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# A new single-step mechanism for partially premixed hydrocarbon combustion

Alejandro Millán-Merino\*, Said Taieb, Pierre Boivin

*Aix Marseille Univ, CNRS, Centrale Marseille, M2P2, Marseille, France*

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## Abstract

We propose a new single-step mechanism for the combustion of arbitrary hydrocarbons and alcohols. Unlike most single-step models, no tabulation is required, as the method builds upon a new analytical description of the thermochemical equilibrium of fuel-oxidizer mixtures including dihydrogen and carbon monoxide – two species usually discarded in one-step descriptions – yielding correct adiabatic temperature. The single-step chemistry includes varying stoichiometric coefficients, ensuring a convergence towards thermochemical equilibrium regardless of the local state. The reaction rate is then carefully adjusted to reproduce accurately premixed flames. To tackle ignition simultaneously, an additional passive scalar advection-diffusion-reaction equation is introduced, with a rate fitted on ignition delays. The scalar then serves as an efficiency to modify the single-step reaction rate in autoignition configurations. The obtained scheme is then validated for a wide range of equivalence ratios on homogeneous reactors, premixed flames, a triple flame, and a counterflow diffusion flame. The new analytical thermochemical equilibrium formulation may also serve in speeding up infinitely fast chemistry calculations.

*Keywords:* Single-step chemistry; Laminar flame speed; Ignition delay time; Partially premixed combustion; Hydrocarbon combustion

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## Introduction

In modeling combustion chambers, implementation of detailed chemistry is a significant challenge for two reasons. First, the number of species can be considerable (e.g., 207 for kerosene fuel [1]), drastically increasing the number of degrees of freedom at each grid point (note that the 3D Navier-Stokes system only counts 5 degrees of freedom). Second, the number of reaction rates to be computed can also be important (1673 for kerosene [1]). For both, the number of species and the number of reactions tend to increase with time, as a better understanding of detailed kinetic processes is acquired.

In reduced chemistry development, the literature [2–6] generally agrees on the following objectives. The first and foremost objective is to accurately reproduce the oxidation heat release, e.g., the burnt gases temperature. This problem is purely a Gibbs energy minimization problem and is therefore independent of the kinetics. In that sense, infinitely fast chemistry schemes are reduced chemistry models that only answer the first objective.

The second objective is to recover a specific set of kinetic properties. These can involve, depending on the model: premixed flame burning velocities [3, 7] and thicknesses [5], thermo-acoustic instabilities [8], ignition delays [9–11], temperature in diffusion flames, strain rate at extinction, detonation structures [12]...

In tackling the first objective, two main strategies exist. (i) The first is to include in the description the minimal set of species allowing to reach the desired accuracy. For lean premixed hydrocarbons, for instance, considering only the major species ( $C_nH_m$ ,  $O_2$ ,  $CO_2$ ,  $H_2O$ ) leads to reasonable burnt gas temperatures [2, 5]. For most hydrocarbons combustion chambers, however, the mixture is only partially premixed, and albeit lean on average, rich and hot regions can exist and must be carefully treated, as they are, e.g., where soot is produced [13]. It is therefore required to add at least a species (e.g., CO in [3, 14]), and a reaction. As noted by Er-raiy et al. [5],  $H_2$  is also required to accurately reproduce burnt temperatures of hydrocarbon-air mixtures, adding yet another species and reaction. (ii) The second strategy consists of altering, one way or another, the heat release or thermodynamic properties controlling the heat release. For instance, Fernández-Tarrazo et al. [2] directly modified the heat release of rich mixtures in the energy equation, while others opted for creating a virtual species for which thermodynamic properties are tabulated from an extensive set of species [5, 6].

Regarding the second objective, several options can be found in the literature recovers the kinetic properties. Starting from the detailed chemistry elementary rates, partial-equilibrium and quasi-steady-state approximations are used in fully analytically derived mechanisms [4, 15], while more systematic methods study the kinetic source term jacobian to obtain the main chemical time-scales (see, e.g., [16–18]). Very

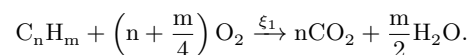
short mechanisms (1-2 steps) tend to resort directly to carefully fitted rates to recover the desired set of kinetic properties [5, 6].

In this study, we propose a new method for constructing single-step mechanisms and apply it to  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ ,  $CH_3OH$ ,  $C_2H_5OH$ , and kerosene surrogate combustion. Section 1 derives a new asymptotic analysis of the thermodynamic equilibrium, which allows considering a single-step mechanism without appreciable loss of accuracy for the burnt gases temperature in the rich region. The formalism proposed can also drastically reduce the cost of infinitely fast chemistry solvers by avoiding the costly Gibbs energy minimization process. Section 2 introduces a novel method to correct the premixed flame velocity based on a Von-Karman analysis. The method relies only on fitting nine parameters based on detailed chemistry calculations or experimental data, but does not require any tabulation. Section 3 presents a new passive scalar approach based on an eigenvalue study of the Jacobian similar to [16–19]. The passive scalar serves as an efficiency function in the single-step chemistry and allows to recover ignition characteristics, in addition to partially-premixed phenomena. Section 4 presents additional evaluations, and conclusions are drawn in Section 5. Supplementary Material includes all parameters and validations for  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ ,  $CH_3OH$ ,  $C_2H_5OH$ , and a fuel surrogate for kerosene  $C_{9.74}H_{20.05}$ .

## 1. Asymptotic analysis of the equilibrium

### 1.1. Leading order solution

The simplest equilibrium approximation may be obtained by assuming total oxidation:



Consider a mixture initially consisting of  $n_{C_nH_m}^0 = \phi$ , and  $n_{O_2}^0 = n + m/4$ , where  $n_i^0$  is the initial mole number of the  $i^{th}$  species, allowing for  $\phi$  to correspond to the classical equivalence ratio definition

$$\phi = \left(n + \frac{m}{4}\right) \frac{n_{C_nH_m}}{n_{O_2}}$$

Assuming total oxidation is equivalent to limiting the reaction molar advancement  $\xi_1$  by the deficient reactant as

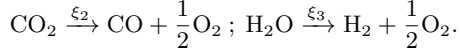
$$\xi_1 = \min(\phi, 1). \quad (1)$$

From the knowledge of  $\xi_1$ , the equilibrium composition is fully characterized. In particular, the burnt gases temperature can be computed from this composition under classical assumptions (e.g., constant pressure and entropy or constant volume and internal energy) [20].

### 1.2. Recombination reactions extension

Above, we have only assumed that the mixture consists of the principal reactants ( $C_nH_m$ ,  $O_2$ ), products ( $CO_2$ ,  $H_2O$ ), and inert gases (e.g.,  $N_2$ ). However,

equilibrium properties of hydrocarbon-air blends highly depend on the set of species considered [2, 3, 5], and it has been corroborated that for typical hydrocarbon-air mixtures at standard conditions at least (CO, H<sub>2</sub>) should be taken into account [5]. Their presence can be included by considering the two dissociation reactions



Species mole numbers are related to reaction molar advancement  $\xi_k$  as

$$n_i = n_i^0 + \sum_{k=1}^3 \nu_{k,i} \xi_k \quad (2)$$

with  $\nu_{k,i}$  the net stoichiometric coefficient (positive for the products and negative for the reactants) in reaction  $k$ . For a complete depletion of C<sub>n</sub>H<sub>m</sub>, we now obtain

$$\xi_1 = \phi, \quad \xi_{ox} = \xi_2 + \xi_3 = \max(\xi_{ox}^0, 0)$$

with

$$\xi_{ox}^0 = \frac{4n+m}{2}(\phi - 1).$$

being the leading order term in the recombination reaction advancement. Note that  $\xi_1$  upper limit is now increased compared to the 1-step description of the example because the two recombination reactions advancement leave more O<sub>2</sub> available for the complete C<sub>n</sub>H<sub>m</sub> oxidation. At this stage, there are two options. (i) We can assume a value for the relative importance of the recombination reactions (i.e.,  $\xi_2 = \beta \xi_{ox}$ ), or (ii) take into account the equilibrium constants to compute ( $\xi_2, \xi_3$ ), as done afterward. Once this is accomplished,  $\xi_1, \xi_2$ , and  $\xi_3$  are known, and the equilibrium is fully defined in the same way as in the previous example.

### 1.3. Asymptotic correction for $\xi_{ox}$

Reminding that exact thermodynamic equilibrium is attained through Gibbs free energy [21]. The total Gibbs free energy of the mixture,  $G$ , is minimal when the condition  $\partial G / \partial n_i = 0$  is satisfied for each species. Combining the constraints between themselves and with Eq. (2) reaches the equilibrium conditions for the recombination reactions as

$$K_2 = \frac{(n_{\text{CO}}^0 + \xi_2) \sqrt{\frac{4n+m}{2}(1-\xi_1) + \xi_{ox}}}{(n_{\text{CO}_2}^0 + n\xi_1 - \xi_2) \sqrt{2N^0 + \frac{m-4}{2}\xi_1 + \xi_{ox}}}, \quad (3)$$

$$K_3 = \frac{(n_{\text{H}_2}^0 + \xi_3) \sqrt{\frac{4n+m}{2}(1-\xi_1) + \xi_{ox}}}{(n_{\text{H}_2\text{O}}^0 + \frac{m}{2}\xi_1 - \xi_3) \sqrt{2N^0 + \frac{m-4}{2}\xi_1 + \xi_{ox}}}, \quad (4)$$

with equilibrium constants  $K_k$  introduced as

$$K_k = \exp\left(-\sum_{i=1}^7 \nu_{k,i} \frac{g_i}{RT}\right) \left(\frac{P^0}{P}\right)^{\sum_{i=1}^7 \nu_{k,i}}. \quad (5)$$

where  $g_i$  is the specific Gibbs energy of the  $i^{\text{th}}$  species,  $\mathcal{R}$  is the ideal gas constant, and  $P^0$  and  $N^0 = \sum_{i=1}^7 n_i^0$  are the reference pressure and the initial mole number concentration. The equilibrium constants are evaluated at the equilibrium temperature and pressure,  $T$  and  $P$ , respectively. Let us now assume that oxidation reaction 1 is complete ( $K_1 \gg 1$ ) while the two recombination equilibrium constants are small ( $K_2, K_3 \ll 1$ ). At leading order,  $K_2 = K_3 = 0$ , we recover exactly the solution from Eq. (1) under the same assumptions. For the first correction order, equations (3) & (4) can be recast as

$$K_{ox} = (\xi_{ox} + n_{ox}^0) \sqrt{\xi_{ox} - \xi_{ox}^0} \quad (6)$$

and

$$K_r = \frac{n_{\text{CO}}^0 + \xi_{ox} - \xi_3}{n_{\text{H}_2}^0 + \xi_3} \frac{n_{\text{H}_2\text{O}}^0 + \frac{m}{2}\phi - \xi_3}{n_{\text{CO}_2}^0 + n\phi - \xi_{ox} + \xi_3} \quad (7)$$

where the following definitions are introduced for simplicity:  $n_{ox}^0 = n_{\text{CO}}^0 + n_{\text{H}_2}^0$ ,  $K_r = K_2/K_3$ , and

$$K_{ox} = \left[ (n_{\text{CO}_2}^0 + n\phi) K_2 + \left( n_{\text{H}_2\text{O}}^0 + \frac{m}{2}\phi \right) K_3 \right] \sqrt{2N^0 + \frac{m-4}{2}\phi}.$$

This set of equations is now decoupled and has an explicit solution. The first equation is a third-order polynomial, while the other is a second-order polynomial. The result of Eq. (6) has a single real solution satisfying the physical constraints  $\xi_{ox} \geq 0$  and  $\xi_{ox} \geq (2n + \frac{m}{2})(\phi - 1)$ :

$$\xi_{ox} = \frac{\Theta}{3} + \frac{(\xi_{ox}^0 - n_{ox}^0)^2}{3\Theta} - \frac{\xi_{ox}^0 + 2n_{ox}^0}{3} \quad (8)$$

with

$$\Theta = \frac{1}{\sqrt[3]{2}} \sqrt[3]{27K_{ox}^2 + \sqrt{27R_o} - 2(\xi_{ox}^0 - n_{ox}^0)^3}$$

$$R_o = 27K_{ox}^4 - 4K_{ox}^2(\xi_{ox}^0 - n_{ox}^0)^3.$$

These expressions are valid when  $R_o \geq 0$ , but a similar formula is provided in supplementary material when  $R_o < 0$ .

For equation (7), the solution that satisfies the physical description of the problem is

$$\xi_3 = \frac{\sqrt{\mathcal{C}_1^2 + 4(K_r - 1)\mathcal{C}_2} + \mathcal{C}_1}{2(K_r - 1)} \quad (9)$$

with

$$\begin{aligned} \mathcal{C}_1 &= n_{\text{CO}}^0 + n_{\text{H}_2\text{O}}^0 + \xi_{ox} + \frac{m}{2}\phi \\ &\quad + (n_{\text{H}_2}^0 + n_{\text{CO}_2}^0 - \xi_{ox} + n\phi) K_r \\ \mathcal{C}_2 &= (n_{\text{CO}}^0 + \xi_{ox})(n_{\text{H}_2\text{O}}^0 + \frac{m}{2}\phi) \\ &\quad - n_{\text{H}_2}^0(n_{\text{CO}_2}^0 - \xi_{ox} + n\phi) K_r. \end{aligned}$$

The equilibrium composition ( $\xi_1, \xi_2, \xi_3$ ) is now defined explicitly through Eqs. (1), (8), & (9). Note, however, that an equilibrium temperature estimate is still required to compute the equilibrium constants (5). In the following, we use the value of  $T$  obtained from the simplified problem of Sec. 1.2, in order to keep the formulation fully explicit. It should be remarked that a higher accuracy may be achieved through a limited number of iterations.

Equilibrium properties of methane-air flame obtained with the present method are compared in Fig. 1 with constant pressure equilibrium computations made with the Cantera suite using the 7 species mechanism. Excellent accuracy is achieved for temperature values when recombination equations are used. For mole fraction profiles, it is clear that the asymptotic correction provides a better agreement with the reference capturing the correct dependency with the equivalence ratio, even in the vicinity of stoichiometry.

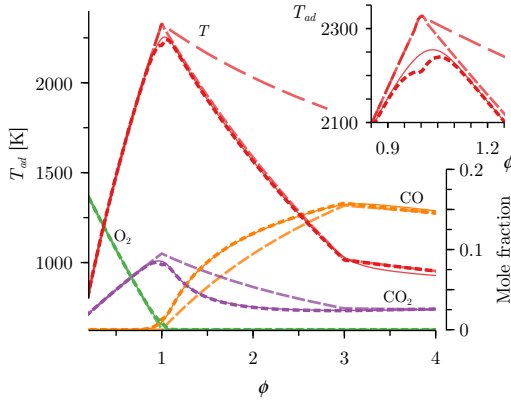
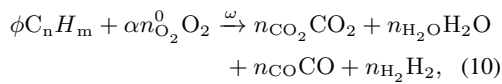


Figure 1: Adiabatic temperature and equilibrium mole fraction profiles versus the equivalence ratio of methane-air mixtures at constant pressure,  $P = 1$  bar, and initial gas temperature,  $T^0 = 300$  K. Solid line: Cantera equilibrium computations with 7 species; Long dashed line: Leading order solution, Eq. (1) and  $\xi_2 = \xi_3 = 0$ ; Short dashed line: Recombination leading order, Eq. (1) with  $\xi_{\text{ox}}^0$  and  $\xi_2 = 0.32\xi_{\text{ox}}^0$ ; Dotted line: Recombination asymptotic correction, Eqs. (1), (8), & (9).

Note that a similar agreement is obtained for  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ , and kerosene  $\text{C}_{9.74}\text{H}_{20.05}$ . Through minor changes, provided in the Supplementary Material, the formulation can also encompass alcohols  $\text{C}_n\text{H}_m\text{OH}$  or any partially oxygenated hydrocarbon  $\text{C}_n\text{H}_m\text{O}_p$ .

## 2. Kinetic mechanism

Let us now define a one-step mechanism as



where  $\alpha = (n_{\text{O}_2}^0 - n_{\text{O}_2})/n_{\text{O}_2}^0$  is the oxygen ratio consumption and  $n_i$  are the stoichiometric coefficients

chosen to match the equilibrium calculated in Sec. 1, taking the local pressure and enthalpy to estimate the equilibrium constants (5).

From this definition, it is clear that no matter the reaction rate, the mixture composition will tend towards the equilibrium composition, allowing for an accurate value of  $T_b$ . This strategy avoids the need to define a virtual species with ad-hoc thermodynamic parameters [5, 6].

Next, let us introduce a general reaction rate for the global reaction (10) as

$$\omega = C_{\text{C}_n\text{H}_m}^{s_F} C_{\text{O}_2}^{s_O} K \text{ with } K = B e^{-\frac{T_a}{T}}, \quad (11)$$

where reaction exponents ( $s_F$  and  $s_O$ ), pre-exponential factor  $B$  and activation temperature  $T_a$  are constant to be defined hereafter.

As pointed out by Franzelli et al. [3], there exists a direct relation between the laminar flame velocity  $V_L$  pressure dependence  $V_L(P) = V_L(P_0) (P/P_0)^\gamma$  and the global order of the reaction through  $s = s_F + s_O = 2(\gamma + 1)$ . Having defined  $s$  from this relation based on detailed chemistry results, we then set on trial and error basis  $s_F = s_O = s/2$ . Following the strategy of [2, 3, 5, 6],  $(B, T_a)$  are then fitted to obtain accurate laminar flame velocity predictions in the lean limit. Results obtained for methane/air mixtures are reproduced in Fig. 2, labeled 1-step N.C.

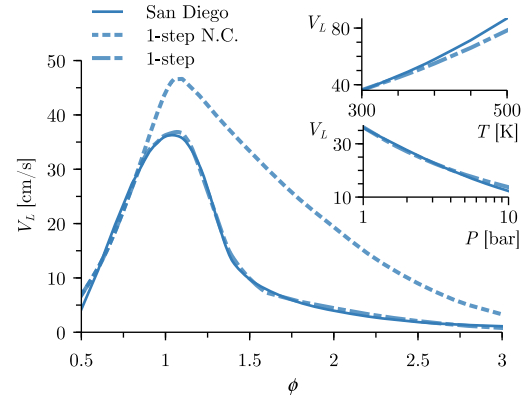


Figure 2: Laminar flame velocity versus equivalence ratio for methane-air mixtures at initial conditions  $T = 300$  K and  $P = 1$  bar. Inset plots represent  $V_L$  variations with initial conditions,  $T$  and  $P$ , for stoichiometric mixtures. Solid line: San Diego, Dashed line: single-step mechanism without correction function, Dot-dash line: present mechanism with the function correction,  $\mathcal{F}$ .

Comparing the obtained results with the reference solution, it is clear that  $V_L$  is overestimated by the single-step mechanism.

Since the global reaction (10) is complete, we may adapt the classical asymptotic solution of Zeldovich, Frank-Kamenetskii, and von Karman to the

reaction rate (11) as

$$V_L^2 = 2\Gamma(s+1) \left(n + \frac{m}{4}\right)^s \left(\frac{T_b}{T_b - T_u}\right)^{s+1} \frac{\rho_b^s}{\rho_u^2} \frac{\lambda}{c_p} \left(\frac{T_b}{T_a}\right)^{s+1} Be^{-\frac{T_a}{T_b}} \left(\frac{\phi}{n_{O_2}^0}\right)^{s_F} \quad (12)$$

with  $\Gamma(s+1)$  the gamma function. From (12), it is clear that the error on  $V_L^2$  may be exactly corrected through the introduction of a correction function  $\mathcal{F} = (V_L^{NC}/V_L^{ref})^2$  in the reaction rate

$$\omega = C_{O_2}^{s/2} C_{C_nH_m}^{s/2} \mathcal{F} K, \quad (13)$$

where  $\mathcal{F}$  gathers the change that  $s_F$  suffers from passing from lean to rich flames. In practice, we found that defining  $\mathcal{F}$  as the product of two  $\phi$ -dependent corrections  $\mathcal{F}_i$  defined as

$$\mathcal{F}_i = 1 - \Delta r_{V_L,i} \left[ 1 - \tanh\left(-\frac{4}{n_{O_2}^0} \frac{\phi - \phi_i}{\Delta\phi_i}\right) \right] \quad (14)$$

is sufficient, with only  $(\Delta r_{V_L,i}, \Delta\phi_i, \text{ and } \phi_i)$  as free parameters. The correction  $\mathcal{F} = \mathcal{F}_1\mathcal{F}_2$  is defined such as its limit is 1 in the lean limit (no correction) and  $(V_L^{NC}/V_L^{ref})^2$  in the rich limit. Separating  $\mathcal{F}$  into two separate functions  $(\mathcal{F}_1, \mathcal{F}_2)$  allows to correct both the laminar flame speed value in the rich limit (via  $\mathcal{F}_1$ ) and at stoichiometry (via  $\mathcal{F}_2$ ), a strategy close to the one proposed by Franzelli et al. [3].

The effect of the correction can readily be seen in Fig. 2, showing that the correction function  $\mathcal{F}$  in (13) successfully corrects the flame velocity dependence over a wide range of equivalence ratios. A similar agreement is shown in Fig. 3, for a wide variety of fuel-air blends ( $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ ,  $CH_3OH$ ,  $C_2H_5OH$ , using the San Diego mechanism as a reference [22] and a fuel surrogate for kerosene  $C_{9.74}H_{20.05}$  obtaining the values from [3]). The model free parameters ( $B$ ,  $T_a$ ,  $s$ ,  $\Delta r_{V_L,1}$ ,  $\Delta\phi_1$ ,  $\phi_1$ ,  $\Delta r_{V_L,2}$ ,  $\Delta\phi_2$ , and  $\phi_2$ ) are provided for each fuel in Supplementary Material.

### 3. Coupling ignition delay times with laminar flame computations

So far, the mechanism proposed allows to accurately reproduce burnt gas temperature (via the study of Sec. 1), and premixed combustion characteristics (Sec. 2). Hereafter, we propose a simple approach allowing to also deal with ignition phenomena as occurring, e.g., in lifted flames.

As duly noted in the literature, chemical time-scales associated with ignition are different from those of premixed flame propagation and tackling both phenomena with a single step is non-trivial [3, 23, 24].

It is well understood that the ignition process can be well represented by chained reactions building up a radical pool, which eventually will trigger heat-releasing reactions [18, 19, 25, 26]. The exponential character

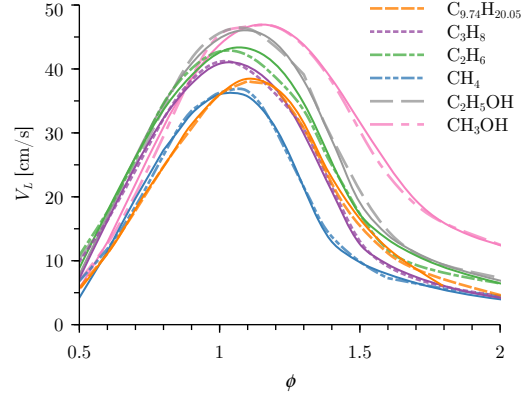


Figure 3: Laminar burning velocities versus equivalence ratio comparison for the reference mechanism and the 1-step model. Initial conditions for the fuel-air mixtures are  $T = 300K$  and  $P = 1bar$ . Solid lines: reference mechanism [3, 22]; Dashed lines: present 1-step mechanism.

arises from the fact that the reaction rate is proportional to the radical pool concentration, leading to an exponential evolution of radical concentrations [19]. Indeed, such dependence is impossible to obtain with the single-step considered (10) [24]: since no radical carrying the chain-reaction is included [18, 26], the rate  $\omega$  (11) only depends on reactants concentrations which are constant in the first approximation.

Let us now illustrate the difficulty of using single-step chemistry for ignition events. As Carbajal-Carrasco et al. remind in [23], the asymptotic analysis describes the dependence of the ignition delay time or autoignition time as

$$\tau_{ig} \propto \frac{T_u^2}{T_a(T_b - T_u)} \frac{1}{K}.$$

It is then straightforward to derive the Arrhenius constant  $K_{ig}$  required for  $\omega$  in Eq. (11) to obtain accurate ignition times. Unfortunately, because of the different time scales involved,  $K_{ig}$  strongly departs from  $K_{V_L}$ , the rate optimized in Sec. 2.

Ignition times predictions as obtained with both  $K_{ig}$  and  $K_{V_L}$  are presented in Fig. 4, confirming the aforementioned point: chemical time-scales relative to propagation and ignition are very different, and the rate optimized for propagation leads to ignition times several orders of magnitude shorter than with detailed chemistry. Similar results are obtained with the other considered fuels.

Two main strategies to circumvent this issue may be found in the literature. One strategy consists in fitting two sets of rates ( $K_{V_L}$  for flame propagation,  $K_{ig}$  for ignition), and switching smoothly between the two based on, e.g., the fresh gases reconstructed temperature [23]. Nonetheless, transitioning between the two can be tricky, and no complex configuration including simultaneously propagation and ignition modes is reported [23, 27]. This approach remains appeal-

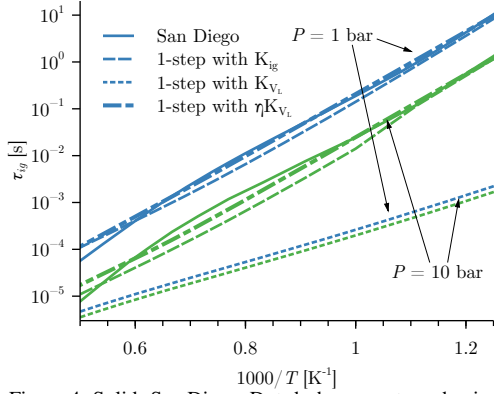


Figure 4: Solid: San Diego, Dot-dash: present mechanism.

ing, as numerical boundedness of mass fractions is trivial when a single progress variable is considered.

The second strategy is to include a second step [3], thereby providing the additional degree of freedom required. Nonetheless, this is done at the expense of an additional reaction, and of an additional species, whose properties have to be carefully adjusted [23].

In the present work, we intend to keep the best of both approaches by introducing a passive scalar. To account for the exponential property of ignition, we propose the introduction of a scalar variable  $\eta \in [0, 1]$ , that will play the role of the radical pool precursors, and will serve as an efficiency in Eq. (13)

$$\omega = C_{O_2}^{sO} C_{C_nH_m}^{sF} \mathcal{F} K \min(\eta, 1), \quad (15)$$

where the min operator is used to avoid rate acceleration in flame regions, where  $\eta > 1$ . The scalar is passive in the sense that it does not enter in the mass or energy balance (no mass, no reference energy), but still follows a classical advection-diffusion-reaction equation as

$$\frac{\partial \rho \eta}{\partial t} + \frac{\partial \rho v_\alpha \eta}{\partial x_\alpha} = \frac{\partial}{\partial x_\alpha} \left( \frac{1}{Le_\eta} \frac{\lambda}{c_p} \frac{\partial \eta}{\partial x_\alpha} \right) + \omega_\eta, \quad (16)$$

where the Lewis number can be case-dependent. In the following, we assumed  $Le_\eta = 0.18$ , a value characteristic of H atom diffusion, but further improvement could be achieved, e.g., by taking into account the molecular composition of the radical pool [19].

The scalar reaction rate  $\omega_\eta$  is then written as

$$\omega_\eta = C_M^{s\eta} B_\eta e^{-\frac{T_{a,\eta}}{T}} (\varepsilon + \eta). \quad (17)$$

The presumed form of the reaction rate  $\omega_\eta$  is inspired by various analytical studies [18, 19, 25] and represents both the initiation reaction(s) and chain reactions.

The initiation reaction, e.g.  $F + O \longrightarrow R$ , is represented by the  $\varepsilon$  term producing the first radicals even when none is present. The initiation reaction is

therefore fundamental: no ignition could occur without it, but its rate is second-order [19, 28] on ignition times prediction.

The branched-chain reactions are taken into account in (17) via the  $\eta$  term, providing the exponential dependence characteristic of ignition [18, 19, 25]. The associated Arrhenius rate  $B_\eta e^{-\frac{T_{a,\eta}}{T}}$  will provide the ignition temperature dependence, while  $C_M^{s\eta}$  will provide the pressure-dependence, as in third-body reactions.

Using asymptotic analysis to solve the coupled global (exothermic) and passive scalar reactions shows that the ignition delay time is proportional to the kinetic parameters as

$$\tau_{ig} \propto \exp \left( \frac{T_a}{T_u} \left[ \frac{B}{B_\eta} \frac{T_b - T_u}{T_u} \varepsilon + 1 \right] \right) \frac{1}{B_\eta} \log \left( \frac{B_\eta}{B} \frac{T_u^2}{T_a(T_b - T_u)} \frac{0.561}{\varepsilon} \right), \quad (18)$$

showing the role of  $\varepsilon$  in the temperature dependence of the ignition delay time. Taking into account the analytical solution of  $\eta$  – see more details in the supplemental material – the reaction rate  $\omega_\eta$  is finally modified as

$$\omega_\eta = C_M^{s\eta} B_\eta e^{-\frac{T_{a,\eta}}{T}} \left( \frac{\varepsilon}{\mathcal{F}} + \eta \right) f_\phi, \quad (19)$$

where factor  $1/\mathcal{F}$  was introduced to eliminate the rectification made in equation (13); and  $f_\phi$  is introduced to describe the  $\phi$  dependence of the ignition delay time. Details on the formula retained for  $f_\phi$  are provided in Supplementary Material but suffice to say, for discussion purposes, that  $f_\phi$  tends to zero in both rich and lean limits, and has a maximum close to the most-reacting mixture.

Ignition time results using the coupled scalar equation are reported in Fig. 4 (see the  $\eta K_{Vi}$  curves), showing that the proposed approach is accurate. Since  $\eta$  becomes large in the premixed flame but is clipped to one in the reaction rate (15), results from Fig. 3 remain unaltered. A similar agreement is reported in Supplementary material for the fuels considered for the study.

#### 4. Additional validations

This Section aims at validating the chemical model developed in Secs. 1–3 in two configurations beyond 1D premixed flames and homogeneous reactors to:

- Verify that the coupling of both reaction rates is satisfying on a simple configuration involving both ignition and propagation.
- Assess the model's capabilities for diffusion flames, even though no particular effort was made in that direction.

##### 4.1. Triple flame

A mixing layer is formed by placing in contact at a given time, two semi-infinite spaces of  $\text{CH}_4$  and Air, in quiescent conditions with a high initial temperature ( $T_u = 1500\text{K}$ ). Chemical reactions occur as the reactants mix, giving rise to self-ignition in the most reactive zone, and evolving in the formation of two premixed fronts, composed of lean and rich stoichiometries, leaving behind the trailing diffusion flame. These structures, so-called triple flames, are often encountered in several classical applications such as jets of fuel in a hot co-current oxidizer (JHL).

The resulting triple-flame structure can be observed in Fig. 5 through the heat release rate contours and the isothermal surfaces. The single-step model predicts an ignition, defined as the maximum heat-release point, delayed by 10% compared to the detailed mechanism, for a corresponding equivalence ratio about 3% higher thanks to  $f_\phi$ . Note that the Figure does not start at  $t = 0$ , voluntarily magnifying twice the prediction errors.

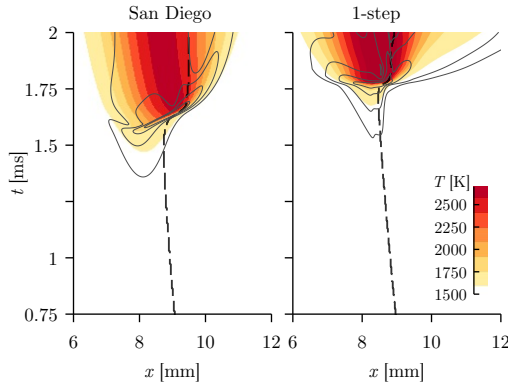


Figure 5: Transient evolution of one-dimensional  $\text{CH}_4/\text{air}$  mixing layer at atmospheric pressure and initial temperature of  $1500\text{K}$  initially located at  $x = 10[\text{mm}]$  with detailed chemistry (left) and current model (right). Black dashed line indicate the location where the mixture is stoichiometric. Solid lines represent isocontours of heat-release rate, while isothermal contours are shown in color.

These results are highly encouraging, as they show no *footprint* of the efficiency scalar  $\eta$ , while other similar corrections leave clear marks on the flow field (see, e.g., the triple flame in [4]).

#### 4.2. Diffusion flame

Even though the mechanism was derived for premixed combustion, diffusion flame may appear locally in partially premixed combustors. It is therefore of interest to check that the scheme will provide – if not excellent – at least consistent and satisfactory results.

Fig. 6 displays a comparison between the single-step and the detailed chemistry [22] computations of counter-flow diffusion flames under atmospheric conditions. The maximum of temperature,  $T_{\text{max}}$ , is presented as a function of the strain rate. The model

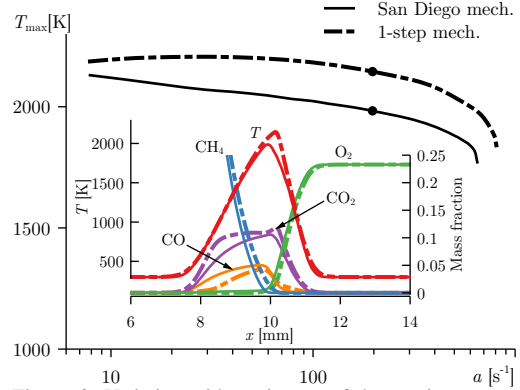


Figure 6: Variation with strain rate of the maximum temperature in a planar  $\text{CH}_4$ -air diffusion flame at atmospheric conditions,  $T_u = 300\text{K}$  and  $P = 1\text{bar}$ , and nozzle separation,  $L = 0.02\text{m}$ . Inset shows the temperature and mass fractions profiles of the major species. Solid lines represent the predictions made with San Diego mechanism [22]. Dash-dot lines represent the result made with the present 1-step mechanism. Dots indicates the strain rate at which the inlet profiles were calculated.

overpredicts the maximum temperatures in diffusion flames by 8%, a typical value for reduced mechanisms [4]. The measured strain rate is also off by 24% ( $a^{\text{SD}} = 650\text{ s}^{-1}$ ,  $a^{\text{1S}} = 807\text{ s}^{-1}$ ). Again this discrepancy is consistent with predictions from existing reduced mechanisms [2, 5].

Having pointed out the limitations of the model in the worst conditions, we can conclude that the model provides a satisfactory agreement for diffusion flames, and may be used for partially-premixed combustor simulations.

## 5. Conclusions and perspectives

One-step chemistry has been built from an analytical description of the thermo-chemical equilibrium for a wide-ranging spectrum of fuel-air mixtures, including  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , and a fuel surrogate for kerosene  $\text{C}_{9.74}\text{H}_{20.05}$ . The formalism proposed offers a simple implementation and does not resort to tabulation. The reaction rate calibration process was able to faithfully reproduce the laminar premixed flame velocity for a wide range of equivalence ratios and initial pressures and temperatures. Coupling with a passive scalar advection-diffusion-reaction equation resulted in excellent induction time estimations, a promising approach towards the simulation of turbulent lifted flames. The use of this model for turbulent partially premixed combustion configurations will be the focus of future studies.

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### Supplementary material

1. The extension of Sec. 1 to arbitrary partially oxygenated fuels  $C_nH_mO_p$ .
2. Derivation of the analytical solution of  $\eta$  (18).
3. The parameters derived in Secs. 2 & 3, for  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ ,  $CH_3OH$ ,  $C_2H_5OH$ , and a fuel surrogate for kerosene  $C_{9.74}H_{20.05}$ .

Note that, for an easy implementation, all required routines are made available at [pierre-boivin.cnrs.fr](http://pierre-boivin.cnrs.fr).

### References

- [1] P. Dagaut, M. Cathonnet, The ignition, oxidation, and combustion of kerosene: A review of experimental and kinetic modeling, *Progress in energy and combustion science* 32 (1) (2006) 48–92.
- [2] E. Fernández-Tarrazo, A. L. Sánchez, A. Linan, F. A. Williams, A simple one-step chemistry model for partially premixed hydrocarbon combustion, *Combustion and Flame* 147 (1-2) (2006) 32–38.
- [3] B. Franzelli, E. Riber, M. Sanjosé, T. Poinso, A two-step chemical scheme for kerosene–air premixed flames, *Combustion and Flame* 157 (7) (2010) 1364–1373.
- [4] P. Boivin, C. Jiménez, A. L. Sánchez, F. A. Williams, An explicit reduced mechanism for  $H_2$ –air combustion, *Proceedings of the Combustion Institute* 33 (1) (2011) 517–523.
- [5] A. Er-Raiy, Z. Bouali, J. Réveillon, A. Mura, Optimized single-step (oss) chemistry models for the simulation of turbulent premixed flame propagation, *Combustion and Flame* 192 (2018) 130–148.
- [6] M. Cailler, N. Darabiha, B. Fiorina, Development of a virtual optimized chemistry method. application to hydrocarbon/air combustion, *Combustion and Flame* 211 (2020) 281–302.
- [7] Z. M. Nikolaou, J.-Y. Chen, N. Swaminathan, A 5-step reduced mechanism for combustion of  $co/h_2/h_2o/ch_4/co_2$  mixtures with low hydrogen/methane and high  $h_2o$  content, *Combustion and Flame* 160 (1) (2013) 56–75.
- [8] A. D. Weiss, A. L. Sánchez, F. A. Williams, Accuracies of reduced mechanisms for predicting acoustic combustion instabilities, *Combustion and Flame* 209 (2019) 405–407.
- [9] P. Boivin, C. Jiménez, A. L. Sánchez, F. A. Williams, A four-step reduced mechanism for syngas combustion, *Combustion and Flame* 158 (6) (2011) 1059–1063.
- [10] P. Boivin, A. L. Sánchez, F. A. Williams, Four-step and three-step systematically reduced chemistry for wide-range  $H_2$ –air combustion problems, *Combustion and Flame* 160 (1) (2013) 76–82.
- [11] P. Boivin, F. A. Williams, Extension of a wide-range three-step hydrogen mechanism to syngas, *Combustion and Flame* 196 (2018) 85 – 87.
- [12] B. Varatharajan, M. Petrova, F. Williams, V. Tangirala, Two-step chemical-kinetic descriptions for hydrocarbon–oxygen–diluent ignition and detonation applications, *Proceedings of the Combustion Institute* 30 (2) (2005) 1869–1877.
- [13] K. Akihama, Y. Takatori, K. Inagaki, S. Sasaki, A. M. Dean, Mechanism of the smokeless rich diesel combustion by reducing temperature, *Sae Transactions* (2001) 648–662.
- [14] A. Misdariis, O. Vermorel, T. Poinso, A methodology based on reduced schemes to compute autoignition and propagation in internal combustion engines, *Proceedings of the Combustion Institute* 35 (3) (2015) 3001–3008.
- [15] F. Mauss, N. Peters, B. Rogg, F. Williams, Reduced kinetic mechanisms for premixed hydrogen flames, in: *Reduced Kinetic Mechanisms for Applications in Combustion Systems*, Springer, 1993, pp. 29–43.
- [16] S. Lam, D. Goussis, The csp method for simplifying kinetics, *International Journal of Chemical Kinetics* 26 (4) (1994) 461–486.
- [17] W. Jones, S. Rigopoulos, Reduced chemistry for hydrogen and methanol premixed flames via rcce, *Combustion Theory and Modelling* 11 (5) (2007) 755–780.
- [18] L. Veggi, P. Boivin, Explicit formulation of the reactivity of hydrogen, methane and decane, *Combustion and Flame* 162 (3) (2015) 580–585.
- [19] P. Boivin, A. Sánchez, F. Williams, Analytical prediction of syngas induction times, *Combustion and Flame* 176 (2017) 489–499.
- [20] T. Poinso, D. Veynante, *Theoretical and numerical combustion*, RT Edwards, Inc., 2005.
- [21] W. C. Reynolds, The element potential method for chemical equilibrium analysis: implementation in the interactive program stanjan, Technical Rept. (1986).
- [22] Chemical-Kinetic Mechanisms for Combustion Applications, [web.eng.ucsd.edu/mae/groups/combustion/mechanism.html](http://web.eng.ucsd.edu/mae/groups/combustion/mechanism.html), v. 2016-12-14.
- [23] L. A. Carbajal-Carrasco, Z. Bouali, A. Mura, Optimized single-step (oss) chemistry for auto-ignition of heterogeneous mixtures, *Combustion and Flame* 227 (2021) 11–26.
- [24] M. L. Boursicaud, L. A. Carbajal-Carrasco, Z. Bouali, A. Mura, Optimized two-step (ots) chemistry models for the simulation of turbulent premixed flame propagation and ignition, Under consideration for publication (2022).
- [25] C. Treviño, F. Mendez, Reduced kinetic mechanism for methane ignition, *Proceedings of the Combustion Institute* 24 (1) (1992) 121–127.
- [26] D. J. Diamantis, D. C. Kyritsis, D. A. Goussis, The reactions supporting or opposing the development of explosive modes: Auto-ignition of a homogeneous methane/air mixture, *Proceedings of the Combustion Institute* 35 (1) (2015) 267–274.
- [27] A. Misdariis, O. Vermorel, T. Poinso, A methodology based on reduced schemes to compute autoignition and propagation in internal combustion engines, *Proceedings of the Combustion Institute* 35 (3) (2015) 3001–3008.
- [28] C. Treviño, F. Solorio, Asymptotic analysis of the high-temperature ignition of  $co/h_2/o_2$  mixtures, *Combustion and flame* 86 (3) (1991) 285–295.