

Kinetic Parameters for Safety of Hydrogen-Containing Mixtures

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The production of clean energy via carbon-neutral fuels has been included in a road map within several international institutions. Among the available alternatives, hydrogen has been largely considered as one of the most promising solutions. However, technologies for its safe storage and optimized combustion are still under development or on a prototypal stage. Hence, the addition of hydrogen to less reactive fuels has been proposed as a supplementary route for short and mid-term solutions. A self-evident example of this trend is the design of infrastructures transporting mixtures of natural gas and hydrogen in a ratio up to 3:1 on a molar basis. In most cases, the addition of hydrogen to pure methane has been considered, so far, narrowing the beneficial effects on the environmental perspective. Indeed, the utilization of bio-derived methane may help to broaden these positive aspects. Nevertheless, the effects of the initial composition on chemical and thermal aspects are still poorly understood. In this perspective, the characterization of the overall reactivity and severity in case of accidental release in terms of laminar burning velocity represents an appealing solution. For these reasons, this work presents a detailed analysis of coupling experimental and numerical investigations to fully understand the involved phenomena. More specifically, the overall reactivity was measured for gaseous mixtures representative for bio-derived methane enriched by hydrogen, at first. Several compositions and initial temperatures were examined at this stage. Then, the validity of a theoretical-based mechanism was tested against experimental data, allowing for further characterization of the investigated species. The most prominent effects of operative conditions on the ignition phenomena were numerically individuated and discussed. The results collected throughout this work provide a robust feature for the detailed evaluation of the normal operations as well as the accidental release of hydrogen-containing fuels.

1. Introduction

Under the impulse of the European Union, several regulations and goals (e.g., Paris agreement) have been set at an international level, promoting research projects dealing with innovative solutions for industrial and transportation sectors. Among the others, the utilization of hydrogen as an energy vector has been indicated as a brilliant solution for the reduction of anthropogenic impact on the environment (Ball and Weeda, 2015). The beneficial effects of the introduction of hydrogen-based systems have been largely demonstrated through the life cycle assessment approach, especially for heavy trucks, maritime (Al-Breiki and Bicer, 2021), and aviation (Bicer and Dincer, 2017) applications. However, the current understanding of hydrogen reactivity and long-term stability have raised several concerns on hydrogen-based technologies (Molkov, 2012). Besides, being an incondensable gas, hydrogen is characterized by low volumetric density and energy density at atmospheric conditions. Hence, compression at ambient temperature and liquefaction through cryogenic temperatures have been considered to make the storage and transportation of pure hydrogen sustainable also from an economic point of view. Other than physical storage, the chemical route has been intensively investigated too. Namely, hydrogenation/dehydrogenation cycles or hydrogen blending with low-value fuels represent the most promising and investigated alternatives of this class (Sharma and Ghoshal, 2015). The former requires dedicated plants transforming the carriers close to the market, whereas the latter allows for the direct utilization of hydrogen in gaseous streams with large content of inert or low-reactive species such as CO₂ and CO. Considering the reduced capital costs associated with the blending solution, it should be preferred for small and medium scales.

Typical examples of largely available low-values mixtures are bio-derived fuels, mostly containing $\text{CH}_4:\text{CO}:\text{CO}_2:\text{H}_2$ (Fischer and Jiang, 2016). Biomass-derived fuels can be produced and used through several industrial processes, such as the gasification of municipal waste (Campoy et al., 2014), digestion processes (Kan et al., 2018) or combined gasification/gas turbine cycles (Pedroso et al., 2017). Besides, different sources can be used for this aim (Indrawan et al., 2018). Hence, the flexibility in the selected process and the nature of the feedstock implies as intrinsic drawback a significant variability of their composition. Changes in composition result in large oscillations in the overall reactivity, making the design of combustor systems challenging (Fischer and Jiang, 2014). In this light, the characterization of the effect of fuel composition on the overall reactivity and safety parameters represents an essential step for the diffusion of this technology (Eckart et al., 2017). Flame structure, shape, and overall kinetics can be summarized under a single parameter: the laminar burning velocity (S_u) (Glassman and Yetter, 2008). To obtain the S_u , experimental, empirical, and numerical routes are possible. Typically, lab-scale burners, such as closed vessels, heat flux burners, counterflow flames, are used for the experimental approach. If desired, Readers are encouraged to check the dedicated review (Egolfopoulos et al., 2014) for additional information on the theoretical and practical aspects involving the cited *apparati*. However, this alternative may result in a time-demanding option since it implies the realization of many experiments to cover all the operative conditions of interest for combustion applications. Conversely, empirical correlations represent the fastest way to assess the S_u since they are usually based on the physical properties of the unburned mixtures and tabulated coefficients. Several equations have been developed so far (Xie and Li, 2020), including Le Chatellier's, Spalding's (Spalding, 1956) Gulder's (Gulder, 1984), and Hirasawa's (Hirasawa et al., 2002) correlations. However, most of them fail once a significant amount of hydrogen is added to the burning mixture (Salzano et al., 2018). The drop in accuracy has been attributed to the peculiarity of hydrogen behaviour in an oxidative environment, leading to unusual interactions. For these reasons, kinetic mechanisms are often suggested for preliminary evaluations of hydrogen-containing fuels. Different approaches can be adopted for their development, including pure theoretical based (i.e., based on parameters deriving by quantum mechanical calculations), lumped parameters, and hybrid approach (combining estimated and theoretical based parameters) (Curran, 2019). Again, the time requested to perform the tasks represents an important aspect to be considered for the selection of the most appropriate option. Indeed, the pure theoretical based option is unfeasible for the generation of detailed kinetic mechanisms since they include hundreds of species and thousands of reactions (Battin-Leclerc, 2008). Conversely, lumped parameters may lack accuracy and flexibility since these mechanisms derive from empirical rules and simplifications. Hence, the hybrid approach should be preferred. The nature of the approach imposes the validation as a preliminary step against experimental data at conditions representative for the analysed systems. Regardless of the selected approach, the knowledge of the overall reactivity (via the determination of the S_u) allows for the estimation of several safety parameters essential for quantitative risk assessment (Pio and Salzano, 2018). In this sense, the evaluation of lower flammability limit (LFL) and upper flammability limit (UFL) at atmospheric conditions represents an essential step for the further development and safe implementation of the discussed solutions.

For these reasons, this work presents a numerical investigation aiming at the evaluation of LFL and UFL of bio-derived mixtures containing hydrogen through the utilization of a detailed kinetic mechanism validated for the investigated conditions.

2. Methodology

The limiting laminar burning velocity theory proposed by Hertzberg (1984) (Hertzberg, 1984) was employed for the sake of LFL and UFL determination. In other words, the compositions resulting in a laminar burning velocity equal to a threshold value, the so-called limiting laminar burning velocity ($S_{u,lim}$), were considered for the determination of flammability limits. According to the cited theory, the $S_{u,lim}$ is a function of thermodynamic and transport properties of the unburned mixtures. The detailed kinetic mechanism developed at the University of Bologna (Pio et al., 2019) was used for the estimation of the required properties as well as for the evaluation of the S_u at different compositions, being extensively validated for the components of the investigated mixtures and analysed conditions. This mechanism was employed by the open-source software Cantera (Goodwin, 2003), assuming a zero-dimensional reactor, running in adiabatic conditions and transient mode at an initial temperature of 300 K and initial pressure of 1 atm. Grid refining parameters were set as follow: maximum first derivative (slope) = 0.07, maximum second derivative (curve) = 0.01, absolute error criteria (ATol) = $1.0 \cdot 10^{-14}$ (for steady-state) or $1.0 \cdot 10^{-12}$ (for transient), relative error criteria (RTol) = $1.0 \cdot 10^{-9}$ (for steady-state) or $1.0 \cdot 10^{-5}$ (for transient). These values were selected after a grid dependency analysis, as reported elsewhere (Pio and Salzano, 2019). Binary, ternary, and quaternary mixtures of $\text{CH}_4:\text{CO}:\text{CO}_2:\text{H}_2$ were investigated in this work, as reported in Table 1 in terms of volumetric percentage. The selected values were identified to be representative of possible mixtures deriving by biomass treatment (Sik Song et al., 2011). Although the scope of this work is

the evaluation of the effect of hydrogen on the reactivity of bio-derived fuels, pure CH₄ as well as its binary mixtures with CO and CO₂ were also investigated, for the sake of comparison.

Table 1. Summary of the fuel composition investigated in this work expressed as a volumetric percentage.

Mixture	CH ₄ [%v/v]	CO [%v/v]	CO ₂ [%v/v]	H ₂ [%v/v]
Mix 1	100	0	0	0
Mix 2	90	0	0	10
Mix 3	80	0	0	20
Mix 4	90	10	0	0
Mix 5	80	20	0	0
Mix 6	80	0	20	0
Mix 7	50	0	50	0
Mix 8	60	0	20	20
Mix 9	40	0	40	20
Mix 10	70	10	0	20
Mix 11	60	20	0	20
Mix 12	40	20	20	20

Results will be also expressed in terms of equivalence ratio (φ , Equation 1) at LFL and UFL:

$$\varphi = \sum_i \frac{\left(\frac{F_i}{O_2}\right)}{\left(\frac{f_i}{ox}\right)} \quad (1)$$

where F and O_2 respectively represent the volumetric fraction of the i -th fuel species and oxygen in the unburned mixture, whereas f and ox stand for the stoichiometric coefficients of the i -th fuel and oxygen in the reaction of complete oxidation. Under these premises, in this work CH₄, CO, and H₂ were considered as fuels species, only. Hence, the variations in terms of flammability limits with respect to Mix 1 (Δ) for the j -th mixture were calculated as defined in Equation 2, distinguished for LFL and UFL to represent in both cases an increase in reactivity for positive values.

$$\Delta_j = \left(\sum_i F_{i,LFL,Mix j}\right) - F_{LFL,Mix 1} \quad \Delta_j = -\left(\sum_i F_{i,UFL,Mix j}\right) + F_{UFL,Mix 1} \quad (2)$$

3. Results and discussion

Figure 1 and Figure 2 report the flammability limits numerically estimated in this work for the fuel compositions considered in Table 1 in presence of air at 300 K and atmospheric pressure, expressed in terms of a ternary plot. For the sake of clarity, species other than CH₄ composing the fuel mixtures (i.e., CO, CO₂, and H₂) were grouped under the nomenclature "Other species". A comparison of equivalence ratios and CH₄ contents at LFL and UFL (Table 2) was included.

Table 2. Equivalence ratio (φ) and CH₄ content at lower and upper flammability limits as estimated using the detailed kinetic mechanism as a function of the initial fuel composition.

Mixture	φ @ LFL	CH ₄ @ LFL [%v/v]	φ @ UFL	CH ₄ @ UFL [%v/v]
Mix 1	0.422	4.24%	2.510	20.86%
Mix 2	0.433	4.22%	2.504	19.92%
Mix 3	0.444	4.16%	2.493	18.83%
Mix 4	0.432	4.21%	2.467	19.69%
Mix 5	0.444	4.16%	2.420	18.41%
Mix 6	0.429	4.26%	2.511	19.83%
Mix 7	0.446	4.28%	2.515	17.28%
Mix 8	0.423	3.83%	2.464	17.08%
Mix 9	0.408	3.48%	2.435	14.49%
Mix 10	0.442	3.96%	2.447	17.43%
Mix 11	0.444	3.75%	2.405	15.91%
Mix 12	0.447	3.43%	2.362	13.26%

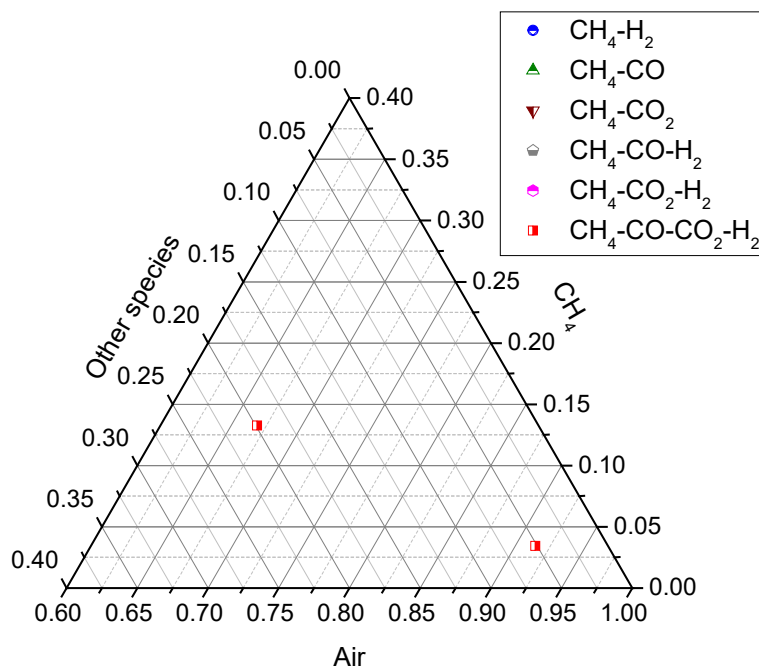


Figure 1. Estimation of the flammability limits of $\text{CH}_4:\text{CO}:\text{CO}_2:\text{H}_2$ mixtures defined in Table 1 in the air at 300 K and 1 atm.

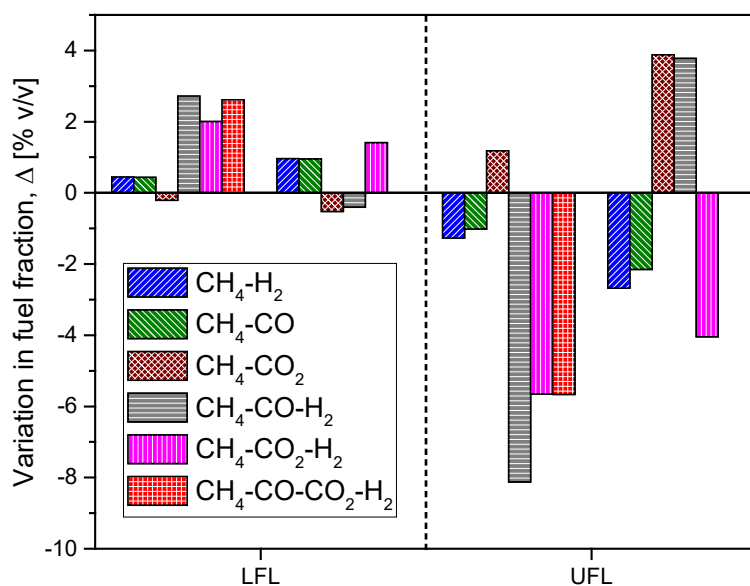


Figure 2. Comparison of the effects of initial composition on flammability limits of $\text{CH}_4:\text{CO}:\text{CO}_2:\text{H}_2$ mixtures defined in Table 1 in the air at 300 K and 1 atm.

The application of the described approach has led to the LFL and UFL respectively equal to 4.24%_{v/v} and 20.86%_{v/v} for pure CH_4 . These estimations represent slightly conservative results with respect to experimental data available in the current literature (Coward and Jones, 1952)(Zlochower and Green, 2009), possibly attributable to the assumption of perfectly adiabatic conditions posed for the numerical analysis. Although CH_4 content at LFL is slightly affected by the fuel composition, the fraction of flammable gases at the corresponding compositions varies from 3.7 %_{v/v} up to 6.9 %_{v/v}. Regardless of the added fuel species, similar LFL can be observed for the binary mixtures investigated in this work. This means that the potential abundance of hydrogen radicals in Mix 2 and Mix 3 does not lead to a boost of hydrogen abstraction, mainly responsible for the production of radicals and, thus of the ignition at lean compositions. Besides, the CH_4 content at LFL slightly decreases, but it is compensated by the added fuel, resulting in higher LFL, i.e., less ignitable mixtures. This result can be considered counterintuitive, at first, if compared with the overall reactivity. Indeed, either H_2 or CO

is characterized by considerably faster S_u than CH_4 , then an increase in the overall reactivity may be expected. However, their addition has a larger impact on the $S_{u,lim}$ than S_u , causing the observed trend. These observations indicate the limited impact of the chemistry of the secondary fuels on the ignitability of CH_4 if additives are limited at $\leq 20\%_{v/v}$, thus confirming the existence of a methane-dominated chemical regime. Conversely, larger UFL can be observed for Mix 2 and Mix 3 with respect to the homologous mixtures containing CO (i.e., Mix 4 and Mix 5). Besides, it is worth noting that these mixtures show significantly larger UFL than Mix 1. However, if the CH_4 content and equivalence ratio at UFL are considered, the highest value is observed for Mix 1. From a chemical point of view, these trends testify that the interactions between ignition mechanisms of the investigated fuels species are low. From a safety point of view, this observation may suggest the utilization of the equivalence ratio as a stand-alone parameter to characterize the ignitable region in the case of stratified mixtures containing different fuel species. In other words, a conservative approach for the determination of flammable areas of gaseous mixtures may consider the equivalence ratio at LFL and UFL of the main fuel (i.e., CH_4 in this case), i.e., 0.42 and 2.51 in this case. Indeed, either the CH_4 fraction or the estimated LFL for the mixtures cannot guarantee a conservative approach on the safe side for all the investigated conditions.

The addition of CO_2 to pure CH_4 (i.e., Mix 6 and Mix 7) produces negligible effects on the estimated LFL and reduces significantly the UFL. These data are in line with the ones published by Chen et al. (2009) (Chen et al., 2009) on the inertisation of methane at ambient conditions. The differences in the abovementioned trends are commonly attributed to the variation of relative weights of thermal and radical aspects on the ignition. In other words, LFL is usually assumed as determined by thermal aspects, thus the variation in thermal inertia of the initial gaseous stream is the main responsible for LFL. Alternatively, UFL is typically considered as ruled by the chemistry of radical species and termination reactions. Hence, in this case, the presence of CO_2 mainly impacts UFL by shifting the equilibrium toward uncompleted oxidation and, thus, modifies the kinetic rates and produced heat. However, the equivalence ratio at UFL is almost unchanged for these mixtures, meaning that the CH_4/O_2 resulting in the ignition is unaltered by inertization up to $50\%_{v/v}$ of CO_2 .

The results reported for ternary and quaternary mixtures investigated in this work show that the simultaneous presence of CO_2 and H_2 has a larger echo on the LFL and UFL. In this sense, it is worth noting that usually the formation of CO_2 in combustion systems is attributed to the reaction R1: $\text{CO} + \text{OH} \rightleftharpoons \text{CO}_2 + \text{H}$. Furthermore, the relevance of CO_2 acting as a third body for the production of HO_2 , namely the reaction R2: $\text{H} + \text{O}_2 (+\text{CO}_2) \rightleftharpoons \text{HO}_2 (+\text{CO}_2)$, has been already reported for gaseous mixtures including the investigated species (Lee et al., 2017). Hence, it is legitimate to assume that the formation of OH and HO_2 is enhanced by the presence of CO_2 due to the reverse reaction of R1 and direct R2, being either CO_2 or H largely available for Mix 8, Mix 9, and Mix 12. The supposed increase in the OH and HO_2 fractions turns in easier ignition at respectively intermediate and low temperatures, following the classical theory of combustion (Law, 2006).

4. Conclusions

This work presents a numerical investigation on the reactivity of gaseous mixtures containing hydrogen, potentially representative for bio-derived streams. A detailed kinetic mechanism was used for the evaluation of the laminar burning velocity at extremely lean and rich compositions, aiming at the quantification of lower and upper flammability limits at atmospheric conditions through the limiting laminar burning velocity theory. To this scope, binary, ternary, and quaternary mixtures of CH_4 , CO, CO_2 , and H_2 were investigated. The effects of initial fuel compositions on the flammability limits in the air were discussed. Observed differences were discussed given elemental reactions involving the added species and possibly determining a significant variation in the estimated parameters. This analysis was intended as support for the sake of accurate characterization of accidental release of gaseous mixtures containing different fuels. Indeed, an alternative approach for the identification of flammable regions in the case of stratified mixtures, such as the ones resulting from an accidental release, was proposed.

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