CH₄/air homogeneous autoignition: a comparison of two chemical kinetics mechanisms

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Abstract

Reactions contributing to the generation of the explosive time scale that characterise autoignition of homogeneous stoichiometric CH₄/air mixture are identified using two different chemical kinetics models; the well known GRI-3.0 mechanism (53/325 species/reactions with N-chemistry) and the AramcoMech mechanism from NUI Galway (113/710 species/reactions without N-chemistry; Combustion and Flame 162:315-330, 2015). Although the two mechanisms provide qualitatively similar results (regarding ignition delay and profiles of temperature, of mass fractions and of explosive time scale), the 113/710 mechanism was shown to reproduce the experimental data with higher accuracy than the 53/325 mechanism. The present analysis explores the origin of the improved accuracy provided by the more complex kinetics mechanism. It is shown that the reactions responsible for the generation of the explosive time scale differ significantly. This is reflected to differences in the length of the chemical and thermal runaways and in the set of the most influential species.

Keywords: methane/air autoignition, detailed chemical kinetics, model reduction, explosive time scale, CSP

1. Introduction

Recent decades have seen significant growth in the number of detailed chemical kinetics mechanisms, the size of which is also increasing with time. These mechanisms relate to fuels with simple or complex structures, and their increasing size generally improves agreement with the experimental data. However, the majority of detailed mechanisms currently constructed face the following limitations:

- the vast majority of elementary reaction rate parameters are estimated as there is no experimentally measured or theoretically calculated data available
- the available experimental data available for validation is limited to several global parameters and only a small number of intermediate species (relative to the size of the model).

Therefore, the origin of the increasing accuracy provided by the kinetics mechanisms of increasing complexity is an open subject.

One of the reaction processes that attracted significant interest from the modelling community, due to its relevance to natural gas, is the oxidation of the CH₄/air mixtures. Listed on Table 1 are various detailed chemical kinetics mechanisms accounting for the oxidation of methane, which were developed the last decades. Naturally, the range of validity of these mechanisms, in terms of initial fuel composition, operating conditions (e.g., stoichiometry, initial pressure and temperature, etc) and reacting configurations (e.g., ignition, flames etc), varies widely. In general, each new mechanism was shown to provide an increasing agreement with the experimental data.

The origin of the increased accuracy provided by the larger and more refined chemical kinetics mechanism is the subject of this work. The approach followed is novel, in that the improvements are identified using an algorithmic methodology. Previous commentaries on methane/oxygen chemical kinetic models discussed advances based on a detailed understanding of specific kinetic phenomenon. For example, early models for CH₄/air between 1958 and 1978 (see Table 1) were improved by adding chemical species and

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reactions to the models for H_2 and CO oxidation. By the 1980s, it was clear that an accurate CH_4 /air oxidation model requires approximately 30 species. Subsequent CH_4 models included more species to account for molecular growth reactions wherein radicals derived from CH_4 could recombine to form larger hydrocarbons (e.g., C_2H_6 , C_2H_4 , C_3H_6 , etc.), especially under rich conditions. These larger models also formed the basis for hierarchical chemical kinetic models, wherein larger hydrocarbon combustion models are built by adding species and reactions to the CH_4 combustion model.

In the 1980s and 1990s, measurements of rate constants using shock tubes and flash photolysis techniques improved, which allowed for CH_4 kinetic models to include more accurate rate constants. In addition, the development of ab initio quantum mechanical simulations and master equation analysis provided high accuracy theoretical calculations for thermochemical parameters (entropy and enthalpy of formation) and rate constants with pressure dependence. Despite these advances in elementary rate constant measurements and calculations, a plethora of CH_4 combustion models with widely varying rate parameters have been published since 1995. This can be attributed to uncertainties in the measurements/calculations and for the need to predict a wide variety of global combustion data, such as ignition delay times, speciation profiles, laminar flame speeds, flame extinction and ignition, flame structure, etc. To overcome these issues regarding uncertainty, GRI-Mech performed a mathematical optimization to fit rate constant parameters against a wide range of experimental data. This led to GRI-Mech, one of the most widely used CH_4/O_2 models to date.

In the present work, GRI-Mech 3.0 is compared against a recent comprehensive CH_4/O_2 model, using an algorithmic methodology to highlight the evolution of CH_4/O_2 models over the past 20 years. These two mechanisms were introduced in 1999 and 2015; the first mechanism involves 53/325 species/reactions (including nitrogen chemistry) and the second one, that is based on AramcoMech 1.3, involves 113/710 species/reactions (excluding nitrogen chemistry) [1, 2].

The analysis will be based on CH_4 /air mixtures because methane is the simplest carbon fuel and currently exists a large number of chemical kinetics mechanisms to model its dynamics. This work concentrates on the influence of the reactions in each of the selected two mechanisms on the dynamics responsible for autoignition. When comparing complex mechanisms, it is often challenging to identify which reactions are responsible for observed differences in predicted combustion properties. In this work, species and reactions in the two

Table 1: The evolution of the size of the chemical kinetics mechanisms for the oxidation of CH_4 /air mixtures. Additional details on these mechanisms are listed in [Appendix A](#).

year	species	reactions	Ref.
1958	11	6	[3]
1970	13	18	[4]
1975	13	23	[5]
1978	23	63	[6]
1979	25	75	[7]
1984	34	140	[8]
1992	31	149	[9]
1994	70	1600	[10]
1995	42	835	[11]
1998	156	680	[12]
1999	38	190	[13]
2000	77	484	[14]
2000	127	1207	[15]
2000	53	325	[1]
2001	37	351	[16]
2007	118	663	[17]
2009	97	779	[18]
2010	230	1328	[19]
2013	253	1542	[20]
2015	157	1011	[21]
2015	113	710	[2]

mechanisms that are related to the explosive dynamics will be identified. The two most influential sets of species and reactions (one set from each mechanism) will be compared. It is expected that the outcome of this comparison will clarify the origin of the differences in the accuracy by which the two mechanisms reproduce the experimental results.

2. The two chemical kinetics mechanisms employed

The two chemical kinetics mechanisms that will be employed here are the quite popular GRI-3.0 mechanism [1] and a mechanism that was introduced recently and was shown to predict the experimental results more accurately [2]; the later mechanism will be referred to next as the Galway mechanism.

The GRI-3.0 mechanism includes 53 species and 325 reactions and its range of validity is 1000 to 2500 K, 10 Torr to 10 atm and $\phi=0.1$ to 5 [1]. The Galway mechanism includes 113 species and 710 reactions and its range of validity is 600 to 1600 K, 7 to 41 atm and $\phi=0.3$, 0.5, 1.0, and 2.0 in air-mixtures [2]. Of the 53 species in the GRI-3.0 mechanism, 35 are included in the Galway mechanism, one species (C_3H_7) is included in two different forms (iC_3H_7 and nC_3H_7) and the remaining 17 species involve nitrogen atoms so they are

Table 2: The reactions in the Galway and the GRI-3.0 mechanisms that contribute the most to the generation of the characteristic explosive time scale.

Galway	GRI-3.0	Reactions
<u>1</u>	<u>38</u>	$\text{H} + \text{O}_2 \leftrightarrow \text{O} + \text{OH}$
<u>2</u>	<u>3</u>	$\text{O} + \text{H}_2 \leftrightarrow \text{H} + \text{OH}$
<u>3</u>	<u>84</u>	$\text{OH} + \text{H}_2 \leftrightarrow \text{H} + \text{H}_2\text{O}$
<u>8</u>	<u>43</u>	$\text{H} + \text{OH} + \text{M} \leftrightarrow \text{H}_2\text{O} + \text{M}$
<u>9</u>	<u>33</u>	$\text{H} + \text{O}_2(+\text{M}) \leftrightarrow \text{HO}_2(+\text{M})$
<u>15</u>	<u>87</u>	$\text{HO}_2 + \text{OH} \leftrightarrow \text{H}_2\text{O} + \text{O}_2$
(15*)	287	$\text{HO}_2 + \text{OH} \leftrightarrow \text{H}_2\text{O} + \text{O}_2$
<u>16</u>	<u>115</u>	$\text{HO}_2 + \text{HO}_2 \leftrightarrow \text{H}_2\text{O}_2 + \text{O}_2$
<u>17</u>	<u>116</u>	$\text{HO}_2 + \text{HO}_2 \leftrightarrow \text{H}_2\text{O}_2 + \text{O}_2$
<u>19f</u>	<u>85b</u>	$\text{H}_2\text{O}_2(+\text{M}) \rightarrow \text{OH} + \text{OH} (+\text{M})$
<u>24</u>	<u>89</u>	$\text{H}_2\text{O}_2 + \text{OH} \leftrightarrow \text{H}_2\text{O} + \text{HO}_2$
<u>27</u>	<u>99</u>	$\text{CO} + \text{OH} \leftrightarrow \text{CO}_2 + \text{H}$
<u>39</u>	<u>32</u>	$\text{CH}_2\text{O} + \text{O}_2 \leftrightarrow \text{HCO} + \text{HO}_2$
<u>72</u>	<u>101</u>	$\text{CH}_2\text{O} + \text{OH} \leftrightarrow \text{HCO} + \text{H}_2\text{O}$
<u>75</u>	<u>161</u>	$\text{CH}_2\text{O} + \text{CH}_3 \leftrightarrow \text{HCO} + \text{CH}_4$
<u>76</u>	<u>121</u>	$\text{CH}_2\text{O} + \text{HO}_2 \leftrightarrow \text{HCO} + \text{H}_2\text{O}_2$
<u>128</u>	<u>53</u>	$\text{CH}_4 + \text{H} \leftrightarrow \text{CH}_3 + \text{H}_2$
<u>129</u>	<u>98</u>	$\text{CH}_4 + \text{OH} \leftrightarrow \text{CH}_3 + \text{H}_2\text{O}$
<u>131f</u>	<u>157b</u>	$\text{CH}_4 + \text{HO}_2 \rightarrow \text{CH}_3 + \text{H}_2\text{O}_2$
<u>145f</u>	<u>119</u>	$\text{CH}_3 + \text{HO}_2 \leftrightarrow \text{CH}_3\text{O} + \text{OH}$
<u>146</u>	<u>118</u>	$\text{CH}_3 + \text{HO}_2 \leftrightarrow \text{CH}_4 + \text{O}_2$
<u>148</u>	<u>155</u>	$\text{CH}_3 + \text{O}_2 \leftrightarrow \text{CH}_3\text{O} + \text{O}$
<u>149</u>	<u>156</u>	$\text{CH}_3 + \text{O}_2 \leftrightarrow \text{CH}_2\text{O} + \text{OH}$
150		$\text{CH}_3 + \text{O}_2(+\text{M}) \leftrightarrow \text{CH}_3\text{O}_2(+\text{M})$
151		$\text{CH}_3\text{O}_2 + \text{CH}_2\text{O} \leftrightarrow \text{CH}_3\text{O}_2\text{H} + \text{HCO}$
152		$\text{CH}_4 + \text{CH}_3\text{O}_2 \leftrightarrow \text{CH}_3 + \text{CH}_3\text{O}_2\text{H}$
154		$\text{CH}_3\text{O}_2 + \text{CH}_3 \leftrightarrow \text{CH}_3\text{O} + \text{CH}_3\text{O}$
<u>189</u>	<u>158</u>	$\text{CH}_3 + \text{CH}_3(+\text{M}) \leftrightarrow \text{C}_2\text{H}_6(+\text{M})$

not included in the nitrogen-free Galway mechanism.

The reactions listed in Table 2 are those in the GRI-3.0 and Galway mechanisms that contribute the most to the generation of the time scale, which characterises the autoignition of a homogeneous stoichiometric ($\phi=1$) CH_4/air mixture at (i) $p(0) = 1$ MPa, $T(0) = 1100$ K and (ii) at $p(0) = 4$ MPa, $T(0)=900$ K. “Edited” reactions are those common in the two mechanisms: bold(blue)/underlined(red) denotes reactions whose parameters (pre-exponential factor, etc) differ moderately/significantly, while italic(magenta) denotes reactions whose directions (fwd and bwd) have been reversed; the parameters of the latter reactions differ significantly, as the underlined.

As it is shown in Table 2, when using the Galway mechanism 28 reactions contribute to the generation of the characteristic (explosive) time scale. In contrast, when using the GRI-3.0 mechanism, only 24 reactions provide a similar contribution. Four reactions of the 28 from Galway mechanism (150, 151, 152 and 154) are not included in the GRI -3.0 mechanism, while one reaction of the 24 from the GRI-3.0 mechanism (287) is not included in the Galway mechanism. Reaction 287 of the GRI-3.0 mechanism that is not represented in the

Galway mechanism will be referred as 15*, as indicated in Table 2, since it is the high pressure version of reaction 15 in the Galway mechanism. In the following, the numbering of the reactions will follow that, under the column headed “Galway”.

3. The ignition delay

The variation of the ignition delay, t_{ign} , with the initial pressure $p(0)$ is displayed in Fig. 1, for $T(0) = 900$ and 1100 K; $\phi = 1$. It is shown that in the $T(0) = 900$ K case, the ignition delay provided by the Galway mechanism is shorter in comparison to the one provided by the GRI-3.0 mechanism, throughout the range of $p(0)$ considered. In the $T(0) = 1100$ K case, this is true only when $p(0) > 3.2$ MPa, while when $p(0) < 3.2$ MPa the ignition delay provided by the Galway mechanism is longer in comparison to the one provided by the GRI-3.0 mechanism. Figure 1 also suggests that the largest differences in t_{ign} are manifested at large values of $p(0)$ when $T(0) = 900$ K and at small values of $p(0)$ when $T(0) = 1100$ K. In general, both chemical kinetics mechanisms produced a similar trend; i.e. a decreasing t_{ign} for increasing $p(0)$.

Regarding the ratio of the ignition delays provided by the two mechanisms, $t_{\text{ign,Gal}}/t_{\text{ign,GRI}}$, Fig. 1 shows that in the $T(0)=900$ K case it decreases monotonically with increasing $p(0)$, while in the $T(0) = 1100$ K case first increases when $p(0) < 0.5$ MPa and then decreases when $p(0) > 0.5$ MPa.

Table 3: The ignition delay t_{ign} [s] for the GRI-3.0 and the Galway chemical kinetics mechanisms for (i) $p(0) = 1$ MPa and $T(0) = 1100$ K and (ii) $p(0) = 4$ MPa and $T(0) = 900$ K; $\phi=1$.

	GRI-3.0	Galway
(i) $p(0)=1$ MPa $T(0) = 1100$ K	0.01674	0.02519
(ii) $p(0) = 4$ MPa $T(0) = 900$ K	0.16319	0.03607

CSP diagnostics will be presented for the homogeneous autoignition of a stoichiometric CH_4/air mixture for the two cases indicated in Fig. 1 by the vertical dashed lines; i.e., (i) $p(0) = 1$ MPa and $T(0) = 1100$ K and (ii) $p(0) = 4$ MPa and $T(0) = 900$ K. These are two typical sets of $p(0)$ and $T(0)$ in the cases at which large differences in t_{ign} are recorded. These two cases will be referred in the following as cases (i) and (ii) respectively; $\phi = 1$. The ignition delays for these two cases are displayed in Table 3. It is shown that in the (i) case $t_{\text{ign,Gal}}$ is about 50% larger to $t_{\text{ign,GRI}}$, while in the (ii) case it is about 80% shorter.

Figure 1: Left: the variation of the ignition delay (t_{ign}) for the two chemical kinetics mechanisms under study, as a function of the initial pressure $p(0)$ for $T(0) = 900$ K (top) and $T(0) = 1100$ K (bottom), $\phi=1$. Right: the evolution of the ratio of the two ignition delays. The vertical lines denote the cases (i) and (ii), for which CSP diagnostics were computed and the related t_{ign} are listed in Table 3.

The evolution of the mass fraction of selected species for the (i) and (ii) cases is shown in Fig. 2. The species profiles are shown as a function of scaled time (t/t_{ign}). At condition (i) the Galway predicts a longer ignition delay time, but the species profiles indicate that important radicals (OH and HO_2) and important intermediate species (CH_2O and H_2O_2) are actually in higher concentrations in the Galway mech compared to GRI-3.0 mech. This is unexpected because one would intuitively think the more reactive model would produce higher concentration of radicals and intermediates. Similar anomalies in the species profiles are shown at conditions (ii) wherein CO concentrations are higher for GRI-3.0 even though it is less reactive compared to Galway mech. This highlights the need for more rigorous methods to identify the reactions affecting explosive time scales.

4. Physical Problem

The adiabatic autoignition of a homogeneous CH_4/air mixture is considered at constant volume. It is assumed that the chemical kinetics mechanism employed involves N species and K reactions. Considering the forward and backward directions of these K elementary reactions as separate unidirectional ones, the governing equations for the species mass fraction and temperature

are:

$$\frac{d\mathbf{y}}{dt} = \frac{1}{\rho} \mathbf{W} \cdot \sum_{k=1}^{2K} \mathbf{S}_k R^k \quad (1)$$

$$\frac{dT}{dt} = \frac{1}{\rho c_v} (-\mathbf{h}_c \cdot \mathbf{W} + RT\mathbf{U}) \cdot \sum_{k=1}^{2K} \mathbf{S}_k R^k \quad (2)$$

where $\mathbf{y}$ is the N -dim. state column vector of the species' mass fraction, $\mathbf{S}_k$ and R^k represent the stoichiometric vector and reaction rate, respectively, of the k -th unidirectional reaction, ρ is the mixture density, $\mathbf{W}$ is a $N \times N$ diagonal matrix with the species' molecular weights in the diagonal, c_v is the heat capacity, $\mathbf{h}_c$ is the N -dim. vector of the species' absolute enthalpies, T is the temperature, R is the universal gas constant and $\mathbf{U} = [1, 1, \dots, 1]$ [22, 23].

5. The CSP algorithm and tools

Eqs. (1) and (2) can be cast in an $(N+1)$ -dimensional system:

$$\frac{d\mathbf{z}}{dt} = \mathbf{g}(\mathbf{z}) = \sum_{k=1}^{2K} \hat{\mathbf{S}}_k R^k = \sum_{n=1}^{N-E+1} \mathbf{a}_n f^n \quad (3)$$

where $\mathbf{z}$ is the $(N+1)$ -dim. state column vector, defined as $\mathbf{z} = [\mathbf{y}, T]^T$, $\mathbf{a}_n$ is the $(N+1)$ -dim. CSP column ba-

Figure 2: The evolution of the mass fractions of various species, as a function of the scaled time t/t_{ign} , for the two mechanisms (Solid/Dashed line represents the Galway/GRI-3.0 mechanism) for (i) $p_0 = 1$ MPa and $T_0 = 1100$ K (top) and (ii) $p_0 = 4$ MPa and $T_0 = 900$ K (bottom); $\phi = 1$.

sis vector of the n -th mode and $f^n = \mathbf{b}^n \cdot \mathbf{g}(\mathbf{z})$ is the related CSP amplitude, where $\mathbf{b}^n$ are the CSP dual $(N+1)$ -dim. row vectors and $\mathbf{b}^i \cdot \mathbf{a}_j = \delta_j^i$ [24, 25]. The amplitudes f^{N-E+2} to f^{N+1} are by definition zero, since they represent the conservation of the E elements in the mechanism. The non-zero amplitudes f^n ($1 \leq n \leq N - E + 1$) are set positive, by properly adjusting the sign of the $(N+1)$ -dimensional row vectors $\mathbf{b}^n$ (and therefore the sign of $\mathbf{a}_n$, so that the orthogonality condition is preserved).

Assuming that the system in Eq. (3) exhibits M time scales that are of dissipative nature and much faster than the rest ($\tau_1 < \dots < \tau_M \ll \tau_{M+1} < \dots < \tau_{N-E+1}$), the following reduced system can be constructed:

$$f^m \approx 0 \quad (m = 1, \dots, M) \quad \frac{d\mathbf{z}}{dt} \approx \sum_{n=M+1}^{N-E+1} \mathbf{a}_n f^n \quad (4)$$

The first of these two relations is an algebraic M -dim. system and defines the Slow Invariant Manifold (SIM), along which the solution evolves, while the second is an $(N+1)$ -dim. system of ODEs that governs the slow evolution of the process on the SIM [26, 27]. The evolution Eq. (4) is free of the fast time scales (τ_1 to τ_M), so that its dynamics are characterized by the fastest of the slow time scales. The identification and analysis of the slow characteristic time scales, among them the

explosive ones, is allowed by the availability of Eq. (4) [28, 29, 30].

The time scales of the system in Eq. (3) are approximated by the relation $\tau_n = |\lambda_n|^{-1}$ ($n = 1, \dots, N - E + 1$), where λ_n is the n -th non-zero eigenvalue of the Jacobian $\mathbf{J}$ of $\mathbf{g}(\mathbf{z})$. This eigenvalue is defined as $\lambda_n = \boldsymbol{\beta}^n \cdot \mathbf{J} \cdot \boldsymbol{\alpha}_n$, where $\boldsymbol{\alpha}_n$ and $\boldsymbol{\beta}^n$ are the n -th right (column) and left (row), respectively, eigenvectors of $\mathbf{J}$. When the real part of λ_n is positive (negative), the related time scale τ_n is an explosive (dissipative) one, since it relates to components of the system that tend to lead it away from (towards to) equilibrium. Taking into account the fact that the vector field $\mathbf{g}(\mathbf{z})$ is the sum of $2K$ terms, the n -th eigenvalue can be expressed as:

$$\lambda_n = \boldsymbol{\beta}^n \cdot \sum_{k=1}^{2K} \text{grad}(\hat{\mathbf{S}}_k R^k) \cdot \boldsymbol{\alpha}_n = c_1^n + \dots + c_{2K}^n \quad (5)$$

where $\mathbf{J} = \text{grad}(\hat{\mathbf{S}}_1 R^1) + \dots + \text{grad}(\hat{\mathbf{S}}_{2K} R^{2K})$ [31, 32] and the magnitude of the term c_k^n is indicative of the contribution of the k -th reaction to the n -th eigenvalue. Consider the case where λ_n is real (the extension to the case where some of the eigenvalues are complex pairs is straightforward [33]). In this case, the c_k^n terms can be either positive or negative; $c_k^n > 0$ implies that the k -th reaction contributes to an explosive character of the n -th time scale τ_n , while $c_k^n < 0$ implies that the k -th reaction

contributes to a dissipative character.

The contribution of each of the $2K$ reactions to the time scale τ_n can be assessed through the related term in Eq. (5), by employing the *Time scale Participation Index* (TPI):

$$J_k^n = \frac{c_k^n}{|c_1^n| + \dots + |c_{2K}^n|} \quad (6)$$

where $n = 1, \dots, N-E+1$, $k = 1, \dots, 2K$ and by definition $\sum_{k=1}^{2K} |J_k^n| = 1$ [31, 32, 33]. J_k^n measures the relative contribution of the k -th reaction to the n -th eigenvalue λ_n and, therefore, to the time scale τ_n . The J_k^n terms can be either positive or negative; positive (negative) J_k^n implies that the k -th reaction contributes to the explosive (dissipative) character of the n -th time scale τ_n . When the positive (negative) terms outweigh the negative (positive) ones the n -th time scale is an explosive (dissipative) one.

The variables (mass fractions or temperature) that (i) are being affected the most by τ_e , and (ii) are functionals in the reaction rates that contribute to the amplitude f^e of the explosive mode will be identified with the *CSP Pointer* (Po), which is defined as:

$$\mathbf{D}^e = \text{diag}[\mathbf{a}_e \mathbf{b}^e] = [a_e^1 b_1^e, \dots, a_e^{N+1} b_{N+1}^e] \quad (7)$$

where, by definition $\sum_{k=1}^N a_e^k b_k^e = 1$ [32, 33, 34, 35]. The magnitude of $D_k^e = a_e^k b_k^e$ measures the relation of the k -th component of $\mathbf{z}$ to the $\mathbf{a}_e f^e$ mode.

Here, the CSP basis vectors $\mathbf{a}_n$ and their dual $\mathbf{b}^n$ will be approximated by the right and left eigenvectors, respectively, of the Jacobian $\mathbf{J}$ of the system in Eq. (3), which provide leading order accuracy [24]; i.e., $\mathbf{a}_n = \boldsymbol{\alpha}_n$ and $\mathbf{b}^n = \boldsymbol{\beta}^n$. The values of the Jacobian $\mathbf{J}$ and the $2K$ Jacobians in Eq. (5) were computed on the basis of analytical expressions.

The TPI indices will be employed in order to investigate the differences in the components of the two mechanisms, GRI-3.0 and Galway, that generate the time scale that characterises the autoignition process. The TPIs will identify reactions that contribute to the generation of this time scale, which is directly related to the ignition delay t_{ign} [31, 36]. Note that the identification and analysis of the slow time scales (explosive or dissipative) via TPI is allowed by the availability of the reduced system, as in Eq. 4, the dynamics of which incorporates the slow time scales of the full system [28, 29, 30], when sufficiently far from the edges of the SIM [37, 38].

6. The explosive dynamics

The evolution of the explosive time scales that are generated in the (i) and (ii) cases is displayed in Fig. 3, as a function of the scaled time t/t_{ign} . As shown in Fig. 3, in both cases considered, two time scales appear during the evolution of the autoignition process that have an explosive character; one fast and one slow, say $\tau_{e,f}$ and $\tau_{e,s}$, respectively. In both cases, $\tau_{e,f}$ initially increases (i.e., the ignition process decelerates) and then remains practically constant until right before the end of the ignition delay. At that point, $\tau_{e,f}$ exhibits a steep decrease (i.e., the process accelerates), which is followed by an equally fast increase, so that it meets the slow explosive time scale, $\tau_{e,s}$. As soon as they meet, they lose their explosive character and they disappear. Note that in the (i) case, $\tau_{e,f}$ is slightly faster with the GRI-3.0 mechanism, while in the (ii) case $\tau_{e,f}$ is faster with the Galway mechanism. This feature correlates perfectly with the findings in Table 3, according to which t_{ign} is shorter when using GRI-3.0 in the first case and when using the Galway mechanism in the second case.

The reactions that are responsible for the generation of $\tau_{e,f}$ and the variables that relate the most to these time scales will be identified at five points along the explosive stage, as shown in Fig. 3. Point P_1 denotes the start of the process ($t = 0$), while point P_5 denotes the point where $\tau_{e,f}$ attains the minimum value and is located very close to the ignition delay ($t_{P5} \approx t_{ign}$); for the (i) case, $t_{P5} = 0.017$ s for the GRI-3.0 mechanism and $t_{P5} = 0.025$ s for the Galway mechanism, while for the (ii) case $t_{P5} = 0.163$ s for the GRI-3.0 mechanism and $t_{P5} = 0.036$ s for the Galway mechanism. Points P_2 - P_4 are equally distributed in the explosive stage.

In order to investigate the dependence of $\tau_{e,f}$ to the temperature, the explosive time scales computed from the (truncated) Jacobian of the species' equation Eq. (1) were compared with those computed from the full Jacobian of the system of Eqs. (1) and (2). When the temperature dependence is weak, the computed two $\tau_{e,f}$ are expected to be similar [31, 39]. The evolution of the resulting $\tau_{e,f}$ for the GRI-3.0 and the Galway mechanisms is displayed in Fig. 4 for the (i) ($p(0) = 1$ MPa and $T(0) = 1100$ K; top row) and (ii) ($p(0) = 4$ MPa and $T(0) = 900$ K; bottom row) cases. Solid (black) lines denote the explosive time scales computed on the basis of the full Jacobian (constructed from Eqs. (1) and (2)), while dashed (blue) lines denote the explosive time scales computed on the basis of the truncated Jacobian (constructed from Eq. (1) only).

Figure 4 shows that, initially, $\tau_{e,f}$ of the full and the truncated Jacobians are either identical or very close

Figure 3: The evolution of the developing explosive timescales τ_e as a function of the scaled time t/t_{ign} , computed with the two mechanisms (Solid/Dashed line represents the Galway/GRI-3.0 mechanism) for (i) $p(0) = 1$ MPa and $T(0) = 1100$ K (top) and (ii) $p(0) = 4$ MPa and $T(0) = 900$ K (bottom); $\phi = 1$. P₁-P₅ denote the points in time where CSP diagnostics were computed.

Figure 4: The evolution of the fastest explosive time scale $\tau_{e,f}$, computed from the full and truncated Jacobians, with the GRI-3.0 and Galway mechanisms for (i) $p(0) = 1$ MPa and $T(0) = 1100$ K (top) and (ii) $p(0) = 4$ MPa and $T(0) = 900$ K (bottom); $\phi = 1$. The full Jacobian is constructed on the basis of the species and energy equations, while the truncated Jacobian is constructed on the basis of the species equation only. P₁-P₅ denote the points in time where CSP diagnostics were computed.

to each other. This indicates that the temperature dependence of $\tau_{e,f}$ is weak. However, close to the ignition delay large deviations are recorded, indicating the temperature dependence is strong. The part of the ignition delay where the two explosive time scales are close relates to the chemical runaway, while the remaining part relates to the thermal runaway [31]. Note that $\tau_{e,f}$ of the truncated Jacobian is larger than that of the full Jacobian, indicating that the influence of the temperature is to accelerate the process. Note also that the GRI-3.0 mechanism relates to a larger chemical runaway regime. This influence of the temperature has also been detected by the CSP Pointer (Po), as it will be discussed in the Sections that follow.

In the case where the GRI-3.0 mechanism is considered, Fig. 4 suggests that points P₁-P₄ belong to the chemical runaway regime for both sets of initial conditions considered. This is also true when using the Galway mechanism for points P₁-P₂ in the (i) case ($p(0) = 1$ MPa and $T(0) = 1100$ K) and for points P₁-P₃ in the (ii) case ($p(0) = 4$ MPa and $T(0) = 900$ K); points P₃ and P₄ in the (i) case and point P₄ in the (ii) case belong to a regime in which chemical and thermal runaways coexist. In all cases shown in Fig. 4, point P₅ belongs to the thermal runaway regime.

7. Diagnostics for the $p(0)=1$ MPa $T(0)=1100$ K case

Table 4 displays the CSP diagnostics for the initial conditions $T(0) = 1100$ K and $p(0) = 1$ MPa ((i) case), as they were computed at the five points P₁-P₅ along the ignition delay, shown in Fig (3). Included in the Table are the TPI indices, which identify the reactions contributing the most to $\tau_{e,f}$, and the Po index which identifies the variables (species' mass fractions and temperature) related the most to $\tau_{e,f}$. Subscripts "f" and "b" associated with reactions denote the forward and backward reactions, respectively. Note that for the set of initial conditions considered here, the ignition delay t_{ign} is shorter when using the GRI-3.0 mechanism, according to Table 3.

At point P₁, Table 4 suggests that for the GRI-3.0 mechanism the reactions that contribute the most to $\tau_{e,f}$ and the related variables are:

while those for the Galway mechanism are:

It is shown that reactions 148f and 131f are major contributors to $\tau_{e,f}$ at $t = 0$ s, in both cases; by 61% and 14% when the GRI-3.0 is used and 28% and 13% when the Galway mechanism is used, respectively. This reflects the fact that the mass fraction of the reactants of these two reactions, CH_3 and HO_2 , are the variables identified the most by the Po. However, when using the Galway mechanism the reaction 152f makes a significant contribution to $\tau_{e,f}$ (by 27%) and the mass fraction of its reactant CH_3O_2 is among the most significant variables. Note that the reaction 152f and its reactant CH_3O_2 are not included in the GRI-3.0 mechanism.

In the region spanned by the points P₂-P₄, Table 4 suggests that the reactions contributing to the generation of $\tau_{e,f}$ differ significantly. Specifically, for the GRI-3.0 mechanism the reactions that contribute the most to $\tau_{e,f}$ and the related variables are:

while for the Galway mechanism these are:

The explosive character of $\tau_{e,f}$ at points P₂-P₄ is promoted the most by reaction 145f, when using either the GRI-3.0 or the Galway mechanism. Reaction 145f converts less reactive methyl and hydroperoxyl radicals to more reactive hydroxyl radicals, while also being exothermic. In both cases, this character is opposed mainly by reaction 189f, assisted by reaction 146f when using the Galway mechanism; both are radical recombination chain terminating reactions leading to ethane in the former and methane and oxygen in the latter. Note

Table 4: Diagnostics results for both chemical mechanisms under study; $p(0) = 1$ MPa, $T(0) = 1100$ K, $\phi = 1$; $t_{ign}=0.0167416$ s for the GRI-3.0 and $t_{ign}=0.0251985$ s for the Galway mechanisms. Number in parentheses denote powers of ten.

	P ₁	P ₂	P ₃	P ₄	P ₅
	$t_1=0.0(0)$ s $\tau_{e,f}=5.52(-4)$ s	$t_2=4.19(-3)$ s $\tau_{e,f}=5.50(-3)$ s	$t_3=8.37(-3)$ s $\tau_{e,f}=4.59(-3)$ s	$t_4=1.3896(-2)$ s $\tau_{e,f}=1.98(-3)$ s	$t_5=1.67415(-2)$ s $\tau_{e,f}=2.52(-7)$ s
	TPI				
GRI-3	<u>148f</u> : +0.61	<u>39f</u> : +0.18	<u>145f</u> : +0.14	<u>145f</u> : +0.16	<u>1f</u> : +0.28
	<u>131f</u> : +0.14	<u>189f</u> : -0.17	<u>189f</u> : -0.14	<u>189f</u> : -0.11	<u>3f</u> : +0.10
	<u>39f</u> : +0.07	<u>145f</u> : +0.12	<u>39f</u> : +0.14	<u>16/17f</u> : -0.08	<u>3b</u> : -0.07
	<u>149f</u> : +0.06	<u>149f</u> : +0.08	<u>128f</u> : -0.08	<u>128f</u> : -0.08	<u>2f</u> : +0.04
	<u>19f</u> : +0.05	<u>128f</u> : -0.07	<u>75f</u> : +0.07	<u>75f</u> : +0.07	<u>27f</u> : +0.04
		<u>148f</u> : +0.05	<u>16/17f</u> : -0.06	<u>39f</u> : +0.06	15*f : -0.03
	Po				
	CH ₃ : +0.72	CH ₂ O : +0.88	CH ₂ O : +0.84	CH ₂ O : +0.69	T : +0.65
	HO ₂ : +0.15	HO ₂ : +0.04	T : +0.06	T : +0.14	O ₂ : -0.33
	CH ₂ O : +0.07				OH : +0.28
					H : +0.26
	$t_1=0.0(0)$ s $\tau_{e,f}=6.68(-4)$ s	$t_2=6.3(-3)$ s $\tau_{e,f}=1.17(-2)$ s	$t_3=1.26(-2)$ s $\tau_{e,f}=1.14(-2)$ s	$t_4=2.09(-2)$ s $\tau_{e,f}=4.62(-3)$ s	$t_5=2.51986(-2)$ s $\tau_{e,f}=1.72(-7)$ s
	TPI				
Galway	<u>148f</u> : +0.28	<u>189f</u> : -0.18	<u>189f</u> : -0.17	<u>189f</u> : -0.13	<u>1f</u> : +0.30
	<u>152f</u> : +0.27	<u>146f</u> : -0.11	<u>146f</u> : -0.11	<u>145f</u> : +0.11	<u>3f</u> : +0.10
	<u>131f</u> : +0.10	<u>149f</u> : +0.08	<u>145f</u> : +0.11	<u>146f</u> : -0.10	<u>3b</u> : -0.07
	<u>150f</u> : +0.09	<u>131f</u> : +0.08	<u>149f</u> : +0.09	<u>149f</u> : +0.09	<u>2f</u> : +0.06
	<u>150b</u> : -0.09	<u>145f</u> : +0.07	<u>131f</u> : +0.08	<u>131f</u> : +0.06	<u>27f</u> : +0.04
	<u>19f</u> : +0.04	<u>154f</u> : +0.07	<u>16/17f</u> : -0.07	<u>1f</u> : +0.06	
		<u>16/17f</u> : -0.06	<u>76f</u> : +0.05	<u>16/17f</u> : -0.06	
	Po				
	CH ₃ O ₂ : +0.54	CH ₂ O : +0.59	T : +0.51	T : +0.76	T : +0.39
	CH ₃ : +0.23	T : +0.24	CH ₂ O : +0.29	C ₂ H ₄ : +0.09	H : +0.32
	HO ₂ : +0.13	C ₂ H ₆ : +0.09	C ₂ H ₆ : +0.12	C ₂ H ₆ : +0.08	OH : +0.32
				H ₂ : +0.07	O ₂ : -0.24

that the fact that at points P₂-P₄ $\tau_{e,f}$ is smaller in GRI-3.0 case is reflected by the dominance of the promoting reaction 145f, while in the Galway case the dominant reactions are the opposing reactions 189f. Other reactions that provide significant contributions to the explosive character of $\tau_{e,f}$ are the chain branching 39f in the GRI-3.0 case and the chain carrying 149f and 131f in the Galway case.

Considering the pointed variables at points P₂-P₄, Table 4 suggests that when using the GRI-3.0 mechanism it is mainly the mass fraction of CH₂O that relates to $\tau_{e,f}$ and followed by the temperature T. In contrast, when using the Galway mechanism it is the temperature that is most significant, followed by the mass fraction of CH₂O and then by that of C₂H₆. Note that the strongest influence of the temperature to $\tau_{e,f}$, in the case of the Galway mechanism, is also manifested in Fig. 4, where the evolution of $\tau_{e,f}$ is displayed when computed by accounting or by neglecting the energy equation.

The chemical paths that relate to the explosive time scale $\tau_{e,f}$ can thus be constructed, as displayed in Fig. 5, by accounting the reactions that exhibit the largest TPIs. The top row of the figure refers to the start of the process ($t = 0$), while the bottom row refers to the points P₂-P₄. For the initiation of the process, the top row of Fig. 5 suggests that both mechanisms provide a similar path, with the exception of reactions 149f and 39f in the GRI-3.0 case being substituted by reactions 150f,b and 152f in the Galway case, all three of which are not included in the GRI-3.0 mechanism. These differences in the $\tau_{e,f}$ -related pathways at P₁ are the cause for the differences in the pathways at points P₂-P₄. As the bottom row of Fig. 5 suggests, only reactions 145f and 189f participate in both pathways developing in the GRI-3.0 and Galway cases. These two reactions are supplemented by reactions 39f and 16/17f in the GRI-3.0 case and by reactions 149f, 146f and 131f in the Galway case. In contrast to the initiation case, these differences

Figure 5: Chemical pathways of the reactions that contribute the most to the generation of $\tau_{e,f}$ (large TPI) for the case (i); $p(0) = 1$ MPa, $T(0) = 1100$ K. Left: the GRI-3.0 mechanism. Right: the Galway mechanism. Top: pathways at the initiation of the process. Bottom: pathways during the chemical runaway regime, right after the start of the process. Bold species (colored blue) are the pointed species. For the notation of the reaction numbers see Table 2.

are not related directly to the differences in the reactions included in the two mechanisms considered, since all the reactions that participate in the two pathways are encountered in both mechanisms. Instead, as discussed next, the differences in the two pathways at points P₂-P₄ are due to the differences encountered during the initiation of the process.

As shown in the upper row of Fig. 5, the Galway mech's initiation process is strongly influenced by reactions 150f,b and 152f. This sequence of reactions combines methyl radicals with oxygen to produce methylperoxy, which in turn reacts with methane to produce methyl radicals and methyl hydroperoxide species ($\text{CH}_3\text{O}_2\text{H}$). The latter species quickly decomposes to methyl and hydroperoxyl radicals. Therefore, the net result of this reaction sequence is a net increase in CH_3 and HO_2 radical production. Recall, these reactions are missing in GRI-3.0, and therefore the initial production of CH_3 and HO_2 radicals produced in the Galway mech is higher. Moving to points P₂-P₄, the higher concentrations of these radicals results in reactions involving them (e.g., 145f, 146f, and 149f) being more pronounced in the Galway mech. GRI-3.0 explosivity is more governed by CH_2O than temperature because this species is directly formed in the early stages (via 149f) and consumed to release heat in the later stages (39f). On the other hand, Galway mech explosivity is

governed more by temperature, because heat release is driven by various radical driven processes (145f, 146f, 149f). The Galway mech is not as dependent on CH_2O oxidation for heat release as GRI-3.0, as this is also suggested by the Po of CH_2O and of temperature in Table 4.

At point P₅, Table 4 shows that the reactions that contribute the most to the explosive time scale $\tau_{e,f}$ and the dominant variables are the same in both the GRI-3.0 and the Galway mechanisms:

GRI	Galway	
(+0.28)	(+0.30)	<u>1f</u> $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$
(+0.10)	(+0.10)	<u>3f</u> $\text{OH} + \text{H}_2 \rightarrow \text{H} + \text{H}_2\text{O}$
(-0.07)	(-0.07)	<u>3b</u> $\text{H} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}_2$
(+0.04)	(+0.06)	<u>2f</u> $\text{O} + \text{H}_2 \rightarrow \text{H} + \text{OH}$
(+0.28)	(+0.39)	T
(+0.10)	(+0.32)	H
(-0.07)	(+0.32)	OH
(+0.04)	(-0.24)	O ₂

This feature indicates that the dynamics at the final part of the explosive stage is described by the same chemistry in both mechanisms. It is the same chemistry encountered in this part (end of explosive stage), when other fuels and a wider range of initial conditions were considered; i.e., H_2 [31], CH_4 [39, 40, 41],

n-heptane [42, 43], DME and EtOH [44, 45]. Regarding the pointed variables at point P₅, Table 4 shows that the temperature is the leading variable, followed by the mass fraction of OH, H and O₂, which are reactants to the dominant reaction 1f.

8. Diagnostics for the p(0)=4 MPa T(0)=900 K case

Table 5 displays the CSP diagnostics for the initial conditions $p(0) = 4$ MPa and $T(0) = 900$ K ((ii) case), as they were computed at the five points P₁-P₅ along the ignition delay, shown in Fig (3). Included are the TPI indices, which identify the reactions contributing the most to $\tau_{e,f}$ and the Po index which identifies the variables (species mass fractions and temperature) related the most to $\tau_{e,f}$. Note that for the set of initial conditions considered here, the ignition delay t_{ign} is shorter when using the Galway mechanism, according to Table 3.

At point P₁, Table 5 shows that, when using the GRI-3.0 mechanism, the reactions contributing the most to $\tau_{e,f}$ and the variables related the most to this time scale are:

(+0.62) 148f	$\text{CH}_3 + \text{O}_2 \rightarrow \text{O} + \text{CH}_3\text{O}$
(+0.13) 131f	$\text{CH}_3 + \text{H}_2\text{O}_2 \leftarrow \text{HO}_2 + \text{CH}_4$
(+0.70)	CH_3
(+0.13)	HO_2

while when using the Galway these are:

(+0.73) 152f	$\text{CH}_4 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3 + \text{CH}_3\text{O}_2\text{H}$
(+0.14) 131f	$\text{CH}_4 + \text{HO}_2 \rightarrow \text{CH}_3 + \text{H}_2\text{O}_2$
(+0.75)	CH_3O_2
(+0.14)	HO_2

The diagnostics at $t = 0$ for the case considered here when using the GRI-3.0 mechanism are exactly the same with those in the case examined previously in Section 7. The diagnostics when using the Galway mechanism are quite similar with those in the case examined in Section 7. The only difference is that reactions 148f and 150f,b provide negligible contribution and the mass fraction of their reactant CH₃ is not among the pointed variables. The reaction 150f forms the methylperoxy radical (CH₃O₂) and 150b is its dissociation back to CH₃ and O₂. The 150f,b reactions appear lower down in the list of important reactions at 900 K because the CH₃O₂ radical is more stable at these temperatures. Thus, CH₃O₂ can react with the fuel (CH₄) via H-atom abstraction in reaction 152f at these lower

temperatures, which drives reactivity at P₁. In particular, when using the GRI-3.0 mechanism reaction 148f contributes the most (66%) to $\tau_{e,f}$, followed by reaction 131f (13%), while when using the Galway mechanism reaction 152f is the largest contributor (73%), followed by reaction 131f (14%); the reaction 148f is included in both mechanisms, while reaction 152f is included only in the Galway mechanism. In both cases the pointed mass fractions refer to species that are reactants to the contributing reactions $\tau_{e,f}$; CH₃ is reactant of 148f, CH₃O₂ is reactant of 152f and HO₂ is reactant of 131f.

As in case (i) discussed previously, Table 5 suggests that in case (ii) the set of reactions that generate $\tau_{e,f}$ at points P₂-P₄ differs significantly, when using the two mechanisms. In particular, the reactions that contribute the most to $\tau_{e,f}$ and the variables related the most, for the GRI mechanism are:

(+0.20 to +0.24) 145f	$\text{CH}_3 + \text{HO}_2 \rightarrow \text{CH}_2\text{O} + \text{OH}$
(+0.06 to +0.20) 39f	$\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{HCO} + \text{HO}_2$
(-0.10 to -0.17) 189f	$\text{CH}_3 + \text{CH}_3(+\text{M}) \rightarrow \text{C}_2\text{H}_6(+\text{M})$
(-0.11 to -0.17) 16/17f	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$
(0.56 to 0.86)	CH_2O
(0.09 to 0.30)	H_2O_2
(0.02 to 0.11)	T

and for the Galway mechanism these are:

(+0.19 to +0.21) 19f	$\text{H}_2\text{O}_2(+\text{M}) \rightarrow \text{OH} + \text{OH}(+\text{M})$
(+0.06 to +0.12) 151f	$\text{CH}_3\text{O}_2 + \text{CH}_2\text{O} \rightarrow$
	$\text{CH}_3\text{O}_2\text{H} + \text{HCO}$
(+0.04 to +0.15) 131f	$\text{CH}_4 + \text{HO}_2 \rightarrow \text{CH}_3 + \text{H}_2\text{O}_2$
(-0.06 to -0.12) 16/17f	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$
(0.41 to 0.60)	H_2O_2
(0.07 to 0.37)	T
(0.18 to 0.31)	CH_2O
(0.01 to 0.12)	CH_3O_2

A first comment on these diagnostics is that the hydrogen chemistry is more active when using the Galway mechanism. This finding agrees very well with the fact that $\tau_{e,f}$ and t_{ign} are shorter in this case. In addition, the influence of the temperature is stronger when using the Galway mechanism, as it is evident by the value of its Po index. This feature agrees fully with the results displayed in Fig. 4 (bottom row), according to which the thermal runaway extends in a larger portion of the ignition delay when using this mechanism.

In particular, Table 5 suggests that when using the GRI-3.0 mechanism, the generation of $\tau_{e,f}$ at points P₂-P₄ is mainly promoted by the two chain carrying reactions 145f and 39f, which are included in the Galway

Table 5: Diagnostics results for both chemical mechanisms under study; $p(0) = 4$ MPa, $T(0) = 900$ K, $\phi = 1$; $t_{ign}=0.1631995$ s for the GRI-3.0 and $t_{ign}=0.0360763$ s for the Galway mechanism.

	P ₁	P ₂	P ₃	P ₄	P ₅
	$t_1=0.0(0)s$ $\tau_{e,f}=3.12(-3)s$	$t_2=4.08(-2)s$ $\tau_{e,f}=3.88(-2)s$	$t_3=8.16(-2)s$ $\tau_{e,f}=3.19(-2)s$	$t_4=1.3546(-1)s$ $\tau_{e,f}=1.51(-2)s$	$t_5=1.631994(-1)s$ $\tau_{e,f}=2.15(-7)s$
	TPI				
GRI-3.0	<u>148f</u> : +0.62	<u>145f</u> : +0.20	<u>145f</u> : +0.24	<u>145f</u> : +0.24	<u>1f</u> : +0.20.
	<u>131f</u> : +0.13	<u>39f</u> : +0.20	<u>39f</u> : +0.15	<u>16/17f</u> : -0.17	<u>3f</u> : +0.08
	<u>19f</u> : +0.09	<u>189f</u> : -0.17	<u>189f</u> : -0.14	<u>189f</u> : -0.10	15*f : -0.07
	<u>39f</u> : +0.07	<u>149f</u> : +0.08	<u>16/17f</u> : -0.11	<u>76f</u> : +0.09	<u>24b</u> : +0.07
	<u>149f</u> : +0.07	<u>75f</u> : +0.06	<u>75f</u> : +0.08	<u>19f</u> : +0.09	<u>3b</u> : -0.06
			<u>146f</u> : +0.06	<u>39f</u> : +0.06	<u>24f</u> : -0.06
	Po				
	CH ₃ : +0.70	CH ₂ O : +0.86	CH ₂ O : +0.82	CH ₂ O : +0.56	T : +1.49
	HO ₂ : +0.13	H ₂ O ₂ : +0.09	H ₂ O ₂ : +0.13	H ₂ O ₂ : +0.30	O ₂ : -0.42
	H ₂ O ₂ : +0.09		T : +0.02	T : +0.11	OH : +0.13
	CH ₂ O : +0.08				H ₂ O : -0.09
	$t_1=0.0(0)s$ $\tau_{e,f}=1.77(-3)s$	$t_2=9.0(-3)s$ $\tau_{e,f}=6.34(-3)s$	$t_3=1.8(-2)s$ $\tau_{e,f}=7.15(-3)s$	$t_4=3.0(-2)s$ $\tau_{e,f}=4.17(-3)s$	$t_5=3.60762(-2)s$ $\tau_{e,f}=9.20(-8)s$
	TPI				
Galway	152f : +0.73	<u>19f</u> : +0.19	<u>19f</u> : +0.20	<u>19f</u> : +0.21	<u>1f</u> : +0.28
	<u>131f</u> : +0.14	<u>131f</u> : +0.15	151f : +0.12	151f : +0.09	<u>3f</u> : +0.09
	<u>19f</u> : +0.08	152f : +0.13	<u>16/17f</u> : -0.09	<u>129f</u> : +0.07	<u>3b</u> : -0.07
	150f : +0.01	<u>16/17f</u> : -0.12	<u>131f</u> : +0.08	<u>76f</u> : +0.07	<u>27f</u> : +0.06
	150b : -0.01	151f : +0.06	<u>76f</u> : +0.06	<u>16/17f</u> : -0.06	<u>8f</u> : -0.05
		154f : -0.05	152f : +0.05	<u>72f</u> : -0.05	<u>9f</u> : -0.05
		150f : +0.05	<u>146f</u> : -0.05	<u>146f</u> : -0.05	
		150b : -0.05			
	Po				
	CH ₃ O ₂ : +0.75	H ₂ O ₂ : +0.60	H ₂ O ₂ : +0.55	H ₂ O ₂ : +0.41	T : +0.79
	HO ₂ : +0.14	CH ₂ O : +0.19	CH ₂ O : +0.31	T : +0.37	O ₂ : -0.31
	H ₂ O ₂ : +0.08	CH ₃ O ₂ : +0.12	T : +0.07	CH ₂ O : +0.18	OH : +0.30
					H : +0.18

mechanism but they have negligible influence on $\tau_{e,f}$ when the latter mechanism is used. When the Galway mechanism is used, the major $\tau_{e,f}$ -promoting reactions are 19f, 131f and 151f; the first two are included in the GRI-3.0 mechanism but exhibit negligible influence on $\tau_{e,f}$ when this mechanism is used, while 151f is not included in the GRI-3.0. In both cases, the major opposing to $\tau_{e,f}$ action originates from the termination reaction 16/17, while an additional opposition originates from the termination reaction 189f when using the GRI-3.0 mechanism. The mass fraction of CH₂O and H₂O₂ are the variables related the most to $\tau_{e,f}$, along with the temperature at P₃ and P₄, whose influence is more pronounced when using the Galway mechanism.

The chemical paths of the reactions that relate the most to the generation of $\tau_{e,f}$ are depicted in Fig. 6, for the two mechanisms; the top row refers to the ini-

tiation of the process ($t = 0$) and the bottom row at the conditions prevailing at points P₂-P₄. A comparison with the pathways in Fig. 5 for the $p(0) = 1$ MPa and $T(0) = 1100$ K case reveals that those for the GRI-3.0 mechanism are similar; i.e. the difference in the initial temperature and pressure did not had an effect, both at the initiation and during the chemical runaway. Regarding the pathways for the Galway mechanism, it is shown that at the initiation of the process the differences are rather small; the significant influence of reactions 148f and 150 in the $p(0) = 1$ MPa and $T(0) = 1100$ K case now is negligible. However, the pathways at points P₂-P₄ are completely different; the influence of hydrogen chemistry is much more pronounced in the $p(0) = 4$ MPa and $T(0) = 900$ K case, mainly via the action of the reaction 19f.

Table 5 suggests that at point P₅ the set of reactions

Figure 6: Chemical pathways of the reactions that contribute the most to the generation of $\tau_{e,f}$ (large TPI) for the case (ii); $p(0) = 4$ MPa, $T(0) = 900$ K. Left: the GRI-3.0 mechanism. Right: the Galway mechanism. Top: pathways at the initiation of the process ($t = 0$). Bottom: pathways in the chemical runaway regime (P₂-P₄), right after the start of the process. Bold species (colored blue) are the pointed species. For the notation of the reaction numbers see Table 2.

that contribute the most to the generation of $\tau_{e,f}$ is not exactly the same when using the two mechanisms, as in the case (i) examined previously, but is quite similar; i.e., for the GRI-3.0 mechanism:

(+0.20)	<u>1f</u>	H + O ₂ → O + OH
(+0.08)	<u>3f</u>	OH + H ₂ → H + H ₂ O
(-0.07)	15*f	OH + HO ₂ → O ₂ + H ₂ O
(+0.07)	<u>24b</u>	H ₂ O ₂ + OH → H ₂ O + HO ₂
(+1.49)		T
(-0.42)		O ₂
(+0.13)		OH

and for the Galway mechanism:

(+0.28)	<u>1f</u>	H + O ₂ → O + OH
(+0.09)	<u>3f</u>	OH + H ₂ → H + H ₂ O
(-0.07)	<u>3b</u>	OH + H ₂ → H + H ₂ O
(+0.06)	<u>27f</u>	CO + OH → CO ₂ + H
(+0.79)		T
(-0.31)		O ₂
(+0.30)		OH

As in case (i) at P₅, the reactions contributing the most to $\tau_{e,f}$ are reactions 1f and 3f. However, now their contribution is significantly higher than in case (i). Sim-

ilarly to case (i) the CO to CO₂ reaction 27f keeps providing only a small contribution at this point.

9. Conclusions

The GRI-3.0 [1] and Galway [2] chemical kinetics mechanisms were employed for simulations of homogeneous, isochoric autoignition of CH₄/air mixtures. The aim of the present study was to identify algorithmically the components of the two mechanisms that contribute the most to the differences in the predicted ignition delay. Two cases, in which large such differences in the ignition delay are recorded, were investigated. The analysis was based on diagnostics generated by CSP algorithmic tools, which allowed the identification, at selected points during the chemical and thermal runaways, of the reactions and species that relate the most to the generation of the explosive time scale and thus to the ignition delay. Among others, such an analysis allows to follow the temporal evolution of the major chemical paths that lead to ignition.

The major findings are the following:

1. The presence of reaction 152f (CH₄+CH₃O₂ → CH₃+CH₃O₂H) and of the species CH₃O₂ in the Galway mechanism (both are absent in GRI-3.0)

have a strong influence in the dynamics during the initial stage of the ignition delay, in promoting ignition, when considering large and low initial temperatures. A similar influence has reaction 150f,b ($\text{CH}_3 + \text{O}_2(+\text{M}) \leftrightarrow \text{CH}_3\text{O}_2(+\text{M})$) (which is also included in the Galway mechanism but is absent from the GRI-3.0), but only when considering high temperatures. Instead, when using the GRI-3.0 mechanism the reaction that dominates the initial stage is 148f ($\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{O}$), which is present in the Galway mechanism but is not shown there to exercise any influence.

2. According to Fig. 1, the largest deviations in t_{ign} are encountered in the case of a low initial temperature (case (ii), in which the Galway mechanism generates much shorter t_{ign}). In this case, it was shown that the reaction that dominates the generation of $\tau_{e,f}$, during the most part of the explosive stage, is the (carbon chemistry related) reaction 145f ($\text{CH}_3 + \text{HO}_2 \rightarrow \text{CH}_2\text{O} + \text{OH}$) when the GRI-3.0 mechanism is employed and the hydrogen chemistry related reaction 19f ($\text{H}_2\text{O}_2(+\text{M}) \rightarrow \text{OH} + \text{OH}(+\text{M})$) when the Galway mechanism is related.
3. The deviations encountered in the case of a large initial temperature (case (i), in which the Galway mechanism generates longer t_{ign}) are attributed to the much more intense activity of the hydrogen chemistry throughout the explosive stage when the Galway mechanism is employed, mainly via reaction 19f ($\text{H}_2\text{O}_2(+\text{M}) \rightarrow \text{OH} + \text{OH}(+\text{M})$). Such an action of 19f has been reported for a large number of fuels [46].
4. Due to the prevailing paths along the ignition delay, the portion of this period in which extends the chemical/thermal runaway regime is larger/smaller in the case where the GRI-3.0 mechanism is employed. This explains the fact that temperature is more influential when using the Galway mechanism.

Note that all these features, notably the influence of reaction 152f at the initial stage of the ignition delay and of reaction 19f throughout the ignition delay, were identified by CSP algorithmic tools. The CSP methodology presented in this manuscript provides new insights into underlying chemical kinetic phenomenon governing global combustion properties. As shown, two kinetic models with widely different reaction mechanisms can predict similar global combustion behavior. Yet, the question remains as to which kinetic model is the best representation of reality. Indeed, answering

such a question is beyond the present scope because of the postdictive nature of both kinetic models utilized [47]. Nevertheless, the CSP approach described herein could be used to study a kinetic model with reaction pathways, rate parameters, and thermochemistry predicted completely by ab initio quantum chemical calculations. Such a predictive model would be a representation of “real” reaction dynamics and not constrained or tuned to match global combustion measurement data. The CSP approach could be used to compare various postdictive models with the predictive model, and find which postdictive model is the most chemically accurate.

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Appendix A. Details on the various mechanisms

[3] 1958 - 11 species, 6 elementary reactions: Methane oxidation at temperatures from 423 to 513K and under pressures from 100 to 375 mm Hg using various mixture compositions ($\text{CH}_4/\text{O}_2 = 1/2, 1/1, 2/1$).

[4] 1970 - 13 species, 18 elementary reactions: The oxidation of methane behind reflected shock waves has been studied in the temperature range of 1350 to 1900K. The mixture compositions studied ranged from 0.2 to 5.0 fraction stoichiometric, and the pressure range was from 1.5 to 4.0 atm.

[5] 1975 - 13 species, 23 elementary reactions: shock-initiated methane oxidation, CH_4/O_2 ratios of 0.5, 1, and 2, for initial reflected shock temperatures in the range 1875 to 2240K

[6] 1978 - 23 species, 63 elementary reactions: The combustion of CH_4 in fuel-rich, $\text{CH}_4/\text{O}_2/\text{Ar} = 9/1/90$, mixtures was studied behind incident shock waves with $1800 < T(\text{K}) < 2700$ at total densities of $1.2 \times 10^{-6} \text{ mol/cm}^3$.

[7] 1979 - 25 species, 75 elementary reactions: Initial conditions studied include temperatures from 1300-1900 K. and mixtures ranging from pure methane to pure ethane, with stoichiometric amounts of oxygen, diluted in argon. Computed ignition delay times and effective activation energies are compared with published experimental shock tube results.

[8] 1984 - 34 species, 140 elementary reactions: Shock-Initiated Ignition in Methane-Propane Mixtures at constant density of approximately $2 \times 10^{-5} \text{ mol/cm}^3$ over a temperature range of 1300-1600K.

[9] 1992 - 31 species, 149 elementary reactions: The initial conditions chosen in our study for computer simulation of the shock-tube conditions vary from 1400 to 2000K and at total densities of from 1.5 to 6.0×10^{-5} mol/cm³.

[10] 1994 - 70 species, 1600 elementary reactions: Methane pyrolysis, partial oxidation and combustion

[11] 1995 - 42 species, 835 reactions: oxidation of methane and ethane, atmospheric pressure and $T(0)=773$ -1573K.

[12] 1998 - 156 species, 680 reactions: The chemical structure of an opposed-flow, methane diffusion flame is studied.

[13] 1999 - 38 species, 190 reactions: modeling of shock-induced ignition in low-dilution CH₄/O₂ mixtures at high pressures (40-260 atm) and intermediate temperatures (1040-1500 K).

[14] 2000 - 77 species, 484 reactions: investigation of methane oxidation in the presence of NO and NO₂ has been made in an isothermal plug-flow reactor at 750-1250K.

[15] 2000 - 127 species, 1207 reactions: -

[1] 2000 - 53 species, 325 reactions: Find more information on the performance of the mechanism at http://www.me.berkeley.edu/gri_mech.

[16] 2001 - 37 species, 351 reactions: The mechanism accounts for the oxidation kinetics of methane, hydrogen, carbon monoxide, ethane, and ethene in flames and homogeneous ignition systems in a wide concentration range. It is tested against a variety of experimental measurements of laminar flame velocities, laminar flame species profiles, and ignition delay times.

[17] 2007 - 118 species, 663 reactions: Shock tube chemical kinetic modeling to simulate ignition and oxidation kinetics of various methane-propane fuel blends at gas turbine pressures. Ignition delay times were obtained behind reflected shock waves for fuel mixtures consisting of CH₄/C₃H₈ in ratios ranging from 90/10% to 60/40%. Equivalence ratios varied from lean ($\phi = 0.5$), through stoichiometric to rich ($\phi = 3.0$) at pressures from 5.3 to 31.4 atm and temperatures as low as 1042 K.

[18] 2009 - 97 species, 779 reactions: The oxidation of NH₃ during oxy-fuel combustion of methane, i.e., at high [CO₂], has been studied in flow reactor conditions. The simulations covered stoichiometries ranging from fuel rich to very fuel lean and temperatures from 973 to 1773 K.

[19] 2010 - 230 species, 1328 reactions: Rapid compression machine and shock-tube conditions for blends of CH₄/n-C₄H₁₀ in "air" at pressures of approximately 10, 16, 20, 25, and 30 atm from fuel-lean to fuel-

rich conditions at two different fuel compositions, 90% CH₄/10% n-C₄H₁₀ and 70% CH₄/30% n-C₄H₁₀, and temperatures from 660 to 1330 K.

[20] 2013 - 253 species, 1542 reactions: A detailed chemical kinetic mechanism was developed to describe the oxidation of small hydrocarbon and oxygenated hydrocarbon species. The mechanism was validated over a wide range of initial conditions and experimental devices, including flow reactor, shock tube, jet-stirred reactor, and flame studies. The mechanism contains accurate kinetic descriptions for saturated and unsaturated hydrocarbons, namely methane, ethane, ethylene, and acetylene, and oxygenated species; formaldehyde, methanol, acetaldehyde, and ethanol.

[21] 2015 - 157 species, 1011 reactions: A detailed chemical reaction mechanism for oxy-fuel combustion of sour gas, a mixture of natural gas (essentially methane (CH₄)), carbon dioxide (CO₂), and hydrogen sulfide (H₂S), is presented.

[2] 2015 - 113 species, 710 reactions: The mechanism accounts for the ignition delay and kinetic modeling of methane, dimethyl ether, and their mixtures at high pressures.

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