



## Full Length Article

# Burning velocity and Markstein length blending laws for methane/air and hydrogen/air blends



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## ABSTRACT

Because of the contrasting chemical kinetics of methane and hydrogen combustion, the development of blending laws for laminar burning velocity,  $u_l$ , and Markstein length for constituent mixtures of CH<sub>4</sub>/air and H<sub>2</sub>/air presents a formidable challenge. Guidance is sought through a study of analytical expressions for laminar burning velocity. For the prediction of burning velocities of blends, six blending laws were scrutinised. The predictions were compared with the measured burning velocities made by Hu et al. under atmospheric conditions [1]. These covered equivalence ratios ranging from 0.6 to 1.3, and the full fuel range for H<sub>2</sub> addition to CH<sub>4</sub>. This enabled assessments to be made of the predictive accuracy of the six laws. The most successful law is one developed in the course of the present study, involving the mass fraction weighting of the product of  $u_l$ , density, heat of reaction and specific heat, divided by the thermal conductivity of the mixture. There was less success from attempts to obtain a comparably successful blending law for the flame speed Markstein length,  $L_b$ , despite scrutiny of several possibilities. Details are given of two possible approaches, one based on the fractional mole concentration of the deficient reactant. A satisfactory empirical law employs mass fraction weighting of the product  $u_l L_b$ .

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## 1. Introduction

There is increasing interest in supplementing natural gas supplies with the addition of hydrogen. This has led to a number of experimental and chemical kinetic [1,2] studies of the burning velocities,  $u_l$ , of such blends with air. The interest in this extends beyond such practicalities to the general problem of deriving satisfactory blending laws for fuel/air mixtures, with very different burning velocities and chemical kinetics. For example, the laminar burning velocity,  $u_l$ , of a stoichiometric mixture at 303 K and 0.1 MPa of CH<sub>4</sub> is 0.35 m/s, whereas that for H<sub>2</sub>/air is 2.05 m/s. This large difference makes the prediction of CH<sub>4</sub>/H<sub>2</sub> burning velocities a particularly challenging test for blending laws.

One of the approaches adopted is based on earlier analytical derivations of expressions for the laminar burning velocity, involving profiles of volumetric heat release rates. An important difference in flame structure between CH<sub>4</sub>/air and H<sub>2</sub>/air flames is revealed by the profiles of the volumetric heat release rates, normalised by their maximum values,  $q/q_{\max}$ , and plotted against the reaction progress variable,  $c$ . Values of such profiles computed from earlier detailed chemical kinetics studies [3] are shown in

Fig. 1 by the two contrasting dotted curves. The full line curve is a more approximate algebraic fit. The maximum heat release rate of the faster burning H<sub>2</sub> mixture occurs at a distinctively lower value of  $c$ . This is a consequence of enhanced molecular transport and low temperature reaction, both attributable to H atoms, with a resulting increase in  $u_l$ . The kinetic modeling in [2] shows how the blend  $u_l$  of CH<sub>4</sub>/H<sub>2</sub> flames increases with the concentration of H. Exceptionally, in hydrogen flames, such is the upstream diffusion of H atoms and the consequent induced reactivity, the concept of a flame thickness based on an inert preheat zone is of limited validity [4]. The contrasting aspects of CH<sub>4</sub> and H<sub>2</sub> flame structures make the development of accurate blending laws for  $u_l$  values of their blends more exacting than the development of such laws for hydrocarbon blends.

The present paper explores the application of six different laws, for predicting the burning velocities of blends of CH<sub>4</sub>/air and H<sub>2</sub>/air, at the same equivalence ratio,  $\phi$ . One of the laws is entirely new and was developed in the course of the present study. Probably the earliest blending law was that of Le Châtelier [5] for predicting the lean flammability limit of a blend, based upon the reciprocal of mole fraction weighting of those of the constituent fuels. A common approach is to employ a property of the constituent mixtures, all at the same  $\phi$ , designated by  $i$  and  $j$  for a binary blend, with an appropriate quantitative weighting of that property. Frequently

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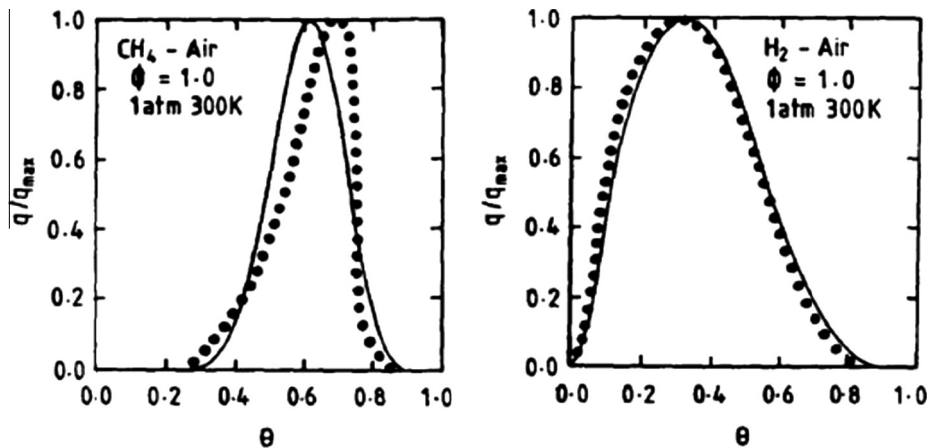
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### Nomenclature

$a$	air mole/fuel mole	$T_{ai}$	activation temperature, based on $u_l \rho_u$ (K)
$a_s$	stoichiometric air mole/fuel mole	$\tilde{T}_a$	activation temperature based on $u_i$ (K)
$c$	reaction progress variable	$T_u$	unburned temperature (K)
$c_p$	mean specific heat at constant pressure (J/mass/K)	$T_b$	burned temperature (K)
$h$	sensible enthalpy (J/mol)	$u_l$	unstretched laminar burning velocity (m/s)
$h_f$	enthalpy of formation (J/mol)	$\bar{x}$	mixture mole fraction
$k_u$	mixture thermal conductivity (J/m/K/s)	$\bar{x}_f$	fuel mole fraction
$k_m$	mean thermal conductivity (J/m/K/s)	$\bar{x}_i$	$i$ 'th constituent mole fraction
$L_b$	burned gas Markstein length (m)	$x$	mass fraction
$Le$	Lewis number	$x_f$	fuel mass fraction
$Ma_b$	burned gas Markstein number	$x_i$	$i$ 'th constituent mass fraction
$\bar{m}_i$	species $i$ mole fraction	$\bar{x}_d$	deficient reactant mole fraction
$\bar{m}_R$	reactant mole fraction	$Z$	Zel'dovich number = $(T_a/T_b^2)(T_b - T_u)$
$P$	pressure (Pa)		
$q$	heat release rate (J/s)		
$q_{\max}$	maximum volumetric heat release rate (J/m <sup>3</sup> s)		
$\bar{Q}$	molar heat of reaction (J/mol)		
$Q$	mass heat of reaction (J/kg)		
$R(c)$	heat release rate source term (J/m <sup>3</sup> s)		
$r$	laminar flame radius (m)		
$S_n$	stretched flame speed (m/s)		
$S_s$	unstretched flame speed (m/s)		
$t$	time (s)		
$T$	temperature (K)		

### Greek symbols

$\alpha$	flame stretch rate (1/s)
$\delta$	flame thickness (m)
$\lambda$	burning velocity eigenvalue
$\nu$	kinematic viscosity (m <sup>2</sup> /s)
$\rho_u$	unburned mixture density (kg/m <sup>3</sup> )
$\rho_b$	burned mixture density (kg/m <sup>3</sup> )
$\phi$	equivalence ratio



**Fig. 1.** Dotted curves show volumetric heat release rate profiles from detailed chemical kinetics, for CH<sub>4</sub>/air and H<sub>2</sub>/air mixtures from [3].  $\theta$  is the reaction progress variable,  $c$ . The full line curve is a more approximate algebraic fit.

the property employed is the laminar burning velocity of the constituent mixtures,  $u_{li}$ , along with mole or mass fractional weightings,  $\bar{x}_i$ , or,  $x_i$ , respectively, of the constituent mixtures. The burning velocity of the blend,  $u_{lb}$ , expressed in terms of the fractional mass concentrations of the constituent fuel/air mixtures,  $x_i$  and  $x_j$  and their respective burning velocities is:

$$u_{lb} = x_i u_{li} + x_j u_{lj}. \quad (1)$$

The expression for fractional mole weighting, indicated by  $\bar{x}_i$  is similar.

Burning velocities also are affected by the flame stretch rate and, for this, a convenient and relevant parameter is the Markstein length,  $L_b$ . This can be derived directly from flame speed measurements in spherical explosions, as in [1]. The chemical kinetic computational studies in [6] show how Markstein lengths can be

derived from these, that are associated, with the laminar burning velocity and the separate effects of both strain rate and flame curvature. This is applied to experimentally measured values in [7]. Normalised by the laminar flame thickness these give the corresponding Markstein numbers. In contrast to  $u_l$ , no blending laws are known to the authors for  $L_b$ .

Two possible approaches for Markstein length blending laws are considered. One is based on weighting the value of  $L_b$  for each constituent mixture by the fractional mole concentration of the deficient reactant (fuel or oxygen). The other, involves fractional mole concentration weighting of the product  $u_l L_b$  for each constituent mixture.

The different blending laws for  $u_l$  and  $L_b$  are first formulated and discussed. Each is then employed to predict the values of these parameters for blends of CH<sub>4</sub>/air and H<sub>2</sub>/air at the same  $\phi$ , over

the same ranges of measurement of spherical explosions as were employed in the experiments in [1]. These cover the full range of CH<sub>4</sub>/H<sub>2</sub> ratios and a wide range of  $\phi$  values. The ratio of predicted to measured values are then compared over these wide ranges, for the different blending laws.

## 2. Mixture compositions

Before introducing possible blending laws, it is first necessary to define how the various constituent mixtures, their blends, and their proportions of fuel, are specified. This requires the composition of constituent mixtures to be expressed in terms of the value of  $\phi$ . For one mole of fuel and  $a$  moles of air:

$$\phi = (1/a)(1/a_s)^{-1}, \quad (2)$$

where  $s$  indicates the moles of air for one mole of fuel in a stoichiometric mixture.

One mole of constituent fuel/air mixture is comprised of:

$$\left[ \frac{1}{1 + (1/\phi)(1/a_s)^{-1}} \right] \text{ mole of fuel and } \left[ \frac{(1/\phi)(1/a_s)^{-1}}{1 + (1/\phi)(1/a_s)^{-1}} \right] \text{ mole of air.} \quad (3)$$

This simplifies to:

$$\left[ \frac{\phi}{\phi + a_s} \right] \text{ mole fuel} + \left[ \frac{a_s}{\phi + a_s} \right] \text{ mole air.} \quad (4)$$

Now consider a binary blend of two constituent fuel/air mixtures, one with fuel  $i$ , the other with fuel  $j$ , both with the same  $\phi$ . Let the blend consist of a mole fraction  $\bar{x}_i$  of the first constituent mixture and of  $\bar{x}_j$  of the second mixture. Note  $\bar{x}_i + \bar{x}_j = 1$ . The composition of one mole of the blend is:

$$\left[ \frac{\phi}{\phi + a_{si}} \right] \bar{x}_i \text{ moles fuel } i + \left[ \frac{\phi}{\phi + a_{sj}} \right] \bar{x}_j \text{ moles of fuel } j + \left[ \frac{a_{si}}{\phi + a_{si}} \right] \bar{x}_i + \left[ \frac{a_{sj}}{\phi + a_{sj}} \right] \bar{x}_j \text{ mole of air.} \quad (5)$$

In general, different fuels,  $i$  or  $j$ , will have different stoichiometric air requirements and this is signified by the appropriate fuel symbol following  $a_s$ . In the present study, for one mole of fuel,  $a_{sH_2} = 2.38$  and  $a_{sCH_4} = 9.52$ .

The mole fraction of fuel  $i$  within the total fuels of  $(i + j)$  is:

$$\bar{x}_{fi} = \left[ \frac{\phi}{\phi + a_{si}} \right] \bar{x}_i \left\{ \left[ \frac{\phi}{\phi + a_{si}} \right] \bar{x}_i + \left[ \frac{\phi}{\phi + a_{sj}} \right] \bar{x}_j \right\}^{-1}. \quad (6)$$

Fractional mass weightings are obtained from mole fractions by multiplying mass by the appropriate molecular weights, and normalising.

## 3. The blending laws

### 3.1. Analytical expressions for burning velocity

A theoretical background is provided for some of the blending laws, not so much by detailed chemical kinetics, as by Spalding's seminal mathematical analyses of the laminar burning velocity [8–10]. His expression for the mass burning rate flux  $u_l \rho_u$ , for a Lewis number of unity, is:

$$u_l \rho_u = \left[ \frac{k_u \int_0^1 R(c) dc}{\lambda (T_b - T_u) c_p^2} \right]^{0.5}. \quad (7)$$

Here  $k_u$  is the thermal conductivity of unburned gas,  $T_u$ , the initial temperature,  $c_p$ , the mean specific heat, and  $\rho_u$  the density of unburned gas. The integral is that of the volumetric heat release

rate source term,  $R(c) = (k/k_u)H\dot{m}$ , in which  $H$  is the mass-based heat of reaction of the fuel, and  $\dot{m}$  its mass volumetric rate of burning, with respect to the reaction progress variable,  $c$ , given by the fractional temperature rise,  $(T - T_u)/(T_b - T_u)$ . The numerical value of  $\lambda$ , the burning velocity eigenvalue, was related by Spalding, in an algebraic expression, to the value of  $c$  at the centroid of a plot of the heat release rate profile, against  $c$ , as in Fig. 1. In terms of Eq. (7), as the maximum of the heat release rate profile moves to lower values of  $c$ ,  $\lambda$  decreases with the centroid distance, and  $u_l$  consequently increases.

Eq. (7) can be expressed as

$$(Qc_p/k_u)^{0.5} u_l \rho_u = \left[ \frac{\int_0^1 R(c) dc}{\lambda} \right]^{0.5}, \quad (8)$$

with  $Q$  the heat of reaction of unit mass of the mixture. Computations in [3] show that higher values of  $Q$  and  $u_l$  are associated with smaller values of  $\lambda$ . The numerator within the larger brackets represents a volumetric heat release rate integrated in  $c$  space. This, with  $Q$ , exerts the dominant influence on  $u_l$ .

If  $S(c)$  represents the product of reactant concentrations, Arrhenius "A" values,  $k/k_u$ , heat of reaction, any effect of non-unity Lewis number,  $Le$ , and the activation temperature for the heat release rate,  $T_a$ , then:

$$\int_0^1 R(c) dc = \int_0^1 S(c) \exp(-T_a/T) dc. \quad (9)$$

Because  $dc/dT = (T_b - T_u)^{-1}$ , it can be shown:

$$\int_0^1 R(c) dc = \int_0^1 S(c) \left[ \frac{T_a}{T^2} (T_b - T_u) \right]^{-1} d \exp(-T_a/T). \quad (10)$$

The high activation energy, asymptotic, assumption [11], that all the heat release occurs at  $T_b$ , results in a value of  $\lambda$  of 0.5 and a single valued volumetric heat release rate,  $q_{\max}$ , at  $c = 1$ . Eq. (10) then becomes:

$$\int_0^1 R(c) dc = \int_0^1 S(1) \left[ \frac{T_a}{T_b^2} (T_b - T_u) \right]^{-1} \exp(-T_a/T_b) = (S(1)/Z) \exp(-T_a/T_b), \quad (11)$$

in which  $Z$  is the Zel'dovich number,  $= (T_a/T_b^2)(T_b - T_u)$ .

Eq. (7) then becomes

$$u_l \rho_u = \left[ \frac{k_m S(1) \exp(-T_a/T_b)}{0.5Z(T_b - T_u)c_p^2} \right]^{1/2}. \quad (12)$$

$$u_l \rho_u = \exp(-T_a/2T_b) \exp \ln \left( \frac{k_m S(1)}{0.5Z(T_b - T_u)c_p^2} \right)^{1/2}, \text{ and} \quad (13)$$

$$u_l \rho_u = \exp \left[ (T_a/2T_b) - \ln \left( \frac{k_m S(1)}{0.5Z(T_b - T_u)c_p^2} \right)^{1/2} \right]. \quad (14)$$

If  $T_{al} = T_a - 2T_b \ln \left( \frac{k_m S(1)}{0.5Z(T_b - T_u)c_p^2} \right)^{1/2}$ , then

$$\frac{T_{al}}{2T_b} = \frac{T_a}{2T_b} - \ln \left( \frac{k_m S(1)}{0.5Z(T_b - T_u)c_p^2} \right)^{1/2}, \text{ and} \quad (15)$$

$$u_l \rho_u = \exp(-T_{al}/2T_b). \quad (16)$$

Here  $T_{al}$  is an activation temperature for the laminar burning mass flux, which is dependent upon pressure,  $P$ , Lewis number,  $Le$ , and  $(T_b - T_u)$ . It follows from Eq. (16) that

$$2 \ln u_i \rho_u = -T_{al}/T_b, \quad \text{and} \quad \frac{d^2 \ln u_i \rho_u}{d1/T_b} = -T_{al}. \quad (17)$$

This is a frequently used expression in asymptotic analyses [12,7]. Hirasawa et al. [13] employed a slightly different activation temperature,  $\tilde{T}_a$ , based on  $u_i$  alone rather than  $u_i \rho_u$ , with:

$$u_i = \exp(-\tilde{T}_a/T_b), \quad \text{or} \quad \ln u_i = -\tilde{T}_a/T_b. \quad (18)$$

### 3.2. Blending laws for $u_i$

The six different blending laws for burning velocity that were scrutinised are summarised and referenced in Table 1. Laws 1 and 2 involve fractional mass [14,15] and mole [16] weightings of  $u_i$ , as already discussed.

The third law is more complex and is based on the further development by Di Sarli and Di Benedetto [2] of Le Châtelier's original blending law. With  $\bar{x}_{fi}$ , the mole fraction of fuel  $i$  in all the fuels, in a binary mixture,

$$u_{lb} = [\bar{x}_{fi}/u_{li} + \bar{x}_{fj}/u_{lj}]^{-1}, \quad \text{with} \quad \bar{x}_{fi} + \bar{x}_{fj} = 1. \quad (19)$$

Law 4 is based on the observation in [3] that the burning velocities of lean fuel/air mixtures, within a given chemical family of fuels, increase linearly with the heat of reaction of one mole of the mixture,  $\bar{Q}$ . This is found from:

$$\bar{Q} = \sum_P \bar{m}_P (h_f - \Delta h) - \sum_R \bar{m}_R (h_f - \Delta h), \quad (20)$$

where the summation subscripts  $R$  and  $P$  refer to reactants and products,  $\bar{m}$  indicates a species mole fraction,  $h_f$  is the enthalpy of formation at the standard state conditions of 298 K and 0.1 MPa, and  $\Delta h$  is the sensible enthalpy. Equilibrium products of combustion at constant pressure and  $T_b$ ,  $h_f$  and  $\Delta h$  were found from the GasEq code [17]. Because of the large chemical differences between  $H_2$  and  $CH_4$ , a blending law for their mixtures, based on such an assumed linearity, is unlikely to be successful.

Law 5 is based on Spalding's expression for the mass rate of burning, in the form of Eq. (8), with mass weighting,  $x_i$  and  $x_j$  of the integrated reaction rate terms of the constituent fuel/air mixtures:

$$\begin{aligned} \left[ (Qc_p/k_u)^{0.5} u_i \rho_u \right]_b &= \left[ \int_0^1 \frac{R(c)dc}{\lambda} \right]_b^{0.5} \\ &= x_i \left[ \int_0^1 \frac{R(c)dc}{\lambda_i} \right]_i^{0.5} + x_j \left[ \int_0^1 \frac{R(c)dc}{\lambda_j} \right]_j^{0.5}. \end{aligned} \quad (21)$$

Alternatively, from Eqs. (8) and (21) applying the fractional mass weighting to the separate  $\left[ (Qc_p/k_u)^{0.5} u_i \rho_u \right]$ , constituent mixture terms gives:

$$(Qc_p/k_u)_b^{0.5} u_{lb} \rho_{ub} = x_i (Qc_p/k_u)_i^{0.5} u_{li} \rho_{ui} + x_j (Qc_p/k_u)_j^{0.5} u_{lj} \rho_{uj}. \quad (22)$$

This new law has two merits, that are particularly relevant to  $CH_4$ /air and  $H_2$ /air blends. First, it is related to the all-important profiles of heat release rate for the constituent mixtures, assumed to be additive, and, second, it invokes the separate thermal conductivities of the two mixtures, which are significantly different. That of  $H_2$ /air, is more than twice that of  $CH_4$ /air, see Fig. 2.

The basis of the sixth law is Eq. (18), from [13]. This is a less direct blending law, in that it is based on blended values of  $\tilde{T}_a$ . Values of  $u_i$  and  $T_b$  are known for each of the constituent mixtures, enabling the respective values of  $\tilde{T}_a$  to be found. These are weighted by their respective mole fractions for each constituent mixture to give  $\tilde{T}_{ab}$  for the blend, from which  $u_{lb}$  can be found, by an inverse process, from Eq. (18).

### 3.3. Blending laws for $L_b$

Finding effective blending laws for  $L_b$  proved to be more difficult. A number of parametric groupings and weightings were explored. Only the two most satisfactory are presented. The first law,  $\bar{x}_{di}$ , was suggested by the role of the Lewis number, based on the deficient reactant, in determining the Markstein number. It involves weighting the  $L_b$  value for each constituent mixture by the mole fraction,  $\bar{x}_{di}$ , of the deficient reactant:

$$L_{bb} = \bar{x}_{di} L_{bi} + \bar{x}_{dj} L_{bj}. \quad (23)$$

For example, under lean conditions, for the measured  $L_{bi}$ , the deficient reactant mole fraction for weighting the constituent mixture  $i$ , is the mole fraction of fuel  $i$ , expressed as a fraction of the two constituent mixture fuel moles and given by  $\bar{x}_{fi}$  in Eq. (6). Here,  $\bar{x}_{di} = \bar{x}_{fi}$ . Under rich conditions, the deficient reactant mole fraction for mixture  $i$  is the mole fraction of oxygen  $\bar{x}_{oi}$  expressed as a fraction of the two constituent mixture oxygen moles, given within Eq. (5). Hence:

$$\bar{x}_{di} = 0.21 \left[ \frac{a_{si}}{\phi + a_{si}} \right] \bar{x}_i \left\{ 0.21 \left[ \frac{a_{si}}{\phi + a_{si}} \right] \bar{x}_i + 0.21 \left[ \frac{a_{sj}}{\phi + a_{sj}} \right] \bar{x}_j \right\}^{-1}. \quad (24)$$

The second law, involves the product,  $u_i L_b$ , for each constituent mixture, fractional mass weightings, and is more empirical. It takes the form:

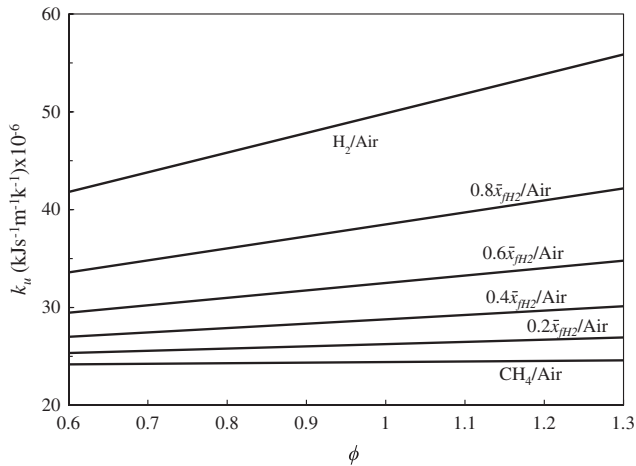
$$u_{lb} L_{bb} = x_i u_{li} L_{bi} + x_j u_{lj} L_{bj}. \quad (25)$$

## 4. Comparisons of measured and predicted values

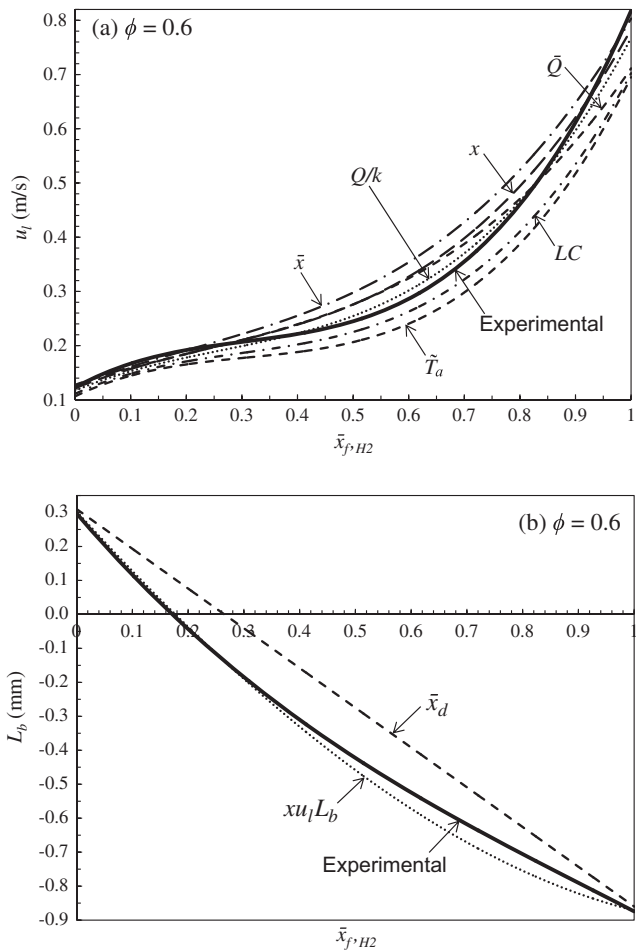
Predicted values of  $u_i$  and  $L_b$  for blends of  $CH_4$ /air and  $H_2$ /air at the same  $\phi$  are compared with the experimentally measured values of  $u_i$  and  $L_b$  of Hu et al. [1], derived from spherical explosions, at 303 K and 0.1 MPa in a cylindrical explosion chamber of 180 mm diameter. Values of  $\phi$  ranged between 0.6 and 1.3, with  $\bar{x}_{f,H_2}$  varying between 0 and 1.0. Predicted and experimental values of  $u_i$  and  $L_b$  values under lean conditions, for  $\phi = 0.6$  and 0.8, are shown in

**Table 1**  
Summary of  $u_i$  blending laws investigated.

	$u_i$ blending law	Ref.	Symbol	$u_p/u_i$	$\sigma$
1	Fractional mass weighting of $u_i$ of constituent mixtures. Eq. (1)	[14]	$x$	1.09	0.06
2	Fractional mole weighting of $u_i$ of constituent mixtures. Eq. (1) modified	[16]	$\bar{x}$	1.2	0.09
3	Modified Le Châtelier law. Fractional mole weighting of constituent fuels. Eq. (19)	[2]	$LC$	0.92	0.04
4	$u_i$ plotted against $\bar{Q}$ per mole of constituent mixture. Eq. (20)	[3]	$\bar{Q}$	1.18	0.08
5	Fractional mass weighting of constituent mixture $u_i \rho_u$ with $(Qc_p/k_u)^{0.5}$ . Eq. (22)	Present work	$Q/k$	1.01	0.03
6	Fractional mole weighting of $\tilde{T}_a$ to obtain blend $\tilde{T}_a$ . Eq. (18)	[13]	$\tilde{T}_a$	0.89	0.04



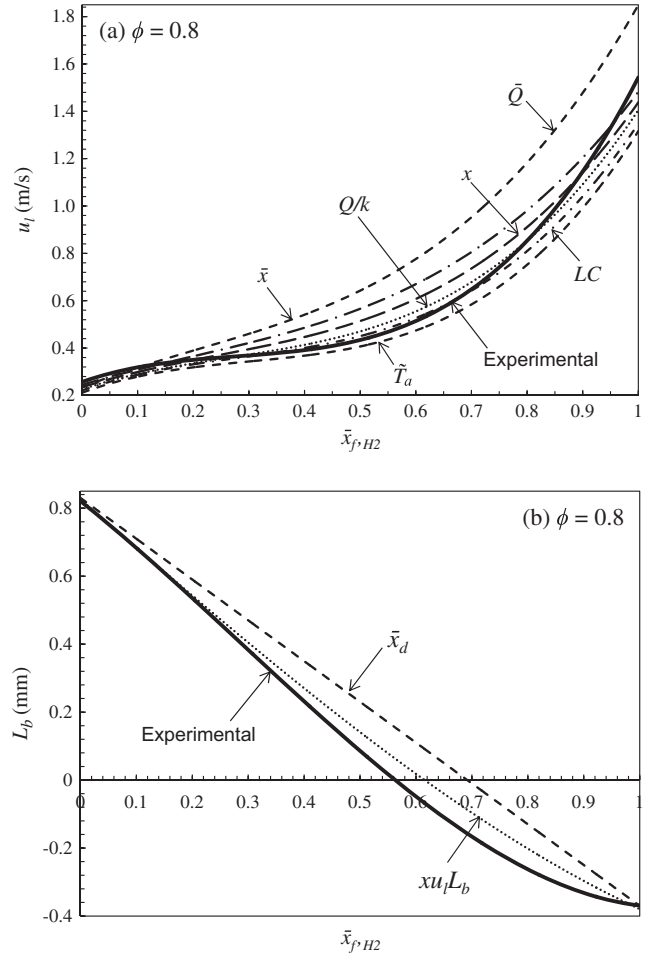
**Fig. 2.** Variation of thermal conductivity,  $k_u$ , with  $\phi$  for methane/air, hydrogen/air, and their blends.  $T_u = 303$  K,  $P_i = 0.1$  MPa. Values from [17].



**Fig. 3.** Predicted and measured values of (a)  $u_l$  and (b)  $L_b$  for  $\text{CH}_4/\text{H}_2/\text{air}$  mixtures, as a function of  $\bar{x}_{f,\text{H}_2}$ ,  $\phi = 0.6$ . Broken, best fit, curves denote predicted values for each law, full line curves denote experimental values measured by Hu et al. [1].

Figs. 3 and 4, and under stoichiometric and rich conditions, for  $\phi = 1.0$  and 1.2, are shown in Figs. 5 and 6.

Measurements of flame speeds were made at flame radii greater than 5 mm, to avoid the influence of ignition energy, and less than 25 mm [1] to avoid cellular flames [18]. There was a linear correlation between flame speed and flame stretch rate [1]. Flame speeds



**Fig. 4.** Predicted and measured values of (a)  $u_l$  and (b)  $L_b$  for  $\text{CH}_4/\text{H}_2/\text{air}$  mixtures, as a function of  $\bar{x}_{f,\text{H}_2}$ ,  $\phi = 0.8$ . Broken, best fit, curves denote predicted values for each law, full line curves denote experimental values measured by Hu et al. [1].

were extrapolated to zero stretch rate and divided by  $\rho_u/\rho_b$  to yield  $u_l$ . Interestingly, such flame speeds would, in fact, be unstable and cellular. Critical Karlovitz stretch factors have been obtained, below which flames become unstable. The more negative the Markstein number, the higher the stretch factor required to maintain its stability [19].

Measured values of  $u_l$  and  $L_b$ , with maximum standard errors of 8.6% and 16.6%, respectively, are shown by the solid curves, while the predicted values are shown by symbols in Table 1 for each of the various blending laws for  $u_l$ .

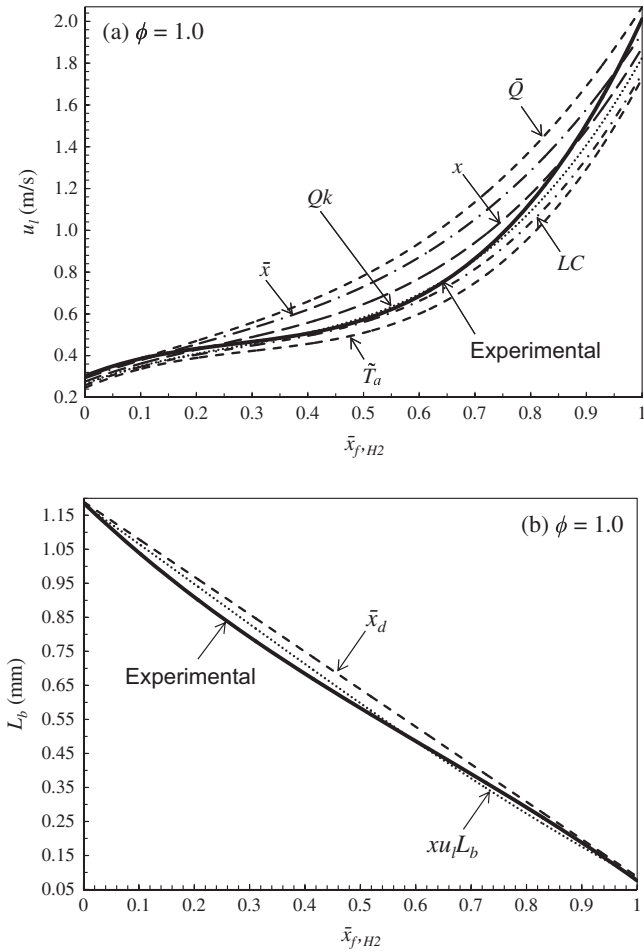
Tables 2 and 3 summarise the ratios of predicted to measured burning velocities,  $u_{lp}/u_l$ , for the different blending laws, for  $\phi = 0.6$  and 0.8 and  $\phi = 1.0$  and 1.2, as a function of  $\bar{x}_{f,\text{H}_2}$ . Likewise, Table 4 summarises the ratio of predicted to measured Markstein lengths,  $L_{bp}/L_b$  for the different blending laws, for  $\phi = 0.6$ –1.2, also as a function of  $\bar{x}_{f,\text{H}_2}$ . For each table, at the bottom of each column, a value of the ratio, averaged over all values of  $\bar{x}_{f,\text{H}_2}$ , is given for the given law and value of  $\phi$ . Below these values are the corresponding standard deviations,  $\sigma$ .

## 5. Discussion

### 5.1. Blending laws for $u_l$

The final two columns in Table 1 give the overall values of  $u_{lp}/u_l$ , averaged over all values of  $\bar{x}_{f,\text{H}_2}$  and  $\phi$ , ranging from 0.6 to 1.3, with



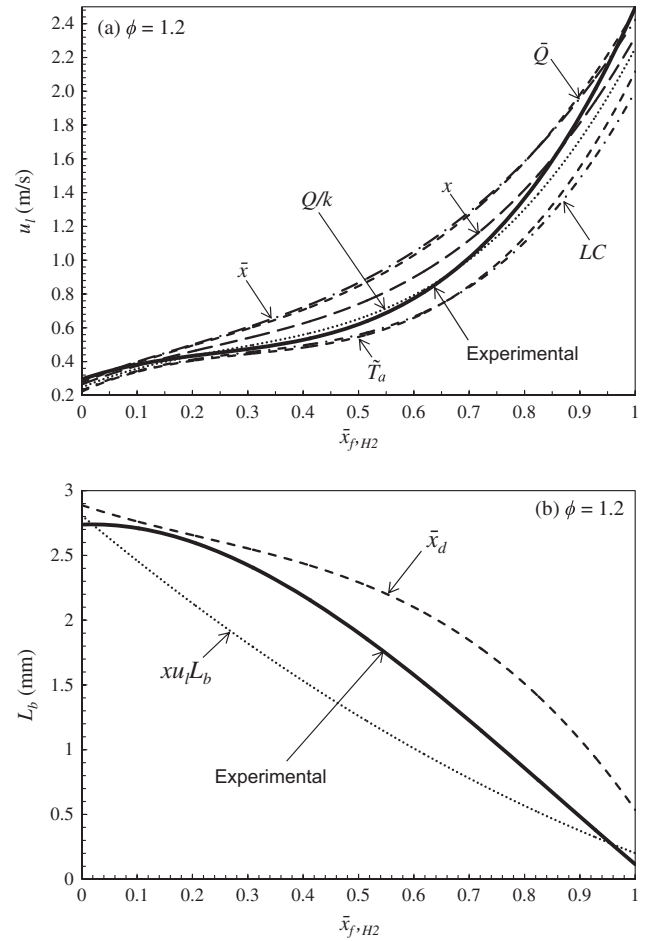


**Fig. 5.** Predicted and measured values of (a)  $u_l$  and (b)  $L_b$  for  $\text{CH}_4/\text{H}_2/\text{air}$  mixtures, as a function of  $\bar{x}_{f,\text{H}_2}$ ,  $\phi = 1.0$ . Broken, best fit, curves denote predicted values for each law, full line curves denote experimental values measured by Hu et al. [1].

their overall standard deviation,  $\sigma$  of such values. The best predictions are those of the  $Q/k$  law. Importantly, this is the only law that gives predictions which are within the 8.6% accuracy of measurement of  $u_l$ . This is not surprising, because it involves more parameters, Eq. (22) is based on the mass fraction weighting of constituent mixture heat release rates, specific heats, and the values of  $k$ . An empirical improvement in the law's accuracy of prediction occurred when  $Q$  was replaced by the molar  $\bar{Q}$ . This reduced the overall average value of  $u_{lp}/u_l$  from 1.05 to 1.01 and decreased  $\sigma$  to 0.04. The second best law is that involving mass weighting. This gives predictions, some of which have errors that exceed 10%.

The worst predictions were those from the  $\bar{x}$  and  $\bar{Q}$  laws. Expectations for the  $\bar{Q}$  law were bound to be low. Fig. 2 in [3] demonstrates the consequences of the two fuels belonging to quite different chemical families. Only for  $\phi = 0.6$  is this law satisfactory. It is rather more surprising that the fractional mole,  $\bar{x}$ , law was so unsatisfactory and inferior to fractional mass weighting. Both of these laws consistently over-estimated  $u_l$ .

Equally consistently, the  $\tilde{T}_a$  law under-estimated values of  $u_l$ . This was based on fractional mole weighting. Fractional mass weighting gave even more pronounced underestimations for this law. In contrast, the  $LC$ , modified Le Châtelier law, which was formulated specifically for  $\text{CH}_4/\text{H}_2$  blends [2], both under and over-estimated  $u_l$ . This was the only law based on the fraction of fuel, rather than of mixture. All the laws became unsatisfactory for  $\phi$



**Fig. 6.** Predicted and measured values of (a)  $u_l$  and (b)  $L_b$  for  $\text{CH}_4/\text{H}_2/\text{air}$  mixtures, as a function of  $\bar{x}_{f,\text{H}_2}$ ,  $\phi = 1.2$ . Broken, best fit, curves denote predicted values for each law, full line curves denote experimental values measured by Hu et al. [1].

values of 1.3 and higher. It was found that the order of merit of the different laws also applied to their performance, over wide ranges of conditions for diverse hydrocarbon/air mixtures, but these predictions were less challenging than those for the present  $\text{CH}_4/\text{air}$  and  $\text{H}_2/\text{air}$  blends.

### 5.2. Blending laws for $L_b$

For the predicted values of  $L_b$ , only those predicted by the  $xu_l L_b$  law at  $\phi = 1.0$  have an accuracy better than the worst measured error of 16.6%. Figs. 4(b) and 5(b) indicate acceptable predictions with this law at  $\phi = 0.8$  and 1.0. The predictions at  $\phi = 1.2$  in Fig. 6(b) are less acceptable. The  $\bar{x}_d$  law consistently over-estimates values, particularly as  $\bar{x}_{f,\text{H}_2}$  is increased, although its performance is satisfactory up to  $\bar{x}_{f,\text{H}_2}$  values of 0.2.

### 5.3. Laminar burn power flux

This is given by the product of mixture density, mass heat of reaction and laminar burning velocity. It is an indicator of the flame power as more  $\text{H}_2$  is added to  $\text{CH}_4$ . Based on the measured values of  $u_l$ , this is shown in  $\text{kW}/\text{m}^2$  in Fig. 7. As the mole fraction of  $\text{H}_2$  is increased, the increased burning velocity of the mixture more than compensates for the lower heat of reaction of hydrogen and the burn power flux increases. The increase is particularly pronounced for  $\bar{x}_{f,\text{H}_2}$  above 0.5.

**Table 2**  
Ratios of predicted to measured burning velocities,  $u_{fp}/u_i$ , for different blending laws,  $\phi$  values of 0.6, and 0.8, as a function of  $\bar{x}_{f,H_2}$ . Values of  $u_i$  for constituent mixtures: at  $\phi = 0.6$ , 0.822 m/s and at  $\phi = 0.8$ , 1.546 m/s for  $H_2$ /air and at  $\phi = 0.6$ , 0.121 m/s, and at  $\phi = 0.8$ , 0.27 m/s for  $CH_4$ /air.

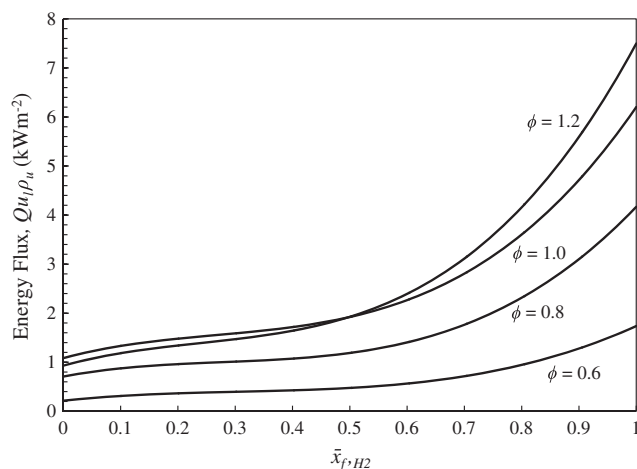
$\bar{x}_{f,H_2}$	$\bar{x}$		$x$		LC		$\bar{T}_a$		$\bar{Q}$		Q/k	
	$\phi = 0.6$	$\phi = 0.8$	$\phi = 0.6$	$\phi = 0.8$	$\phi = 0.6$	$\phi = 0.8$	$\phi = 0.6$	$\phi = 0.8$	$\phi = 0.6$	$\phi = 0.8$	$\phi = 0.6$	$\phi = 0.8$
0.1	1.10	1.03	1.07	1.00	1.02	0.97	0.99	0.94	1.08	1.06	1.05	0.97
0.2	1.09	1.07	1.04	1.02	0.94	0.96	0.90	0.91	1.05	1.13	0.99	0.97
0.3	1.11	1.13	1.05	1.06	0.91	0.97	0.85	0.91	1.05	1.24	0.98	0.99
0.4	1.12	1.20	1.04	1.11	0.87	0.99	0.80	0.92	1.04	1.34	0.96	1.03
0.5	1.13	1.29	1.04	1.18	0.85	1.04	0.78	0.94	1.04	1.46	0.96	1.08
0.6	1.23	1.27	1.14	1.16	0.91	1.01	0.83	0.91	1.12	1.48	1.04	1.06
0.7	1.19	1.30	1.10	1.19	0.88	1.03	0.81	0.94	1.07	1.53	1.02	1.09
0.8	1.18	1.14	1.11	1.06	0.90	0.93	0.84	0.86	1.06	1.38	1.04	0.99
0.9	1.13	1.05	1.08	1.00	0.93	0.91	0.90	0.87	1.00	1.29	1.04	0.96
Av.	1.14	1.16	1.07	1.08	0.91	0.98	0.86	0.91	1.06	1.32	1.01	1.02
$\sigma$	0.05	0.11	0.03	0.08	0.05	0.04	0.07	0.03	0.03	0.16	0.03	0.05

**Table 3**  
Ratios of predicted to measured burning velocities,  $u_{fp}/u_i$ , for different blending laws,  $\phi$  values of 1.0, and 1.2, as a function of  $\bar{x}_{f,H_2}$ . Values of  $u_i$  for constituent mixtures at  $\phi = 1.0$ , 2.05 m/s and at  $\phi = 1.2$ , 2.51 m/s, for  $H_2$ /air and at  $\phi = 1.0$ , 0.353 m/s and  $\phi = 1.2$ , 0.326 m/s for  $CH_4$ /air.

$\bar{x}_{f,H_2}$	$\bar{x}$		$x$		LC		$\bar{T}_a$		$\bar{Q}$		Q/k	
	$\phi = 1.0$	$\phi = 1.2$	$\phi = 1.0$	$\phi = 1.2$	$\phi = 1.0$	$\phi = 1.2$	$\phi = 1.0$	$\phi = 1.2$	$\phi = 1.0$	$\phi = 1.2$	$\phi = 1.0$	$\phi = 1.2$
0.1	1.04	1.14	1.01	1.08	0.98	1.00	0.96	0.99	1.07	1.12	0.98	1.04
0.2	1.11	1.28	1.04	1.16	0.98	1.02	0.94	1.00	1.15	1.26	0.99	1.08
0.3	1.08	1.23	0.99	1.09	0.91	0.90	0.86	0.88	1.13	1.21	0.93	0.99
0.4	1.17	1.32	1.05	1.15	0.94	0.91	0.88	0.89	1.23	1.30	0.97	1.03
0.5	1.30	1.36	1.16	1.17	1.02	0.90	0.94	0.88	1.38	1.33	1.06	1.04
0.6	1.20	1.27	1.07	1.09	0.93	0.82	0.85	0.81	1.29	1.24	0.97	0.97
0.7	1.27	1.35	1.14	1.17	0.99	0.88	0.91	0.88	1.37	1.33	1.04	1.05
0.8	1.12	1.17	1.02	1.04	0.89	0.80	0.84	0.82	1.20	1.16	0.94	0.95
0.9	1.05	1.06	0.99	0.98	0.91	0.81	0.87	0.85	1.13	1.07	0.95	0.93
Av.	1.15	1.24	1.05	1.10	0.95	0.89	0.89	0.89	1.22	1.23	0.98	1.01
$\sigma$	0.09	0.10	0.06	0.07	0.04	0.08	0.04	0.07	0.11	0.09	0.04	0.05

**Table 4**  
Ratios of predicted to measured Markstein lengths,  $L_{fp}/L_b$ , for different blending laws, with  $\phi$  values of 0.6–1.2, as a function of  $\bar{x}_{f,H_2}$ . Values of  $L_b$ , for constituents mixtures at  $\phi = 0.6$ , –0.86 mm, at  $\phi = 0.8$ , –0.37 mm,  $\phi = 1.0$ , 0.087 mm and at  $\phi = 1.2$ , 0.2106 mm for  $H_2$ /air and at  $\phi = 0.6$ , 0.31 mm, at  $\phi = 0.8$ , 0.83 mm, at  $\phi = 1.0$ , 1.19 mm, at  $\phi = 1.2$ , 2.81 mm for  $CH_4$ /air.

$\bar{x}_{f,H_2}$	$\bar{x}_d$				$xuL_b$			
	0.6	0.8	1.0	1.2	0.6	0.8	1.0	1.2
0.2	–0.95	1.18	1.07	1.10	0.46	1.09	1.05	0.88
0.4	0.54	1.21	1.13	1.09	1.14	0.93	1.08	0.68
0.6	0.80	–1.22	0.98	1.13	1.17	–0.20	0.90	0.54
0.8	0.83	0.52	1.23	2.75	1.01	0.81	1.09	1.03
Av.	0.31	0.42	1.10	1.52	0.94	0.66	1.03	0.79
$\sigma$	0.85	1.14	0.11	0.82	0.33	0.58	0.09	0.22



**Fig. 7.** Energy flux variation as a function of  $\bar{x}_{f,H_2}$ , for  $\phi = 0.6, 0.8, 1.0$  and  $1.2$ .

## 6. Conclusions

Six blending laws for laminar burning velocity have been tested as predictors for  $CH_4$ /air and  $H_2$ /air blends over a wide range. Because of their different chemical kinetics and burning velocities, such blends provide a good test of the suitability of the different blending laws. Their performances, in descending order of merit, for each weighting law, are Q/k, mass, mole,  $\bar{T}_a$ , mixture mole  $\bar{Q}$ , and mole. The Q/k law also has the best theoretical basis, through its heat release rate/reaction progress variable profile. Quite empirically, it is improved when  $\bar{Q}$  is substituted for Q. Interestingly, as the proportion of  $H_2$  increases, the heating flux of a laminar flame sharply increases, as the effect of increasing burning velocity dominates over that of decreasing heat of reaction. This first attempt to find an accurate blending law for the Markstein length proved to be more difficult, but two were suggested. One of the problems is the rather wide error bands for the measured values. Further chemical kinetic studies of both strained and curved flames would improve understanding in this area.

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