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Experimental and Numerical Evaluation of Low-Temperature Combustion of Bio-Syngas

Gianmaria PIO¹, Antonio RICCA², Vincenzo PALMA², Ernesto SALZANO^{1,*}

¹ *Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali,
Università di Bologna, via Terracini 28, 40131 Bologna (IT)*

² *Dipartimento di Ingegneria Industriale, Università di Salerno,
via Giovanni Paolo II 132, 84084 Fisciano, Salerno (IT)*

*Author to whom correspondence should be addressed: ernesto.salzano@unibo.it

Abstract

Environmental regulations have strongly incentivized the development of alternative technologies and renewable sources for the energy supply, including bio-syngas and low-temperature combustion. However, accurate estimation methods for low-temperature chemistry of these mixtures are still missing. Hence, experimental data with the limited impact of fluid dynamics aspects are strongly required. To this aim, the heat flux burner has been adopted in this work for the measurements of the laminar burning velocity. Data were compared to evaluate the accuracy of the kinetic mechanism developed at the University of Bologna (KIBO) and existing mixing rules. Hirasawa's correlation has been found as the most reliable empirical correlation. Furthermore, the KIBO model has been validated and compared with existing models for the investigated conditions. These results have allowed for the evaluation of the effects of fuel composition on the preferable reaction paths and on the NO_x production rate.

Keywords: Laminar burning velocity, bio-syngas, combustion, heat flux burner, NO_x formation

1. Introduction

The increasing demand for sustainable and environmentally friendly energy sources, complying with the international regulations on this subject (e.g. Euro VI and EPA emission regulations), has intensively incentivized the development of alternative fuels and combustion systems [1][2]. Among the others, the reduction of operative temperature in the combustion chamber and the utilization of biomass-derived fuels have been largely studied and are still considered as promising solutions [3][4][5]. Indeed, the performance of traditional gas turbine designed for the combustion of natural gas, commonly assumed as pure methane, has been successfully tested in case of syngas combustion, in terms of energy efficiency and environmental performances [6]. The incorporation of biomass integrated gasification, pyrolysis or fermentation processes to gas turbine combined cycle, internal combustion engines, and other energy production systems, has been positively evaluated on the technical and the economic basis [7][8]. The resulting mixtures, often referred as bio-syngas [4], have been successfully utilized in combustion systems, allowing the utilization of several feedstocks such as agriculture residues or municipal solid waste [9][10]. On the other hand, the resulting fuel mixtures, which is mainly composed by hydrogen, carbon monoxide, carbon dioxide, and methane [11], are characterized by large fluctuations on the gaseous composition which reduce the engine efficiency considerably [12] (Table 1). The addition of hydrogen to the unburned mixture is thus encouraged [13] to enhance the overall reactivity and compensate for the aforementioned reduction.

Table 1. Range of composition for biogas and bio-syngas from biomass gasification [14] [15].

Substance (%v)	Biogas	Bio-syngas
H ₂	0-1	22-32
CH ₄	50-75	8-11
CO ₂	25-50	21-30
CO	0	28-36
N ₂	0-10	0

In this framework, in-depth chemical knowledge is essential for the development and implementation of cleaner combustion strategies to satisfy the emission regulations [16][17][18]. To this aim, the development of accurate, comprehensive and detailed kinetic mechanisms is strongly desirable to evaluate the produced amount of either energy or pollutants [19]. The latter can be assessed by means of suitable kinetic models [20]. However, most of the available detailed kinetic mechanisms are developed and validated at engine-relevant conditions, whereas low-temperature reaction rates are only extrapolated [21]. Hence, additional experimental data at low pressure and temperature may broaden the range of validity of the numerical approach and allow for the individuation of global optimized conditions for combustion and process purpose. Moreover, this analysis represents an essential step and the basis for high-pressure investigations necessary to simulate bio-syngas combustion in gas turbines [22].

For these aims, the overall reactivity can be correlated to a physic-chemical property of fuel oxidant mixture under given operative conditions, i.e. the laminar burning velocity (S_u) [17]. This parameter is often utilized because of the limited impact of fluid dynamics aspects and simplicity in the evaluation of the overall kinetic and thermal phenomena as a stand-alone parameter [16]. It represents the transformation velocity and it can be related to the spatial velocity, by adding the unburnt gas velocity term [23], thus to the produced heat. Moreover, it can be adopted for the design of combustion chambers because S_u represents an indirect measurement of the overall system reactivity, i.e. the Damköhler number. Indeed, this dimensionless number relates the time scale, or alternately the velocity, of reaction and transport phenomena. Several experimental systems have been developed for the evaluation of the S_u . Among the others, the counter-flow flame method, the spherical bomb technique, and the flat flame burners have been intensively adopted for research purpose in the last years [24]. Although their apparent simplicity, unrecognized and often neglected interactions between the observed phenomena and the

adopted setup have led to wide variability and systematic scatter in the reported data [25]. The more recent heat flux method (HFM), which belongs to the flat flame burner class [26], is particularly important because it does not require stretch rate correction, thus HFM has the potential to reduce the impact of systematic errors on the measurements. Nonetheless, the consistency of experimental data obtained by means of HFM has been recently discussed by Alekseev and Konnov (2018) also for the hydrogen flames [27], indicating good accordance between numerical and experimental data in a wide range of conditions.

The unification of chemical phenomena in a single parameter allows the implementation in computational fluid dynamic models accounting for reactive scenarios [28] and the evaluation of the accuracy of mixing rules for bio-syngas. The latter assumes particular significance if the non-ideal behavior, due to the presence of hydrogen and carbon monoxide, limiting the application of some of the most common rules (e.g. Le Chatelier's rule) is considered [29]. However, the empirical correlations counting the flame temperature (e.g. Hirasawa's rule) or having an exponential term (e.g. Gulder's correlation) [30] may be successfully adopted in case of non-hydrocarbons presence, as well. Alternatively, detailed kinetic mechanisms can be adopted either for the estimation of the S_u or for the direct implementation in computational fluid dynamics (CFD), although in the reduced form, of reaction rates for the evaluation of more complex scenarios [31]. Kinetic mechanisms consist of a list of hundreds of species, including radicals, and elementary reactions. They are commonly structured by following a hierarchical approach, i.e. the chemistry of hydrogen and other light compounds are included in a core model, supplementary reactions are added if needed to include the chemistry of larger species [32]. These models include thermodynamics, transport, and kinetic rate databases, estimated by numerical methods, e.g. electronic structure (ab initio) methods, statistical theory [33]. Quite obviously, this approach leads to a roughly exponential increase of the number of reactions with respect to the number of species included in the reaction mechanisms [24], requiring the adoption of procedures to reduce their size and validate the resulting mechanisms [18].

In this light, the analysis of multivariable systems, such as reactive mixtures described by detailed kinetic mechanisms where hundreds of reactions are involved, can be performed by isolating and comparing the effect of the variation of one parameter on the overall estimation. This approach is often referred to as sensitivity analysis and it is commonly applied to the analysis of chemical systems [34][35] and kinetic mechanisms [36]. The combination of chaos and Bayesian inference methods with this approach has been intensively studied for the reduction of the uncertainties and the optimization of the Arrhenius parameters in kinetic models [37][38]. Similarly, the reaction significance analysis [39] allows the comparison of numerical and experimental results. It is considered as a promising technique, especially for the characterization of the combustion systems [15], because of the ability to quantify the relevance of the kinetic parameters with respect to an experimental database regardless of the extent of reaction or time. For these reasons, the reaction significance analysis was adopted in this work, however, referred to as sensitivity analysis, for the sake of simplicity.

The characterization of combustion properties by means of detailed kinetic mechanisms allows the evaluation of products distribution, representing an essential part of the analysis of reactive systems [40]. Indeed, this feature can be particularly relevant for the estimation of the content of the most important gaseous pollutants (e.g. CO, CO₂, HC, particulate matter precursors, NO_x) and temperature distribution, thus for the optimization of the operative conditions in terms of either amount of produced energy or pollutant production. Several articles have been published on the formation/consumption rate of NO_x in case of syngas and biogas (including their blends) combustion [41][42][43], individuating the preferable paths and the key reactions ruling the rate of the involved phenomena. Albeit, the relevance of the NO_x chemistry, current models are still considered far to be suitable to guarantee a correct implementation and control of NO_x production [20].

In this framework, experimental data of S_u were considered for the sake of a detailed kinetic model and mixing rules evaluation. Successively, numerical analyses on the reaction system aiming to the individuation of the chemical interactions between the chemistry of pure fuels and their mixtures were performed and presented.

Eventually, the effect of the initial mixture composition on the final concentration of pollutants in the product stream was numerically estimated.

2. Methodology

For the sake of clarity, the methodological section was divided accordingly, to separate the information regarding the experimental procedures and the adopted system from the information regarding the numerical approaches.

2.1. Experimental methods

The heat flux burner adopted in this work mainly consists of 1) a plenum chamber, where a grid was placed to guarantee homogeneous gas velocity; 2) a cylindrical, holed burner plate where thermocouples were conveniently placed to monitor the temperature distribution at different radial position; 3) a cooling jacket designed to keep the plenum chamber temperature at a constant value of 25 °C and 4) a heating jacket enveloping the burner plate, where ethylene glycol at 85 °C was fed. Ancillary systems for the regulation of the flow rate and composition of the feeding gas and for the data acquisition were utilized. A schematic representation of the described experimental apparatus was presented (Figure 1).

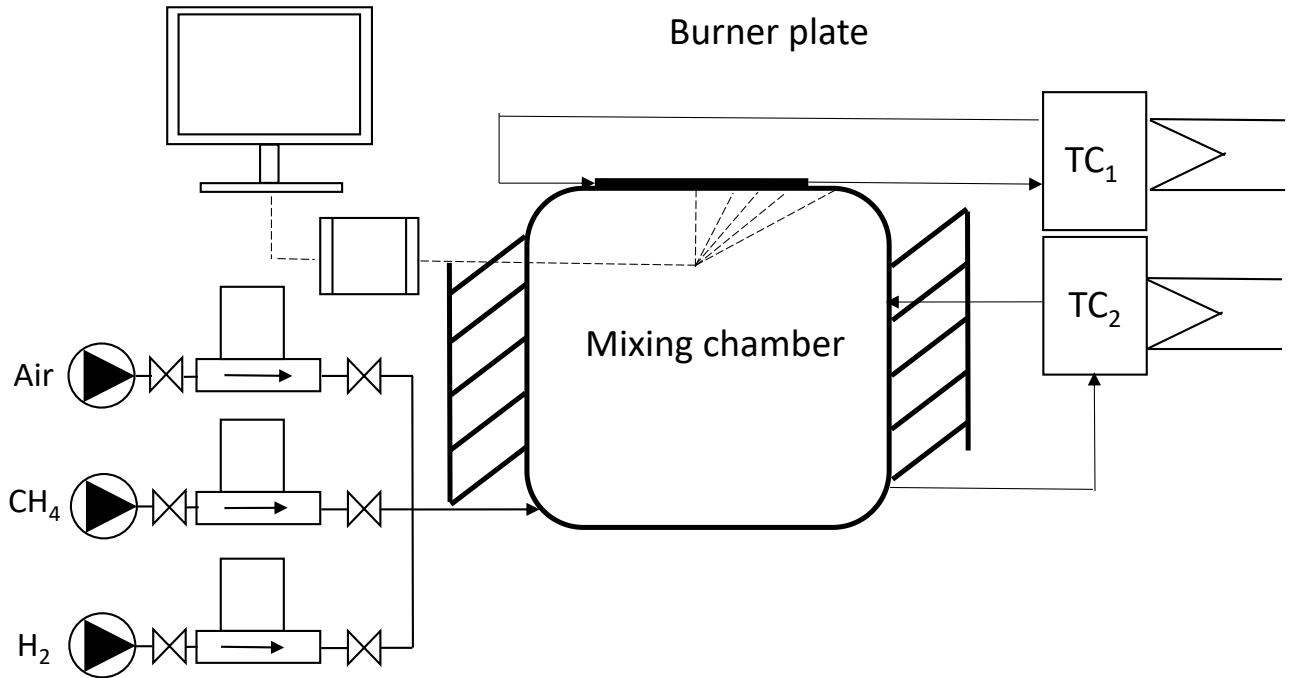


Figure 1. Schematic representation of the adopted experimental apparatus. TC₁ and TC₂ represent the temperature control systems for the burner plate and mixing chamber, respectively.

The heating/cooling systems guarantee that the temperature profile (T) assumes a parabolic trend with respect to the plate radius (r), with a coefficient (A) depending on the unburned gas velocity [44].

$$T(r) = T_{r=0} + Ar^2 \quad (1)$$

The S_u is assumed as the condition at which temperature profile is homogenous, i.e. A is null. However, stable flames cannot be experimentally obtained at these conditions [45]. Hence, the S_u is calculated by varying the gas velocity in order to obtain small positive and negative values of A and consequently interpolating the corresponding gas velocity.

Considering the described procedure and experimental system adopted in this work, several sources of uncertainties in the obtained results can be found and taken into account for the sake of experimental error bars evaluation. More specifically, the uncertainties regarding the erroneous measurement of gas velocity fed to the burner ($\delta S_{u,Q}$), plate temperature profile ($\delta S_{u,T}$) or inaccuracies in the evaluation of the parameter A , all leading to errors in the interpolation process ($\delta S_{u,A}$), were estimated, as suggested by the detailed analysis on the HFM measurement uncertainties presented by Bosschaart and De Goey (2003) [45] and Nonaka and Pereira (2016) [46]. The first was evaluated considering the combination of the uncertainties on the flowrate of each compound forming the gaseous mixture, thus is related to the adopted mass flow controllers (MFCs). The second was estimated based on the thermocouple scatter. The third was calculated by adding in Equation 1 the $\delta S_{u,T}$ and isolating the $\delta S_{u,A}$ term (Equation 2).

$$\delta S_{u,A} = (2 \cdot \delta S_{u,T})/r^2 \quad (2)$$

The obtained results were unified in the single parameter δS_u , representing the overall uncertainties related to the S_u measurements, as reported in Equation 3.

$$\delta S_u = [\delta S_{u,Q}^2 + \delta S_{u,T}^2 + \delta S_{u,A}^2]^{1/2} \quad (3)$$

The gaseous composition was unequivocally determined and expressed in terms of equivalence ratio (φ) and added compound ratio (R_i), assuming methane as the primary species for the fuel composition, i.e. R_i equal to zero means pure methane. The former quantifies the molar ratio of fuel to oxidant with respect to the stoichiometric coefficients of the reactions for the complete oxidation (Equation 4), the latter the fuel composition (Equation 5).

$$\varphi = \sum \frac{m_f/m_{ox}}{(m_f/m_{ox})_{st}} \quad (4)$$

$$R_i = m_i/m_f \quad (5)$$

where m represents the mole, the subscripts st , i , f and ox stand for stoichiometric conditions, the i -th species composing the unburned mixture excluding air (i.e. methane, carbon monoxide or carbon dioxide), f the global fuel mixture and ox the oxidant agent. It is worth noting that the experimental data presented in this work refer to binary fuel containing methane and carbon monoxide or dioxide since experimental S_u and detailed discussion on the implication of hydrogen addition on methane/air premixed flames chemistry have been already published by the same research group [47].

Analogously to the procedure described for the estimation of δS_u , the uncertainties related to the mixture composition were estimated. In this case, the uncertainties sources were related to the equivalence ratio ($\delta\varphi$) and to the added compound ratio (δR_i), both related to the uncertainties of the MFCs. Additional information on the experimental system, the adopted procedure for the collection of S_u data and the evaluation of the uncertainties, either on S_u or mixture composition, can be found in previous work performed by the same group [47].

2.2. Numerical procedure

The obtained experimental results were considered, together with additional data retrieved in the current literature, for the validation of the detailed kinetic mechanism developed at the University of Bologna, named KIBO [48], where the nitrogen chemistry reported by Glarborg et al. (2018) [20] was included. The resulting mechanism consists in about 125 species and 600 reactions, and it has been selected since previous works have demonstrated its ability to accurately predict the light alkanes chemistry in co-presence of non-hydrocarbons species [49].

The S_u estimations were performed by using the open-source software Cantera [50], mono-dimensional, adiabatic, laminar flames. A grid dependency analysis has been previously performed [51] to optimize the simulation parameters in terms of the results accuracy and computational costs for base case conditions (i.e. stoichiometric methane/air mixture at 298 K and 1 bar). This analysis results in the following parameters: ratio equal to 3, slope equal to 0.07 and curve equal to 0.14 as grid refining parameters; relative error criteria ($RTol$) and absolute error criteria ($ATol$) equal to $1.0 \cdot 10^{-9}$ and $1.0 \cdot 10^{-14}$ for the steady-state problem and $1.0 \cdot 10^{-5}$ and $1.0 \cdot 10^{-14}$, respectively.

Collected data were adopted for the evaluation of the empirical parameters of the Gulder's correlation [52] (Equation 6) and Hirasawa's correlation [53] (Equation 7).

$$S_{u,mix} = \chi \cdot \varphi^\eta \cdot \exp^{-\xi \cdot (\varphi - \sigma - \sum_i x_i \Omega_i)^2} \cdot \prod_i (1 + \gamma_i \cdot x_i^{\tau_i}) \quad (6)$$

where χ , η , σ , ξ , Ω , γ , and τ are fitting parameters depending on temperature and fuel species, whereas the subscripts *mix* and *i* stand for the mixture and *i*-th component properties, respectively.

$$S_{u,mix} = \exp \left[\frac{(R_i \cdot n_i \cdot T_{ad,i})}{\sum_i n_{mix} \cdot T_{ad,mix}} \ln(S_{u,i}) \right] \quad (7)$$

where n represents the sum of the moles of products and inert obtained by the combustion of 1 mole of the investigated fuel and T_{ad} is the adiabatic flame temperature. It should be noted that the weighted average values were adopted for the evaluation of the unknown mixture parameters required in Equations 6 and 7. For the sake of simplicity, σ was assumed to equal to 1, since previous analyses have indicated that this hypothesis does not affect the prediction quality of this correlation and allows the reduction of the number of unknown fitting parameters [54]. Indeed, under this assumption, χ assumes the meaning of stoichiometric burning velocity of the primary fuel (methane in our case).

Sensitivity analyses were performed at 298 K, 1 bar for a stoichiometric composition to provide further indications on the low-temperature chemistry of the investigated mixtures. The results were presented in terms of normalized sensitivity coefficient (NSC), defined as in the following equation, or in terms of variation of this parameter

$$NSC_i = (k_i/S_u) \cdot \frac{\partial S_u}{\partial k_i} \quad (8)$$

where k_i represents the reaction rate coefficient of the i -th reaction expressed in the Arrhenius equation form. Hence, reactions promoting the system reactivity will assume positive NSCs, whereas reactions inhibiting the system reactivity negative NSCs. In order to include both cases, the absolute value of NSC was selected as the sorting parameter, i.e. the most impacting reactions were selected, sorting them by decreasing absolute value of NSC.

3. Results and discussions

The experimental and numerical S_u data obtained in this work at 298 K and 1 bar were presented together with data retrieved from the literature. More specifically, syngas compositions containing R_{CO_2} equal to 0.2 and 0.5 have been compared with data collected by Nonaka et al. (2006) [46], Zahedi et al. (2014) [55] and Kumar et al. (2019) [56] by using flat burners (Figure 2, left). Similarly, methane/carbon monoxide mixtures in the air having R_{CO} equal to 0.1 and 0.2 have been experimentally and numerically investigated. For the sake of discussion, data collected from Konnov et al. (2008) [57] using the HFM were also added, although characterized by R_{CO_2} of 0.05 and 0.15 (Figure 2, right). For the sake of clarity, data collected in this work have been reported for pure CH_4 flames exclusively. A comparison with respect to other experimental systems can be found elsewhere [47].

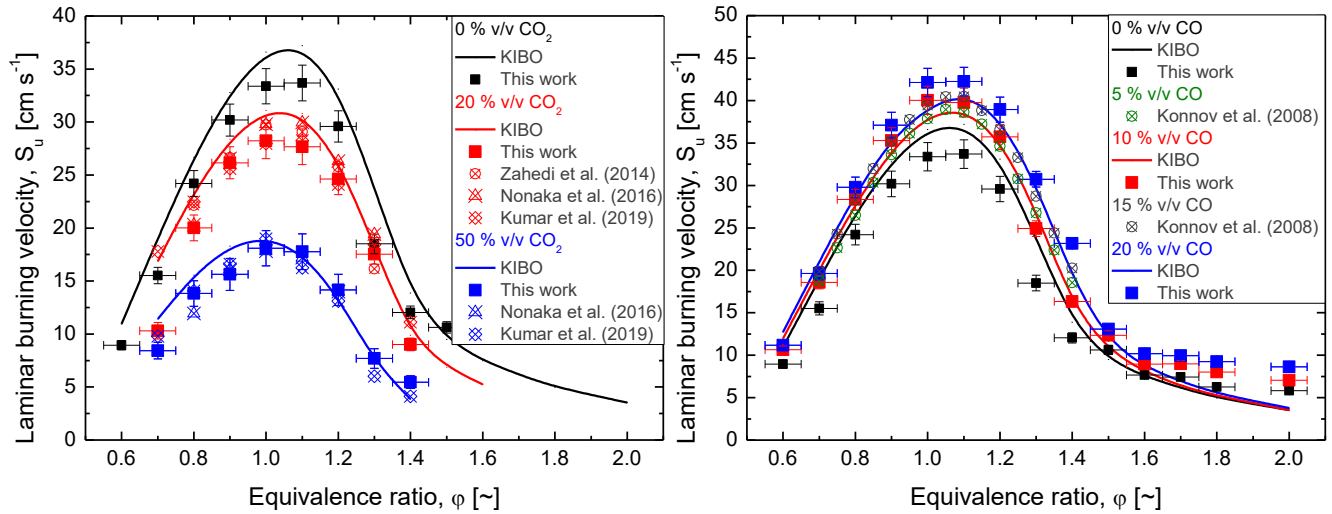


Figure 2. The effect of CO_2 (left) and CO (right) addition on CH_4 S_u in the air at 298 K and 1 bar.

It is worth noting that the experimental data reported by different authors are fairly in agreement if considering the experimental errors. This observation confirms the reliability of the adopted system and the consistency of the measurements, possibly due to comparable procedures and operative conditions adopted, e.g. the heating fluid was fed at a similar temperature, included within the interval 353 - 358 K.

The model KIBO seems to underestimate the effect of CO on the overall reactivity of CH₄ premixed flames, whereas the S_u estimations for $R_{CO_2} = 0.5$ are fairly in agreement with experimental data. In this light, the kinetic parameters related to the reactions $CO + OH \rightleftharpoons CO_2 + H$ and $HCO (+M) \rightleftharpoons H + CO + (+M)$ were substituted in a modified version of KIBO (referred as “modified model”), as suggested by Li et al. (2007) [58], in $k_3 = 2.23 \cdot 10^5 \cdot T^{1.89} \cdot \exp(583/T[K])$ cm³/mol/s and $k_4 = 4.75 \cdot 10^{11} \cdot T^{0.66} \cdot \exp(-7485/T[K])$ cm³/mol/s, respectively. It is worth noting that, although different coefficients are included in most of the detailed kinetic mechanisms (e.g. [59][60][61][62][63]) for these reactions, negligible variations can be observed in terms of reaction rates at high temperature only, confirming the need of additional analysis at low temperature. Nevertheless, Li et al. (2007) [58] parameters result in reaction constants (i.e. k_3 and k_4) closer to the ones resulting from Gri-mech 3.0 mechanism [63], often considered as a benchmark [48], than KIBO. On the other hand, KIBO constants are closer to Saudi Aramco mechanism constants. However, by comparing KIBO and the modified model, negligible variations on the S_u of binary mixtures can be observed at lean and rich conditions. Conversely, a significant increase in the overall reactivity can be observed for near-stoichiometric compositions for the modified model, increasing the estimation accuracy for a binary mixture containing CO, but reducing the predictive quality of CO₂ containing mixtures. Regardless of the adopted version, significant effects of reactant composition on the fundamental burning velocity ($S_{u, max}$), intended as the maximum S_u at a given temperature and pressure conditions, can be observed. $S_{u, max}$ is essential for the evaluation of the maximum reactivity, thus either for kinetic or safety aspects. This parameter is commonly detected at compositions slightly richer than the stoichiometry for hydrocarbons/air mixtures, because of the combination of chemical and thermal aspects [64]. Notwithstanding that, CO addition tends to shift the peak at richer composition and higher values, whereas CO₂ presence leads to lower values at almost stoichiometric conditions. Moreover, the effect of CO₂ addition was found to be more relevant for rich than lean compositions. Quite obviously, the discrepancies between the $S_{u, max}$ can be attributed to the differences in the reactivity of the mixture, i.e. oxidized species act as a diluent, thus reducing the concentrations of the reactants and the reaction rate. However, the observations regarding the conditions at which $S_{u, max}$ occurs denote the effect of thermal properties on the reactivity of the unburned mixtures, accordingly to the laminar flame theory [65], where the S_u is assumed proportional to the thermal diffusivity and T_{ad} . This hypothesis can be supported by the comparison of the T_{ad} with respect to mixture composition (Figure 3). It is worth noting that these values have been obtained by means of the thermodynamic database included in the KIBO mechanism for the calculation of the thermophysical properties of the chemical species involved, thus they are not affected by the reaction constants included in the model.

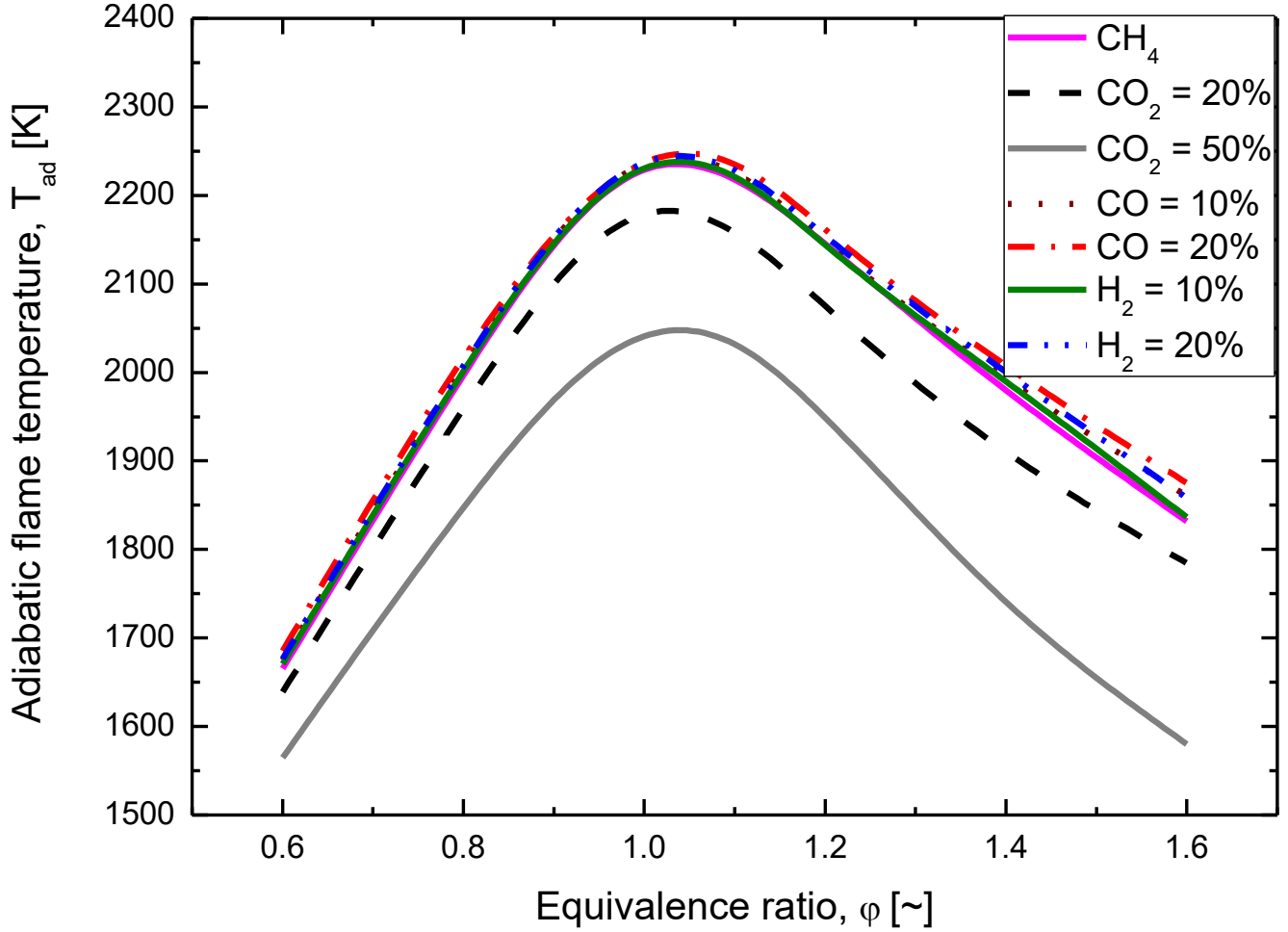


Figure 3. The adiabatic flame temperature in the air with respect to the unburned composition of methane-based mixtures at initial temperature and pressure of 298 K and 1 bar, respectively, as obtained by using the KIBO thermodynamic database.

The maximum T_{ad} is anticipated at stoichiometric composition by the addition of CO_2 , as reported by Nonaka et al. (2016) [46], whereas is almost unaffected by the presence of the other species. It is worth noting that the H_2 -enriched methane T_{ad} is slightly lower than the corresponding CO -enriched mixture T_{ad} , although the S_u has the opposite trend and similar dependence on the equivalence ratio. These discrepancies can be caused by the increase in thermal diffusivity for rich mixtures containing H_2 , more modestly reported in case of CO addition [66]. These observations are particularly relevant if the equality of stoichiometric coefficient of H_2 and CO in the complete oxidation reaction is considered, i.e. the molar compositions are the same once ϕ and R_i are given. Hence, T_{ad} represents an essential parameter to evaluate the effect of air content in the mixture. However, because of the nitrogen presence acting as a thermal diluent, it cannot be considered as a standalone parameter for the estimation of the S_u values because of the coexistence of thermal and kinetic aspects. Indeed, the former can be due to the higher heat of combustion per volume of the CO , whereas the latter could be related to the enhanced availability of H radicals in case of H_2 addition, resulting in increased overall reactivity. In light of these considerations, the adoption of Arrhenius-like empirical correlations for the estimation of mixture reactivity assumed an enhanced significance. Hence, Gulder's and Hirasawa's correlations were adopted for the evaluation of binary fuel reactivity, at first. The parameters corresponding to the former correlation were calculated based on the experimental data collected in this work for CO and CO_2 addition, or were retrieved from previous works for the case of hydrogen-enriched methane [47] (Table 2), whereas adiabatic flame temperatures and pure compounds S_u required for the

latter correlation were estimated numerically by using the KIBO mechanism. Note that the fitting parameters τ were imposed greater than zero, to avoid meaningless expressions in case of mole fraction null.

Table 2. Fitting parameters of the Gulder's correlation for the investigated mixtures at 298 K and 1 bar.

CH ₄			CO ₂			CO			H ₂		
W [cm·s ⁻¹]	η	ξ	γ	τ	Ω	γ	τ	Ω	γ	τ	Ω
37.20	0.47	6.07	-1.70	0.50	0.08	0.10	1.00·10 ⁻⁹	0.80	0.10	0.10	0.24

The obtained fitting parameters were utilized for the estimation of the S_u of bio-syngas mixtures. The content of each species has been selected considering the typical compositions deriving from the gasification plants in case of different biomass (i.e. cellulose, pinewood, and crude glycerol) [67] (Table 3). It is worth noting that the N₂ content originally attributed to the mixture in the cited literature was added to the CO₂ fraction, for the sake of simplicity.

Table 3. Mixture compositions assumed as representative of different biomass-derived gases.

Biomass	Mixture	CH ₄ [%v/v]	CO ₂ [%v/v]	CO [%v/v]	H ₂ [%v/v]
Crude glycerol	Mix 1	11.50	9.70	19.70	59.10
Cellulose	Mix 2	6.50	29.30	35.50	28.70
Pine Wood	Mix 3	4.36	32.33	27.92	35.39

Numerical results, including empirical rules, the original version of KIBO and a modified version including Li's coefficients predictions, were compared with experimental data [47][67] for different compositions and stoichiometry (Figure 4). Data related to binary mixtures were obtained in this work by means of HFB, whereas bio-syngas S_u has been retrieved from the current literature, at different stoichiometry, constant ambient temperature, and atmospheric pressure.

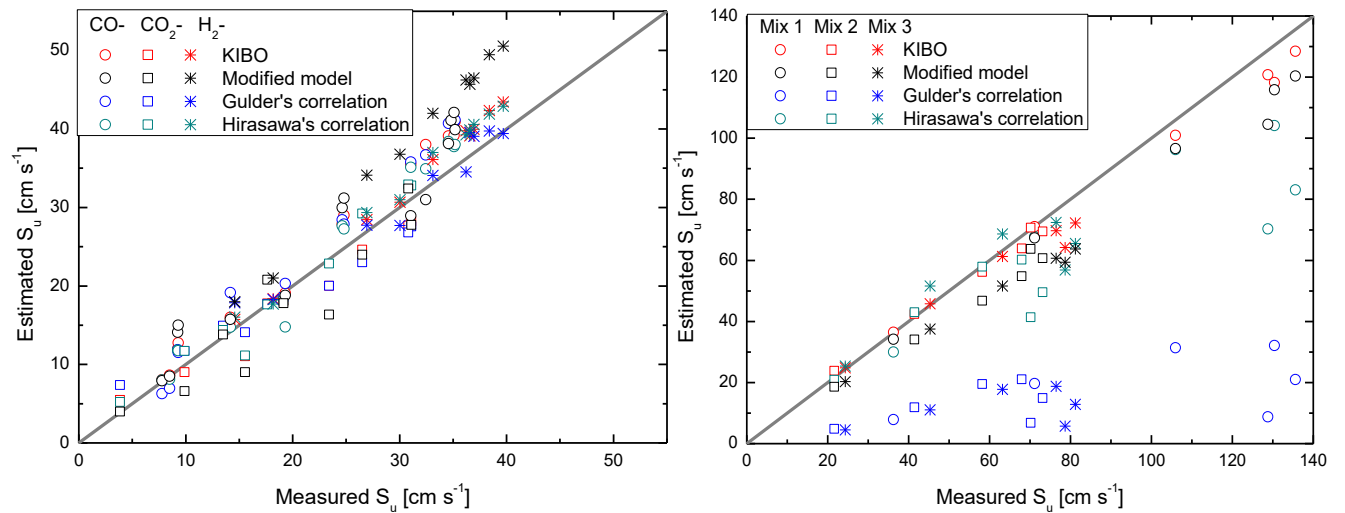


Figure 4. Comparison of numerical methods for the prediction of binary (left) and bio-syngas (right) S_u as a function of fuel composition and stoichiometry.

The obtained results confirm the accuracy of all the adopted methods, i.e. Gulder's and Hirasawa's correlations, and both versions of KIBO mechanism, for the prediction of binary fuels reactivity expressed in terms of S_u . In particular, it is worth mentioning that the investigated modifications in detailed kinetic mechanism lead to significant over prediction of H_2 and CO enriched methane and underprediction of the S_u of Mix 3. Besides, considering all the investigated conditions and compositions, KIBO shows higher accuracy with respect to the modified model, thus the original version was adopted for further analyses, exclusively.

It should be noted that the artificial T_{ad} for CO_2 was defined and calculated by linear extrapolation of the data obtained by the compositions investigated in this work (i.e. R_{CO_2} equal to 0.20 and 0.50), to make possible the estimation of T_{ad} data for mixtures containing different amounts of CO_2 . The obtained $T_{ad, mix}$ were compared with numerical estimations, resulting in differences within the 5% for all the investigated conditions.

Undoubtedly, the proposed formulation of the Gulder's correlation is inadequate to estimate the reactivity of the bio-syngas mixtures with good accuracy, although it is suitable for the evaluation of the investigated binary mixtures. This observation indicates the complexity of the interactions occurring in the case of fuels consisting of more than two chemical species. On the other hand, Hirasawa's correlation and KIBO mechanism are fairly in agreement with the experimental data reported in this work, irrespective to the fuel composition. This is particularly relevant if the starting database and bio-syngas compositions are compared, i.e. bio-syngas mixtures analysed in this work present a higher content of H_2 (up to 59 %v/v) and CO (up to 33 %v/v) than the experimental and numerical conditions utilized for the validation/parameter calculation (where both species contents are lower than 20 %v/v), indicating the general nature of these approaches. These observations are essential for the development of accurate models suitable for the evaluation of reactivity in presence of non - chemical aspects (e.g. turbulence), i.e. for computational fluid dynamic (CFD) analyses involving bio-syngas combustion. Moreover, the accuracy of mixing rule that does not necessarily require demanding calculations may be considered for the development of control software for engine fed by renewable fuels, currently affected by their instability in the composition and limiting their application [68].

The validation of the adopted kinetic mechanism allows further studies on the effect of molecular addition to the CH_4 / air flames structure and system exothermicity. In this sense, the sensitivity analysis was performed for pure methane at stoichiometric conditions with air, at first. The resulting data were utilized to select the 20 most representative reactions (Table 4), in terms of the absolute value of NSC.

Table 4. Main reactions for stoichiometric methane/air mixture, sorted by decreasing absolute value of NSC. Please note that the reaction parameters are reported in the Lindemann form for the falloff reactions, i.e. the subscript 0 and ∞ stand for the kinetic low and high concentration of third body M, respectively. Otherwise, in the modified Arrhenius form, for all the other reactions.

Label	Reaction Equation	a [mol, cm, s, K]*	b	E _a [cal / mol]
1	$\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$	$3.52 \cdot 10^{16}$	- 0.70	17069.79
2	$\text{CH}_3 + \text{H} (+\text{M}) \rightleftharpoons \text{CH}_4 (+\text{M})$	$a_{\infty} = 1.27 \cdot 10^{16}$ $a_0 = 2.48 \cdot 10^{33}$	$b_{\infty} = - 0.63$ $b_0 = - 4.76$	$E_{a\infty} = 382.89$ $E_{a0} = 2440.01$
3	$\text{CO} + \text{OH} \rightleftharpoons \text{CO}_2 + \text{H}$	$4.40 \cdot 10^6$	1.50	- 740.92
4	$\text{HCO} (+\text{M}) \rightleftharpoons \text{CO} + \text{H} (+\text{M})$	$1.86 \cdot 10^{17}$	- 1.00	17000.48
5	$\text{H} + \text{OH} (+\text{M}) \rightleftharpoons \text{H}_2\text{O} (+\text{M})$	$4.00 \cdot 10^{22}$	- 2.00	0.00
6	$\text{CH}_3 + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{S-CH}_2$	$4.00 \cdot 10^{13}$	0.00	2502.39
7	$\text{CH}_4 + \text{H} \rightleftharpoons \text{CH}_3 + \text{H}_2$	$1.30 \cdot 10^4$	3.00	8037.76
8	$\text{H} + \text{O}_2 (+\text{M}) \rightleftharpoons \text{HO}_2 (+\text{M})$	$a_{\infty} = 4.65 \cdot 10^{12}$ $a_0 = 5.75 \cdot 10^{19}$	$b_{\infty} = 0.44$ $b_0 = -1.40$	$E_{a\infty} = 0$ $E_{a0} = 0$
9	$\text{O}_2 + \text{T-CH}_2 \rightleftharpoons \text{CO} + \text{H} + \text{OH}$	$6.58 \cdot 10^{12}$	0.00	1491.40
10	$\text{CH}_4 + \text{OH} \rightleftharpoons \text{CH}_3 + \text{H}_2\text{O}$	$1.60 \cdot 10^7$	1.83	2782.03
11	$\text{HCO} + \text{O}_2 \rightleftharpoons \text{CO} + \text{HO}_2$	$7.58 \cdot 10^{12}$	0.00	409.89
12	$\text{CH}_3 + \text{O} \rightleftharpoons \text{CH}_2\text{O} + \text{H}$	$8.43 \cdot 10^{13}$	0.00	0.00
13	$\text{H} + \text{HCO} \rightleftharpoons \text{CO} + \text{H}_2$	$5.00 \cdot 10^{13}$	0.00	0.00
14	$\text{C}_2\text{H}_5 (+\text{M}) \rightleftharpoons \text{C}_2\text{H}_4 + \text{H} (+\text{M})$	$a_{\infty} = 1.11 \cdot 10^{10}$ $a_0 = 3.99 \cdot 10^{33}$	$b_{\infty} = 1.04$ $b_0 = - 4.99$	$E_{a\infty} = 36768.64$ $E_{a0} = 40000.00$
15	$\text{O}_2 + \text{S-CH}_2 \rightleftharpoons \text{CO} + \text{H} + \text{OH}$	$3.13 \cdot 10^{13}$	0.00	0.00
16	$\text{CH}_3\text{OH} (+\text{M}) \rightleftharpoons \text{CH}_3 + \text{OH} (+\text{M})$	$a_{\infty} = 1.90 \cdot 10^{16}$ $a_0 = 2.95 \cdot 10^{44}$	$b_{\infty} = 0.00$ $b_0 = -7.35$	$E_{a\infty} = 91729.92$ $E_{a0} = 95460.09$
17	$\text{H}_2 + \text{O} \rightleftharpoons \text{H} + \text{OH}$	$5.06 \cdot 10^4$	2.67	6290.63
18	$\text{H}_2 + \text{OH} \rightleftharpoons \text{H} + \text{H}_2\text{O}$	$1.17 \cdot 10^9$	1.30	3635.28
19	$\text{HCO} + \text{OH} \rightleftharpoons \text{CO} + \text{H}_2\text{O}$	$3.00 \cdot 10^{13}$	0.00	0.00
20	$\text{CH}_3 + \text{O}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{OH}$	$3.30 \cdot 10^{11}$	0.00	8941.20

* Units must be intended as raised to powers, depending on the reaction order

Then the effects of CO, CO₂ or H₂ addition on CH₄ chemistry were evaluated in terms of percentage variation from the corresponding methane NSC (Figure 5), following the equation $100\% \cdot (\text{NSC}_{\text{CH}_4} - \text{NSC}_{\text{mix}}) / \text{NSC}_{\text{CH}_4}$.

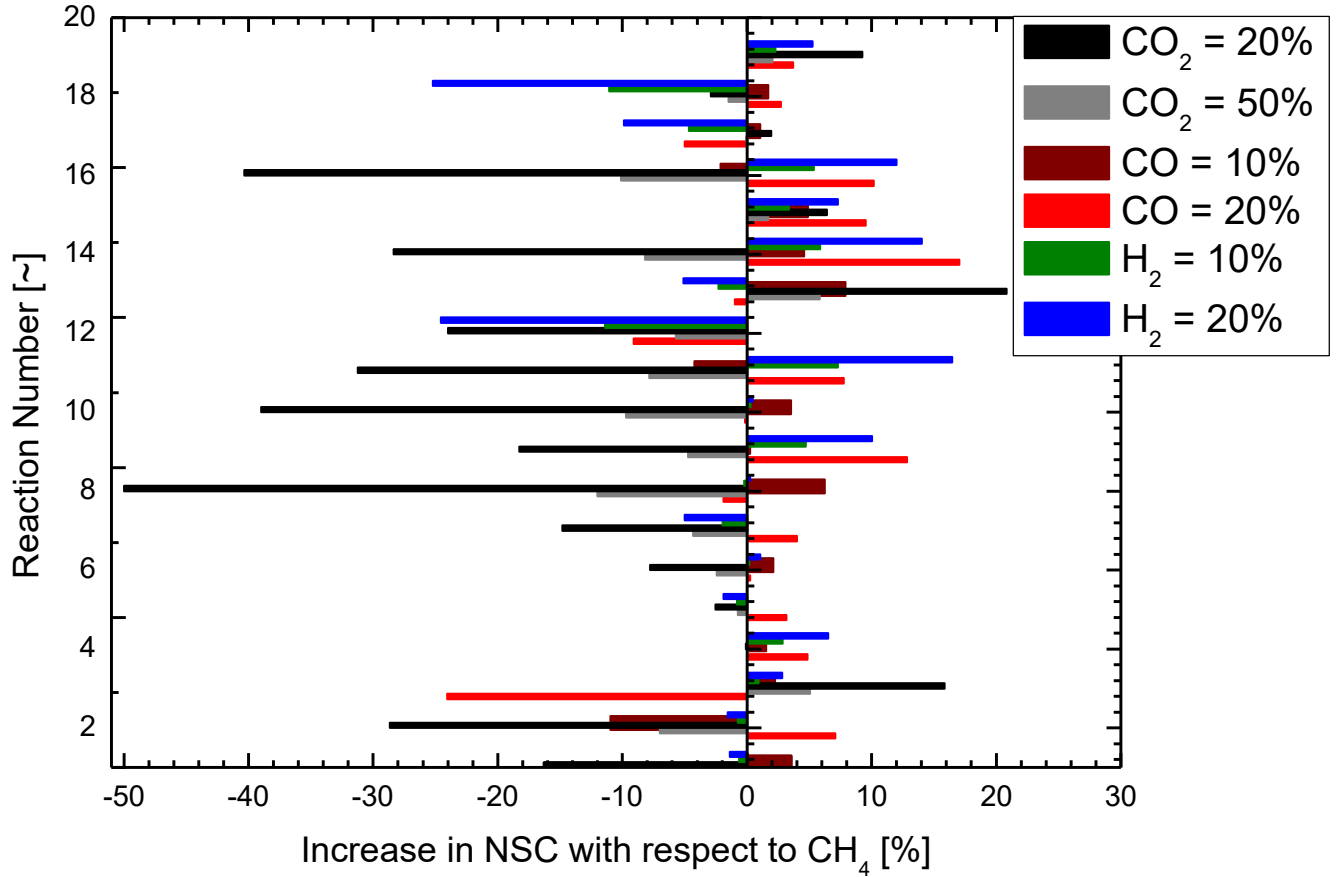


Figure 5. The effect of CO, CO₂ or H₂ addition on CH₄ chemistry, in terms of variation of NSC calculated by using the KIBO mechanism.

As expected, the reactions 1 and 2 are weakly affected by the fuel composition, with an exception for the case with elevated CO₂ content. This trend can be attributed to the reduced availability of the H atom in the unburnt mixture. On the contrary, the reaction 3 assumes reduced relevance in the flame structure determination and could represent the main cause of the aforementioned shift of $S_{u, max}$ and $T_{ad, max}$, being one of the main exothermic steps. The significant variations of its relevance when CO₂ has added results in a detrimental effect on the reactions forming CO, e.g. reactions 9 and 11, because of the reduction in the consumption rate. The NSC trends reported for the reactions 2, 8, 14 and 16 depict the elevated third body collision factors for CO₂ and indicate the main chemical effects reducing the overall reactivity. Moreover, the results presented for reactions 2, 8 and 10 confirm the relevance of CH₃ termination and HO₂ radicals in the bio-syngas combustion, as highlighted in the comprehensive analysis of chemical kinetics at medium and elevated temperatures [14].

Quite obviously, the addition of CO leads to augmented relevance of reaction 3, being reactants more available, and reducing the significance of reaction 1 at the same time. Whereas the addition of H₂ in the same quantity does not suggest significant variations in the corresponding NSC. On the contrary reactions, 12 and 18 have opposite trends. The effect of fuel composition on reaction 4 is negligible, confirming its relevance for CH₄ rich mixtures [66]. The reactions involving C₂H₆, either recombination or decomposition, have been indicated as determining the formation of pollutants in case of biogas combustion [39] and representing the first step toward the formation of soot particles [69]. Knowing this, the trend reported for the reaction 14 should suggest a reduced impact of species deriving from C₂H₆ in case of CO₂ addition, thus reduced amount of produced pollutants. This hypothesis can be confirmed by the estimation of the NO_x content in the combusted mixture with respect to unburned composition (Figure 6).

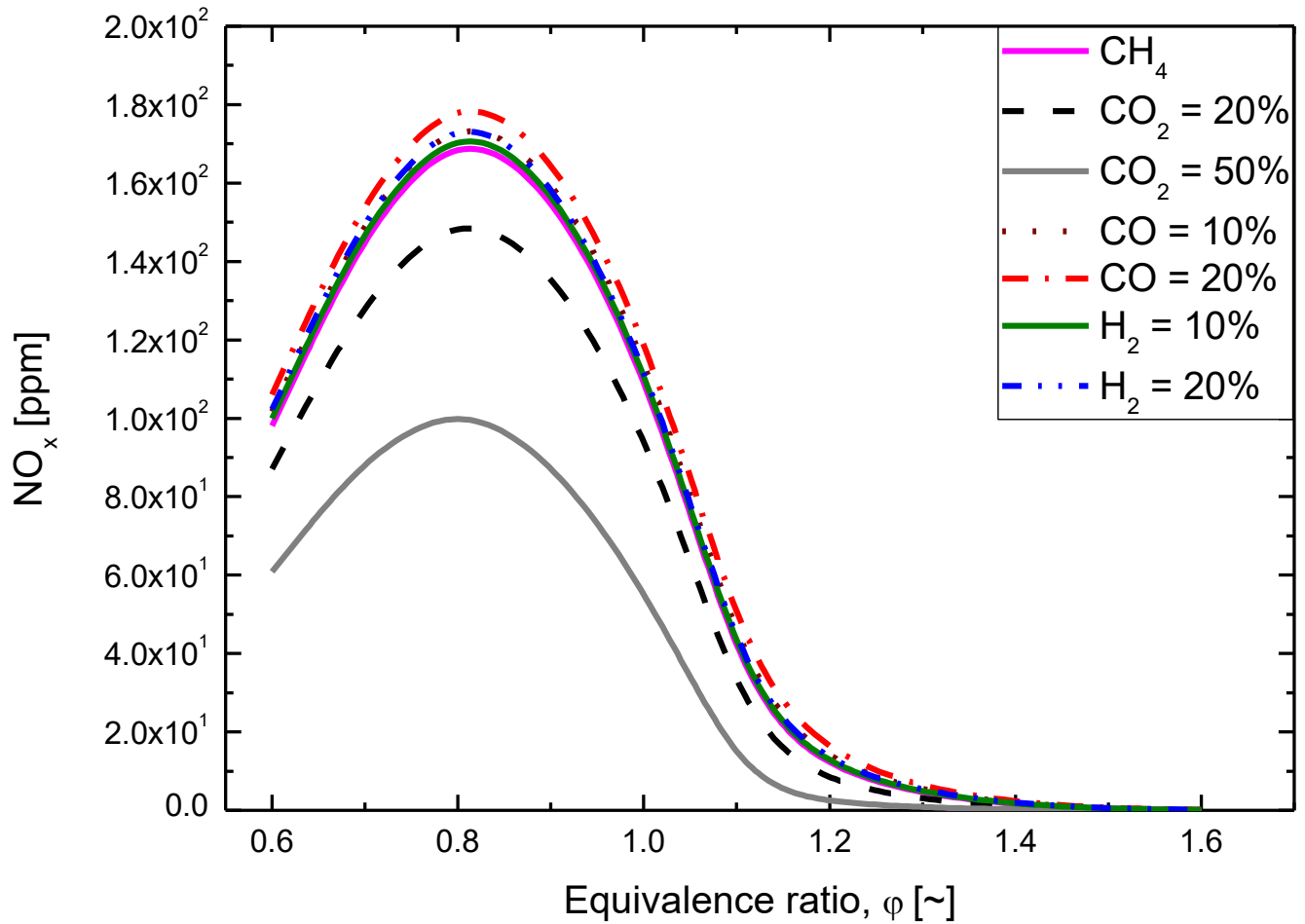


Figure 6. Estimated NO_x content in the product mixtures as a function of unburned composition at 298 K and 1 bar, as obtained by using the KIBO thermodynamic database.

Results indicate that the addition of CO_2 considerably lowers the amount of NO_x produced, in accordance with the values of adiabatic flame temperature previously reported. These results are in line with the observation reported by Fischer and Jiang (2015) at elevated initial temperature [70] and Mardani et al. (2019) [71] where significant reduction of hot spots was reported within the defined computational domain in moderate or intense low-oxygen dilution (MILD) conditions. Moreover, it can be observed that the addition of CO and H_2 has similar effects on NO_x production. Besides, these results are in line with data reported by Van Huynh and Kong (2013) [72], where NO_x content was found mainly affected by the NH_3 tenor, and with significantly lower effect of CO, CO_2 and H_2 , and data reported by Shih and Liu (2014) [73], where significant increases in produced NO_x were observed for hydrogen content higher than 40%, exclusively. It is worth noting that the NO_x peak location with respect to the equivalence ratio is weakly affected by the fuel composition, confirming the existence of the methane-dominated chemical regime in case of non-hydrocarbons addition [74]. Considering that the reactions between hydrocarbons radicals and nitrogenous species are negligible [70], the formation of NO_x can be mainly attributable to the direct oxidation of N_2 or, in smaller quantity, to the oxidation of NNH. Indeed, Zeldovich and NNH mechanisms have been indicated as relevant in the case of H_2 and CO combustion by ab initio quantum chemical calculations [75]. The limited, but valuable, significance of NNH route in the production of NO during bio-syngas combustion may be indicated by the extended results of the sensitivity analysis, where either the reaction $\text{N}_2 + \text{O} \rightleftharpoons \text{N} + \text{NO}$ or

$\text{NNH} + \text{O} \rightleftharpoons \text{NH} + \text{NO}$ are indicated as the main route for NO production, with the former assuming larger NSC than the latter for all the investigated compositions. Hence, the aforementioned reduction in the production rate of O radical in case of CO_2 addition can be the cause of the reported trend for pollutants formation, coupled with the reduced flame temperature. Indeed, the latter limits the Zeldovich thermal-NO mechanism, ruling the NO formation at stoichiometric composition [55]. The negligible contribution of the prompt mechanism was confirmed by the reduced amount of NO_x obtained, regardless of the fuel composition, at rich conditions, where prompt NO mechanism is dominant [20].

4. Conclusions

In this work, the effect of bio-syngas composition on its reactivity and energy production was experimentally and numerically studied at low temperature and atmospheric pressure, in terms of laminar burning velocity. Pollutants production rate has been evaluated under these conditions by means of detailed kinetic mechanism.

Experimental data for CO and CO_2 enriched CH_4 premixed with air were collected by means of heat flux burner at 298 K and 1 bar and compared with existing data. The effects of fuel composition on the overall reactivity and adiabatic flame temperature were analyzed in detail.

A kinetic mechanism (i.e. KIBO) and empirical-based mixing rules (i.e. Gulder's and Hirasawa's rules) were tested and evaluated in comparison with measurements collected in this work and retrieved in the literature. Gulder's correlation strongly underestimates the reactivity of bio-syngas mixtures, indicating that this approach is inadequate to evaluate the chemical interactions of the studied quaternary fuels, in contrast with elevated accuracy resulting from the application of Hirasawa's correlation. These results confirm the key role of adiabatic flame temperature for laminar burning velocity determination. Indeed, both parameters follow the same trend with respect to either the fuel composition or air content. In this sense, the concept of artificial adiabatic flame temperature for CO_2 was introduced and adopted for the implementation of Hirasawa's correlation, i.e. to estimate the mixture flame temperature. Results are fairly in agreement with the temperature values obtained by numerical estimations. This notion can be useful for the estimation of safety parameters in case of CO_2 dilution as well, e.g. when the concept of critical adiabatic flame temperature is applied to the estimation of flammability limits [76]. A comparison between existing kinetic mechanisms has confirmed the elevated accuracy of KIBO model for the prediction of gaseous chemistry in an oxidative environment for a wide range of compositions and operative conditions. The agreement between experimental measurements and KIBO estimation extend the operative conditions in which this mechanism could be considered as validated and allow the evaluation of the chemical effects of non-hydrocarbons addition on methane chemistry in an oxidative environment. This aspect represents an essential step toward the individuation of optimized conditions in terms of combustor design and pollutants emissions.

Preferred reaction paths were highlighted by means of sensitivity analyses, allowing the individuation of 20 ruling reactions. The kinetic effects of CO_2 were highlighted and separated by thermal dilution effects, indicating the phenomena potentially causing the shift of the maximum values of the laminar burning velocity and adiabatic flame temperature toward stoichiometric composition. The significance of CH_3 termination reaction and HO_2 radical formation in the bio-syngas combustion was observed at low temperature, as well. Differences between the effects of H_2 and CO addition were indicated and discussed. The relevance of C_2H_6 chemistry in the formation of pollutant precursors was related to the formation of pollutants. The effect of fuel composition and air content on NO_x (mostly NO) production was estimated in terms of resulting concentration and ruling production mechanisms. These results indicate thermal-NO and NNH mechanisms as ruling routes for the formation of NO_x , attributing negligible relevance to the prompt mechanism, under the investigated conditions. Hence, the limited availability of O radical in case of CO_2 addition was highlighted as potentially causing the reduction of NO_x .

The reported results guarantee accurate estimation of system reactivity by means of empirical correlation suitable for bio-syngas combustion and applicable to generic fuel mixtures. Moreover, the validated kinetic mechanism permits the evaluation of chemical interactions and products distribution with respect to unburned composition, allowing the optimization of operative conditions in terms of either power output or pollutant emissions. Eventually, the accurate estimation of combustion properties, e.g. laminar burning velocity, for a wide range of fuel composition including the typical values deriving from biomass facilitates the design and optimization of combustors and post-combustor treatments.

Nomenclature

A	Second-order coefficient of the temperature profile
a	Pre-exponential factor of the modified Arrhenius form
$ATol$	Absolute error criteria
b	Temperature exponent of the modified Arrhenius form
CFD	Computational fluid dynamics
E_a	Activation energy of the modified Arrhenius form
HFM	Heat flux method
k_i	Reaction rate coefficient of the i -th reaction
KIBO	Kinetic mechanism developed at the University of Bologna
m_f	Mole of fuel in the initial mixture
MFC	Mass flow controller
m_i	Mole of the generic i -th species in the initial mixture
m_{ox}	Mole of oxygen in the initial mixture
n	Sum of the moles of products and inert obtained by the combustion of 1 mole of the investigated fuel in the air
NSC_i	Normalized sensitivity coefficient for the i -th reaction
r	Plate radius
R_i	Molar fraction of additional species i in the fuel mixture
$RTol$	Relative error criteria
S_u	Laminar burning velocity
$S_{u,mix}$	Laminar burning velocity of gaseous mixtures
T	Temperature
T_{ad}	Adiabatic flame temperature
TC_1	Temperature control system for heating/cooling of the burner plate

TC ₂	Temperature control system for heating/cooling of the plenum chamber
T _{r=0}	Temperature measured at plate center
x _i	molar fraction of the i-th species

Greek letters

$\chi, \eta, \sigma, \zeta, \Omega, \gamma,$ and τ_i	Fitting parameters of the Gulder's correlation
$\delta\phi$	Uncertainties related to the equivalence ratio
δS_u	Overall uncertainties related to the obtained value of the laminar burning velocity
$\delta S_{u,A}$	Uncertainties related to the interpolation process
$\delta S_{u,Q}$	Uncertainties related to the feeding velocity
$\delta S_{u,T}$	Uncertainties related to the temperature profile measurement
δR_i	Uncertainties related to the added compound ratio
ϕ	Equivalence ratio

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