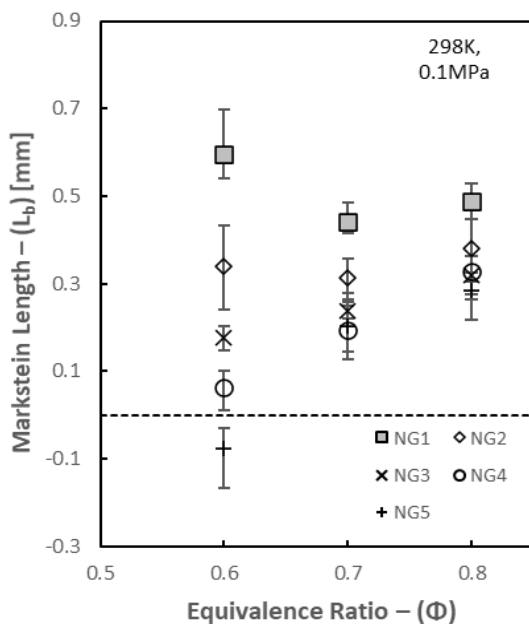
The first term on the right-hand side  $[(D_T \cdot Le_{eff})]$  reflects the diffusive influence. The second term  $[\exp(-T_a/2T_{ad})]$ , represents the Arrhenius factor, which incorporates the relative influence of the global activation energy through the activation temperature  $[T_a = (E_a/R_u)]$  and the adiabatic flame temperature. These individually represent the kinetic ( $T_a$ ) and thermal ( $T_{ad}$ ) influences on flame speed. With respect to Le formulation, it was determined from Fig. 11 that an Le<sub>H</sub> and Le<sub>D</sub> formulation best captured changes in thermo-diffusive behaviour for the CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> and CH<sub>4</sub>/H<sub>2</sub> blends at an Φ = 0.65, respectively. This conclusion is maintained irrespective of the theoretical relationship employed relating L<sub>b</sub> to Le, and consequently applied for the following analysis. Eqn. 15 can be differentiated to determine the sensitivity of each individual pathway on the overall influence of the flame propagation. Thus, the overall sensitivity coefficient can be expressed as:

$$\frac{1}{U_L} \cdot \frac{dU_L}{dx} = \frac{1}{2 \cdot D_T \cdot Le} \cdot \frac{d(D_T \cdot Le)}{dx} - \frac{1}{2 \cdot T_{ad}} \cdot \frac{2 \cdot T_a}{dx} + \frac{T_a}{2 \cdot T_{ad}^2} \cdot \frac{2 \cdot T_{ad}}{dx} \quad \text{Eqn. (16)}$$

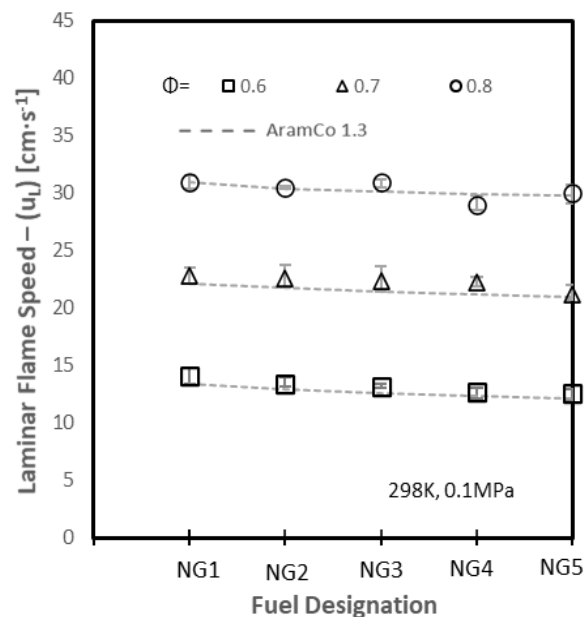
where 'x' is the volume fraction of either H<sub>2</sub> or C<sub>3</sub>H<sub>8</sub> in the individual fuel blend. Note that the three terms on the right-hand side denote the influence of the diffusive, kinetic, and thermal effects, respectively. Sensitivity analysis for the blends considered is presented in Fig. 14, with a positive and

negative sensitivity factor representing flame speed enhancement and inhibition, correspondingly. For the  $\text{CH}_4/\text{H}_2$  and  $\text{CH}_4/\text{C}_3\text{H}_8$  blends, enhancement in flame speed is principally an Arrhenius effect (kinetic), principally through the reduction of overall activation energy and thus the activation temperature. For identical volumetric additions up to 15%,  $\text{C}_3\text{H}_8$  blends yield a greater reduction in  $E_a$  than  $\text{H}_2$ , with  $\text{H}_2$  having a greater influence for higher fractions, due to their molecular weights. This trend is well captured by both experimental and modelling flame speed results (Fig. 10), with  $\text{H}_2$  addition above 30% resulting in significantly greater flame speeds than for the equivalent  $\text{C}_3\text{H}_8$  case. With respect to the thermal pathway, its impact is modest in comparison to the kinetic effect, with the influence of the thermal pathway correlating with nominal modelled changes in adiabatic flame temperature, with  $\text{C}_3\text{H}_8$  and  $\text{H}_2$  addition resulting in changes in adiabatic flame temperature of  $< 50 \text{ K}$  and  $< 25 \text{ K}$ , respectively. In terms of the diffusive pathway,  $\text{C}_3\text{H}_8$  and  $\text{H}_2$  result in sensitivity of similar strength, but with opposite sensitivity, consistent with their  $Le$  trends, increasing and decreasing, respectively. The conclusions drawn thus far, can be used to explain the differences in flame speeds between the ultra-lean  $\text{CH}_4/\text{C}_3\text{H}_8$  and  $\text{CH}_4/\text{H}_2$  blends, with up to 30% volumetric additions of  $\text{C}_3\text{H}_8$  or  $\text{H}_2$  resulting in similar flame enhancement of  $\text{CH}_4$ -based fuels, and  $\text{H}_2$  having greater influence for higher fractions. It should be noted however, that conclusions should be taken qualitatively rather than from a quantitative perspective, given there exists several different theoretical formulations to evaluate the same fundamental property (e.g.  $E_a$ , see Section 4.1). Furthermore, differences are to be expected by applying different reaction mechanisms, due to the number of identical reactions within each mechanism that have different associated Arrhenius coefficients [70]. However, it is noted that qualitative trends should remain valid, and thus performing such sensitivity analysis from first principles remains relevant providing useful insights.

#### 5.4 Tertiary Natural Gas and Hydrogen Blends



**Fig. 15** – Measured  $L_b$  for various NG for selected NG compositions



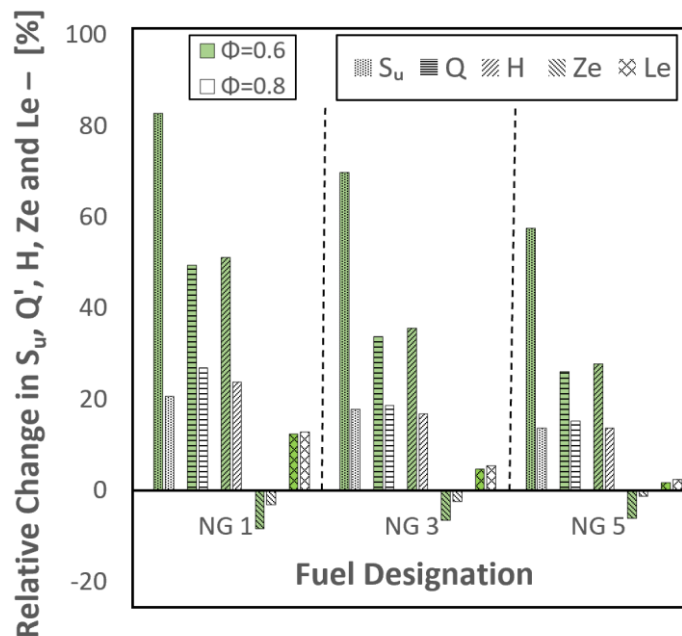
**Fig. 16** – Measured and Modelled  $u_L$  values for selected NG compositions

Having examined and quantified the lean combustion characteristics of  $\text{C}_{1-4}$  alkanes and binary blends of  $\text{CH}_4/\text{C}_3\text{H}_8$  and  $\text{CH}_4/\text{H}_2$ , an understanding of the impact of tertiary blends was considered. Plausible short-term variations in hydrogen-enriched multi-component natural gas (NG)

flame combustion characteristics were experimentally and numerically investigated, with compositions of mixtures detailed in Table 1.

Measured  $L_b$  of NG/H<sub>2</sub> blends are illustrated in Fig. 15. Evidently, at the richest conditions ( $\Phi=0.80$ ),  $L_b$  behaviour is consistent with that previously measured for pure CH<sub>4</sub>, C<sub>3</sub>H<sub>8</sub> and CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> binary mixtures (see Fig. 4), with H<sub>2</sub> (15% by vol.) yielding nominal influence on flame stability characteristics (positive  $L_b$ ,  $Le > 1$ ) as expected. However, significant changes in flame behaviour are observable at leaner conditions, with small variations in NG composition (CH<sub>4</sub>:C<sub>3</sub>H<sub>8</sub> molar ratio) discernibly influencing flame-stretch propagation characteristics, with NG1 and NG5 containing the largest fractions of C<sub>3</sub>H<sub>8</sub> and CH<sub>4</sub>, respectively, behaving in analogous manner to that of pure C<sub>3</sub>H<sub>8</sub> (positive  $L_b$ ) and CH<sub>4</sub> (negative  $L_b$ ) at  $\Phi=0.60$  (see Fig.4). From a preferential-diffusional perspective, H<sub>2</sub> and C<sub>3</sub>H<sub>8</sub> promote opposite lean CH<sub>4</sub> based flame stability behaviour, with the influence of H<sub>2</sub> prominent for NG 3 – 5, which exhibit decreasing  $L_b$  as conditions get leaner. NG5, the blend containing the highest fraction of CH<sub>4</sub> (lowest C<sub>3</sub>H<sub>8</sub> fraction), is observed to display a negative  $L_b$ , indicating an acceleration of the flame with stretch, behaviour equivalent to results presented for 100% CH<sub>4</sub> and CH<sub>4</sub>/H<sub>2</sub> (85/15%,  $\Phi=0.60$ , Fig 4). Conversely, NG1 exhibits increasing  $L_b$  as  $\Phi$  decreases, with the influence of H<sub>2</sub> counteracted by the higher fraction of C<sub>3</sub>H<sub>8</sub>. Khan et al., [19], measured  $L_b$  for various H<sub>2</sub>-enriched NG (CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub>) compositions, showing a reduction in  $L_b$  with decreasing heavier hydrocarbon fraction for a fixed volumetric H<sub>2</sub> addition, in good agreement with trends illustrated in Fig. 15.

Fig. 16 presents the measured laminar burning velocities of the NG/H<sub>2</sub> mixtures ( $\Phi=0.6 - 0.8$ ), with lines representing modelled values using the Aramco 1.3 mechanism. Generally, a marginal decrease in  $U_L$  is measured with decreasing C<sub>3</sub>H<sub>8</sub> fraction (NG 1  $\rightarrow$  NG 5), with leanest flames most prominently affected. As can be seen, this trend very well captured by the Aramco 1.3 reaction mechanism. At equivalent  $\Phi$ , the previously tested binary blends (CH<sub>4</sub>/H<sub>2</sub> & CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> [85/15% vol.]), CH<sub>4</sub>-based fuels exhibited equivalently enhanced reactivity at leanest conditions, upon H<sub>2</sub> or C<sub>3</sub>H<sub>8</sub> addition, in good agreement with  $U_L$  values observed for the tested NG blends.



**Fig. 17** – Relative changes, normalised to pure CH<sub>4</sub>, in  $S_u$ ,  $Q'$ , H radical, Ze and Le between NG 1 – 3 – 5, at  $\Phi=0.60$  & 0.80

The sensitivity analysis performed in Section 5.3 (see Fig. 14), concluded that observed augmentations in flame propagation of ultra-lean ( $\Phi=0.65$ )  $\text{CH}_4/\text{H}_2$  and  $\text{CH}_4/\text{C}_3\text{H}_8$  (up to 50% vol.) was principally an Arrhenius effect, through the reduction of the global activation energy. Consistent with modelling details described earlier (Section 5.2), Fig. 17 depicts relative changes in global activation energy (through  $Z_e$ ), normalised to that of pure  $\text{CH}_4$ , for NG1 (lowest  $\text{CH}_4$  content), NG3, and NG5 (highest  $\text{CH}_4$  content), for  $\Phi=0.60$  and  $0.80$ , alongside modelled relative changes in unstretched flame speed ( $S_u$ ), volumetric heat release rates ( $Q'$ ), concentration of mole fractions of H radicals, and effective Lewis Number ( $Le_{\text{eff}}$ ). Evidently, at the leanest conditions, NG compositions with the highest  $\text{C}_3\text{H}_8$  content (NG 1) display greatest reduction in  $Z_e$  ( $E_a$ ), consistent with enhanced augmentation in measured  $S_u$ . It is noted that the relative changes in adiabatic flame temperature exhibited by the NG blends are negligible (<2%), irrespective of  $\Phi$  specified, re-affirming that changes in attained laminar flame speeds are principally kinetic in nature and not thermal. Since all NG compositions tested contain equal volumetric  $\text{H}_2$  fractions, changes in  $E_a$  are principally related to variations in  $\text{CH}_4:\text{C}_3\text{H}_8$  content. Furthermore, as previously discussed,  $\text{H}_2$  and  $\text{C}_3\text{H}_8$  fuels display higher heat of combustion per mass than  $\text{CH}_4$ , hence measured changes in flame speed are directly correlated to changes in  $Q'$ , with production of key radicals, notably H, influencing  $\text{CH}_4$  oxidation mechanisms. As expected, NG blends containing the highest volumetric concentrations of  $\text{C}_3\text{H}_8$  for a fixed  $\text{H}_2$  enrichment level (15% by vol.) yield greatest augmentations in modelled  $Q'$ , with enhancement promoted with decreasing  $\Phi$ , as illustrated in Fig. 17. The same trend exists with respect to predicted H radical production concentrations, in good agreement with measured  $U_l$  trends.

## Conclusions

The influence of changing Le on-flame behaviour of lean  $\text{CH}_4$ ,  $\text{CH}_4/\text{C}_3\text{H}_8$  and  $\text{CH}_4/\text{H}_2$ , and  $\text{H}_2$ -enriched natural gas mixtures has been investigated in detail, employing the spherically expanding flame configuration to measure flame speed and corresponding Markstein length. From this work the following can be concluded:

- Equal volumetric additions of either  $\text{H}_2$  and  $\text{C}_3\text{H}_8$  to  $\text{CH}_4$  flames (up to 30% by vol.) result in similar enhancement of burning rate with opposing susceptibility to preferential diffusional instability. It is noted the influence of  $\text{H}_2$  and  $\text{C}_3\text{H}_8$  yield greatest influence at leanest conditions, a reflection of each individual fuels' Le behaviour. At a fixed equivalence ratio of 0.65, limited changes in composition provide a marked change in the premixed flame response with the addition of  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$  to  $\text{CH}_4$ , with  $L_b$  plateauing clearly identifiable for  $\text{C}_2\text{H}_6$ , less so for  $\text{C}_3\text{H}_8$ .
- A diffusional based Lewis Number formulation ( $Le_D$ ) yielded best correlation with measured stretch related behaviour of lean ( $\Phi \leq 0.7$ )  $\text{CH}_4/\text{H}_2$  mixtures containing up to 50%  $\text{H}_2$ , whilst a heat-release model ( $Le_H$ ) resulted in better agreement with lean  $\text{CH}_4/\text{C}_3\text{H}_8$  mixtures, with the formulation linking Le to  $L_b$  proposed by Bechtold and Matalon resulting in good quantitative and qualitative agreement.
- Modelling studies suggest that measured augmentations in flame propagation of ultra-lean  $\text{CH}_4$ -based fuels upon  $\text{H}_2$  or  $\text{C}_3\text{H}_8$  addition is predominantly a consequence of enhanced production of key radicals, notably H, facilitating  $\text{CH}_4$  oxidation mechanics, with  $\text{C}_3\text{H}_8$  yielding a greater influence than  $\text{H}_2$  for equal volumetric fractions.
- A sensitivity analysis related to the major flame enhancing pathways (thermal, kinetic, diffusive) has shown that enhanced flame propagation of lean  $\text{CH}_4/\text{H}_2$  and  $\text{CH}_4/\text{C}_3\text{H}_8$ , is principally an Arrhenius effect (kinetic), predominantly through the reduction of the activation temperature. The diffusive pathway was comparable in strength for both blends, but with opposite sensitivities, consistent with their respective Le trends.

- Changes in measured  $L_b$  behaviour of lean hydrogen enriched natural gas (for a fixed volumetric  $H_2$  fraction, 15% vol.) result from variations in fuel composition, with blends containing lowest and highest heavier hydrocarbon content exhibiting analogous stretch-related behaviour to that of pure  $CH_4$  and  $C_3H_8$ , due to preferential-diffusional preferences. Greatest relative changes in flame speed due to variations in heavier hydrocarbon content of the chosen natural gas-hydrogen blends were observed at leanest conditions. Modelling suggests that flame speed changes are principally linked to a reduction in activation energy (kinetic), with differences corresponding to variations in volumetric heat release rates and production of key radicals.

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