



**HAL**  
open science

# Premixed flame heat release based optimum global single-step chemistry for H<sub>2</sub>, CH<sub>4</sub>, and C<sub>3</sub>H<sub>8</sub> mixtures with air

Maria Clara de Jesus Vieira, Luis Fernando Figueira da Silva

## ► To cite this version:

Maria Clara de Jesus Vieira, Luis Fernando Figueira da Silva. Premixed flame heat release based optimum global single-step chemistry for H<sub>2</sub>, CH<sub>4</sub>, and C<sub>3</sub>H<sub>8</sub> mixtures with air. 2021. hal-03324397v1

**HAL Id: hal-03324397**

**<https://hal.science/hal-03324397v1>**

Preprint submitted on 23 Aug 2021 (v1), last revised 3 Feb 2022 (v2)

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Premixed flame heat release based optimum global single-step chemistry for H<sub>2</sub>, CH<sub>4</sub>, and C<sub>3</sub>H<sub>8</sub> mixtures with air

Maria Clara de Jesus Vieira · Luís  
Fernando Figueira da Silva

Received: date / Accepted: date

**Abstract** Despite the significant development of comprehensive detailed chemical kinetics mechanisms for combustion simulation in the past decades, reduced descriptions of the chemical process still enable engineering and direct numerical simulations. This work proposes a new formulation for the heat release rate of laminar premixed flame which extends the classical one-step Arrhenius global kinetics using a kinetically controlled assumption for the scalar controlling the final reaction steps. The proposed methodology considers that the heat release rate as a function of temperature is known and obtained via a freely propagating laminar premixed flame model together with various detailed chemical kinetics mechanisms. The resulting formulation involves three free parameters, one of which is the Zel'dovich number. The proposed formulation is characterized for H<sub>2</sub>, CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> mixtures with air and compared to several detailed chemical mechanisms, exhibiting errors between 6 % and 15 % for the first of these and smaller than 6 % for the hydrocarbons. The three free parameters are determined for a range of equivalence ratios and seem to be mixture properties. In particular, the Zel'dovich number exhibits a minimum around stoichiometry. The hydrocarbons fuels are also characterized when diluted by CO<sub>2</sub>, which is motivated by its presence in Brazilian pre-salt oil wells. The new free parameters are not influenced by dilution, whereas the Zel'dovich number is found to increase.

**Keywords** Single-step chemistry · Premixed combustion · Laminar flames · Zel'dovich number · Heat release rate

**Mathematics Subject Classification (2020)** MSC 80A25 · MSC 80A32

---

Maria Clara de Jesus Vieira  
*Corresponding author*  
Pontifícia Universidade Católica do Rio de Janeiro  
Department of Mechanical Engineering, 22451-900, Rio de Janeiro, Brazil  
E-mail: mariaclara@viejira@gmail.com

Luís Fernando Figueira da Silva  
Pontifícia Universidade Católica do Rio de Janeiro  
Department of Mechanical Engineering, 22451-900, Rio de Janeiro, Brazil  
*Present address:* Pprime UPR3346 CNRS, ENSMA and University of Poitiers

## 1 Declarations

### 1.1 Funding

This work was supported by Petrobras contract no. 5900.0111688.19.9 under the technical monitoring of Dr. P. R. Pagot. Support was also received from Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brazil) under the Research Grant No. 304444/2018-9. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001.

### 1.2 Conflicts of interest/Competing interests

Not applicable

### 1.3 Availability of data and material

Not applicable

### 1.4 Code availability

Not applicable

## 2 Introduction

Despite the decades-long quest for comprehensive detailed chemical kinetics mechanisms for gas-phase combustion [14,9], affordable engineering predictions and detailed computational fluid dynamics direct simulations still resort to simplified descriptions. In recent years, this has fostered, for instance, the development of virtual kinetics mechanisms [5] that rely on an optimization of the thermodynamic, transport and reaction properties. Optimized single-step chemistry models have also been developed to reproduce the burned gases temperature, the laminar flame speed and the laminar flame thickness based on the temperature gradient for the simulation of turbulent premixed flame propagation [8]. This has also been applied for studies of auto ignition of heterogenous mixtures, where the objective is to determine the ignition delay [6]. These studies also provide an ample discussion on the different requirements that simplified chemical models should satisfy.

In the present study an original single-step chemistry approximation method is presented, which involves an expression of heat release rate from the global chemical reaction controlled by a progress variable based on temperature, augmented by a Arrhenius type relaxation towards equilibrium. This method enables the Zel'dovich number determination, regardless the mixture equivalence ratio, also. The basic underlying assumption is that the combustion heat release rate is a function of temperature, obtained here, via detailed chemical kinetic computations. The new method effectiveness is demonstrated for hydrogen, methane and

propane mixtures with air on the basis of a priori analysis of the temperature-based reactive scalar reaction rate. Furthermore, CO<sub>2</sub> diluted hydrocarbons are also considered due to the interest in assessing the behavior of such mixtures for the sake of industrial applications.

Indeed, in a recent survey by ANP (The Brazilian Oil, Gas and Biofuels National Agency) [3], it is estimated that the so called pre-salt production will dominate the national oil and natural gas scenario. The composition of combustible gases from those pre-salt wells is considerably different from existing ones, mainly due to the presence of carbon dioxide (CO<sub>2</sub>) in its composition. Typically, the percentage of CO<sub>2</sub> in the hydrocarbon gas produced ranges from 0% to 80% [3], which justify the choice of fuel diluent composition used here. Note that CO<sub>2</sub> may also be found in gases produced by mature wells, since it is injected to help displace the oils from the bedrock. To represent the fuel in such wells, methane and propane and their mixtures with air are considered.

The present manuscript is organized as follows, the proposed methodology is described in the next section (Section 3). In Section 4 the results of the heat release expression are presented and discussed for the three considered fuels and different detailed chemistry mechanisms. It includes two subsections regarding to undiluted fuel/air mixtures and CO<sub>2</sub> diluted fuel/air mixtures, respectively. Finally, in Section 5, the main observations are reported as a conclusion.

### 3 Methodology

A new formulation for a single scalar based reaction rate is now presented. The proposed methodology considers that the heat release rate as a function of temperature is known,  $\dot{q}_{num}$ . In this work  $\dot{q}_{num}$  is obtained using CHEKMIN's freely propagating laminar premixed flame code, together with various detailed chemical kinetics mechanisms, to be specified further on. Therefore, for the sake of convenience,  $\dot{q}_{num}$  is expressed as a function of a progress variable,  $\theta$ , and a parameter,  $\gamma$ , associated with the chemical reaction heat release:  $\theta = (T - T_u)/(T_b - T_u)$  and  $\gamma = (T_b - T_u)/T_u$ , where  $T$  is the temperature,  $T_b$  is the adiabatic combustion temperature and  $T_u$  is the unburned gases temperature. A chemical equilibrium calculation code is used to determine  $T_b$ .

In the literature [7], an expression for the heat release rate from a global chemical reaction controlled by a minor reagent can be found as:

$$\dot{q}(\theta, Y) \propto Y^n \exp \left\{ \frac{\beta(\theta - 1)}{(1 + \gamma\theta)/(1 + \gamma)} \right\}. \quad (1)$$

In this equation  $Y$  is the normalized mass fraction of the deficient reagent,  $n$  is usually identified as the reaction order,  $\beta = E_a(T_b - T_u)/RT_b^2$  is the Zel'dovich number and, thus, the exponential term corresponds to the Arrhenius law for a global reaction. In the case where the Lewis number of this controlling reagent is unitary, it is possible to write that  $Y = 1 - \theta$ , and thus  $\dot{q}(\theta, Y) \rightarrow \dot{q}(\theta)$  only.

It is worth emphasizing that the hypotheses that lead to the derivation of Eq. (3) are not valid in the stoichiometry region. To illustrate this limitation, Fig. 1 shows the comparison between  $\dot{q}_{num}$  and  $\dot{q}$  for a stoichiometric methane/air mixture, in which  $n = 1$  is presumed and  $\beta$  was obtained by an optimization process that aims to minimize the Euclidean norm  $\|\dot{q}_{num} - \dot{q}\|$ . Here,  $\dot{q}_{num}$  has

been obtained from simulation results using the GRI 3.0 mechanism [11]. In this figure, and throughout this work, the heat release rate is normalized concerning the corresponding integrals.

$$I_q = \int_0^1 \dot{q} d\theta, \quad (2)$$

which is found to be a convenient way to compare the heat release rate for various fuels and equivalence ratios.

Figure 1 clearly shows that the simplified global reaction rate does not correctly describe  $\dot{q}_{num}$ . Indeed, the initial slope of  $\dot{q}_{num}(\theta)$  is smaller than that of  $\dot{q}(\theta)$ , indicating that the numerical value of  $\beta$  is smaller than that obtained using Eq. (1). Note that the Zel'dovich number,  $\beta$ , controls the increase of  $\dot{q}(\theta)$  in the lower temperature range, i.e., for  $\dot{q} \leq \dot{q}_{max}$ , where  $\dot{q}_{max}$  is the maximum heat release rate. Furthermore, both the maximum heat release rate and the relaxation toward the equilibrium when  $\theta \rightarrow 0$  are not well described by the simple functional dependency. This is not surprising, given that the assumptions involved in the derivation of Eq. (1) at the vicinity of the stoichiometry do not hold.

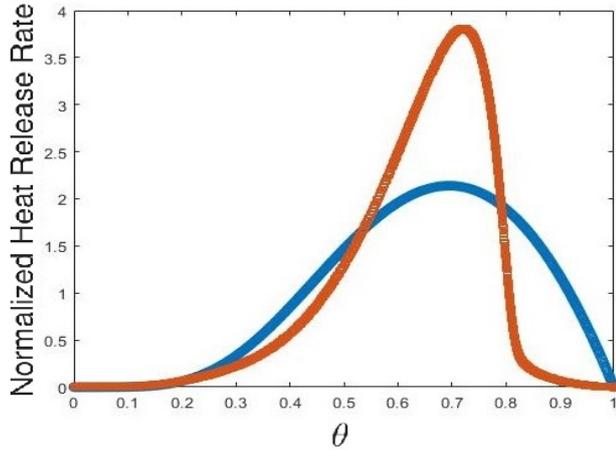


Fig. 1: Normalized heat release rate as a function of the progress variable for a stoichiometric methane/air mixture. Result of simplex optimization of Eq. (1) concerning a variable ( $\beta$ ) with  $n = 1$ . Red dots represents the simulation with the GRI 3.0 mechanism [11] and the blue dots represents the optimization results.

To better describe the variation of  $\dot{q}_{num}$  when  $\theta \rightarrow 1$ , in this paper the following expression is proposed:

$$Y = 1 - \exp[\beta'(1 - 1/\theta)]. \quad (3)$$

This expression considers that the limiting normalized reactant scalar,  $Y$ , is controlled by an Arrhenius type dependency:

$$\frac{d \ln(Y - 1)}{d(1/\theta)} = -\beta', \quad (4)$$

which introduces a first relaxation parameter,  $\beta'$ , that aims to approximate the decrease of  $\dot{q}_{num}$  with  $\theta$  from its maximum value. The integration of this equation leads to Eq. (3). Thus,  $Y$  can be interpreted as being representative of the chemical species that govern the tendency to equilibrium in the final stages of reaction. This  $\beta'$  parameter is then associated to the heat release during the final stages of the global reaction.

Furthermore, in the present formulation  $n$  is not interpreted as the reaction order, but as a free parameter loosely related to the complexity of the tendency of the chemical process towards equilibrium. Note that this formulation guarantees that  $Y(\theta = 1) = 0$ , i.e., the global reaction rate is zero at equilibrium.

Therefore, to approximate the behavior of  $\dot{q}_{num}(\theta)$ , the following expression is proposed:

$$\dot{q}(\theta) \propto \{1 - \exp[\beta'(1 - 1/\theta)]\}^n \exp \left\{ \frac{\beta(\theta - 1)}{(1 + \gamma\theta)/(1 + \gamma)} \right\}, \quad (5)$$

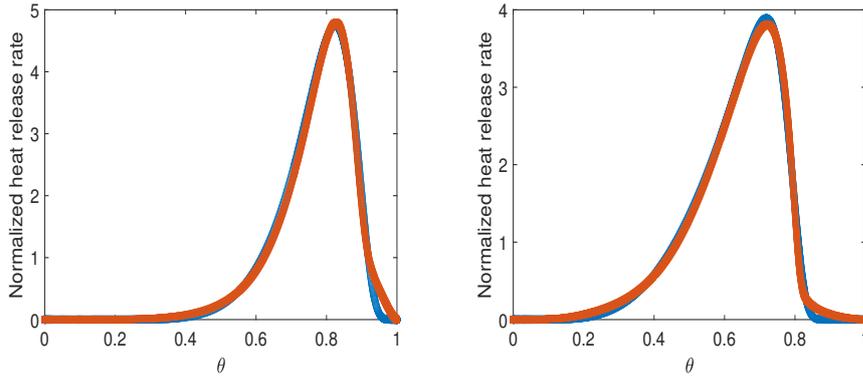
where  $\beta$ ,  $\beta'$  and  $n$  are parameters to be determined. The new parameters,  $\beta'$  and  $n$ , control, respectively, the decrease of  $\dot{q}$  for values of  $\theta$  immediately greater than that corresponding to  $\dot{q}_{max}$  and the behavior of  $\dot{q}(\theta)$  close to  $\theta \rightarrow 1$ . Since these two parameters are characteristic of the final stages of combustion, it is expected that, within the limits of very lean or very rich mixtures, they depend less on the nature of the fuel and mainly on the mixture C/H/O ratio. To determine  $\beta$ ,  $\beta'$  and  $n$  an optimization, aiming to minimize the norm  $\|\dot{q}_{num} - \dot{q}\|$  uses the basic simplex method [12,4]. In all cases the results are verified to ensure that a global minimum error is attained.

## 4 Results and Discussion

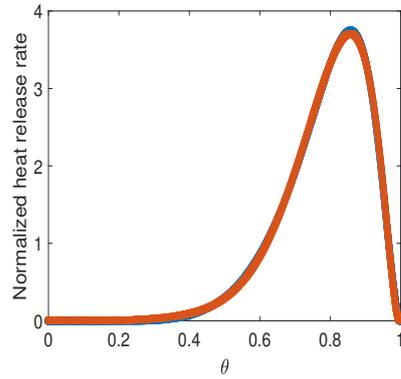
The determination of the reaction rate parameters is carried out for H<sub>2</sub>/air, CH<sub>4</sub>/air/CO<sub>2</sub> and C<sub>3</sub>H<sub>8</sub>/air/CO<sub>2</sub> mixtures. For each mixture and undiluted fuel are considered at least two different kinetics mechanism: Keromnes Mech [10] and Alekseev Mech [2] for hydrogen mixtures, GRI 3.0 [11], San Diego Mech [1] and USC II Mech [13] for methane mixtures and San Diego Mech and USC II Mech for propane mixtures. Subsequently, for CO<sub>2</sub> diluted fuel mixtures the GRI 3.0 is considered for methane, and San Diego Mech for propane. These mechanisms are chosen as representative of the combustion chemical kinetics of these different fuels [9]. For the sake of simplicity a pressure of 1 bar and an unburned gases temperature of 300 K are considered, only.

To provide a first assessment of the proposal formulation behavior for methane/air mixtures, Figures 2a, 2b and 2c, in which are shown the heat release rates,  $\dot{q}_{num}$  and  $\dot{q}$ , normalized by their integrals, illustrate one of the worst and best cases of optimization obtained with the new formulation, which have 4 %, 3 % and 0.9 % of error, respectively. In this figure, the red curve represents the numerical result obtained with kinetic mechanisms,  $\dot{q}_{num}$ , and the blue curve represents the optimization resulting from the use of Eq. (5). The analysis of this figure underscores

the excellent agreement between  $\dot{q}_{num}$  and  $\dot{q}$  during the initial phase of the chemical reaction, that is,  $\dot{q} \leq \dot{q}_{max}$ . In addition, the decrease of  $\dot{q}$  after  $\dot{q}_{max}$  is also very well described by the formulation proposed here. It is also observed that the most significant discrepancies occur for  $\theta \rightarrow 1$ , that is, in the region close to the chemical equilibrium. In the proposed formulation, this behavior is controlled by the parameter  $n$ . These findings suggest that  $\beta'$  and  $n$  are in fact properties of the chemical reaction.



(a) Lean mixture,  $\phi = 0.6$ , parameters:  $\beta = 5.2$ , (b) Stoichiometric mixture,  $\phi = 1.0$ , parameters:  $\beta = 2.3$ ,  $\beta' = 17.7$  and  $n = 105$ .  $\beta' = 16.6$  and  $n = 6.2$ .



(c) Rich mixture,  $\phi = 1.4$ , parameters:  $\beta = 3.9$ ,  $\beta' = 11.8$  and  $n = 1.8$ .

Fig. 2: Normalized heat release rate as a function of the progress variable for methane/air mixtures. Red dots represents the simulation with GRI 3.0 mechanism [11] and the blue dots represents the Eq. (5) optimization results.

A systematic analysis for three different fuel/air mixtures is now performed to further explore this formulation results.

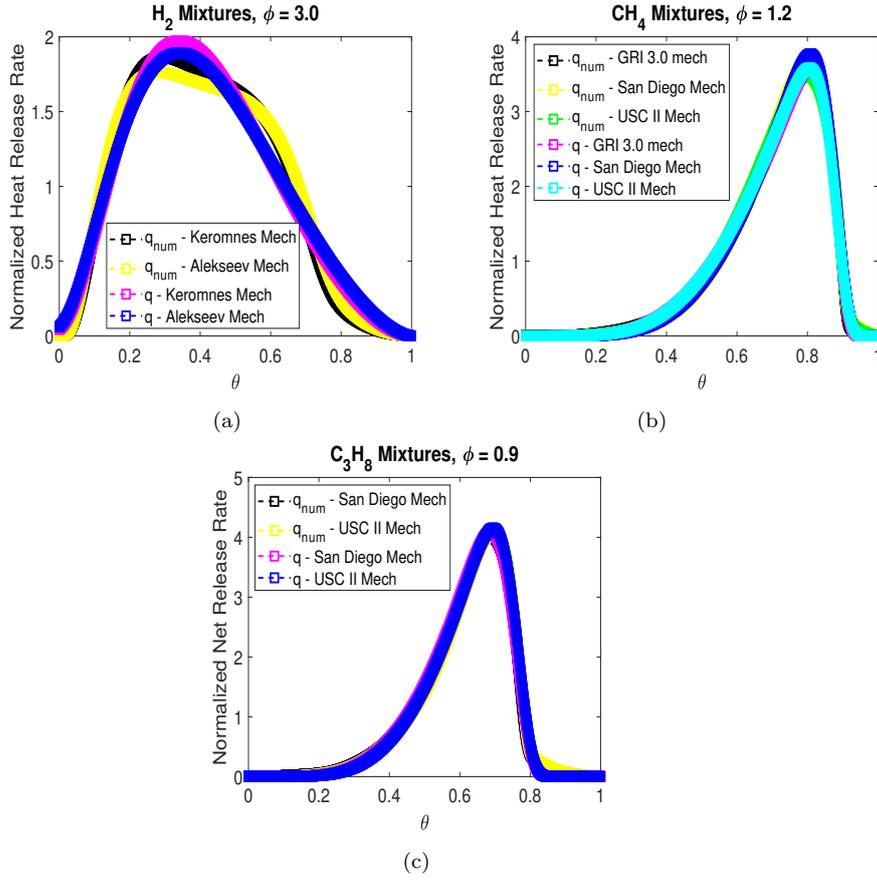


Fig. 3: Normalized heat release rate as a function of the progress variable comparison for the different kinetics mechanism used: (a) H<sub>2</sub>/air mixture,  $\phi=3.0$ , (b) CH<sub>4</sub>/air mixture,  $\phi=1.2$  and (c) C<sub>3</sub>H<sub>8</sub> mixture,  $\phi = 0.9$ .

#### 4.1 Undiluted fuel/air mixtures

Figs. 3a, 3b and 3c present the heat release rate comparison between  $\dot{q}$  calculated with Eq. (5) and that by considering the different detailed chemical kinetics mechanisms for H<sub>2</sub>, CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub>, respectively. The heat release rate is depicted in situations where the worst agreement between  $\dot{q}$  and  $\dot{q}_{num}$  is observed, i.e.,  $\phi = 3.0$ ,  $\phi = 1.2$  and  $\phi = 0.9$  for H<sub>2</sub>, CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> mixtures with air, respectively. For the three different undiluted fuel/air mixtures the qualitative agreement between  $\dot{q}$  and  $\dot{q}_{num}$  is remarkable. The comparison between these results indicate that, for H<sub>2</sub>/air, some discrepancies exist between  $\dot{q}$  and  $\dot{q}_{num}$  for the different chemical kinetic mechanisms, whereas the results obtained for CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> are nearly identical. This good agreement is seen even for the rich H<sub>2</sub>/air mixtures, which exhibits a peak of  $\dot{q}$  for  $\theta \approx 0.3$ , i.e., significantly departed from the burned gases.

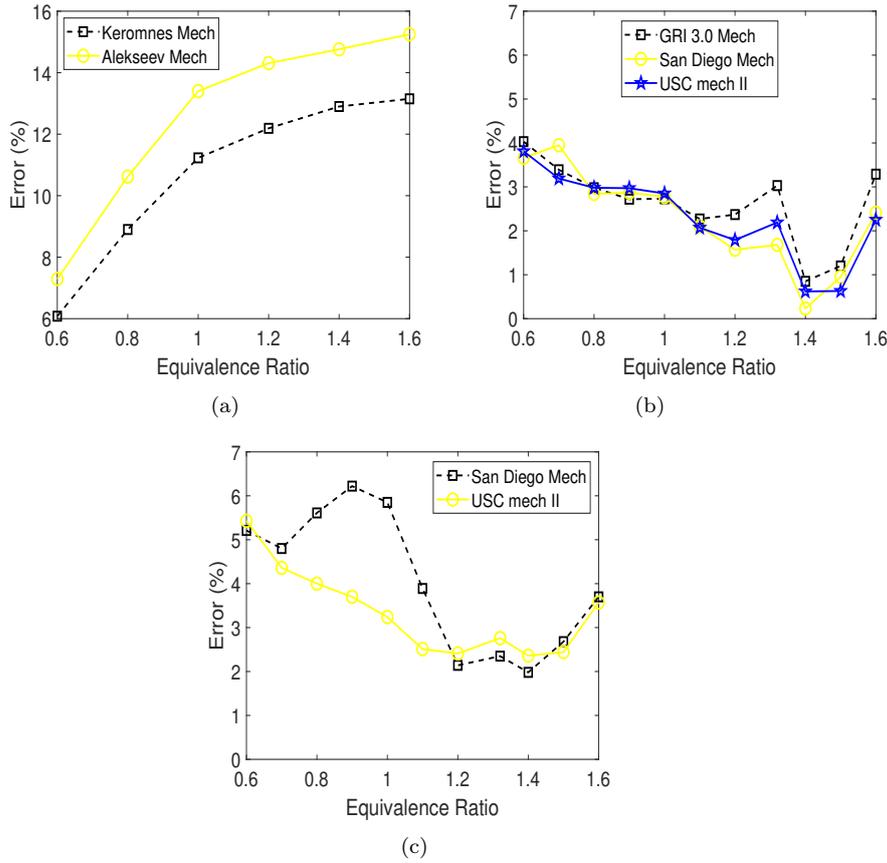


Fig. 4: Error comparison between  $\dot{q}$  using Eq. (5) results and the simulation using detailed chemical kinetics mechanisms,  $\dot{q}_{num}$ , as a function of the equivalence ratio: (a)  $\text{H}_2/\text{air}$  mixtures (b)  $\text{CH}_4/\text{air}$  mixtures (c)  $\text{C}_3\text{H}_8$  mixtures.

To quantify the errors associated with the present formulation throughout an equivalence ratio range, the Euclidean norm of the heat release rate error between the numerical simulation with detailed kinetic mechanisms and the proposed methodology is presented in Figs. 4a, 4b and 4c. For  $\text{H}_2/\text{air}$  mixtures the error varies from 6 % to 16 % and both chemical mechanisms exhibit the same error bias with equivalence ratio, albeit with different values. A remarkable feature concerning  $\text{CH}_4/\text{air}$  mixtures is the nearly identical behavior and value of the error with equivalence ratio, which is found to occur for rich propane mixtures also, but not for lean ones. Indeed, for  $\text{CH}_4/\text{air}$  mixtures and  $\text{C}_3\text{H}_8$  mixtures the error is smaller than for the  $\text{H}_2/\text{air}$  mixtures with values varying from 0.5 % to 4 % and 2 % to 6.5 %, respectively.

To further characterize the proposed reaction rate formation, Figs. 5a, 6a and 7a presents the results of the Zel'dovich number,  $\beta$ , as a function of the equivalence ratio,  $\phi$ , for  $\text{H}_2/\text{air}$ ,  $\text{CH}_4/\text{air}$  and  $\text{C}_3\text{H}_8/\text{air}$  mixtures. The Zel'dovich

number is seen to exhibit a non monotonic behavior with a minimum value at the stoichiometric region. In all cases there are rather small differences among the kinetics mechanisms results, with the most significant lying at the very rich equivalence ratio for methane mixtures. This agreement between chemical mechanisms is an indication that  $\beta$  is a property for the considered fuel/air mixtures. It should be emphasized that the proposed formulation does not exhibit singular behavior in the stoichiometry region, enabling  $\beta$  to be determined across the mixtures flammability range. For hydrogen/air mixtures the Zel'dovich number varies between 0.8 and 3, whereas it is possible to observe that for methane/air mixtures, the Zel'dovich number varies between 2 and 5.2. For propane mixtures, the Zel'dovich number varies between 2 and 11. The Zel'dovich number for  $\phi = 1$  is  $\beta = 1.0$ , 2.3 and 2.47 for mixtures of hydrogen, methane and propane, respectively. It is interesting to note that, except for very lean or very rich mixtures, the computed Zel'dovich number cannot be considered "large".

In Figs. 5b, 6b and 7b is shown the behavior of the  $\beta'$  parameter, which is defined in Eq. (4) as a function of the equivalence ratio, for the different fuels and baseline detailed chemical kinetic mechanisms. For each of the different fuels considered,  $\beta'$  exhibits a quite different behavior. In the case of hydrogen/air mixtures,  $\beta'$  varies from 0.1 and 1. For these mixtures,  $\beta'$  exhibits a behavior analogous to the Zel'dovich number, i.e., with a minimum around the stoichiometry region. For methane/air mixtures  $\beta'$  varies between 2 and 30 being nearly constant for  $\phi \leq 1$ , but increasing, then decreasing for rich mixtures. Indeed, for very lean mixtures the values vary between 15 and 20 depending on the choice of chemical kinetic mechanism. The significant increase occurs in the region with equivalence ratio between 1 and 1.2. Then, from  $\phi = 1.2$ ,  $\beta'$  decreases to 1.6. Nevertheless, for hydrogen/air and methane/air mixtures, the qualitative variation of  $\beta'$  with  $\phi$  also suggests this could be a property of the mixtures. However, a similar agreement between the different chemical mechanism is not seen in Fig. 7c for the propane/air mixtures, except for  $\phi \geq 1.2$ . Indeed, for mixtures of propane/air, the values of  $\beta'$  vary between 2 and 20, for the USC II Mech only and exhibits a non-monotonic behavior between equivalence ratio 0.6 and 1.2 and, subsequently, a decreasing behavior from equivalence ratios 1.3 up to 1.6. Regarding the different kinetics mechanisms used, the main differences are observed for the hydrocarbon mixtures, i.e., for the methane mixtures around  $\phi = 1.2$  and propane mixtures for  $\phi \leq 1.2$ . Such a qualitative agreement between the different chemical kinetic mechanisms results suggest that  $\beta'$  is a property of the studied mixtures also.

The behavior of the parameter  $n$  with the mixture equivalence ratio is shown in the Figs. 5c, 6c and 7c for the different fuels and kinetic mechanism studied. In the case of hydrogen/air mixtures  $n$  varies from 1.2 to 1.8, peaking at the vicinity of stoichiometry. Even if the qualitative behavior is similar, quantitative differences can be seen for the two chosen mechanisms values for  $\phi \geq 1$ . Furthermore for H<sub>2</sub>/air,  $n$  assumes values significantly smaller than those for the methane and propane mixtures. Indeed, it is possible to observe that, for methane/air mixtures,  $n$  non monotonically varies approximately between 1 and 120, with the highest values close to stoichiometry. For  $\phi \geq 1.3$  the value is almost constant, with  $n \approx 1$ . For the propane/air mixtures, when the San Diego Mechanism is used, the behavior of  $n$  is constant for  $0.6 < \phi < 1.1$ . Beyond this range,  $n$  shows a decreasing behavior up to equivalence ratio 1.2. As with methane mixtures, for  $\phi \geq 1.3$  it presents a constant behavior with values of  $n \approx 1$ .

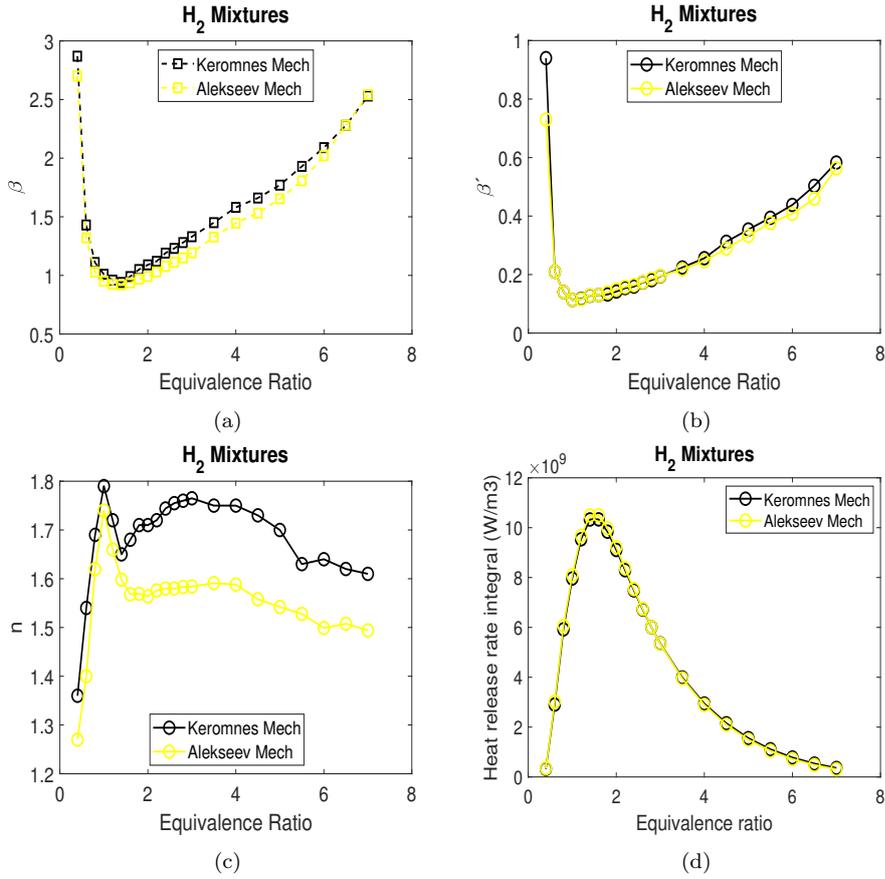


Fig. 5: Results for H<sub>2</sub>/air mixtures with two different kinetics mechanism: Keromnes Mech (black) and Alekseev Mech (yellow). Behavior as a function of the equivalence ratio of (a) Zel'dovich number, (b)  $\beta'$  parameter, (c)  $n$  parameter, (d) Heat release rate normalization integral.

For the sake of completeness, the heat release rate integral of Eq. (2) can be seen in Figs. 5d, 6d and 7d, where the results for the mixtures of hydrogen/air, methane/air and propane/air are represented, respectively. The adequate description of  $I_q$  is indeed crucial for practical flame computations, as is the functional description of the thermodynamic and transport properties, which may be effected using polynomial fits as well, but are not object of this study. As it could have been expected, in these figures, it is possible to observe that the integral of the heat release rate has a behavior similar to the laminar flame front speed, with the maximum in the stoichiometric region.

It is worth mentioning that fits to the above studied parameters are given in the supplementary material.

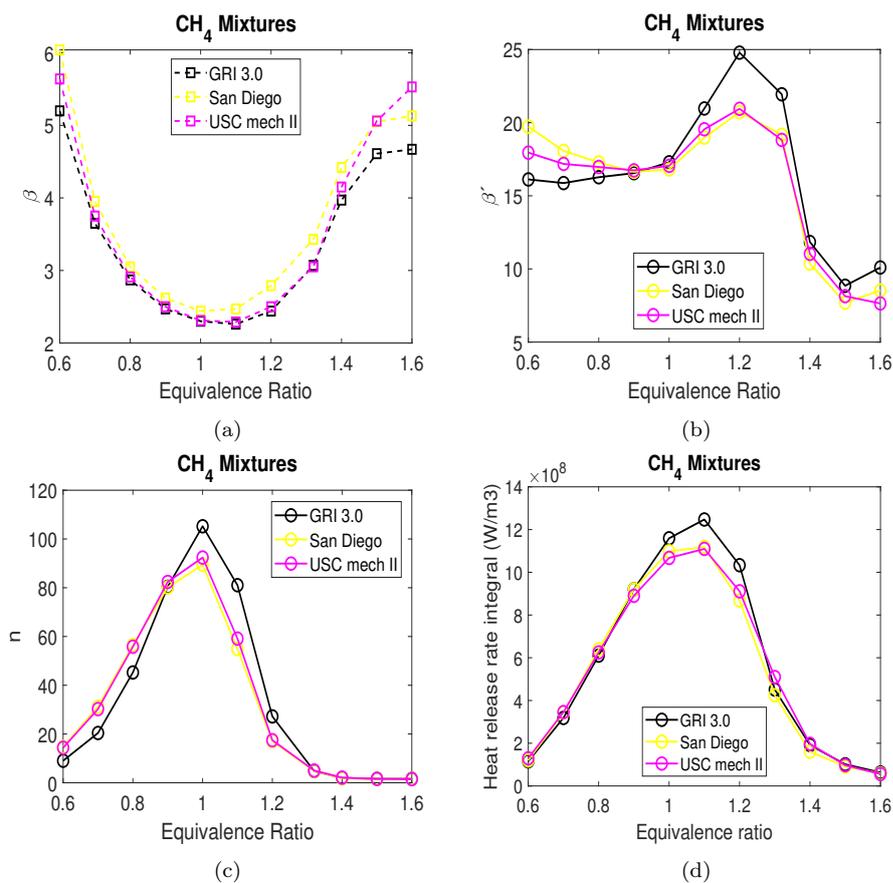


Fig. 6: Results for CH<sub>4</sub>/air mixtures with three different kinetics mechanisms: GRI 3.0 (black), San Diego Mech (yellow) and USC Mech II (magenta). Behavior as a function of the equivalence ratio of (a) Zel'dovich number,  $\beta$ , (b)  $\beta'$  parameter, (c)  $n$  parameter, (d) Heat release rate normalization integral.

#### 4.2 CO<sub>2</sub> diluted hydrocarbon/air mixtures

To further assess the variation of Eq. (5) parameters with the mixture studied, CO<sub>2</sub> diluted methane or propane are now considered. The chemical kinetic mechanisms of GRI 3.0 Mech, USC II Mech and San Diego Mech are considered. The specific choice of dilution percentage is motivated by the relevance of such diluted fuels to the gas mixtures produced by mature oil and gas wells, for instance. Therefore, the CO<sub>2</sub> percentages used here refers to the fuel, not the mixture, dilution.

Figures 8a and 9a present the results found for the Zel'dovich number in mixtures of methane/air/diluent and propane/air/diluent with the fuel diluent varying between 0 % and 75 %. For both fuel/air mixtures used,  $\beta$  increases with the fuel dilution percentage. For instance, for the methane mixtures the minimum ( $\phi = 1$ ) Zel'dovich number is 2.3, 2.63 and 3.4 for 0 %, 25% and 50% CO<sub>2</sub> dilution,

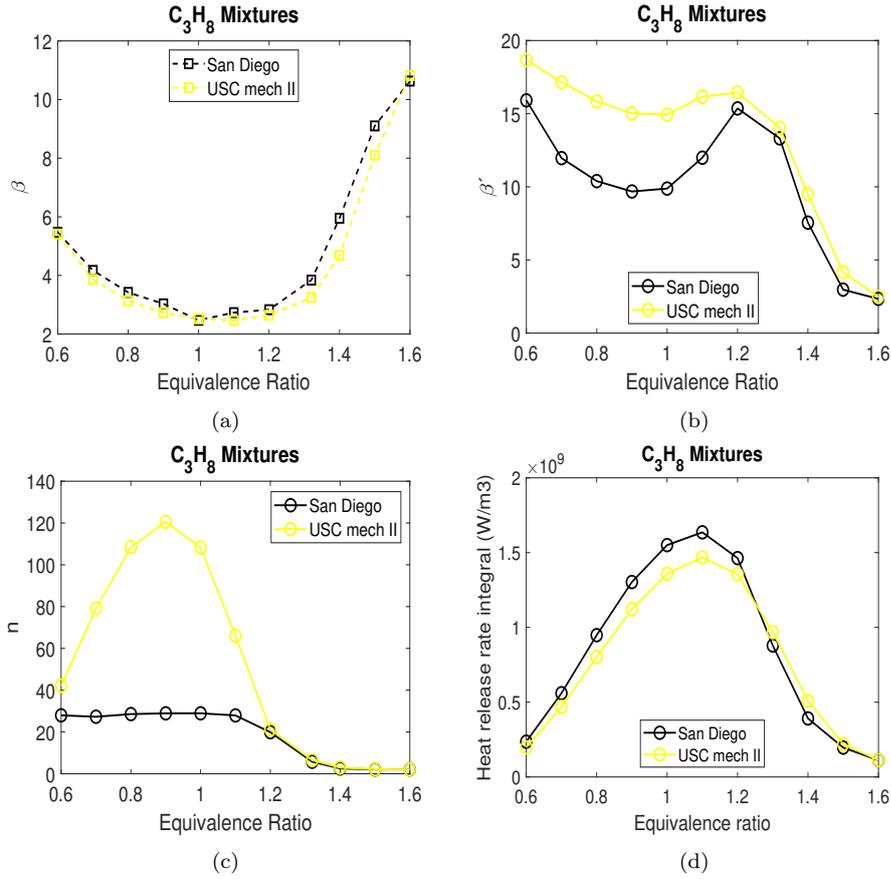


Fig. 7: Results for  $C_3H_8$ /air mixtures with two different kinetics mechanism: San Diego Mech (black) and USC Mech II (yellow). Behavior as a function of the equivalence ratio of (a) Zel'dovich number,  $\beta$ , (b)  $\beta'$  parameter, (c)  $n$  parameter, (d) Heat release rate normalization integral.

respectively. In addition, in the propane mixtures the values for 0 %, 25%, 50% and 75% are 2.47, 3.03, 3.42 and 4.64, respectively.

It is interesting to note that both parameters  $\beta'$  and  $n$ , in Figs. 8b, 8c, 9b and 9c, are slightly dependent on the dilution of the fuel by  $CO_2$  in both methane mixtures and propane mixtures. Furthermore, it is notable that for  $\phi \ll 1$  or  $\phi \gg 1$  the values of  $\beta'$  are very similar for both fuel mixtures. Unsurprisingly, the heat release rate integral decreases with the fuel dilution percentage by  $CO_2$  throughout the equivalence ratio range, as is evidenced in Figs. 8d and 9d.

For the sake of completeness, the Euclidean norm of the heat release rate error between the numerical simulation with detailed kinetic mechanisms and the proposed methodology is presented in Figs. 10a and 10b. For methane/air/diluent mixtures the error varies between 1 % and 5 %. For propane/air/diluent mixtures,

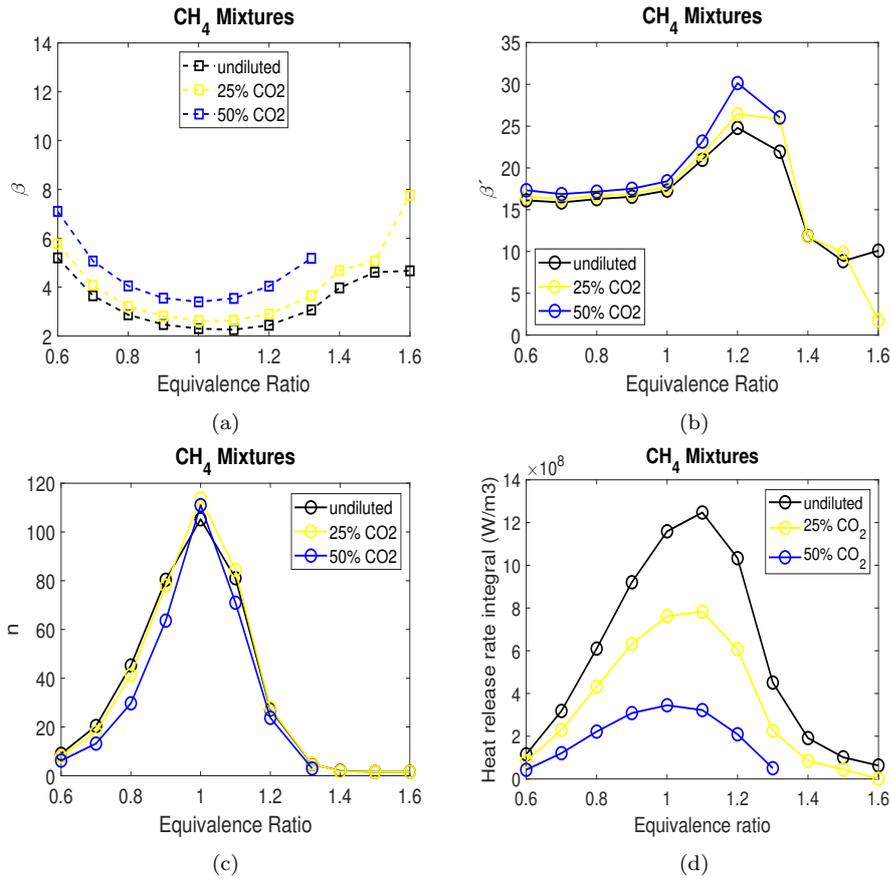


Fig. 8: Results for CH<sub>4</sub>/CO<sub>2</sub>/air mixtures behavior as a function of the equivalence ratio. (a) Zel'dovich number,  $\beta$ , (b)  $\beta'$  parameter, (c)  $n$  parameter, (d) Heat release rate normalization integral.

it varies between 2 % and 7 %. A remarkable feature is that the error value is nearly independent of the fuel dilution percentage.

## 5 Conclusion

A new formulation for a single-step reaction rate is proposed. This formulation is controlled by four non dimensional parameters: (1) the equilibrium obtained temperature increase, (2) the Zel'dovich number, (3) one describing the heat release initial decay beyond the maximum value and (4) another controlling the final stages of the heat release rate process. The latter three are obtained via an optimization that minimizes the error with respect to the heat release rate of a laminar premixed flame expressed in terms of a temperature based reactive scalar. This rate is here determined numerically using detailed chemical kinetics mechanisms.

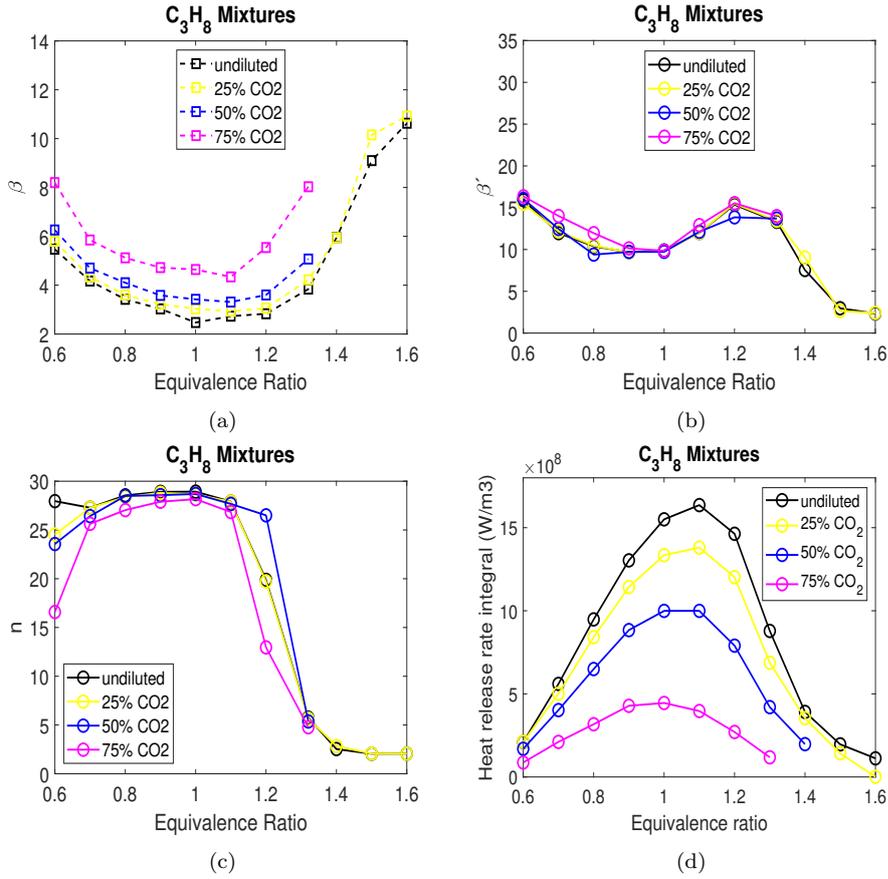


Fig. 9: Results for  $C_3H_8/CO_2/air$  mixtures behavior as a function of the equivalence ratio. (a) Zel'dovich number,  $\beta$ , (b)  $\beta'$  parameter, (c)  $n$  parameter, (d) Heat release rate normalization integral.

The proposed formulation was shown to qualitatively describe the heat release rate as a function of this scalar for three different fuels,  $H_2$ ,  $CH_4$  and  $C_3H_8$ , and for several baseline detailed chemistry mechanisms. Furthermore, the Euclidean norm of the heat release rate error between the numerical simulation with detailed kinetic mechanisms and the proposed formulation was determined for equivalence ratios ranging between 0.6 and 1.6. For methane mixtures, this error varies between 1 % and 5 %. For propane mixtures, it varies between 2 % and 7 %. The  $H_2$  mixtures exhibits errors between 6 % and 15 %. Such error values are similar, in magnitude, with those with which laminar flame speeds are measured.

For all the mixtures studied the heat release rate integral behaves similarly to the laminar flame front speed, with the maximum in the stoichiometric region decreasing with dilution addition. The computed Zel'dovich number exhibits with a minimum at the stoichiometric region and increases with dilution  $CO_2$  for all fuels studied.

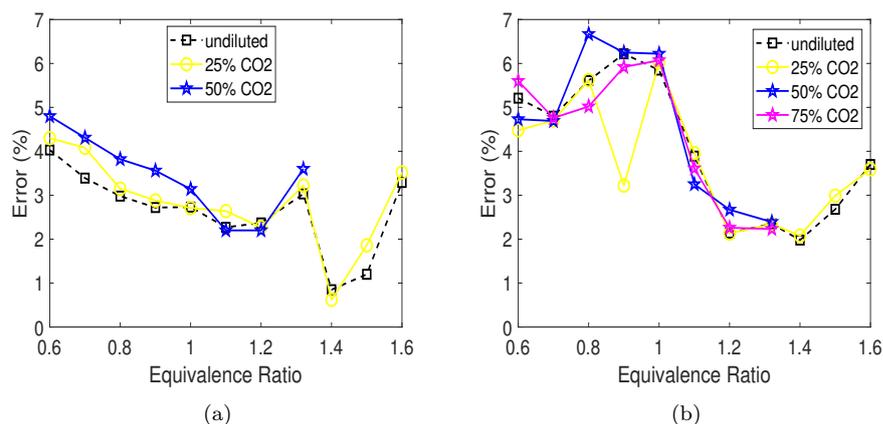


Fig. 10: Error comparison between the Eq. (5) results and the simulation using chemical kinetics mechanisms: (a) CH<sub>4</sub>/CO<sub>2</sub>/air mixtures, (b) C<sub>3</sub>H<sub>8</sub>/CO<sub>2</sub>/air mixtures.

The first new parameter,  $\beta'$ , presents a different behavior for the fuels studied. Indeed, for H<sub>2</sub> it is similar to that of the Zel'dovich number, but the same was not seen for the hydrocarbons/air mixtures. For the latter this parameter is independent of CO<sub>2</sub> dilution. The second new parameter,  $n$ , also shows a different behavior for all fuels, but is not significantly influenced by CO<sub>2</sub> dilution. This parameter also shows values significantly greater for hydrocarbons mixtures than for hydrogen mixtures, i.e., for methane it presents a maximum of the order of 110 and for hydrogen it presents a maximum around 1.8. The obtained results suggests that the new formulation parameters could be considered as properties of the reactive mixtures and not numerical artifacts.

The proposed formulation is still to be applied to solving combustion problems involving the studied gas mixtures. Interesting questions for further studies are the extension to different pressure ranges, to fuels consisting of a mixture of species, such as H<sub>2</sub>/CO, and to larger molecular weight hydrocarbons, which may exhibit a negative temperature coefficient dependency. Furthermore, a posteriori testing of the developed reaction rate formulation is still to be performed, for instance, by determining the laminar flame speed of the studied mixtures.

**Acknowledgements** This work was supported by Petrobras contract no. 5900.0111688.19.9 under the technical monitoring of Dr. P. R. Pagot. Support was also received from Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brazil) under the Research Grant No. 304444/2018-9. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001. This work was performed while L.F. Figueira da Silva was on leave from the Institut Pprime (CNRS, France). Helpful discussions with Dr. Nabiha Chaumeix (CNRS, France) are gratefully acknowledged.

## References

1. Chemical-Kinetic Mechanisms for Combustion Applications, San Diego Mechanism web page, Mechanical and Aerospace Engineering (Combustion Research), University of California at San Diego. URL <http://combustion.ucsd.edu>
2. Alekseev, V.A., Christensen, M., Konnov, A.A.: The effect of temperature on the adiabatic burning velocities of diluted hydrogen flames: A kinetic study using an updated mechanism. *Combust. Flame* **162**, 1884–1898 (2015). DOI <https://doi.org/10.1016/j.combustflame.2014.12.009>
3. ANP: Estudo sobre o aproveitamento do gás natural do pré-sal (2020). Available in: <http://www.anp.gov.br/arquivos/estudos/aproveitamento-gn-pre-sal.pdf>, Accessed in October 18<sup>th</sup> 2020
4. Bezerra, M.A., dos Santos, Q.O., Santos, A.G., Novaes, C.G., Ferreira, S.L.C., de Souza, V.S.: Simplex optimization: A tutorial approach and recent applications in analytical chemistry. *Microchem. J.* **124**, 45–54 (2016). DOI [10.1016/j.microc.2015.07.023](https://doi.org/10.1016/j.microc.2015.07.023)
5. Cailler, M., Darabiha, N., Veynante, D., Fiorina, B.: Building-up virtual optimized mechanism for flame modeling. *P. Combust. Inst.* **36**, 1251–1258 (2017). DOI <https://doi.org/10.1016/j.proci.2016.05.028>
6. Carbajal-Carrasco, L.A., Bouali, Z., Mura, A.: Optimized single-step (OSS) chemistry for auto-ignition of heterogeneous mixtures. *Combust. Flame* **227**, 11–26 (2021). DOI [10.1016/j.combustflame.2020.12.026](https://doi.org/10.1016/j.combustflame.2020.12.026)
7. Clavin, P.: Dynamic behavior of premixed flame fronts in laminar and turbulent flows. *Prog. Energ. Combust.* **11**, 1–59 (1985)
8. Er-raiy, A., Bouali, Z., Réveillon, J., Mura, A.: Optimized single-step (OSS) chemistry models for the simulation of turbulent premixed flame propagation. *Combust. Flame* **192**, 130–148 (2018). DOI [10.1016/j.combustflame.2018.01.038](https://doi.org/10.1016/j.combustflame.2018.01.038)
9. Konnov, A.A., Mohammad, A., Kishore, V.R., Kim, N.I., Prathap, C., Kumar, S.: A comprehensive review of measurements and data analysis of laminar burning velocities for various fuel+air mixtures. *Prog. Energ. Combust.* **68**, 197–267 (2018). DOI [10.1016/j.pecc.2018.05.003](https://doi.org/10.1016/j.pecc.2018.05.003)
10. Kéromnès, A., Metcalfe, W.K., Heufer, K.A., Donohoe, N., Das, A.K., Sung, C.J., Herzler, J., Naumann, C., Griebel, P., Mathieu, O., Krejci, M.C., Petersen, E.L., Pitz, W.J., Curran, H.J.: An experimental and detailed chemical kinetic modeling study of hydrogen and syngas mixture oxidation at elevated pressures. *Combust. Flame* **160**, 995–1011 (2013). DOI <https://doi.org/10.1016/j.combustflame.2013.01.001>
11. Smith, G.P., Golden, D.M., Frenklach, M., Moriarty, N.W., Eiteneer, B., Goldenberg, M., Bowman, C.T., Hanson, R.K., Song, S., Gardiner, W.C., Lissianski, V.V., Qin, Z.: GRI-Mech 3.0. URL [http://www.me.berkeley.edu/gri\\_mech/](http://www.me.berkeley.edu/gri_mech/)
12. Spendley, W., Hext, G.R., Himsforth, F.R.: Sequential application of simplex designs in optimisation and evolutionary operation. *Technometrics* **4**, 441–461 (1962). DOI [10.1080/00401706.1962.10490033](https://doi.org/10.1080/00401706.1962.10490033)
13. Wang, H., You, X., Joshi, A.V., Davis, S.G., Laskin, A., Egolfopoulos, F., Law, C.K.: USC Mech Version II. High-Temperature Combustion Reaction Model of H<sub>2</sub>/CO/C<sub>1</sub>-C<sub>4</sub> Compounds. URL [http://ignis.usc.edu/USC\\_Mech\\_II.htm](http://ignis.usc.edu/USC_Mech_II.htm)
14. Westbrook, C.K., Dryer, F.L.: Chemical kinetic modeling of hydrocarbon combustion. *Prog. Energ. Combust.* **10**, 1–57 (1984). DOI [10.1016/0360-1285\(84\)90118-7](https://doi.org/10.1016/0360-1285(84)90118-7)