The Temperature and Pressure Dependences of the Laminar Burning Velocity: Experiments and Modelling

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Abstract

The laminar burning velocity at standard conditions, i.e. atmospheric pressure and initial temperature of 298 K is invaluable for characterization of combustion properties of the given fuel, for understanding of the underlying chemistry, validation of kinetic models, calibration of turbulent flame models, etc. However, in general applications, from domestic appliances to engines and gas turbines, pressure and initial temperature of the mixture are often higher than standard ones. Elucidation of the temperature and pressure dependences is therefore important both from practical and fundamental points of view: many engineering and CFD codes implement empirical power law equations to evaluate burning velocity at elevated conditions often not covered in laboratory experiments; comparison of the power exponents \( \alpha \) (for temperature dependence) and \( \beta \) (for pressure dependence) obtained from experiments and derived from different kinetic mechanisms provides an independent tool for model validation and analysis; finally, interpreting measurements obtained at different temperatures and/or pressures using these relations helps to check that the data are not biased by some systematic or random errors.

1. Introduction

The adiabatic laminar burning velocity is a fundamental parameter of any combustible mixture, which depends on the stoichiometric ratio, pressure and temperature. It is remarkable that different expressions for this concept are still used in textbooks on combustion and in many research papers. For instance Lewis and von Elbe [1, 2], and Tanford and Pease [3] used the term “burning velocity”, while Coward and Hartwell [4, 5] and others used the term “fundamental speed of flame propagation” or “fundamental flame speed”. Coward and Payman [6] discussed the appropriateness of this term, which originates from the expression “la vitesse normale” introduced by Mallard and Le Chatelier [7], and suggested it as preferable. Nowadays, however, the words “flame speed” are often used instead of the term “fundamental flame speed”, the replacement which can be misleading. Indeed, the flame speed of the burner stabilized flames is zero, while at other conditions it can be affected by stretch, heat losses and bulk flow movement. Therefore, the use of the words “flame speed” without adjective “fundamental” should be discouraged.

By definition, the laminar burning velocity, \( S_{\text{L}} \), is the velocity of a steady one-dimensional adiabatic free flame propagating in the doubly infinite domain. Other definitions specific for a particular method of measurements were discussed as well, yet it was concluded that “it seems impossible to give a precise definition for burning velocity which will be equally applicable to plane and spherical flames” [8]. It is, however, unfeasible to perform experiments with plane flames in the doubly infinite domain both from obvious practical and from fundamental points of view; indeed, planar flames are intrinsically unstable in open domains due to thermal expansion across the flame front. This Landau-Darrieus instability leads to wrinkling and flame surface growth producing flame acceleration. The laminar burning velocity is, therefore, not a measurable quantity; it is derived from other observables using different assumptions or theoretical models. The ultimate uncertainty of the experimentally obtained burning velocity is thus defined both by the uncertainty (accuracy) of the measurements and by the accuracy (validity) of the underlying models. The laminar burning velocity at standard conditions, that is, atmospheric pressure and initial temperature of 298 K is invaluable for characterization of combustion properties of the given fuel, for understanding of the primary chemistry and for validation of kinetic models. Although comparison of the laminar burning velocities with 1-D modelling is often used for validation of detailed reaction mechanisms, one should remember that the majority of the measurements performed prior to 1980’s possess significant spread and could deviate from the “real” values by as much as a factor of 2, e.g. [9]. A greater part of the methods for measuring laminar burning velocities involves curved (Bunsen type), stretched (counter-flow) or spherical time-varying flames. Wu and Law [10] demonstrated experimentally that flame stretch due to flame front curvature and/or flow divergence must be taken into account in the data processing. Experimental difficulties generating uncertainties in measuring burning velocities could be common or different for different methods. They are analyzed in the present overview to demonstrate a range of remaining problems and challenges in the measurements.

2. Temperature and pressure dependences

In general applications, from domestic appliances to engines and gas turbines, pressure and initial temperature of the mixture are often higher than standard ones. Certain applications like industrial gas turbines require pressures as high as 30 atm and operate at temperatures close to minimum ignition temperature. It is therefore important to quantify the effects of pressure and initial temperature on the adiabatic laminar burning velocity of many practical fuels. These effects were often interpreted using empirical correlations as
outlined below. Moreover, in determining turbulent burning velocities or other flame properties, an accurate correlation of the laminar burning velocity is essential [11, 12]. It is thus not surprising that investigations of the laminar burning velocity at different initial temperatures and pressures are numerous and have quite long history.

2.1. Correlations for temperature dependence

Different empirical correlations describing variation of the laminar burning velocity, $S_L$, with initial temperature have been developed. For example, experiments performed in 1950’s and 1960’s [13, 14] were often approximated by equations in the form

$$S_L = A + BT^n$$

where $T$ is initial temperature of the mixture. The most popular correlation describing the effect of initial temperature on the laminar burning velocity

$$S_L = S_{L0} \left( \frac{T}{T_0} \right)^n$$

(2),

where $T_0$ is the reference temperature and $S_{L0}$ is the burning velocity at this temperature, was used in this or equivalent form also since 1950’s, e.g. [15, 16]. Variations of the mixture composition and pressure in other measurements indicated that power exponent coefficient, $\alpha$, varies with pressure and equivalence ratio. Therefore complex equation in the form

$$S_L = CT^n P^{1+BT}$$

(3)

was proposed by Babkin and Kozachenko [17]. Coefficients $C$, $\alpha$, $D$ and $E$ in Equation (3) were found different for different equivalence ratios and pressure ranges. Pressure dependence of the power exponent coefficient, $\alpha$, in Eq. (2) was sometimes neglected or averaged, e.g. [18], yet its variation with equivalence ratio was studied both in lean and rich flames, as it will be discussed in the following.

2.2. Correlations for pressure dependence

The first experiments demonstrating the effect of pressure on the burning velocity have been performed by Ubbelohde and Koelliker [19], who covered the range from 1 to 4 bars. Since then the measurements were often interpreted using empirical power-law pressure dependence

$$S_L = S_{L0} \left( \frac{P}{P_0} \right)^\beta$$

(4),

where $S_{L0}$ is the burning velocity at reference conditions (usually at 1 atm), and $P_0$ is the reference pressure. This power-law Eq. (4) has its rationale in early theories of flame propagation. The very first (on the priority see Manson [20]) thermal theory of Mallard and Le Chatelier [7] considered only heat and mass balance and indicated inverse dependence of $S_L$ with pressure. Jouguet [21], Crussard [22], Nusselt [23], and Daniell [24] developed this theory explicitly introducing an overall reaction rate $W$. Zeldovich and Frank-Kamenetsky [25] further advanced this theoretical approach showing that the mass burning rate $m = \rho S_L$ is proportional to the square root of the overall reaction rate $W$. Since $W$ is proportional to $P^n \exp(-E_a/RT)$, where $n$ is the overall reaction order, the mass burning rate shows a power exponent dependence of $n/2$. The power exponent $\beta$ is therefore

$$\beta = \frac{n}{2} - 1$$

(5),

which is 0 for bimolecular reactions and -0.5 for the first order reactions. This consideration is still in use for explaining changes of the overall reaction order with pressure, e.g. [26, 27].

Another type of the pressure dependence correlation,

$$S_L = S_{L0} \left( 1 + \beta_2 \log(P/P_0) \right)$$

(6)

was first proposed by Agnew and Graiff [28]. Sharma et al. [18] and Bose et al. [29] interpreted their measurements using Eq. (6) and presented discrete coefficients $\beta_2$ for several equivalence ratios. Iijima and Takeno [30] derived a similar correlation with the parameter $\beta_2$ linearly dependent on the stoichiometry. Equations (4) and (6) are in fact related through series expansion as was noticed by Dahoe and de Goey [31], although the values of $\beta_1$ and $\beta_2$ are not equal.

An entirely different correlation

$$S_L = S_{L0} \exp \left( b_1 - \frac{P}{P_0} \right)^\beta$$

(7)

was proposed by Smith and Agnew [32]. Since the parameters $b$ and $x$ were found to be dependent on the composition of the oxidizer and the burning velocity at reference conditions, respectively, it was not attempted by others, except by Konov et al. [33] for sub-atmospheric methane + hydrogen + air flames.

Other empirical correlations describing pressure and temperature dependence of the burning velocity were suggested as well, since, as it is mentioned above, the power exponent $\beta$ is different at different pressures, initial temperatures and varies with mixture composition. Babkin and Kozachenko [17] performed extensive studies of methane + air flames covering a wide range of equivalence ratios, initial temperatures and pressures. They demonstrated that the power exponent $\beta$ decreases with the increase of pressure within the range from 1 to 8 atm, while in the range from 8 to 70 atm the exponent is almost constant. It has its maximum value in near-stoichiometric mixtures decreasing towards lean and rich mixtures. Even after this seminal study of Babkin and Kozachenko [17], correlations in the form of equation (4) or (6) are often used, knowing that the power exponent $\beta_1$ or coefficient $\beta_2$ does not have a constant value.

2.3. Data consistency – role of $\alpha$ and $\beta$

Typical presentation of the laminar burning velocity measurements is in coordinates $S_L$ vs. equivalence ratio, $\phi$. Figure 1 shows such an example for methane + air flames at selected pressures up to 5 atm [34]. Experiments denoted as “present work” were performed from $P = 1.5$ to 5 atm and for $0.8 < \phi < 1.4$ using the heat flux method. For comparison, experimental data from the literature [27, 35, 36, 37, 38, 39] have been included together with predictions of GRImech 3.0 and USC Mech II. For this type of graphs further discussion can be focused on agreement/disagreement of different sets of measurements and on agreement/disagreement between experiments and model predictions. It is, however, difficult to assess if the data obtained at different pressures, even from the same set, are
consistent or not. It will be shown in the following that analysis of the pressure (or temperature) dependence provides a powerful tool for this assessment. Indeed, since the laminar burning velocity of the given fuel depends on the stoichiometric ratio, pressure and temperature only, $S_L = f(\phi, P, T)$, interpretation of experimental and modeling results using correlations outlined above provides additional dimensions which allow for elucidation of possible outliers or inconsistency.

![Graphs showing burning velocities vs equivalence ratio for different pressures](image)

**Fig. 1.** Comparison of the burning velocities of methane + air flames from experimental (symbols) and simulation (lines) results for 2, 3, 4 and 5 atm as functions of equivalence ratio [34].

### 2.3.1. Pressure dependence of methane flames

The pressure dependence of methane flames has been extensively studied. Andrews and Bradley [14] reviewed available experimental data before 1972 and proposed the correlation $S_L = 43 \ P^{-0.5}$ cm/s for stoichiometric mixtures at pressures above 5 atm. Dahoe and de Goey [31] reviewed and interpreted available experimental data using Equation (4) or (6). Goswami et al. [34] extended this analysis using their own data shown in Fig. 1 and comparing with the literature as summarized below.

In the log-log coordinates, the most frequently used power-law pressure dependence (Eq. (4)) should become a straight line. This was indeed observed for all equivalence ratios with minor deviations at $\phi = 0.8$ and 1.4 and pressure of 1.5 atm. Calculations performed using GRImech 3.0 [39] and USC Mech II [40] have also been processed to derive power exponents $\beta_1$ (Eq. (4)). Although the modeling results plotted in a log-log scale look quite linear, careful analysis shows that they do not exactly follow Eq. (4). This is in line with earlier observations [17, 26, 27], which demonstrated that the overall reaction order decreases with the pressure increase from 1 to 5 atm.

The power exponents $\beta_1$ (Eq. (4)) derived from the experiments of Goswami et al. [34] are compared with the selected literature data in Fig. 2. In this graph the older measured values for which no stretch correction was implemented are not shown. Uncertainties in the power exponents were evaluated using the least-squares method taking the typical uncertainty of the measured burning velocity of 0.8 cm/s into account. Most recently Dirrenberger et al. [41] obtained close values of the power exponent $\beta_1$ in lean flames of methane using the same heat flux method. Also shown are values of
the power exponents derived from the modeling using both GRImech 3.0 and USC Mech II.

2.3.2. Pressure dependence for other hydrocarbons

Combustion of methane as the main constituent in natural gas has been a key field of research for many years. Methane (or natural gas) is burnt, premixed or non-premixed, in a large variety of conditions: at room and elevated initial temperatures, at atmospheric and high pressures. Much less experiments have been performed with other hydrocarbons also present in natural gas.

Goswami [47] has recently measured burning velocities of ethane + air and propane + air flames at pressures up to 5 atm using the heat flux method. Figures 3 and 4 taken from Goswami [47] compare available stretch-corrected data for these mixtures at atmospheric pressure. Significant spread of the data even at 1 atm is obvious, yet it is well established that burning velocities of hydrocarbon flames decrease with the pressure rise very similarly to methane flames, e.g. [48, 49]. In other words, the pressure dependence of the burning velocity in the form of Eq. (4) satisfactorily describes existing measurements [50].

Detailed analysis of the burning velocities for many hydrocarbons aimed at the evaluation of their consistency is yet to be done, therefore Figure 5 [47] presents only power exponents $\beta_1$ (Eq. (4)) derived from the experiments performed using the heat flux method. In lean mixtures ethane and propane flames possess close values of the power exponents, while in rich mixtures those for ethane are higher than for other fuels studied. One may note that Metghalchi and Keck [50] found significantly different values of the power exponent for propane in the range of equivalence ratios 0.8 – 1.2.
Fig. 4. Comparison of the burning velocities of propane + air flames at 1 atm as a function of equivalence ratio. Available stretch-corrected data: [49, 51, 52, 53], present work denotes Goswami [47].

Interestingly, in the recent study of Dirrenberger et al. [41] devoted to the pressure dependence of n-pentane flames, the power exponents determined in the range 0.7 < Φ < 0.9 are found increasing from -0.37 to -0.33 in good agreement with those shown in Fig. 5 for ethane and propane. It could be speculated that the pressure dependence of the burning velocities of lean flames for normal alkanes has close similarity, yet further analysis and more experiments should be performed.

2.3.3. Different behavior for H2 pressure dependence

Hydrogen + air flames behave largely different as compared to the flames of hydrocarbons. It was early realized that burning velocity of hydrogen flames may increase with the pressure rise, e.g. [30]. Moreover, the overall reaction order, n, (see Equation (5)) varies non-monotonically with pressure and is considerably different for different equivalence ratios [55]. At certain combinations of equivalence ratio and pressure, the effective reaction order of hydrogen flames can assume negative values.

Unstretched laminar burning velocities of hydrogen flames at high pressures are available mostly from constant volume bombs [56, 57, 58, 59, 60, 61]. The systematic measurements in hydrogen + air mixtures [56] are shown in Fig. 6 and compared with the Konnov [62] hydrogen model predictions. It is interesting that the calculated burning velocities converge with the experiments as the pressure increases. Good agreement of these experiments with the calculations could not be expected in rich mixtures at atmospheric and moderate pressures because the measurements of [56, 63] were found consistently lower than other data from the literature [62]. This was recently confirmed by Dayma et al. [61] who covered pressure range from 0.2 till 3 atm. Non-monotonic behavior in this study was substantiated and supported by the modeling using kinetic schemes of Burke et al. [64] and of Keromnes et al. [65].

Fig. 5. Variation of the power exponent β1 (Eq. (4)) with equivalence ratio at elevated pressures for methane, ethane, and propane flames, taken from Goswami [47].

Fig. 6. Unstretched laminar burning velocities for hydrogen + air flames at standard temperature as a function of initial pressure [62]. Measurements: symbols; calculations: lines with corresponding small symbols. Equivalence ratios: crosses: 0.75; diamonds: 1.05; squares: 1.8; [56]; solid circles: 3 [56]; open circles: 3 [12].

Measurements of the laminar burning velocities were also conducted using different technique based on particle tracking velocimetry and image processing for burner-stabilized flames in a high-pressure chamber [12]. These results for equivalence ratio = 3 are shown in Fig. 6 to illustrate significant disagreement of the available experimental data at elevated pressures, which is much higher than expected experimental uncertainty.

Negative pressure dependence of the mass burning rates was experimentally proved and analyzed in the
mixtures H$_2$ + O$_2$ + diluent (He, Ar or CO$_2$) also studied in spherical flames by Burke et al. [66]. It was demonstrated that many contemporary hydrogen kinetic schemes fail to predict these observations and require further improvement.

They were compared with several kinetic models as well, as shown in Fig. 7. Again, all tested mechanisms except GRImech 3.0 overpredict these results with increasing relative divergence at higher pressures approaching 10 atm.

The composition of the mixtures studied in flat non-stretched [67] and spherical [61, 66] flames was different. However, analysis of the comparison between different experimental data and essentially the same collection of hydrogen kinetic schemes indicate that the measurements, especially in lean flames, are probably inconsistent and call for further investigation. Experimental difficulties generating uncertainties in measuring burning velocities from spherical flames have recently been discussed in several publications, e.g. by Wu et al. [68] and Varea et al., [69]. This inconsistency is also manifested in the analysis of the temperature dependence of hydrogen flames outlined in the following Section 2.3.5.

2.3.4. Temperature dependence of methane flames

Temperature dependence of the laminar burning velocity provides another dimension for the data consistency. Andrews and Bradley [14] reviewed experiments with methane flames prior to 1972 and noted considerable scatter in both the magnitude of the burning velocity and its rate of increase with temperature. For stoichiometric flames they derived correlation $S_p = 10 + 0.000371T^2$. Since then it was generally accepted that the power exponent $\alpha$ for methane flames is 2, while for other hydrocarbon + air mixtures it ranges between 1.5 and 2 [70]. Metghalchi and Keck [50, 71] investigated the effect of temperature on the burning velocities of several fuels using Equation (2) and proposed linear function of the power exponent $\alpha$ with equivalence ratio independent of the fuel type: $\alpha = 2.18 - 0.8(\phi - 1)$ in the range of equivalence ratios 0.8 – 1.2. Dahoe and de Goey [31] processed essentially the same experimental data as did Andrews and Bradley [14] using both Equations (1) and (2). They concluded that mean value of $\alpha$ in Equation (2) for stoichiometric methane + air flames is 1.89 with apparent scattering from 1.5 to 2.2.

Konnov [72] further analyzed the temperature dependence of methane flames focusing on comparison of the power exponents $\alpha$ obtained experimentally and derived from predictions of two kinetic schemes: the Konnov mechanism and the GRI-mech 3.0 in the range of equivalence ratios from 0.5 to 2. This comparison together with recent updates is shown in Fig. 8. Both models are in good agreement with the measurements in methane + air flames in the range of $\phi$ from 0.8 to 1.2 [18, 44, 73, 74]. Furthermore, they qualitatively reproduce rapid increase of $\alpha$ from stoichiometric to very lean methane mixtures.

![Graph showing laminar burning velocity vs pressure for different gases and mixtures](image1)

**Fig. 7.** Laminar burning velocity of 85:15 % H$_2$ + N$_2$ with 1:7 O$_2$:He oxidizer at $\phi = 0.6$ and 298 K. Symbols: Goswami et al. [67]; lines: predictions of different models.

![Graph showing temperature power exponent vs equivalence ratio](image2)

**Fig. 8.** Power exponent coefficient, $\alpha$, in Eq. (2) for methane + air flames. Crosses: [74], open diamonds: [44], solid diamonds: [73], open circles: [29], solid circle: [75], open squares: [36], solid triangles: [17], open triangles: [18], long-dash line: [30], dash-dot line: [76], dash- double dot line: [45], dash-triple dot line: [77], red solid line: [78], blue stars: [41]. Solid line: modeling using the Konnov mech., short-dash line: modeling using the GRI-mech. 3.0.

Unexpected non-monotonic behavior of $\alpha$ was found in rich methane + air flames [72]. Both calculated dependences peak at $\phi = 1.4$, at higher equivalence ratios they level off approaching $\alpha = 2$. In the dedicated experiments of Yan et al. [79] notable decrease of the
power exponent was confirmed from \( \phi = 1.3 \) towards \( \phi = 1.45 \). Most recently Dirrenberger et al. [41] extended determination of the power exponent \( \alpha \) up to \( \phi = 1.7 \) essentially confirming predictions of the two models. This variation of the power exponents \( \alpha \) clearly indicates significant changes in the combustion chemistry that is modification of the relative role of the elementary reactions, as discussed by Konnov [72] and Yan et al. [79]. Moreover, Goswami et al. [34] pointed out on the resemblance and relation of the anomalous behavior of the power exponent \( \beta \). (Fig. 2) and power exponent \( \alpha \) suggesting a general coupling of the flame response on the pressure and temperature variation.

What can be concluded and learned from the comparison shown in Fig. 8?

- The temperature power exponent \( \alpha \) obtained experimentally and derived using two kinetic models shows parabola-like variation from lean to moderately rich mixtures. Linear variation expressions of \( \alpha \) with equivalence ratio suggested by Metghalchi and Keck [50, 71], Iijima and Takeno [30], Stone et al. [76], and Takizawa et al. [77] should not be used.
- The powers exponents derived from earlier experiments of Babkin and Kozachenko [17] and Lauer and Leukel [73] may possess rather high uncertainty due to inaccuracies in the measurements of the laminar burning velocity itself caused by the lack of stretch correction.
- The results of Bose et al. [29] are obvious outliers.
- Two essentially different kinetic schemes: the Konnov mechanism and the GRI-mech. 3.0 predict very close power exponents for methane flames. This unexpected insensitivity was observed for other fuels as well and will be discussed in the following.

### 2.3.5. Temperature dependence of hydrogen flames

Measurements of the laminar burning velocity of hydrogen flames are as numerous as those of methane. However, available data on the effect of temperature on the burning velocities of \( \text{H}_2 + \text{air} \) flames interpreted using correlation \( S_l = S_{l0} (T/T_{0})^\alpha \) are rather scarce. Heimel [16] and Milton and Keck [80] determined discrete values of the power exponent \( \alpha \), while Liu and MacFarlane [81] proposed linear correlations below and above the maximum of the burning velocity as a function of equivalence ratio with the junction value of \( \alpha = 1.571 \). Iijima and Takeno [30] covered practically the same range of equivalence ratios \( 0.5 < \phi < 4 \) and observed modest increase of \( \alpha \) without a minimum.

These measurements were analyzed by Konnov [72], who calculated laminar burning velocities of hydrogen + air flames in the range of equivalence ratios from 0.35 to 8.5. From the calculations the power exponents \( \alpha \) were derived as shown in Fig. 9. Modeling results confirmed small variation of \( \alpha \) in the range of \( \phi \) from 1 to 3. In the very lean and very rich mixtures, however, the temperature power exponent increases dramatically. Sensitivity analysis revealed the reason of this behavior [72].

Apart from the studies mentioned above, where the power exponent \( \alpha \) was derived directly, a number of works [82, 83, 84, 85, 86, 87] presented burning velocities of \( \text{H}_2 + \text{air} \) flames at room and elevated temperatures without evaluation of the power exponent in the form of Eq. (2). For these studies, the power exponent \( \alpha \) was extracted with a least-square fit procedure by Alekseev et al. [88]. All available and extracted values of \( \alpha \) from the experimental data are shown in Figure 9.

![Fig. 9. Power exponent \( \alpha \) for \( \text{H}_2 + \text{air} \) flames at standard conditions. Solid symbols and thick lines: experiments [16, 30, 80, 81, 89], open symbols: fit to experimental data [82, 83, 84, 85, 86, 87], made by Alekseev et al. [88]; thin lines: modeling.](image)
The two models, as well as the previous version of the mechanism [62], were found to give almost identical results. Comparing the calculations to the experimental data, it can be observed that they are in a reasonable agreement with the most recent measurements of Krejci et al. [86]. The data of Krejci et al. [86] also possess less scattering for the $\alpha(\phi)$ dependence than the measurements of Hu et al. [82]. However, in the very lean mixtures ($\phi<0.5$), a solid conclusion cannot be drawn due to the large discrepancies in the experimental data. Notably, at $\phi = 0.3$ there are three measurements available, from Verhelst et al. [89], Bradley et al. [84] and Das et al. [85], which differ by about a factor of 5. Also, all modeling studies shown in Figure 9 predict a trend of rapid rise of $\alpha$ in lean mixtures, which is supported by the data of Krejci et al. [86] and Das et al. [85]. The latter is the only study, which indicates a very high $\alpha$ in a very lean mixture. However, it should be noted that in this case $\alpha$ is based on just two temperature points in a narrow interval of 25 K (298K and 323K), though the rise of the burning velocity was considerable. Nevertheless, the results extracted from Das et al. [85] are valuable as a possible evidence for a trend found in the modeling, yet should not be seen as an attempt to determine exact value of $\alpha$ at $\phi = 0.3$.

It should be also noted that Das et al. [85] employed the counterflow technique. In the other studies of very lean $\mathrm{H}_2+\text{air}$ flames, Bradley et al. [84] and Verhelst et al. [89], a spherical bomb method was used. For these last two cases, the flame configuration was unstable due to a high Lewis number at $\phi = 0.3$. This could be seen as one of the possible reasons for the remaining discrepancy.

What can be concluded and learned from the comparison shown in Fig. 9?

- The contemporary kinetic models for hydrogen combustion are capable to reproduce the experimental data in a wide range of conditions.
- It was shown that the temperature exponent cannot be treated as a constant for hydrogen flames, even to a first approximation. For a given fuel-oxidizer mixture, it strongly depends on equivalence ratio, diluent content and correlation temperature interval.
- A rapid increase of $\alpha$ in very lean mixtures was observed.
- New experimental measurements in the very lean $\mathrm{H}_2+\text{air}$ mixtures are required to confirm the quality of the model prediction for these conditions.

### 2.3.6. Peculiarities of the temperature dependence

Nowadays it is a common practice to compare new measurements of the burning velocity with the modelling using several kinetic schemes, if available, to validate them and to recommend the most suitable one for the given fuel. When measurements are performed at different initial gas temperatures, the temperature dependence in the form of empirical Equation (2) can also be analysed. As was exemplified by Konnov [72], the power exponent, $\alpha$, can be derived from the modelling and compared with experimental data. Such analyses are illustrated for methane and hydrogen flames in the previous sections. They clearly indicate outliers and help to reveal inconsistency in the measurements.

On the other hand, close examination of the models’ behaviour demonstrates that the mechanisms showing large difference in prediction of the burning velocities can be very close with respect to the prediction of the power exponents $\alpha$. This has been earlier observed for methane [72], ethanol [90], hydrogen [88] and other fuels. To elucidate the underlying reasons of this observation, a dedicated study for methyl formate, MF, flames was performed by Christensen et al. [91] as summarized in the following.

Laminar burning velocities of methyl formate and air flames were determined at atmospheric pressure and initial gas temperatures of 298, 318, 338 and 348 K. Measurements were performed in non-stretched flames, stabilized on a perforated plate burner at adiabatic conditions, generated using the heat flux method. The measurements at 338 K shown in Fig. 10 are compared to modelling using the mechanisms of Glaude et al. [92] and Dievart et al. [93]. The Dievart mechanism is in better agreement with the present experiments in lean and slightly rich flames, while the Glaude mechanism is systematically over predicting the experimental results. Included in the figure as well are the data of Wang et al. [94] obtained at 333 K with good agreement.

![Fig. 10. Laminar burning velocities of MF+air as a function of $\phi$ at 338 K. Symbols: experimental data and lines: modelling. Squares and circles: Christensen et al. [91]; diamonds: Wang et al. [94] at 333 K. Solid line: Dievart et al. [93] and dotted line: Glaude et al. [92].](image)
al. [92] and Dievart et al. [93]. The calculated values are in relatively good agreement although there is an increasing discrepancy between the experimental and calculated coefficients $\alpha$ towards richer flames, as the experimental coefficients are larger. Both mechanisms show a minimum located at equivalence ratio 1.2.

Despite over predicting the experimental results of $S_L$, the Glaude et al. [92] mechanism is good at predicting the temperature dependence of the laminar burning velocity. To investigate the deviations seen at rich conditions as well as the kinetics behind the temperature dependence, a separate sensitivity analyses were performed with the Glaude et al. and the Dievart et al. mechanisms at 298 K. The normalized sensitivity of the laminar burning velocity with respect to the rate constant, $k$, is commonly defined as

$$Sens(S_L, k) = \frac{\partial S_L}{\partial k} S_L$$

(8)

The 20 most sensitive reactions for $S_L$ of stoichiometric mixture are presented in Fig. 12. The results indicate that the laminar burning velocity is sensitive to reactions from the $H_2 - O_2$ subset as well as to $C_1$ chemistry. The sensitivity spectra for both mechanisms are essentially very close.

The sensitivity analysis of the laminar burning velocity as above is commonly used to reveal key reactions responsible for the differences between model and experiment or between models. Intriguing was, however, that two mechanism largely different in predicting the burning velocities (Fig. 10) show close performance with respect to the temperature dependence prediction, Fig. 11.

To gain further insight into the relation of the temperature dependence and the key reactions, a sensitivity analysis of the power exponent $\alpha$ has been performed for the first time [91]. As mentioned above, the normalized sensitivity of the laminar burning velocity can be described by Eq. (8). In a similar manner the normalized sensitivity of the power exponent with respect to the rate constant, $k$, can be defined as

$$Sens(\alpha, k) = \frac{\partial \alpha}{\partial k} \alpha$$

(9)

By utilizing that the sensitivity of the power exponent and the laminar burning velocity both are functions of $k$, and that the temperature dependence is described by Eq. (2), the partial derivatives with respect to $k$ can be calculated using the product rule. It can then be shown that the normalized sensitivity of the power exponent with respect to $k$ can be obtained as

$$Sens(\alpha, k) = \frac{Sens(S_L, k) - Sens(S_L, 0)}{ln(T/T_0) \alpha}$$

(10)

In this equation $T_0$ refers to the reference temperature of 298 K and $T$ to the arbitrary elevated temperature (398 K in the study of Christensen et al. [91]).

Figure 13 shows normalized sensitivity coefficients of the power exponent for stoichiometric mixture. When comparing the sensitivity of $S_L$, Fig. 12, and the sensitivity of $\alpha$, Fig. 13, one can see some important differences. Most noticeable is that the sensitivity coefficients of the power exponent are roughly 1 order of magnitude smaller than the sensitivity coefficients of $S_L$. There are also several reactions in the sensitivity of $S_L$ that are displayed with opposite sign in the sensitivity spectra of $\alpha$. This indicates that as the temperature is increased from 298 to 398 K, several chain promoting reactions become less important and...
these reactions are now displayed with negative sensitivity. The same is true for several chain inhibiting reactions that display positive sensitivities in Fig. 13. One last observation is that while the two mechanisms displayed similar results for the sensitivities of the laminar burning velocity in shape and reaction ranking, the sensitivity coefficients of α are more scattered.

Fig. 13. Normalized sensitivity coefficients for the power exponent α of MF-air flames at φ = 1.0.

This analysis explains why the mechanisms showing large difference in prediction of the burning velocities can be very close with respect to the prediction of the power exponents α. In fact, the normalized sensitivity coefficients for the power exponent are roughly one order of magnitude smaller than commonly used normalized sensitivity coefficients for the burning velocity. This means that if the differences in reaction rate constants of two models are manifested in, say, 20% difference in the burning velocity, one may expect only 2% difference in the power exponent α.

It also implies that comparison of the experimental alpha coefficients and those derived from the modelling, as shown in Fig. 11, cannot be used for kinetic model validation, as has been suggested in other studies, unless the model is significantly incapable in the burning velocity prediction. On the other hand, this comparison can serve for analysis of experimental data consistency. Indeed, since the models are more “robust” in calculation of the alpha coefficients, substantial deviation between experiments and modelling most probably indicates potential problems in the measurements. This analysis of experimental data consistency has recently been demonstrated for hydrogen + air mixtures [88], where contradiction of several datasets and modelling was evidenced in lean flames.

3. Experimental uncertainties

Quite often measurements of the laminar burning velocities are reported with a stated accuracy of 1-2%. These evaluations are usually based on the accuracy of equipment used. In practice, however, scattering of available data at the same conditions of temperature, pressure and equivalence ratio often exceeds 5 and even 10% as illustrated in Figs. 1, 3, 4, and 6 above. There are several reasons for this inconsistency.

- Firstly, technical details important in data processing are most often not reported in archival publications. Thus each attempt of measurements in a new laboratory and even re-visiting the same experiment after some time has passed at the same place is unique since operating experiment and data processing involves the effect of operator.

- Second, both equipment and theory behind each of the methods mentioned above are in a constant development.

- Moreover, there are no protocols in place to renounce older data even if the author himself or herself realized that the published results were incorrect or highly uncertain. This leads to an accumulation of results hardly suitable for model validation due to large degree of scatter.

Several reviews devoted to comparison of the experimental approaches and of the results obtained deserve to be mentioned. In 1953 Linnett [8] described the following methods: (1) Egerton-PoWling flat flame method; (2) Soap bubble method; (3) Closed spherical vessel method; (4) Cylindrical tube method; (5) Bunsen burner method. In the seminal review of Andrews and Bradley [95] in 1972 essentially the same methods were further scrutinized and the maximum burning velocity of methane + air flame at 1 atm and 298 K of 45 ±2 cm/s was recommended. Enlightening Fig. 14 composed by Law [96] is basically an extension of the similar figure compiled by Andrews and Bradley [95]. Law [96] has emphasized that after the work of Wu and Law [10], which demonstrated the importance of the stretch correction in the data processing, the uncertainty of the burning velocity measurements was reduced to less than ±8 cm/s (the scattering in Andrews and Bradley [95] plot was of the order of ±25 cm/s), while contemporary measurements together with non-linear stretch correction are indeed consistent within ±2 cm/s.

Although the stretch correction is extremely important, other experimental difficulties generating uncertainties in measuring burning velocities were realized and reviewed. These difficulties could be common or different for different methods; some methods for measuring burning velocity are now considered obsolete. Ranzi et al. [97] and Nilsson and Konnov [98] limit their discussion to four methods: Bunsen burner, spherical flames, counter-flow flames and flat flames stabilized using the heat flux method. In the recent review of E golopoulos et al. [99] only the last three were carefully analyzed and compared. This review summarizes the state of the art in the data quality and demonstrates a range of remaining problems and
challenges in the measurements. Many exciting developments in the field presented and analyzed by Egolfopoulos et al. [99] open new prospects in the improvement of the theoretical and experimental approaches.

![Graph](image)

Fig. 14. Variation of measured maximum laminar burning velocities of CH₄ + air mixtures at standard conditions as a function of year of publication, taken from Law [96].

**Concluding remarks**

In most practical situations combustion is accompanied by flames. With a few exceptions like detonations or explosions, flames of different natures and appearances propagate in engines, in domestic appliances, in gas-turbine combustion chambers, etc. It is therefore natural that laboratory studies of flames provide valuable information on combustion characteristics important both for solution of engineering problems and for development and validation of combustion models.

The laminar burning velocity and its temperature and pressure dependences is important both from practical and fundamental points of view: many engineering and CFD codes implement empirical power law equations to evaluate burning velocity at elevated conditions often not covered in laboratory experiments.

Moreover, comparison of the power exponents $\alpha$ (for temperature dependence) and $\beta$ (for pressure dependence) obtained from experiments and derived from different kinetic mechanisms provides an independent tool for model validation and analysis. The power exponents $\alpha$ are not very sensitive to the rate constants implemented in the modeling; therefore they are more suitable for analysis of consistency of the measurements and helps to check that the data are not biased by some systematic or random errors.

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**References**