



Laminar Burning Velocity of Multi-Component Gaseous Mixtures

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The laminar burning velocity is the essential parameters for the safe design of equipment and process. Indeed, the knowledge of this parameter allows for the definition of flammability limits, minimum oxygen concentration and the gas deflagration index, K_g . Recently, the interest in the laminar burning velocity has raised because of the increased use of complex gaseous mixtures derived from biological (biogas), or pyrolysis and gasification (syngas) processes. Due to the large number of components of these gases, simplified correlations for the definition of the additivity of the burning velocity are questionable. Furthermore, the presence of carbon monoxide, hydrogen sulphide, ammonia and hydrogen, or other non-hydrocarbon substances, may strongly affect the correlation results. Le Chatelier's formula e.g. may produce an error of over 25% with respect to the experimental data for simple mixtures based on two hydrocarbon fuels.

In this work, a review of the main additivity rules for the definition of the laminar burning velocity for multi-component mixtures (≥ 3 fuels) is given, starting from the pioneering correlations and analysis of Spalding. The equations have been compared and validated with respect to experimental data. A comparison with the results obtained by using more recent advanced kinetic mechanism, which can be adopted for the prediction of mixture reactivity, is also given.

1. Introduction

In the recent years, the attention of researchers on chemical and safety aspects of complex fuel mixtures is growing due to the increasing utilization of biofuels as alternative fuel in power generation, automotive industries, or for aviation transportation. In this light, a key parameter in the design of industrial processes is the laminar burning velocity (S_u), which condenses several information regarding the reactivity and the exothermicity of the system. Furthermore, it is also essential for safety, because it allows for the definition of flammability limits, minimum oxygen concentration and other important safety parameters. Moreover, S_u allows the development and the validation of detailed kinetic mechanisms (Pizzuti et al., 2016).

Several experimental techniques can be applied to measure S_u . Rallis and Garforth (1980) have divided experimental rigs in stationary and propagating flame equipment. The former is based on the flowrate measurement - in stationary conditions - of the premixed fuel-oxidant mixture. The second is based on the determination of the flame propagation in homogeneous and quiescent flammable mixtures. Bunsen burner, flat-flame and heat flux methods are example of stationary flames apparati, whereas cylindrical tube vessel, soap bubble method and spherical constant-volume vessel method are example of propagating flame apparati. Both systems are nowadays diffused worldwide. Theoretical and experimental analyses, which consider the critical aspects of the experiments and the systematic errors, can be found elsewhere (Hermanns, 2007). However, there is a lack in the definition of sound-based correlations for the effect of additivity of substances on the S_u of gaseous or vapour mixtures, at least for practical and industrial use. In the following, a review of existing empirical or semi-empirical correlations and more recent methodologies, is given. Hence, the use of detailed kinetic models is discussed.

2. Empirical correlations

The main empirical correlations adopted for the evaluation of the laminar burning velocity of complex mixtures ($S_{u,mix}$) composed by n gases or vapours i , are given in the following:

$$S_{u,mix} = \frac{1}{\sum_i^n \frac{z_i}{S_{u,i}}} \quad (1)$$

$$S_{u,mix} = \sum_i^n x_i S_{u,i} \quad (2)$$

$$S_{u,mix} = \sum_i^n h_i S_{u,i} = \sum_i^n \left(\frac{\Delta H_{c,i} x_i}{\sum_i^n \Delta H_{c,i} x_i} \right) S_{u,i} \quad (3)$$

where z_i is the molar fraction of the i -fuel in the mixture, x_i is the molar fraction of i -fuel in the fuel-air mixture, $S_{u,i}$ is the laminar burning velocity of the pure component i , $\Delta H_{c,i}$ and h_i are the enthalpy of combustion and the enthalpy of formation of the pure component i , respectively. More in details, the $S_{u,mix}$ can be estimated by using a linear correlation with respect to $S_{u,i}$ or their inverse, e.g. Le Chatelier's rule (Eq. 1), weighted arithmetic mean based on mole/mass fraction of i -th component (x_i) (Eq. 2) or energy fraction (h_i) obtained by the heat of combustion (ΔH_c) (Eq. 3), as reported by Sileghem et al. (2012).

The main drawback limiting the use of these correlations is the availability of $S_{u,i}$ data for all investigated fuels and conditions. Coppens et al. (2007) have given a correlation based on Gülder's correlation (Gülder, 1984). The equation has been generalized for ternary and more complex fuel blends, as reported in Eq. 4.

$$S_{u,mix} = W \cdot \phi^\eta \exp^{-\xi(\phi - \sum_i x_i \Omega_i)^2} \cdot \prod_i (1 + \gamma_i \cdot x_i^\tau) \quad (4)$$

In Eq.4), W , η , ξ , σ , Ω , Υ and τ are fitting parameters depending on temperature and fuel species, ϕ is the equivalence ratio calculated as reported in Eq. 5.

$$\phi = \frac{\left(\frac{n_f}{n_{ox}} \right)}{\left(\frac{n_f}{n_{ox}} \right)_{st}} \quad (5)$$

where n represents the number of moles in the unburned mixture, and the subscripts f , ox and st the fuel, oxygen and stoichiometric conditions, respectively. Noteworthy, Eq. 4 could be presented as an Arrhenius-like correlation where the exponential term (representing the apparent activation energy) is a function of gaseous composition and unburned gas temperature, thus confirming the complexity of reaction system.

A more theoretical and general approach could be desirable, in order to reduce the number of experiments and the systematic error connected to the experimental uncertainties. On this regard, the pioneering work of Semenov reported and validated for hydrocarbons mixtures by Dugger et al. (1952), represents the first study where burning velocity of fuels was estimated by means of the thermodynamic properties of the gaseous mixture, by using a first order kinetic equation and mass diffusivity, D :

$$S_{u,mix}^2 = \frac{2K_f}{\rho_0 c_{p,0}^2 (T_f - T_0)^2} \left(\frac{T_0}{T_f} \right) \left(\frac{K}{\rho D} \right)_f \left(\frac{n_0}{n_f} \right) \left(\frac{RT_f^2}{E} \right)^2 A e^{-\frac{E}{RT_f}} \quad (6)$$

where A and E are the pre-exponential factor and activation energy of global reaction rate equation assumed as first order kinetic, respectively, K the conductivity, c_p the specific heat, ρ the density, T the temperature, n the mole number involved into the reactive system including the inert (N_2 from air in our case), and R the ideal gas constant. The subscript f represents the adiabatic flame conditions and 0 the unburned mixture conditions.

Starting from the observation reported by Semenov, a semi-empirical correlation has been proposed by Spalding (1956) based on the hypothesis of additive mass-based reaction rate with respect to the fuel mixture composition:

$$S_{u,mix}^2 = \left(\frac{K}{(\rho_0 c_p (T_f - T_0))^2} \right)_{mix} \sum_i^n \omega_i \left(\frac{(\rho_{0,i} c_{p,i} (T_f - T_0) S_{u,i})^2}{K_i} \right) \quad (7)$$

where ω_i represents the mass ratio of fuel i plus the corresponding amount of oxidant to the total mass of (fuel + oxidant). Eq. 7 has been further simplified by Yumlu (1968) assuming the additivity of conductivity and heat release rate for the pure components:

$$S_{u,mix}^2 = \sum_i^n \omega_i S_{u,i}^2 \quad (8)$$

Finally, an example of logarithmic correlation has developed by Hirasawa et al. (2002). The Hirasawa's rule is based on the hypothesis of the flame temperature as the dominant parameter in the burning velocity determination of the fuel blends, at atmospheric pressure.

$$S_{u,mix} = \exp \left[\sum_i^n \left(\frac{z_i n T_{f,i}}{n_{mix} T_{f,mix}} \ln(S_{u,i}) \right) \right] \quad (9)$$

3. Kinetic models

An alternative route to predict $S_{u,mix}$ consists in the use of detailed, chemical reaction mechanism. Quite clearly, the main drawback limiting the use of detailed kinetic models related to the mechanism is represented by the computational time needed to perform the simulations. A possible solution is represented by the reduction of the species and reaction number, however with negligible effects on the numerical results. The model developed by Lawrence Livermore National Laboratory (LLNL) for diesel surrogate (Pei *et al.*, 2015) have considered more than 1500 species in the detailed version, whereas two reduced version are given with 679 and 323 species, respectively. For the sake of brevity, a short list of kinetic models is given in Table 1. Data are classified by typology (i.e. detailed or skeletal mechanisms) and reference fuels analysed for the tuning of the reaction mechanism.

Table 1. Kinetic mechanism list

Mechanism name	Typology	Reference compound
Gri-Mech 3.0 (Smith <i>et al.</i> , 1995)	Detailed	H ₂ /CO/C ₁ -C ₄ Compounds
MIT (Richter and Howard, 2002)	Detailed	C ₁ -C ₆ , Oxygenated Compounds
Jet Surf 2.0 (Sirjean <i>et al.</i> , 2009)	Detailed	Diesel and Biodiesel Surrogates
TUE (Konnov, 2009)	Detailed	C ₁ -C ₄ , Oxygenated Compounds
LLNL Gasoline surrogate (Mehl <i>et al.</i> , 2011)	Detailed/Skeletal	Gasoline Surrogate
Creck complete (Ranzi <i>et al.</i> , 2012)	Detailed	Hydrocarbons, Oxygenated Compounds
USC Mech II (Wang, 2013)	Detailed	H ₂ /CO/C ₁ -C ₄ Compounds
Diesel surrogate (Stagni <i>et al.</i> , 2015)	Skeletal	Diesel and Biodiesel Surrogates
LLNL Diesel surrogate (Pei <i>et al.</i> , 2015)	Detailed/Skeletal	Diesel Surrogate
Aramco Mech 2.0 (Li <i>et al.</i> , 2016)	Detailed	C ₁ -C ₄ , Oxygenated Compounds
UCSD complete (UCSD, 2016)	Skeletal	Diesel and Biodiesel Surrogates
KIBO (Pio <i>et al.</i> , 2018)	Detailed	C ₁ -C ₄ Compounds

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In the following, we have adopted a kinetic mechanism developed at University of Bologna, which has been indicated as the best fitting model for C₄ and lighter hydrocarbons in previous work (Pio *et al.* 2018).

Results and Discussion

In order to assess the mixing rules for the prediction of $S_{u,mix}$, the experimental data reported by Nilsson *et al.* (2017) for Methane/Ethane/Propane/Hydrogen mixtures with air were only considered in this work. More specifically, the effect of equivalence ratio on the $S_{u,mix}$ of fuel mixture consisting of 40%v of methane, 5%v of ethane, 5%v of propane and 50%v of hydrogen at 300 K and 1 bar was studied. Results are reported in Figure 1. Required thermodynamic parameters, the $S_{u,i}$ and the fitting coefficients were obtained by means of monomolecular and binary data reported by Nilsson *et al.* (2017). Following Varma *et al.* (1999), a statistical analysis based on Fractional Bias (FB) and Normalized Mean Square Error (NMSE) was also performed (Figure

2). Acceptance criteria of $|FB| < 0.5$ and $NMSE < 0.3$ were adopted. Noteworthy, all the reported correlations respect the acceptance criteria, except for the weighted average (Eq. 2).

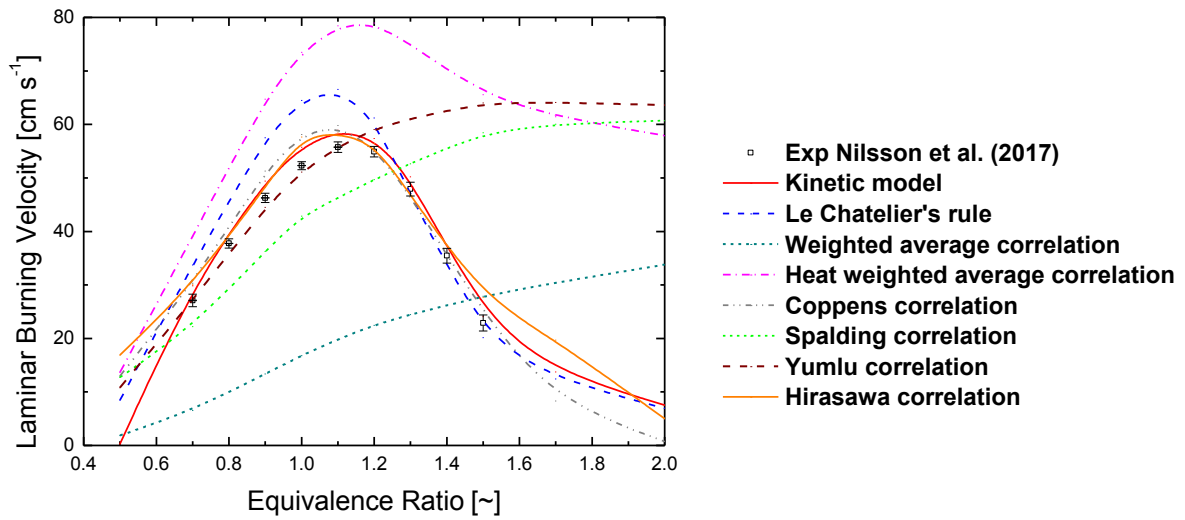


Figure 1. $S_{u,mix}$ for Methane/Ethane/Propane/Hydrogen/Air mixtures (300 K, 1 bar). Experimental data by Nilsson et al. (2017).

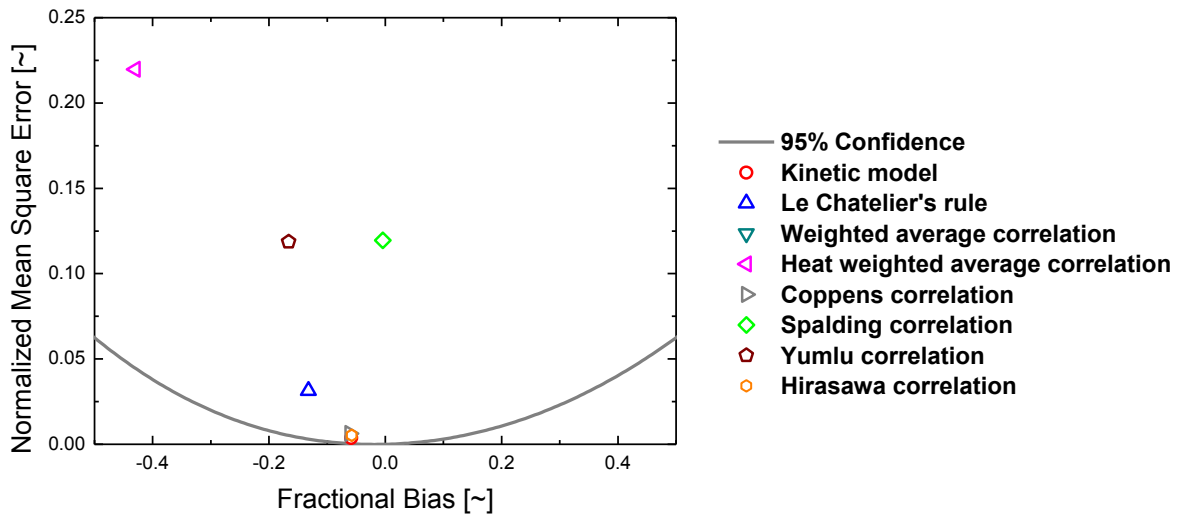


Figure 2. Fitting evaluation.

Results suggest that heat weighted average (Eq. 3), Spalding (Eq. 7) and Yumlu (Eq. 8) correlations are not suitable for $S_{u,mix}$ estimation, especially for rich mixtures, being the effect of hydrogen $S_{u,i}$ too relevant. In addition, Le Chatelier's mixing rule (Eq. 1) overpredicts the nearly stoichiometric $S_{u,mix}$. Coppens (Eq. 4) and Hirasawa (Eq. 9) correlations are suitable for the prediction of experimental and kinetic mechanism data. This observation is confirmed by Figures 1 and 2, which show almost overlapped points for Coppens, Hirasawa correlations and detailed kinetic model. Indeed, they are placed close to the origin of the axis, thus representing the perfect correspondence with experimental data.

Conclusions

The development of simplified correlations for the estimation of complex fuel mixtures represents a crucial step in process development and safety. Indeed, the use of a singular equation instead of detailed kinetic models consisting in several Arrhenius equations considerably reduces the computational costs and time required to for

the estimation of chemical reaction rate, as required in the use of RANS (Reynolds Average Navier-Stokes) based CFD model.

For the specific test case shown in this work, simplified correlations based on weighted arithmetic mean (Eq. 2) and Le Chatelier's rule (Eq. 1) have been confirmed to be inadequate, in particular when relevant amount of non-hydrocarbon substances as hydrogen are added (Basco et al., 2012; Nur et al., 2015). The data based on Eq. 3 and 10 suggest the flame temperature as the dominant factor. This observation is confirmed by the modified Coppens' correlation (Eq. 4), which can be expressed as an Arrhenius-like correlation, hence implicitly ruled by the flame temperature and the gaseous composition. Eventually, as also reported by Dirrenberger et al. (2011), Coppens' additivity rule is the most accurate correlation for the estimation of the Laminar Burning Velocity of a wide range of fuel mixtures, including natural gas and hydrogen.

Further study will be addressed to the introduction of non-hydrocarbon species (Salzano et al., 2012a; 2012b; Barba et al., 2017)

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