

Alma Mater Studiorum Università di Bologna
Archivio istituzionale della ricerca

Automatically generated model for light alkene combustion

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:

Pio, G., Dong, X., Salzano, E., Green, W. (2022). Automatically generated model for light alkene combustion. COMBUSTION AND FLAME, 241, 1-30 [10.1016/j.combustflame.2022.112080].

Availability:

This version is available at: <https://hdl.handle.net/11585/890886> since: 2022-07-18

Published:

DOI: <http://doi.org/10.1016/j.combustflame.2022.112080>

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>).
When citing, please refer to the published version.

(Article begins on next page)

This is the final peer-reviewed accepted manuscript of:

Gianmaria Pio, Simona Renda, Vincenzo Palma, Ernesto Salzano, Safety parameters for oxygen-enriched flames, Journal of Loss Prevention in the Process Industries, Volume 65, 2020, 104151, ISSN 0950-4230.

The final published version is available online at:

<https://doi.org/10.1016/j.jlp.2020.104151>

Rights / License:

The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>)

When citing, please refer to the published version.

Safety parameters for Oxygen-Enriched Flames

Gianmaria **PIO**¹, Simona **RENDA**², Vincenzo **PALMA**², 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

The utilization of low-quality gaseous fuel from biomass gasification and the abundance of oxygen-rich streams obtained as a by-product of nitrogen-air separation by membrane technology has incentivized the development of sustainable oxygen-enriched combustion technologies in the last decades. However, a dearth of experimental and numerical analysis addressing the reactivity and safety aspects of these mixtures at initial low temperatures can be observed in the current literature.

In this work, the heat flux burner was adopted for the measurement of the laminar burning velocity of methane in oxygen enriched air at different equivalence ratios. Results were compared with numerical data obtained by means of detailed kinetic mechanisms developed at the University of Bologna and the Gas Research Institute (GriMech3.0). Simplified correlations for the estimation of the laminar burning velocity with respect to the oxygen content at any equivalence ratio were developed, tested and evaluated.

An elemental reaction-based function was found appropriate for the estimation of the overall reactivity of the investigated mixtures. Besides, numerical analyses were performed to characterize the flame structures in terms of temperature and product distribution under several initial conditions. These results gave further insights into the reaction mechanisms of gaseous fuels in the case of oxygen-enriched air, highlighting potential bottlenecks for kinetic model refinements. Eventually, relevant safety parameters were estimated, in particular the flammability range of the fuel/oxidant mixture, in terms of lower and upper flammability limits.

Keywords: Laminar Burning Velocity; Flammability Limits; Oxygen Enriched Air; Premixed Flame; Detailed kinetic; Heat Flux Burner.

Highlights:

- Experimental determination of methane/oxygen/nitrogen laminar burning velocity
- Heat Flux Burner as a new methodology for the definition of safety parameters
- Validation and comparison of detailed kinetic mechanisms for oxygen enriched flames
- Individuation of the flammability range for the fuel/oxidant mixture
- Development and comparison of simplified correlations for the safety parameters

Nomenclature

a, b, c, d	Fitting parameters (Equation 8)
$ATol$	Absolute error criteria
c_p	Thermal capacity
\mathfrak{D}	Dilution index
E	Oxygen enrichment factor (Equation 5)
f, g, h	Generic functions (Equation 9)
\vec{g}	Gravitational acceleration
HFM	Heat flux method
LFL	Lower flammability limit
LOC	Limiting Oxygen Concentration
K	Thermal conductivity
M	Mixtures mole fraction
$RTol$	Relative error criteria
S_u	Laminar burning velocity
$S_{u,d}$	Laminar burning velocity for diluted mixtures
T	Temperature
UFL	Upper flammability limit

Subscripts

0	Initial conditions
Air	Air as oxidant
b	Burned conditions
F	Flame
f	Fuel
I	Ignition
lim	Limiting
N	Nitrogen
O	Oxygen
st	Stoichiometric
u	Unburned conditions

Greek symbols

α	Thermal diffusivity
ε	Fitting parameter (Equation 4)
$\xi, \eta, \gamma, \nu, \sigma, \Omega, W$	Fitting parameters (Equations 1 and 3)
ρ	Density of gas
τ_R	Characteristic reaction time
φ	Equivalence ratio
χ, ψ	Fitting parameters (Equation 6)

1. Introduction

The potential utilization of post-combustion strategies to reduce the emissions of pollutants such as carbon capture and sequestration (CCS) has strongly promoted the adoption of oxygen and oxygen-enriched air in energy production systems [1]. Besides, the implementation of membrane-based processes for the production of nitrogen from the air separation makes the resulting by-product, i.e. oxygen-enriched stream having oxygen content up to 40 %v/v, inexpensive [2]. Furthermore, the increased combustion efficiency due to the higher reactivity of the oxidant allows for the recovery of low-quality fuels, such as bio-syngas purification streams, waste gases, tail gases. Thus avoiding flaring option [3][4] and allowing for retrofitting of existing plants [5]. However, these unconventional techniques are still characterized by poorly controlled combustion, requiring investigations on the characterization of macroscopic (e.g. pollutant emissions and combustion temperature) and microscopic (e.g. flame structure, and burning velocity) phenomena [6]. To this aim, several studies have been performed in the last years on turbulent or non-premixed flames [7][8][9]. Nevertheless, detailed investigations on oxygen/nitrogen/fuel premixed flames at low initial temperatures are rare [10][11][12], although this approach has the potential to provide useful indications on the chemical phenomena involved and on the performance and safety of promising combustion systems for oxygen enriched air (e.g. porous medium gas burner) [13]. Bearing in mind the variability in the composition of bio-syngas resulting from different sources [14] and the existence of a methane-dominated chemical regime in the case of complex gaseous mixtures [15][16], preliminary investigations on methane flames are essential in several fields, including the evaluation of safety aspects [17][18]. The laminar burning velocity (S_u) is considered one of the most representative properties for the evaluation of kinetic mechanisms in oxidative conditions because it contains several pieces of information regarding the reactivity, the thermal properties, the flame shape and the geometry of the flame [19][20]. The heat flux burner can be adopted to collect experimental data, because of the reduced impact of fluid dynamics [21]. However, some limitations for the determination of elevated S_u by means of this technique should be considered during the selection of the investigated operative conditions, i.e. the challenging burner design required for S_u higher than 100 cm/s, the reduced stand-off distances in the case of higher initial temperatures leading to radical quenching over the plate, and the difficulties in flame stabilization in the case of pressure beyond 10 bar [21].

Alternatively, empirical correlations can be adopted for preliminary estimations, for instance, the effects of the fuel/oxidant ratio on the S_u can be evaluated by using the correlations proposed by Gülder [22]:

$$S_u = W \cdot \varphi^\eta \cdot e^{-\xi(\varphi-\sigma)^2} \quad (1)$$

where W , η , σ and ξ are empirical parameters depending on the experimental conditions and gaseous mixture, and φ is the equivalence ratio (Equation 2), defined as the ratio between the molar fraction (m) of the fuel (f) to the oxidant (oxygen, ox) in feeding and stoichiometric (st) conditions.

$$\varphi = \frac{\left(\frac{m_f}{m_{ox}}\right)}{\left(\frac{m_f}{m_{ox}}\right)_{st}} \quad (2)$$

However, the Gülder's correlation can be used for pure fuel/air mixtures, only, whereas the modification proposed by Coppens et al. [23] (Equation 3) allows for the evaluation of the effects of fuel composition:

$$S_u = W \cdot \varphi^\eta \cdot e^{-\xi(\varphi - \sigma - \sum(\Omega \cdot m_i))^2} \cdot \prod(1 + \gamma \cdot m_i^\nu) \quad (3)$$

The latter correlation requires the definition of three additional (γ , ν , and Ω) to take into account of the effects of multi-component fuels. Previous studies have observed that σ may be posed equally to the unity to reduce the degree of freedom in the estimation of empirical parameters, with a negligible effect on the estimation quality [24]. A similar correlation can be obtained for the oxygen-enriched case starting from the correlation developed by Metghalchi and Keck [25] (Equation 4), which gives the actual laminar burning velocity at any oxygen content ($S_{u,d}^\varphi$), if the S_u of fuel/air mixtures at the same equivalence ratio ($S_{u,air}^\varphi$) and the dilution index (\mathfrak{D}) are provided. The original equation can be conveniently modified, replacing \mathfrak{D} by the oxygen ratio E (Equation 5):

$$S_{u,d}^\varphi = S_{u,air}^\varphi \cdot [1 + \varepsilon \cdot (E - E_{air})] \quad (4)$$

$$E = \frac{m_{o_2}}{m_{o_2} + m_{in}} \quad (5)$$

where the subscripts *in*, *air* and O_2 refer to inert (i.e. nitrogen in this case), air, and oxygen, respectively; ε is an empirical parameter depending on the experimental conditions (mainly temperature and pressure) and gaseous mixture. The superscript φ in Equation 4 is added to underline the dependence on the equivalence ratio. It is worth noting that Equation 4 can be considered as a specific case of Equation 3 having ν equal to 1 if oxygen is considered as additional fuel. Alternatively, a new correlation for the estimation of the overall reactivity of the mixtures can be developed, based on the Arrhenius-like equation. To include the effects of composition, leading to different ruling reaction pathways in combustion systems, the frequency factor can be replaced by the laminar burning velocity of fuel/air mixture at stoichiometric composition ($S_{u,air}^{st}$), the activation energy by a function of the equivalence ratio, and flame temperature by a function of oxygen enrichment factor. These assumptions result in Equation 6.

$$S_u = S_{u,air}^{st} \cdot \varphi^\psi \cdot \left(\frac{E}{E_{air}}\right)^\omega \cdot e^{-\chi \left(\frac{\varphi-1}{E_{air}}\right)^2} \quad (6)$$

where χ , ω and ψ are empirical parameters.

Eventually, numerical methods, such as detailed kinetic mechanisms, can be implemented to estimate the S_u [26]. These models allow for the characterization of chemical interactions between reactants, intermediates, and products, as well as the estimation of the flame structures.

Accurate and robust methods for the estimations of the S_u in a wide range of conditions may be beneficial for the characterization of safety parameters, as well. In particular, flammability limits, and limiting oxygen content can be estimated in accordance with the well-established limiting laminar burning velocity theory proposed by Hertzberg (1984) [27].

In this work, the effect of the initial composition on S_u was evaluated experimentally by using the heat flux burner [15][28]. The collected measurements were compared with numerical predictions resulting from the application of detailed kinetic mechanisms extensively validated in previous studies [11][29], and the correlations previously proposed. The effect of the initial composition on the flammability range of the fuel/oxidant was estimated, as well.

2. Materials and Methods

Considering the different approaches utilized in this work, the description of methodological procedures adopted in this work was conveniently reported into two sub-sections, relying on experimental and numerical analyses, respectively.

2.1. Experimental analysis

The heat flux burner utilized in this work is composed of a feeding section, a burner, and a data acquisition system. In the first section, the gaseous stream flow rate and composition are controlled and mixed through Bronkhorst mass flow controllers and pipelines. The second section consists of a plenum chamber, where the premixing and homogeneity of the temperature and composition of the gaseous mixture are guaranteed, and a perforated burner plate. The radial plate temperature distribution is measured by using thermocouples conveniently located at different distances from the plate center and monitored through a data acquisition system.

The temperature of the plenum chamber is controlled by using a cooling jacket fed by water at 295 K. Similarly, the temperature of the burner plate is controlled utilizing a jacket where ethylene glycol at the temperature of 358 K was fed. The temperature of both liquids is controlled by thermostats. A simplified representation of the described system is given in Figure 1, whereas additional information and features on the burner plate geometry can be found in Figure 2.

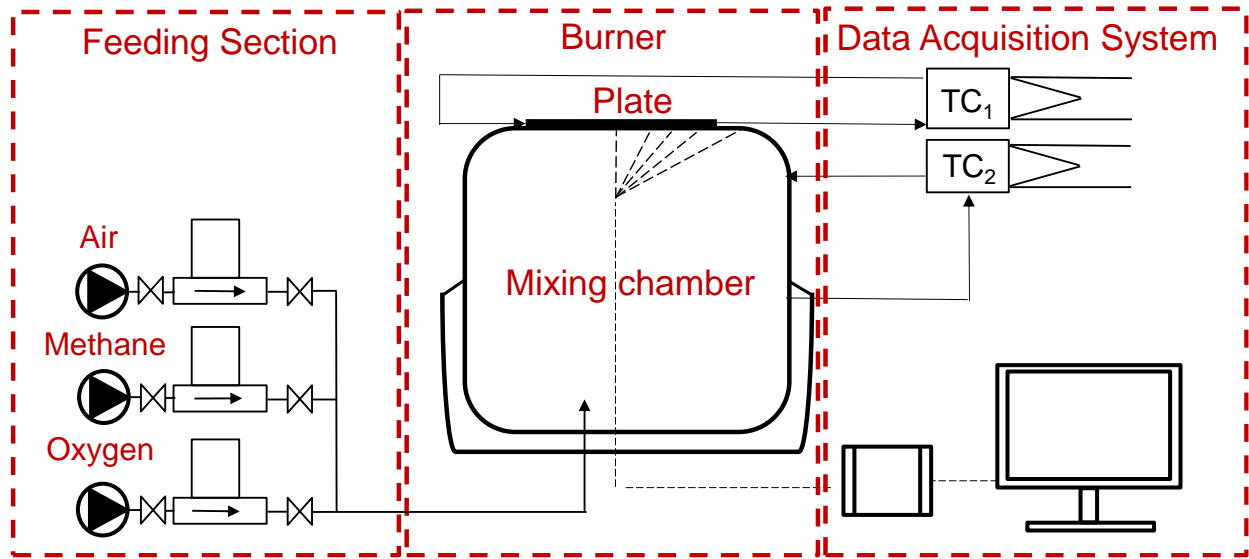


Figure 1. Schematic representation of the experimental system adopted in this work.

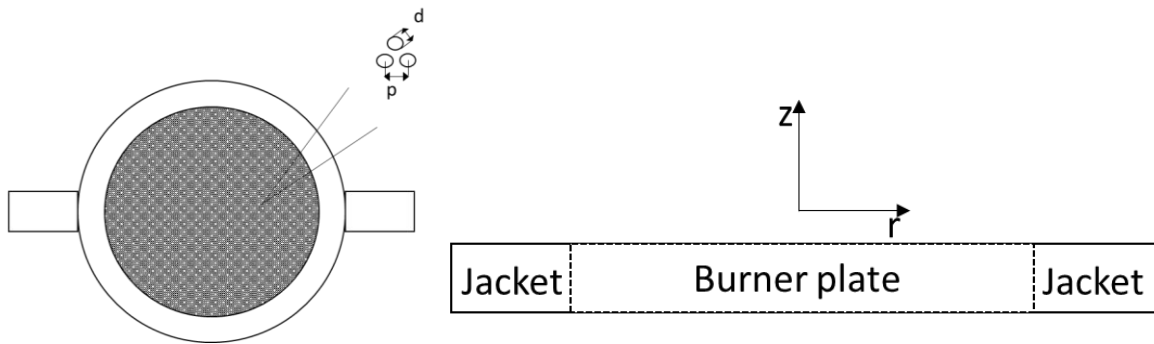


Figure 2. Schematic representation of top and side views of the burner head, including a focus on the dimensions and layout of holes (d = hole diameter, p is the center to center pitch). The origin of coordinates is placed on the axis of symmetry and below the plate

The feeding system is designed to guarantee the fuel/oxidant premixing and homogeneous composition with respect to the radial position on the plenum plate. Thermocouples were added to monitor the inlet and outlet temperatures of the jacket fluid and the plenum chamber temperature. Indeed, the difference between the outlet and inlet values of the heating jacket (ΔT_j) was adopted as an additional monitoring parameter to guarantee the absence of angular temperature profile, i.e. the plate temperature was considered homogeneous with respect to the angular position only in case of measured ΔT_j smaller than 1 K. Air and oxygen enriched air were adopted as oxidant agents, 295 K and 1 bar as the unburned conditions to study the methane premixed flame. In particular, the S_u of methane/nitrogen/oxygen mixtures having E ranging from 0.21 to 0.40 and ϕ from 0.5 and 1.5 were experimentally determined. These values were selected in accordance with the restrictions on the heat flux method applicability previously cited [21]. Several plate temperature distributions were measured by changing the initial flow rate for a given composition. Quadratic coefficients

were calculated assuming a parabolic trend of the temperature with respect to the distance from the plate center. Hence, the laminar burning velocity was obtained by interpolation as the velocity giving null coefficient, i.e., representing adiabatic conditions. Additional information on the adopted procedure can be found elsewhere [16].

The evaluation of the experimental error was performed by considering the temperature measurements, the unburned gas velocity, and the interpolation process as possible sources of uncertainties for the S_u collected data and the combination of uncertainties of the mass flow controllers for estimation of the corresponding experimental error of the equivalence ratio, adopting the procedure described in detail elsewhere [15].

2.2. Numerical analysis

The premixed flame was modeled assuming mono-dimensional and adiabatic conditions, by using the open-source code Cantera [30], the detailed kinetic mechanism developed at the University of Bologna (KiBo) [29] and the well-known GriMech3.0 mechanism [31]. KiBo represents a semi-empirical chemical model optimized in terms of accuracy and required computational costs to describe the oxidation of light hydrocarbons. It consists of 600 reactions and 125 species and is suitable for the estimation of S_u of gaseous mixtures containing chemicals lighter than C₅, sulfur- and nitrogen-based species in a wide range of conditions [32][29]. The adopted grid parameters were ratio equal to 3, slope equal to 0.07 and curve equal to 0.14, for the refiner function, 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 $1.0 \cdot 10^{-14}$ for time stepping problem, respectively. These values result in a typical grid of 250 - 350 points and were selected based on the results obtained by a grid sensitivity analysis reported in previous work [33]. The resulting temperature profile and species distribution were utilized to distinguish the reactive zone and evaluate the effect of initial condition on the flame structure.

The accuracy of the correlations presented (i.e. Equation 3 and Equation 6) and of the detailed kinetic mechanisms adopted (i.e. KiBo and GriMech3.0) was estimated against experimental data collected in this work and retrieved from the current literature. Methane related parameters obtained in a previous investigation [24] were adopted in Equation 3 and Equation 6, whereas oxygen enriched parameters were calculated to minimize the overall discrepancies between predicted values and experimental measurements collected in this work. To avoid meaningless results, experimental data were divided into two groups, one for the estimation of fitting parameters (referred to as the training dataset) and the other for the evaluation of estimation accuracy (referred to as the test dataset), in accordance with the founding principles of the machine learning approach [34].

Finally, the values of Upper Flammability Limit (UFL), Lower Flammability Limit (LFL) and the Limiting Oxygen Concentration (LOC) were assumed as the composition giving the S_u equal to the threshold value ($S_{u,lim}$) defined in Equation 7.

$$S_{u,lim} = \sqrt[3]{2\alpha \cdot \vec{g} \cdot \frac{\rho_b}{\rho_u}} \quad (7)$$

where \vec{g} , α , ρ_b , and ρ_u represent the gravitational acceleration effective thermal diffusivity of the mixture, burned and unburned densities. The required properties were calculated by using the thermodynamic and transport databases included in the detailed kinetic mechanism KiBo.

3. Results and Discussion

The effects of initial composition on methane/nitrogen/oxygen premixed flames were analysed by using either experimental or numerical approaches. Results are reported in the following.

3.1. *The Effect of Oxygen Enrichment Factor*

The experimental data collected at the unburned temperature of 295 K obtained in this work at different E and φ are shown in Figure 3. In the figure, additional experimental data obtained at the same conditions, as reported in the literature [35][20][36], and numerical predictions resulting from the implementation of KiBo and GriMech3.0 were also reported for the sake of comparison.

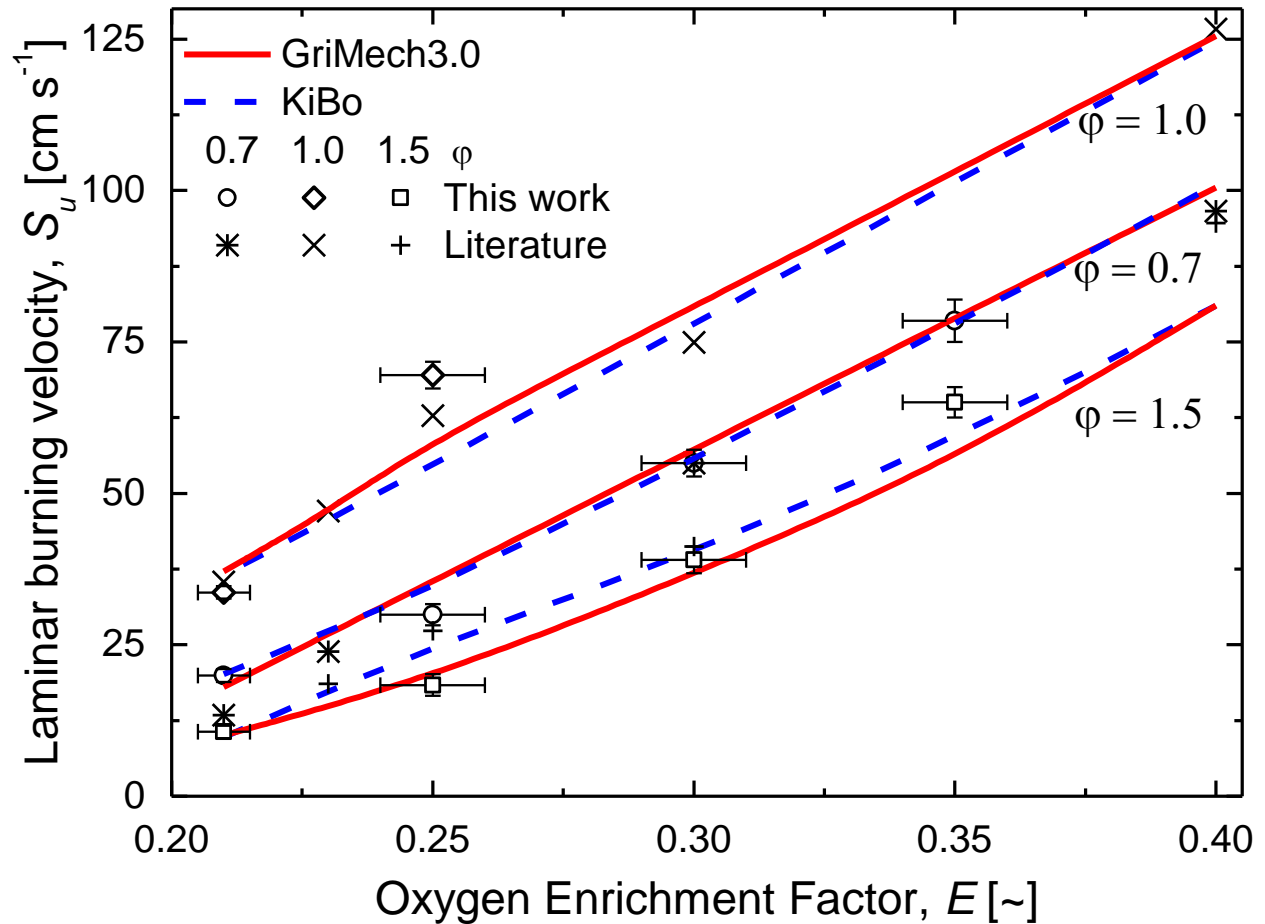


Figure 3. The effect of oxygen addition on the laminar burning velocity (S_u) of methane/nitrogen/oxygen mixtures for three equivalence ratios ($\phi = 0.7; 1.0; 1.5$). Open symbols: experiments, this work (\square : $\phi=1.5$; \circ : $\phi=0.7$; \diamond : $\phi= 1.0$). Cross symbols: experimental data from literature [35][20][36] ($+$: $\phi=1,5$; $*$: $\phi=0.7$; x : $\phi= 1.0$). Blue dashed lines: KiBo; Red solid lines: GriMech3.0.

For any given value of oxygen enrichment factor, the laminar burning velocity follows the typical trend with respect to the equivalence ratio, where an increase in ϕ leads to higher S_u for lean compositions and lower S_u for rich compositions, in accordance with the trend of the adiabatic flame temperature [37]. However, it should be said that kinetic phenomena proportional to fuel concentration push the peak of S_u/ϕ curves toward richer compositions, typically within the range 1.1 -1.2 for most of the hydrocarbons [26]. Additional information on this topic will be discussed in the following. A linear trend with respect to E can roughly represent the stoichiometric and lean data reported in Figure 3, exclusively. The differences between rich and non-rich compositions can be attributed to the ruling phenomena determining the overall reactivity, i.e. when the former composition is investigated, the chemistry of fuel radicals is predominant, whereas in the latter case, thermal aspects assume elevated relevance. This hypothesis is in accordance with the well-known theory developed for the estimation of the effect of temperature on the lower and upper flammability limits [38]. The kinetic models can fairly reproduce both trends. Moreover, numerical results are in line with estimations reported in the literature for lean mixture [39][40][41], as well.

Nevertheless, discrepancies can be observed for rich fuel at higher oxygen content. The possible causes of these disagreements will be analyzed in the following.

3.2. The Combined Effects of Oxygen Enrichment Factor and Equivalence Ratio

The effect of oxygen enrichment for different equivalence ratios is reported in Figure 4.

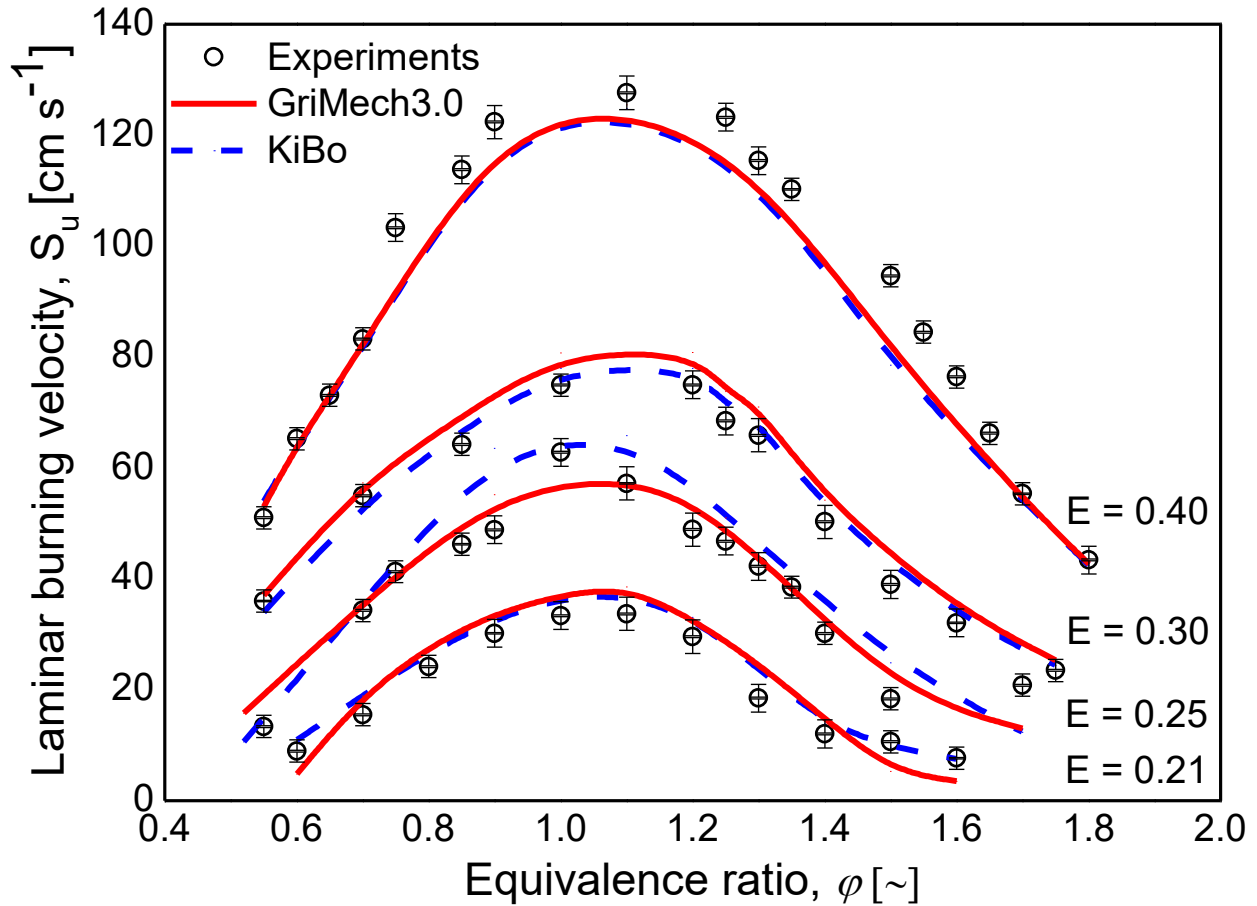


Figure 4 The effect of equivalence ratio on the laminar burning velocity (S_u) of methane/nitrogen/oxygen mixtures for different oxygen factors, E . Open symbols: experimental data collected in this work and retrieved from the literature [35][20][36]. Blue dashed lines: KiBo; Red solid lines: GriMech3.0.

It is worth mentioning that, both detailed kinetic mechanisms can fairly represent experimental measurements collected in this work and retrieved from the current literature under the investigated conditions, including the shift toward richer compositions of conditions where the maximum value of the S_u is reached. However, a tendency to slightly underestimate the S_u of near-stoichiometric mixtures can be observed, especially for elevated E . Additional information on the combined effects of E and ϕ on the chemical behavior of methane can be collected by analyzing the flame structures at different initial compositions. More specifically, temperature profile, reactants, and

main combustion products (i.e. H_2 , H_2O , CO , and CO_2) distribution were reported with respect to the distance from the burner plate, as calculated by the kinetic model. For the sake of brevity, lean ($\varphi = 0.7$) and rich ($\varphi = 1.5$) equivalence ratios, using air ($E = 0.21$) and oxygen enriched air ($E = 0.35$) are here reported (Fig. 5), exclusively.

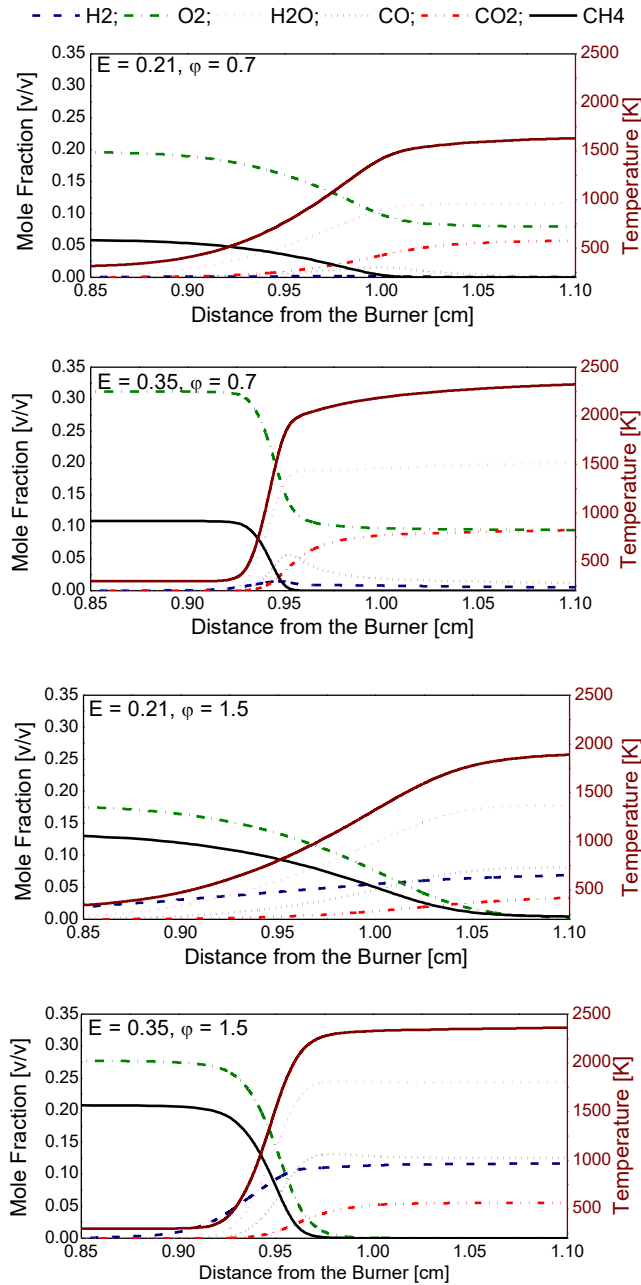


Figure 5. Flame structures of methane/nitrogen/oxygen mixtures at different initial compositions.

As expected, either the temperature or mole fraction profiles reported in Figure 5 indicate that higher oxygen content leads to a narrower reactive zone. Indeed, the decay of reactant mole fractions (or the increase in temperature) is anticipated for the air case, whereas the achievement

of equilibrium values is observed at higher distances to the burner plate with respect to a mixture having $E = 0.35$. This trend can be attributed to the enhanced kinetics of the chain-branching reaction $\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$, due to the increased availability of reactants, making faster the reaction responsible for most of the heat-release-rate [42]. Furthermore, substantial hydrogen production can be observed in the isothermal zone, especially in rich composition, confirming the hypothesis of the non-inert preheat zone. It is worth noting that similar adiabatic flame temperatures can be observed for different equivalence ratios at higher E . Besides, the CO peaks are considerably more pronounced in the case of oxygen enrichment, suggesting that oxygen significantly interacts with the degradation path of CH_4 leading to the formation of CO, whereas the further oxidation to CO_2 mainly occurs with alternative oxidative agents. These observations are in line with the results of sensitivity analysis performed by Wu et al. (2009) [43] for methane/air flames, where the formation of CO is mainly attributed to the oxidation of methane dehydrogenation product (i.e. methyl radical, CH_3) by means of the reaction $\text{O} + \text{CH}_3 \rightarrow \text{H} + \text{H}_2 + \text{CO}$, whereas the CO_2 production is attributed to the reaction $\text{OH} + \text{CO} \rightleftharpoons \text{H} + \text{CO}_2$. This hypothesis is of particular meaning for biomass-derived fuels since several studies have indicated that the latter reaction has a significant impact on the overall reaction path in the case of fuels containing CO_2 [44][45]. Hence, future numerical works aiming to the improvement of detailed kinetic mechanisms, especially for rich compositions, should be devoted to the estimations of these reaction rate coefficients.

3.3. Comparison of the Empirical Correlations

The obtained experimental data were adopted for the estimation of the parameters in Equations 3 and 6 by means of the minimum least square method, as described in detail into the methodological section. The resulting parameters were reported in Table 1.

Table 1. Fitting parameters calculated for Equations 3 and 6.

Parameter	$W = S_{u,air}^{st}$ [cm s ⁻¹]	ω [~]	ψ [~]	χ [~]	ξ [~]	η [~]	γ [~]	ν [~]	σ [~]	Ω [~]
Value	36.0	2.0	0.5	4.5	4.7	0.5	25.0	1.0	1.0	0.1

Both equations indicate a square root dependence of the S_u with respect to the φ (i.e. η and ψ equal to 0.5). On the other hand, in the Equation 3, the reaction order with respect to oxygen was found to be equal to 1, in compliance with the assumption of the linear proportional relation of S_u with respect to E for the pre-exponential coefficient [46], whereas a quadratic trend with respect to E was suggested by Equation 6, following the elementary rate law. To clarify the possible reasons for these discrepancies, both correlations can be rewritten in a more general form as follow

$$\frac{S_u}{S_{u,air}^{st}} = f(\varphi) \cdot g(E) \cdot e^{-h(\varphi,E)} \quad (9)$$

where f , g , and h are functions of the parameters reported in the brackets. This form allows for the evaluation of the relative contribution of each parameter involving the determination of the S_u . Indeed, recalling that linear trends were observed at stoichiometric and lean compositions for experimental data, it is possible to conclude that the combined effect of E and φ , i.e. $h(\varphi, E)$, is negligible under these conditions. On the other hand, the latter function assumes a larger significance for richer compositions.

The estimation quality of the correlation proposed in this work is evidenced in Figure 7, where experimental data obtained at similar initial temperature and pressure [35][20][36] and part of the measurements collected in this work (i.e. excluding the data adopted for the estimation of the empirical parameters) were displayed against numerical predictions. In this plot, the accuracy of the utilized detailed kinetic mechanisms was analysed, as well.

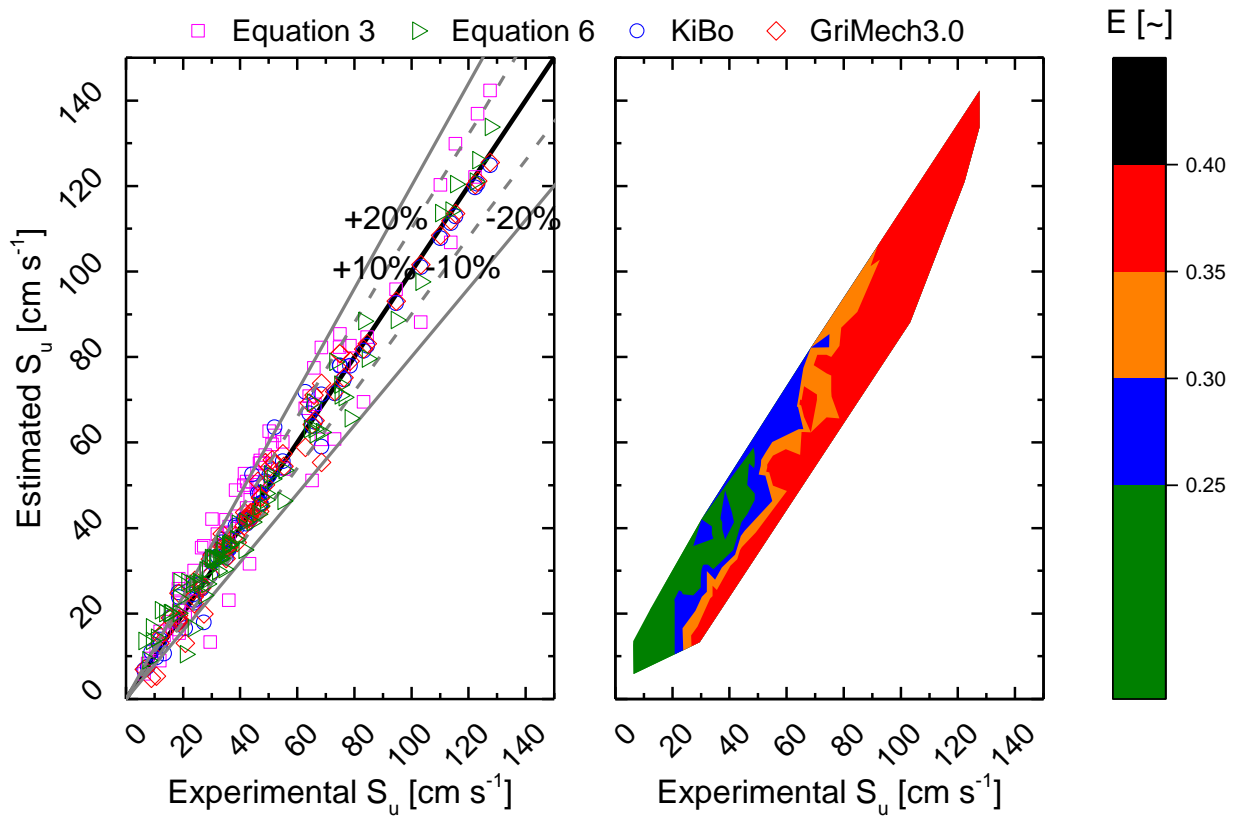


Figure 6. Comparison of experimental and estimated S_u (Eq. 3, Eq. 6, KiBo and GriMech3.0 models).

It is worth mentioning that for elevated values of S_u , namely at elevated oxygen enrichment and equivalence ratio, the estimations are within the $\pm 10\%$ of the range with respect to the experimental values analyzed, regardless of the adopted approach, although fitting parameters of both correlations derive from lower E . However, significant underestimation can be observed for lower values when $E = 0.40$, especially for Equation 3. This observation implies that simplified approaches need further improvement to guarantee satisfactory agreement with experimental data

at extreme conditions. Considering the whole dataset, Equation 6 gives more accurate estimations than Equation 3, suggesting the adoption of an elemental reaction-based approach for the estimation of the overall reactivity under the investigated conditions. Besides, negligible differences can be observed at elevated S_u between KiBo and GriMech3.0.

3.4. Estimation of the flammability limits

Considering the elevated accuracy demonstrated by Equation 6, with coefficients reported in Table 1, this correlation was implemented for the estimation of the flammability limits and limiting oxygen concentration of the investigated mixtures following the procedure described in the methodological section. The obtained results were compared with experimental data retrieved in the current literature [47][48] and reported in Figure 7. At this stage, flammability limits estimated at $E < 0.21$ and $E > 0.40$ were added for the sake of discussion.

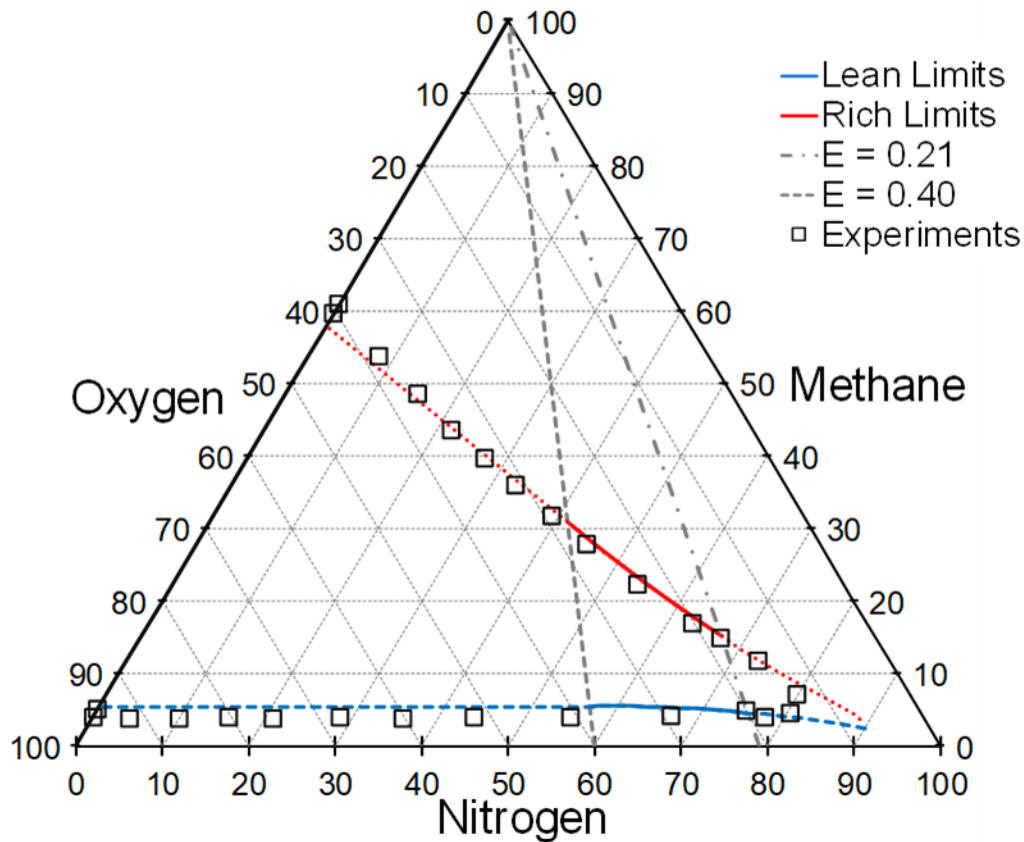


Figure 7. Comparison of flammability range of methane/nitrogen/oxygen mixture at atmospheric pressure and 295 K. Symbols represents experimental data reported in the literature [47][48], whereas lines stand for numerical predictions obtained by Equation 6 and Table 1. Please note that dashed lines were drawn to underline that extrapolation was performed.

Although the empirical parameters included in Equation 6 were calculated by using data obtained at E within the range of 0.21 - 0.40, numerical estimations are in compliance with experimental measurements at E not included in the original range, as well.

The estimated LFL, UFL in the air are 4.46 %v/v and 15.14 %v/v respectively, which are in a very good agreement with experimental data obtained by several standard techniques [49]. The estimated LOC in nitrogen is 7.5 %v/v, which corresponds to the slightly richer than the stoichiometric mixture at $E = 0.075$. This value, resulting from the combination of detailed kinetic models implemented in adiabatic conditions and fundamental-based experimental system (i.e. the heat flux burner), gives more conservative values than the visual methodology, spherical bomb or critical adiabatic flame temperature (CAFT) approaches, where LOC in nitrogen is typically close to 9.9 %v/v [50].

The agreement between the two data sources for LFL and UFL for oxygen-enriched compositions is undoubtedly facilitated by the direct proportionality with respect to E . However, it is worth to mention that the $S_{u,lim}$ is almost constant for rich mixtures, whereas a power-law correlation (Equation 10) fairly represents the obtained trend of the threshold value with respect to E for lean conditions

$$S_{u,lim} = 114.55 \cdot E^{1.82} \quad (10)$$

Meaning that under these conditions the variation in the adiabatic flame temperature at UFL is limited, in accordance with the CAFT [51] method. On the other hand, the $S_{u,lim}$ obtained in the lean cases are strongly affected by the increase in the E , mainly because of the corresponding increase in the adiabatic flame temperature, thus affecting the burned mixture density.

4. Conclusions

Experimental and modeling data for the laminar burning velocity of methane flames in oxygen enriched air have been collected and analysed in this work. The tendency of the selected kinetic mechanism to underpredict this parameter, especially for near stoichiometric and elevated oxygen enrichment factor, was indicated. Empirical correlations for the estimation of these parameters were developed, successfully implemented and compared for the representation of the available dataset. Quadratic law and square root law satisfactorily represent the laminar burning velocity trends with respect to the oxygen enrichment factor and equivalence ratio, respectively. The effects of the reactant composition on the laminar flame structure were evaluated, as well. Providing additional insights for the individuation of ruling reaction paths, helping further refinements of kinetic modes.

In conclusion, the safety parameters of methane/nitrogen/oxygen mixtures have been evaluated either experimentally, by means of the heat flux burner, or based on simple correlations resulting

from combustion fundamentals and detailed kinetic models. This methodology can be easily extended to any fuel mixture.

References

- [1] C. Allouis and F. Chiariello, "Effect on O₂ enrichment and CO₂ dilution on rapeseed oil combustion in a stationary burner," *Exp. Therm. Fluid Sci.*, 73, 49–55, 2016.
- [2] F. Wu, M. D. Argyle, P. A. Dellenback, and M. Fan, "Progress in O₂ separation for oxy-fuel combustion—A promising way for cost-effective CO₂ capture: A review," *Prog. Energy Combust. Sci.*, 67, 188–205, 2018.
- [3] E. Salzano, A. Basco, F. Cammarota, V. Di Sarli, and A. Di Benedetto, "Flammability of Syngas / CO₂ Mixtures in Oxygen-Enriched Air," *Ind. Eng. Chem. Res.*, 51, 1–6, 2012.
- [4] J. Chen, L. Mu, J. Cai, P. Yao, X. Song, H. Yin, and A. Li, "Pyrolysis and oxy-fuel combustion characteristics and kinetics of petrochemical wastewater sludge using thermogravimetric analysis," *Bioresour. Technol.*, 198, 115–123, 2015.
- [5] I. Glassman and R. A. Yetter, *Combustion*, 4th ed. Elsevier B.V, 2008.
- [6] A. Vandael, J. P. Chica Cano, S. de Persis, and G. Cabot, "Study of the influence of water vapour and carbon dioxide dilution on flame structure of swirled methane/oxygen-enriched air flames," *Exp. Therm. Fluid Sci.*, 113, 2020.
- [7] S. A. Zelepouga, A. V. Saveliev, L. A. Kennedy, and A. A. Fridman, "Relative effect of acetylene and PAHs addition on soot formation in laminar diffusion flames of methane with oxygen and oxygen-enriched air," *Combust. Flame*, 122, 76–89, 2000.
- [8] A. N. Mazas, B. Fiorina, D. A. Lacoste, and T. Schuller, "Effects of water vapor addition on the laminar burning velocity of oxygen-enriched methane flames," *Combust. Flame*, 158, 2428–2440, 2011.
- [9] N. Merlo, T. Boushaki, C. Chauveau, S. De Persis, L. Pillier, B. Sarh, and I. Gökalp, "Combustion characteristics of methane-oxygen enhanced air turbulent non-premixed swirling flames," *Exp. Therm. Fluid Sci.*, 56, 53–60, 2014.
- [10] L. Tian, L. Liu, and R. Duan, "Experimental investigation on oxygen diluted partially premixed and oxygen enriched supplemental combustion for low emission," *Energy*, 156, 144–153, 2018.
- [11] G. Pio and E. Salzano, "Evaluation of safety parameters of light alkenes by means of detailed kinetic models," *Process Saf. Environ. Prot.*, 119, 131–137, 2018.
- [12] C. F. Chen, C. M. Shu, H. C. Wu, H. H. Ho, and S. P. Ho, "Ethylene gas explosion analysis under oxygen-enriched atmospheres in a 20-liter spherical vessel," *J. Loss Prev. Process Ind.*, 49, 519–524, 2017.
- [13] M. M. Abdelaal, M. K. El-Riedy, and A. M. El-Nahas, "Effect of oxygen enriched air on porous radiant burner performance and NO emissions," *Exp. Therm. Fluid Sci.*, 45, 163–

168, 2013.

- [14] Q. Zhou, C. S. Cheung, C. W. Leung, X. Li, X. Li, and Z. Huang, "Effects of fuel composition and initial pressure on laminar flame speed of H₂/CO/CH₄ bio-syngas," *Fuel*, 238, 149–158, 2019.
- [15] E. Salzano, G. Pio, A. Ricca, and V. Palma, "The effect of a hydrogen addition to the premixed flame structure of light alkanes," *Fuel*, 234, 1064–1070, 2018.
- [16] G. Pio, A. Ricca, V. Palma, and E. Salzano, "Low temperature combustion of methane/alkenes mixtures," *Fuel*, 254, 2019.
- [17] H. Chen, *Gas Explosion Technology and Biomass Refinery*. Springer, 2015.
- [18] G. Pio and E. Salzano, "Flammability parameters of liquified natural gas," *J. Loss Prev. Process Ind.*, 56, 424–429, 2018.
- [19] C. Xu and A. A. Konnov, "Validation and analysis of detailed kinetic models for ethylene combustion," *Energy*, 43, 19–29, 2012.
- [20] S. De Persis, F. Foucher, L. Pillier, V. Osorio, and I. Gökalp, "Effects of O₂ enrichment and CO₂ dilution on laminar methane flames," *Energy*, 55, 1055–1066, 2013.
- [21] A. A. Konnov, A. Mohammad, V. R. Kishore, N. Il Kim, C. Prathap, and S. Kumar, "A comprehensive review of measurements and data analysis of laminar burning velocities for various fuel+air mixtures," *Prog. Energy Combust. Sci.*, 68, 197–267, 2018.
- [22] O. L. Gulder, "Correlations of laminar combustion data for alternative S.I. engine fuels," *SAE Tech. Pap.*, 1984.
- [23] F. H. V. Coppens, J. De Ruyck, and A. A. Konnov, "Effects of hydrogen enrichment on adiabatic burning velocity and NO formation in methane + air flames," *Exp. Therm. Fluid Sci.*, 31, 437–444, 2007.
- [24] G. Pio and E. Salzano, "Laminar Burning Velocity of Methane, Hydrogen, and Their Mixtures at Extremely Low-Temperature Conditions," *Energy & Fuels*, 32, 8830–8836, 2018.
- [25] M. Elia, M. Ulinski, and M. Metghalchi, "Laminar Burning Velocity of Methane–Air–Diluent Mixtures," *J. Eng. Gas Turbines Power*, 123, 190, 2001.
- [26] E. Ranzi, A. Frassoldati, R. Grana, A. Cuoci, T. Faravelli, A. P. Kelley, and C. K. Law, "Hierarchical and comparative kinetic modeling of laminar flame speeds of hydrocarbon and oxygenated fuels," *Prog. Energy Combust. Sci.*, 38, 468–501, 2012.
- [27] M. Hertzberg, "The Theory of Flammability Limits, Flow Gradient Effect and Flame Stretch," *United States Dep. Inter.*, 1984.
- [28] G. Pio, A. Ricca, V. Palma, and E. Salzano, "Experimental and numerical evaluation of low-temperature combustion of bio-syngas," *Int. J. Hydrogen Energy*, 45, 1084–1095, 2020.
- [29] G. Pio, D. Barba, V. Palma, and E. Salzano, "A Numerical Study on the Effect of

Temperature and Composition on the Flammability of Methane–Hydrogen Sulfide Mixtures,” *Combust. Sci. Technol.*, 191, 1541–1557, 2019.

- [30] D. G. Goodwin, “An Open Source, Extensible Software Suite FOR CVD Process Simulation,” 2003.
- [31] G. P. Smith, D. M. Golden, M. Frenklach, N. W. Moriarty, B. Eiteneer, M. Goldenberg, C. T. Bowman, R. K. Hanson, S. Song, W. C. Gardiner Jr., V. V Lissianski, and Z. Qin, “GRI-Mech 3.0,” http://www.me.berkeley.edu/gri_mech/. 2000.
- [32] G. Pio, V. Palma, and E. Salzano, “Comparison and validation of detailed kinetic models for the oxidation of light alkenes,” *Ind. Eng. Chem. Res.*, 57, 7130–7135, 2018.
- [33] G. Pio and E. Salzano, “The effect of ultra-low temperature on the flammability limits of a methane/air/diluent mixtures,” *J. Hazard. Mater.*, 362, 224–229, 2019.
- [34] A. T. Kolokouris, “MACHINE LEARNING.,” *Byte*, 11, 225–231, 1986.
- [35] B. Lewis and G. Von Elbe, *Combustion, Flames and Explosions of Gases*. Elsevier B.V, 1987.
- [36] S. Wang, Z. Wang, Y. He, X. Han, Z. Sun, Y. Zhu, and M. Costa, “Laminar burning velocities of CH₄/O₂/N₂ and oxygen-enriched CH₄/O₂/CO₂ flames at elevated pressures measured using the heat flux method,” *Fuel*, 259, 116152, 2020.
- [37] J. Oh and D. Noh, “Laminar burning velocity of oxy-methane flames in atmospheric condition,” *Energy*, 45, 669–675, 2012.
- [38] F. P. Lees, *Loss Prevention in the Process Industries Hazard Identification, Assessment and Control*, 1. Elsevier B.V, 1996.
- [39] R. P. Lindstedt, F. C. Lockwood, and M. A. Selim, “Detailed kinetic modelling of chemistry and temperature effects on ammonia oxidation,” *Combust. Sci. Technol.*, 99, 253–276, 1994.
- [40] B. Shi, D. Shimokuri, and S. Ishizuka, “Methane/oxygen combustion in a rapidly mixed type tubular flame burner,” *Proc. Combust. Inst.*, 34, 3369–3377, 2012.
- [41] K. Zhang, G. Hu, S. Liao, Z. Zuo, H. Li, Q. Cheng, and C. Xiang, “Numerical study on the effects of oxygen enrichment on methane/air flames,” *Fuel*, 176, 93–101, 2016.
- [42] Y. Lafay, B. Renou, G. Cabot, and M. Boukhalfa, “Experimental and numerical investigation of the effect of H₂ enrichment on laminar methane-air flame thickness,” *Combust. Flame*, 153, 540–561, 2008.
- [43] C. Y. Wu, Y. C. Chao, T. S. Cheng, C. P. Chen, and C. T. Ho, “Effects of CO addition on the characteristics of laminar premixed CH₄/air opposed-jet flames,” *Combust. Flame*, 156, 362–373, 2009.
- [44] C. Liu, B. Yan, G. Chen, and X. S. Bai, “Structures and burning velocity of biomass derived gas flames,” *Int. J. Hydrogen Energy*, 35, 542–555, 2010.
- [45] H. Zhao, J. Fu, F. M. Haas, and Y. Ju, “Effect of prompt dissociation of formyl radical on

- 1,3,5-trioxane and CH₂O laminar flame speeds with CO₂ dilution at elevated pressure,” *Combust. Flame*, 183, 253–260, 2017.
- [46] B. Galmiche, F. Halter, F. Foucher, and P. Dagaut, “Effects of dilution on laminar burning velocity of premixed methane/air flames,” *Energy and Fuels*, 25, 948–954, 2011.
- [47] H. F. Coward and G. W. Jones, “Limits of flammability of gases and vapors,” 1952.
- [48] M. G. Zabetakis, “Flammability Characteristics of Combustible Gases and Vapors,” 1999.
- [49] D. Razus, M. Molnarne, and O. Fuß, “Limiting oxygen concentration evaluation in flammable gaseous mixtures by means of calculated adiabatic flame temperatures,” *Chem. Eng. Process. Process Intensif.*, 43, 775–784, 2004.
- [50] D. Razus, M. Molnarne, C. Movileanu, and A. Irimia, “Estimation of LOC (limiting oxygen concentration) of fuel-air-inert mixtures at elevated temperatures by means of adiabatic flame temperatures,” *Chem. Eng. Process. Process Intensif.*, 45, 193–197, 2006.
- [51] R. Li, Z. Liu, Y. Han, M. Tan, Y. Xu, J. Tian, J. Chai, and J. Liu, “Extended adiabatic flame temperature method for lower flammability limits prediction of fuel-air-diluent mixture by nonstoichiometric equation and nitrogen equivalent coefficients,” *Energy and Fuels*, 31, 351–361, 2017.