# A CSP-BASED SKELETAL MECHANISM GENERATION PROCEDURE: AUTO-IGNITION AND PREMIXED LAMINAR FLAMES IN *N*-HEPTANE/AIR MIXTURES

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**Abstract.** We use a procedure based on the decomposition into fast and slow dynamical components offered by the Computational Singular Perturbation (CSP) method to generate automatically skeletal kinetic mechanisms for the simplification of the kinetics of n-heptane oxidation. The detailed mechanism of the n-heptane oxidation here considered has been proposed by Curran et al. and involves 561 species and 2538 reactions. We show that the comprehensive skeletal kinetic mechanisms so generated are able to reproduce the main features of n-heptane auto-ignition at constant pressure, with different initial pressures, temperatures and equivalence ratios. A skeletal mechanism generated with respect to auto-ignition phenomena, which includes only 66 species out of the original 561, has been shown to provide accurate calculations of premixed laminar flames.

# 1 Introduction

To reduce the CPU time and memory overhead required to solve reactive flows with hydrocarbon oxidation chemistry, there exists two main routes, one aimed at trimming non-important species and reactions from the detailed mechanism, the other at producing a (small) number of global reaction steps, whose rates are computed on the basis of the elementary rates; the latter approach, usually referred as "model reduction" can effectively be applied in series after the first which is usually referred as "model simplification".

Among the model simplification techniques, there exist methods aimed at reducing the number of reactions [1, 2], and others at reducing that of species (and the related reactions), such as the Directed Relation Graph (DRG) method [3], and related variants [4]. These model simplification techniques share a common feature, that is, the parameters used to estimate the relative importance of reactions are all constructed on manipulation of the production/consumption terms rating the kinetics of individual species. None of these methods attempts at including explicitly any sort of dynamical characterization in the formulation of the simplification procedure.

As of today, the only approach devoting consideration to this issue is due to Valorani et al. [5, 6], where a skeletal reduction algorithm is introduced in which the criterion for selecting the important reactions and species is based on their relevance to the fast or slow dynamics of a prescribed set of species of interest. The algorithm presented in [5, 6] is based on the fast/slow decomposition offered by the CSP method [7]. This formulation offers a significant advantage in the automatic nature of the reduction strategy, involving minimal input and enhanced confidence in the resulting skeletal mechanisms.

In particular, to decide on the relative importance of a species to the kinetics of the target species, the algorithm proposed in [5, 6] inquires about both (i) the species contribution to the fast components of the reaction rates of the CSP radicals and (ii) the slow components of the reaction rates of the remaining species. All species deemed important for both the fast and slow kinetics are retained, because the skeletal mechanism is required to accurately reproduce both (i) the fast relaxation towards, and (ii) the slow evolution on the slow invariant manifold, respectively.

The base algorithm for model simplification presented in [5, 6] was found to produce very accurate skeletal mechanisms for both the GRI-Mech 1.2 and 3.0 mechanisms for methane oxidation and for both ignition delay times, premixed laminar flame speeds and opposed flame structures.

The base procedure trims the unimportant reactions by comparing the corresponding CSP indices with a single user-defined parameter  $\alpha$ , independently of the species considered and of the size of the set of important reactions. This approach can have shortcomings in particular instances. For example, NO kinetics depend on very few reactions, whereas the temperature evolution depends on many. This yields a typical maximum importance index for NO that is much larger than that for temperature. This situation might eventually lead to overly conservative skeletal mechanisms. To avoid this difficulty, it was proposed in [8] to scale the CSP indices before trimming the reactions on the basis of  $\alpha$ . In this paper, we will carry out a comparative error analysis aimed at verifying which of the two algorithmic options, the one not involving and the other involving the scaling of the CSP indices, is the most suited for achieving accurate skeletal mechanisms. The results of this analysis will be reported and discussed in Sec. 5.

Since the CSP analysis has a local nature, whereas a skeletal mechanism is required to have global validity, the procedures presented in [5, 6, 8] might overlook the existence of couplings among species of non-local nature. The accuracy of the skeletal mechanisms generated under these circumstances might not be entirely satisfactory. To circumvent this limitation, one can imagine a modification of the base procedure aimed at capturing non-local couplings. This can be done by introducing an additional iterative loop over the set of computed states, such that within this loop the procedure automatically updates the species of interest, starting from a user-specified set, until all possible dependencies have been satisfied. This modification is discussed in Sec. 6.

In Sec. 7, we generated a number of comprehensive skeletal mechanisms valid for the constant pressure auto-ignition of *n*-heptane/air mixtures, for a pressure of 1 bar and for equivalence ratios in the range 0.5 - 2.0. The detailed mechanism of the *n*-heptane oxidation here considered has been proposed by Curran et al. [9] and involves 561 species and 2538 reactions. We are interested in constant pressure auto-ignition because we want to verify if it is possible to obtain accurate results for laminar premixed flames with skeletal mechanisms generated in a simple configuration, like the homogeneous ignition.

To this aim, we produced one set of mechanisms relative to the range of initial temperatures 600-1250 K, and another to 1000-1250 K. The rationale for constructing skeletal mechanisms tailored to two different initial temperature ranges stems from the conjecture that in a laminar flame it is not essential to include the low temperature kinetics, regardless of the fact that the premixed reactants will be set at 400K. In fact, the results reported in Sec. 8, which refer to planar, atmospheric, stoichiometric laminar premixed flames, will offer an empirical confirmation of the validity of this conjecture. In particular, we found that a simplified mechanism including only 66 species and generated with reference to the high temperature regime only, is able to yield a rather satisfactory description of the flame, both in terms of laminar flame speed, equilibrium temperature and field variables across the flame structure.

# 2 The CSP Method

The CSP method was originally conceived for the analysis of spatially homogeneous (finite-dimensional) stiff systems for which fast and slow timescales are separated by a substantial gap, this circumstance being typical in combustion systems. The presence of such a gap is generally responsible for the existence of a slow invariant manifold (SIM) [10], a lower-dimensional exponentially attractive locus of the phase (composition) space, where the dynamics is solely governed by the spectrum of slow timescales and which therefore embeds the asymptotic behavior of the system. The CSP method provides an accurate estimate of the manifold [11, 12], a crucial step if a reduced system is to be achieved for which a subset of slow variables is left to evolve on the manifold and the remaining fast variables follow from the equation of the manifold itself. The CSP method was also extended to reactive flows governed by systems of PDEs [13, 14], the main focus of all these contributions being the analysis of the role of the transport operators in the development and the nature of slow manifolds. A brief outline of the necessary CSP theoretical tools will be given in what follows. Consider a generic set of PDEs governing the evolution of a reactive flow involving  $N_S$  species:

$$\frac{d\mathbf{u}}{dt} = \mathbf{L}_C + \mathbf{L}_D + \mathbf{f}(\mathbf{u}) = S\mathbf{R}$$
(1)

where  $\mathbf{u}(\mathbf{x},t) = (Y_1, ..., Y_{N_S-1}, T)^T$  is a N-dimensional ( $N = N_S$ ) vector of scalar unknowns, namely concentrations and temperature, the N-dimensional vectors  $\mathbf{L}_C = \{L_C^i\}$ and  $\mathbf{L}_D = \{L_D^i\}$  formally denote the convective and diffusive spatial operators respectively, and where  $\mathbf{f}(\mathbf{u})$  is a source term describing the production and/or consumption of species by finite rate chemical kinetics. The RHS is generally cast in a CSP canonic form represented by the composition of a  $(N \times N_P)$  generalized stoichiometric matrix  $S = \{\mathbf{S}_k\}$ and a  $N_p$ -dimensional generalized reaction rate vector  $\mathbf{R} = \{R^k\}, N_P = 2(N_R + N)$  indicating the total number of processes comprising  $N_R$  chemical reactions (forward and backwards) and the species diffusion and convection. As discussed in [13, 14], the RHS of Eq. (1) can be expanded in terms of a set of "local" CSP vectors or "modes"  $\mathbf{a}_i$  and their corresponding dual vectors  $\mathbf{b}^i$ , taken to be the eigenvectors of the Jacobian matrix of the chemical source term  $\mathbf{f}(\mathbf{u})$  (ordered in decreasing eigenvalues), as:

$$\frac{d\mathbf{u}}{dx} = \sum_{i=1}^{N} \mathbf{a}_i h^i \tag{2}$$

where  $h^i$  are referred to as modal amplitudes and are defined as:

$$h^{i} = \mathbf{b}^{i} \cdot (\mathbf{L}_{C} + \mathbf{L}_{D} + \mathbf{f}(\mathbf{u})) = (\mathbf{b}^{i} \cdot S)\mathbf{R}$$
(3)

so that the system may be recast as:

$$\frac{du^i}{dx} = \sum_{r=1}^M a^i_r \sum_{k=1}^{N_P} \left( \mathbf{b}^r \cdot \mathbf{S}_k \right) R^k + \sum_{s=M+1}^N a^i_s \sum_{k=1}^{N_P} \left( \mathbf{b}^s \cdot \mathbf{S}_k \right) R^k \tag{4}$$

where the contributions to the  $M \leq N$  fastest modes, associated to the M largest eigenvalues, are separated from the N - M slowest. Note that the number M of fast modes may be estimated using the criterion described in [13], which, to within a user specified tolerance, declares the first M modes "exhausted", i.e.,  $h^i \approx 0$  (i = 1, M). The latter constraints are the defining equations of the SIM as approximated by the CSP vectors. The decomposition into fast and slow modes prompts the introduction of a "slow" importance index  $(I_k^i)_{slow}$  assessing the relative importance of the k-th process (either a reaction or a convection/diffusion transport) in the prodution/consumption of the *i*-th species in the context of its slow evolution on the manifold. In addition, it prompts the introduction of a "fast" importance index  $(I_k^i)_{fast}$  assessing the relative importance of the k-th process on the species affected the most by the M fastest time scales (referred to as CSP "radical species" [13]). The CSP slow and fast importance indices may be defined as:

$$(I_k^i)_{slow} = \frac{\sum_{s=M+1}^N a_s^i (\mathbf{b}^s \cdot \mathbf{S}_k) R^k}{\sum_{j=1}^N \left| \sum_{s=M+1}^N a_s^i (\mathbf{b}^s \cdot \mathbf{S}_j) R^j \right|}$$
(5)

$$(I_k^i)_{fast} = \frac{\sum_{r=1}^M a_r^i (\mathbf{b}^r \cdot \mathbf{S}_k) R^k}{\sum_{j=1}^{N_P} \left| \sum_{r=1}^M a_r^i (\mathbf{b}^r \cdot \mathbf{S}_j) R^j \right|}$$
(6)

For a given species, the elementary reactions with the largest  $(I_k^i)_{slow}$  are the rate controlling reactions for that species [15], as they are the most responsible for its slow evolution on the manifold. On the other hand, elementary reactions with the largest  $(I_k^i)_{fast}$  will be the main contributors to the fast relaxation process towards the manifold, quickly readjusting any perturbation of the system state back onto the manifold. Given a particular reactive flow problem for which an index database is constructed, it is through the analysis of such database that the detailed kinetic mechanism simplification may be accomplished, retaining the reactions which globally exhibit a significant contribution to the (fast/off-manifold, slow/manifold-constrained) evolution of given subsets of species, and discarding the less relevant reactions.

## 3 The generation procedure

The base algorithm for skeletal reduction presented in [5, 6] involved three main stages: (1) at each computed system state, a set of locally important species is identified iteratively, with reference to a user-defined set of target species, by adding species appearing in reactions both involving the target species and having the proper CSP important indices larger than a user-defined threshold  $\alpha$ ; (2) the comprehensive set of important species is defined as the union of all sets of locally important species; (3) the definition of the skeletal mechanism is completed by including all those reactions solely involving species in the comprehensive set of important species.

The base procedure presented in [5, 6] trims the unimportant reactions by comparing the proper CSP indices, measuring the relative importance of each reaction to the time rate of change of, say, the *i*-th species, with a single, user-defined, parameter  $\alpha$ .

However, it has been pointed out in [8] that an alternative measure can be introduced, which involves first scaling each original CSP index  $I_k^i$  with  $I_{max}^i = max[I_m^i; m \in (1, N_r^i)]$ , and then enforcing the comparison with  $\alpha$ . This is equivalent to saying that the importance of reactions is checked against a tolerance  $\alpha I_{max}^i$ . As a result, the tolerance is different for each species. This option ensures that the most important reaction for each of the species included in the set of locally important species is surely considered during the iterative procedure independently from the choice of the parameter  $\alpha$ . Therefore, at the local level, scaling the indices ensures that the simplified kinetics will always include the most important pathways for the set of locally important species.

#### 4 Error measures

The accuracy of skeletal mechanisms, as constructed with the three algorithm options illustrated in the previous section, can be estimated by comparing the auto-ignition evolutions found using the skeletal and the detailed mechanisms.

The accuracy assessment adopted here will involve the computation of the relative error of the equilibrium temperature,  $E_{eq} = (T_{eq} - T_{eq,ref})/T_{eq,ref} = \Delta T_{eq}/T_{eq}$ , and the relative error on ignition delay time,  $E_{ign} = (\tau_{ign} - \tau_{ign,ref})/\tau_{eq,ref} = \Delta \tau_{ign}/\tau_{ign}$ , where the subscript ref denotes the values obtained with the detailed mechanism.

As definition of the ignition delay time  $\tau_{ign}$ , we take the time interval starting from the beginning of the auto-ignition process and ending at the time at which the heat release rate peaks. In *n*-heptane oxidation at low initial temperatures, a two-stage ignition can take place; in this case, the largest heat release rate peak occurs during the second stage ignition.

Simplified mechanisms might exhibit ignition delay times significantly different from those of the detailed mechanism as a consequence of the elimination of chain branching/propagation reactions that can promote or postpone the onset of ignition.

For this reason, the error on the ignition delay time is extremely sensitive to the approximation introduced by replacing the detailed with simplified mechanisms. A typical situation, related to a two-stages ignition case found for a  $(1 \text{ n-C}_7\text{H}_{16}/11 \text{ O}_2/44 \text{ N}_2)$  mixture with an initial pressure set at 13.5 bars and an initial temperature of 850K, is illustrated in Fig. 1. The ignition delay time is over-predicted, nearly correct, and underpredicted for the 138, 128, and 127-species mechanisms, respectively. This suggests that the error on the ignition delay time, being based on a single value quantity, can feature a non monotonic convergence to zero.



Figure 1: Error defined on the basis of the ignition delay time; temperature in Kelvin, time in seconds.

To obtain an error measure less sensitive than the error on the ignition delay time, we resorted to an integral measure of the deviation of the trajectories of the state variables in the phase space where the fuel is chosen as independent parameter. The trajectories found for the temperature and  $C_2H_5$  as a function of  $n-C_7H_{16}$  are shown in Fig. 2 for the same skeletal mechanisms (138, 128, and 127 species) adopted to generate Fig. 1. From

Fig. 2, it is apparent that the error on temperature and  $C_2H_5$  from the 127-species to the 138-species decreases rather monotonically. These findings prompted the introduction of the following error measure:

$$E(Y^{i}) = \frac{1}{Y_{0,fuel}} \int_{Y_{0,fuel}}^{0} \left| \frac{Y^{i}(Y_{fuel}) - Y^{i}_{ref}(Y_{fuel})}{Y^{i}_{ref}(Y_{fuel})} \right| dY_{fuel} \qquad i = 1, N$$
(7)

where  $Y_{0,fuel}$  is the initial fuel mass fraction,  $Y_{ref}^i(Y_{fuel})$  and  $Y^i(Y_{fuel})$  are the mass fractions of the *i*-th species evaluated along solution trajectories as computed by adopting the reference (Curran) and the simplified mechanisms, respectively. The errors  $E(Y^i)$  can be summed up over all species (and the temperature as well) to yield  $E_{all} = \sum_{i \in all} E(Y^i)$ , and/or over the set of species included in the target set to yield  $E_{target} = \sum_{i \in target} E(Y^i)$ . The error  $E_{target}$  is expected to be much smaller than  $E_{all}$ , since, by construction, the skeletal mechanisms are tailored over the target species only.



Figure 2: Error defined on the basis of integral norms of trajectory differences in phase space; temperature in Kelvin, species in mass fractions.

## 5 Performance Assessment

We have anticipated the existence of two options on how to measure the relative importance of reactions, namely by means of the original non scaled or the modified scaled values of the CSP indices, respectively. In this section, we want to assess quantitatively the relative merits of these options. To this aim, we carried out a comparison of the performance of the two options on the basis of the accuracy analysis of the simulation of the constant *volume* auto-ignition of a  $(1 \text{ n-C}_7\text{H}_{16}/11 \text{ O}_2/44 \text{ N}_2)$  mixture for an initial pressure set at 13.5 bars and an initial temperature of 850K.

Fig. 3 reports the errors on the target species,  $E_{target}$ , on all species,  $E_{all}$ , on the equilibrium temperature,  $E_{eq}$ , and the ignition delay time,  $E_{ign}$ , as obtained by adopting the non scaled indices. All the results in this section refer to a target set including only the temperature. From Fig. 3, one can observe that the dependence of the errors  $E_{target}$  and  $E_{all}$  displays an evolution with respect to the number of species retained in the skeletal mechanisms smoother than the error  $E_{ign}$  especially in the range below 250 species. This is a confirmation that the errors  $E_{target}$  and  $E_{all}$  are measures of the accuracy of the skeletal mechanism more convincing than  $E_{ign}$ . Next, it is also confirmed that  $E_{target}$  is several orders of magnitude smaller than  $E_{all}$ . The error on the equilibrium temperature  $E_{eq}$  is very small (< 10<sup>-8</sup>) for all mechanisms with more than 120 species. Finally, the error  $E_{target}$  remains below 1% all the way down to 100 species, whereas  $E_{ign}$  exceeds 20% when the number of species drops below 150-170.



Figure 3: Non-scaled indices and converged-iterations method: errors on target species,  $E_{target}$ , on all species,  $E_{all}$ , on equilibrium temperature,  $E_{eq}$ , and ignition delay time,  $E_{ign}$ .

Fig. 4 reports all errors as obtained by adopting the *scaled* indices. As observed for the non scaled indices, the dependence of the errors  $E_{target}$  and  $E_{all}$  is smoother than  $E_{ign}$ , this indicating that scaling the indices does not improve this trend. The error  $E_{target}$  is several orders of magnitude smaller than  $E_{all}$ , as also noted for the non scaled indices. The error  $E_{eq}$  is very small for a number of species larger than 170, but becomes sensibly larger below this threshold. The order of magnitude of  $E_{target}$  and  $E_{ign}$  is comparable to that observed for the non scaled indices.



Figure 4: Scaled indices and converged-iterations method: errors on target species,  $E_{target}$ , on all species,  $E_{all}$ , on equilibrium temperature,  $E_{eq}$ , and ignition delay time,  $E_{ign}$ .

On the basis of the findings reported in Figs. 3 and 4 one could conclude that both the non scaled and the scaled indices are able to generate valid simplified mechanisms. Indeed, we used in the past [5, 6] both approaches with satisfactory results.

A more stringent comparison of the two approaches can be drawn by displaying the errors of the two methods on the same figure.

Fig. 5 shows that the error  $E_{ign}$  is slightly less irregular for the scaled indices option, but with the same order of magnitude, this making the two methods essentially equivalent to this respect.

Fig. 6 shows that  $E_{target}$  is slightly lower for the scaled indices option, whereas  $E_{all}$  is significantly smaller, especially in the (100-200)-species range, and smoother throughout for the scaled indices option. This result seems to offer the strongest empirical motivation for preferring the scaled indices option, besides this approach seeming the soundest of the two from a theoretical point of view.

Fig. 7 shows that  $E_{eq}$  is much lower for the non scaled indices option when the number of species drops below 170, as noted previously. It is not yet clear as of today what causes this unwelcomed behavior; work is in progress to explore this issue. However, the other errors also attain large values in the same range as the one where the equilibrium temperature is found inaccurate. Therefore, simplified mechanisms with such a large degree of simplification are not acceptable for their poor accuracy independently of the option adopted for the indices.

To summarize, the outcome of the comparative analysis carried out in this section



Figure 5: Comparison of methods #1 and #2: errors on ignition delay time



Figure 6: Comparison of methods #1 and #2: errors on target species, on all species

have not been able to single out which of the two options should be the most preferable, although some findings could suggest that the scaled indices option could yield slightly more accurate skeletal mechanisms that exhibits a smooth dependence on the number of



Figure 7: Comparison of methods #1 and #2: errors on equilibrium temperature

retained species over the whole range of interest.

A further result of this section is that the errors based on the integral norm introduced in Eq. (7) are measures for assessing the skeletal mechanisms accuracy more reliable than the error on the ignition delay time.

## 6 Addition of an outer loop to the base procedure

CSP analysis has a local nature, whereas the skeletal mechanism is required to have global validity. For this reason, the base procedure presented in [5, 6] might overlook the existence of couplings among species of non-local nature. To illustrate this point, let us consider that a set,  $\{\mathbf{u}_n\}_{n=1}^{N_{st}}$ , of state points, with  $\mathbf{u}_n$  having  $N_{dim}$  entries (species, thermodynamic variables), is analyzed by adopting the base procedure and according to some arbitrary ordering.

It is possible that, over a region of states (say, for  $n = 1, \tilde{N}$ ), a subset of the  $N_{dim}$  state vector entries (say, Group 1) is decoupled from the rest (say, Group 2), while these two groups of entries are in fact coupled over a different region of states (say  $n = \tilde{N} + 1, N_{st}$ ). In such a case, if all species in the target set belong to Group 1, then in the region  $(n = 1, \tilde{N})$ the base procedure will not take into account all the possible significant dependencies of the species in Group 2 that were identified as important for the species in the target set in the other region  $(n = \tilde{N} + 1, N_{st})$ . Of course, the accuracy of the skeletal mechanism generated under these circumstances might not be entirely satisfactory.

To circumvent this limitation, one could imagine adding one extra stage to the base procedure, that is, a stage involving an "outer" iteration over the set of computed states, such that the set of target species at each next outer iteration is set equal to the comprehensive set of important species found at the end of the previous iteration. The outer iterations stop when the comprehensive set at the end of the swap on the states remains equal to the target set. The addition of the outer loop to the base procedure realizes a reduction algorithm able to account for both local and non-local couplings.

To assess the effects of carrying out the extra stage, we explored how much the error on the ignition delay time (adiabatic, isochoric process) of a stoichiometric *n*-heptane/air mixture, initially at  $p_0=13.5$  bar and  $T_0=850$  K, decreases, and how much the size of the comprehensive set of important species grows, with the number of outer iterations.

From inspection of the results shown in Fig. 8, which are obtained by using the scaled indices, one can conclude that, although carrying out the extra stage is theoretically justified, the net result of its application is a moderate accuracy improvement and a much smaller degree of simplification for a given threshold on the importance of the reactions. Clearly, the findings of this test are specific and constitute no theoretical proof nor practical guarantee that can have general validity. However, it is worth recalling that the validity of any skeletal mechanism needs to be assessed *a posteriori*, since the skeletal mechanism offering the best combination of accuracy and speed-up needs to be searched on a 1-parameter family, with  $\alpha$  being the parameter, of mechanisms. Therefore, the outer loop must be used only when the base algorithm is failing to return skeletal mechanisms of satisfactory accuracy, this situation arising in coincidence of kinetics featuring dynamical couplings among species of significant non-local nature.



Figure 8: Percent error on ignition delay time and number of species in the skeletal mechanism as a function of the number of outer iterations; *n*-heptane/air mixture,  $\varphi = 1$ ,  $p_0 = 13.5$  bar,  $T_0 = 850$  K.

## 7 Comprehensive Mechanism Generation in Auto-Ignition

A family of skeletal mechanisms for *n*-heptane/air  $(O_2/3.76 N_2)$  mixtures, at atmospheric pressure (1atm), different ranges of initial temperatures and of equivalence ratios have been generated with reference to the constant *pressure*, auto-ignition process in an adiabatic, closed system.

Two simplification campaigns have been carried out. In the first campaign, the database of CSP indices (slow and fast importance indices, pointers to CSP radicals) has been generated on the basis of simulations relative to four initial temperatures (600/700/1000/1250 K) and three equivalence ratios (0.5/1.0/2.0). All the results in this section refer to a target set including temperature, *n*-heptane and CO<sub>2</sub>.

Fig. 9 shows the ignition delay time predicted by two skeletal (139 and 120 species) and the detailed mechanisms over a range of initial temperatures. The three sets of curves in Fig. 9 refer to the three equivalence ratios (0.5/1.0/2.0). For convenience, we will refer to the two skeletal mechanisms for low-to-high temperature kinetics with 139 and 120 species as M#2 and M#3, respectively, whereas the detailed mechanism will be referred to as M#1.



Figure 9: Skeletal mechanisms for low-to-high temperature kinetics: errors on ignition delay time; solid lines refer to the detailed mechanism, small symbols to the comprehensive skeletal mechanisms, wide filled circles denote the states where the CSP inputs have been computed; p = 1 atm,  $\varphi = 0.5/1.0/2.0$  from top to bottom.

Fig. 10 reports the relative errors, maximum and averaged over all the states where the CSP inputs have been computed (shown as filled black circles markers in Fig. 9), on ignition delay time found with different degree of simplifications.



Figure 10: Skeletal mechanisms for low-to-high temperature kinetics: errors on ignition delay time averaged over all the states where the CSP inputs have been computed (shown as filled black circles markers in Fig. 9).

In the second campaign, only initial temperatures in the high range (1000/1250 K) have been considered. Fig. 11 shows the ignition delay time predicted by two skeletal (72 and 66 species) and the detailed mechanisms over a range of initial temperatures. The two skeletal mechanisms for high temperature kinetics with 72 and 66 species will be referred to as M#3 and M#4, respectively.

Fig. 12 reports the relative errors, averaged over all the states where the CSP inputs have been computed (shown as filled black circles markers in Fig. 11), on ignition delay time found with different degree of simplifications.

The findings reported in Figs. 9-12 demonstrate that (i) the accuracy of the skeletal mechanisms is a function of the parameter  $\alpha$ , i.e., the errors grow, as expected, with a reduction of the number of species; (ii) the skeletal mechanisms are able to replicate qualitatively the correct kinetic behavior over the proper range of initial temperatures, with errors below 10-20% until the number of species does not drop below 120 for the low-to-high temperature regime (Fig. 10), and below 66 for the high temperature regime (Fig. 12); (iii) the largest discrepancies for the mechanisms M#2 and #3 including 139 and 120 species out of the original 561 (Fig. 9) are found in the intermediate temperature regime, whereas the mechanisms M#4 and #5, including 72 and 66 species (Fig. 11), becomes inaccurate as the initial temperature drops below 1000K, that is below the states with the lowest temperature where the CSP inputs have been computed; (iv) since the CPU speed-up achievable by adopting skeletal instead of detailed mechanisms, as already demonstrated elsewhere, scales quadratically with the number of species retained in the mechanism, then the 66 species mechanism can achieve a speed-up of the order of



Figure 11: Skeletal mechanisms for high temperature kinetics: errors on ignition delay time; solid lines refer to the detailed mechanism, small symbols to the comprehensive skeletal mechanisms, wide filled circles denote the states where the CSP inputs have been computed; p = 1 atm,  $\varphi = 0.5/1.0/2.0$  from top to bottom



Figure 12: Skeletal mechanisms for high temperature kinetics: errors on ignition delay time averaged over all the states where the CSP inputs have been computed (shown as filled black circles markers in Fig. 11).

 $(561/66)^2 \approx 72$  and the 120 species mechanism can achieve a CPU speed-up of order 22.

## 8 Comprehensive Mechanism Validation in Premixed flames

The skeletal mechanisms generated for low-to-high (M#2 and M#3) and high (M#3 and M#4) temperature kinetics have been adopted to compute the planar laminar flame structures (by using PREMIX) for a premixed mixture of *n*-heptane/air ( $O_2/3.76 N_2$ ), initially at the temperature of 400K, burning at atmospheric pressure.

The laminar flame speeds and the near-equilibrium temperature of the products found with the five mechanisms and for a stoichiometric mixture have been collected in Tab. 1. These data suggest that to reproduce the main features of a laminar flame it is not essential to account for the low temperature kinetics; in fact, even the mechanism M#4, including only 66 species, is able to reproduce quite accurately the correct flame speed and equilibrium temperature.

mech	# spec	$S_L  [\mathrm{cm/s}]$	T [K]
M#1	561	72.33	2333
M#2	139	71.23	2330
M#3	120	71.92	2329
M#4	72	71.40	2330
M#5	66	71.65	2330

Table 1: Laminar flame speed and equilibrium temperature computed with the detailed and four simplified mechanisms.

The errors incurred in the reproduction of the flame structure will be considered in the following. Figs. 13 and 14 illustrates the absolute flow velocity and temperature fields across the flame, respectively. Clearly, all the four skeletal mechanisms yield a rather satisfactory approximation of the main kinematic and thermodynamical variables.

Fig. 15 and 16 show enlarged views of the dependence of temperature and mole fraction of  $C_2H_4$  with respect to the mole fraction of *n*-heptane. The largest discrepancies of the results found by the simplified mechanisms occur in the range of fuel mole fractions smaller than  $10^{-2}$ . Note that the errors on  $C_2H_4$  are rather small although it is not a target species.

#### 9 CONCLUSIONS

This paper has achieved three main goals. First, we carried out a thorough error analysis aimed at verifying which of the two algorithmic options involving or not the scaling of the CSP indices is the most suited for achieving accurate skeletal mechanisms. The comparative analysis showed that although both options produce valid mechanisms, scaling the indices seems to offer a smoother dependence of the accuracy with respect to the number of species retained in the mechanism, and for this reason seems to be the most preferable.

Second, by using the scaled index option, we generated two series of accurate skeletal mechanisms for n-heptane oxidation, one series valid for both a wide range of initial



Figure 13: flame structure; absolute flow velocity (cm/s) vs space (cm); small black circles refer to the detailed mechanism



Figure 14: flame structure; temperature (cm/s) vs space (cm); small black circles refer to the detailed mechanism

temperatures and equivalence ratios, and the other only for the high temperatures regime (and for different equivalence ratios).

Finally, we verified that it is possible to use skeletal mechanisms generated with respect to auto-ignition phenomena for computing premixed laminar flames with high accuracy, especially with respect to macroscopic parameters such as laminar flame speed and equilibrium temperature, and also velocity, temperature and major species fields across the flame.



Figure 15: flame structure; T as a function of  $n-C_7H_{16}$ ; small black circles refer to the detailed mechanism



Figure 16: flame structure;  $C_2H_4$  as a function of  $n-C_7H_{16}$ ; small black circles refer to the detailed mechanism

This test showed that for a premixed laminar flame it is not essential to include the low temperature kinetics of n-heptane. This allowed us to obtain a satisfactory approximation of the flame structure with a rather small mechanism, labeled as M#4 in the main body of the paper, which includes only 66 species out of the original 561.

These findings empirically demonstrate that the reduction can be performed in a simple configuration, like the homogeneous auto-ignition considered in this paper and the resulting reduced mechanism applied successfully to a more complex configuration such as a premixed or counterflow flame, or, even, a fully multidimensional CFD reactive flow simulation.

It is noteworthy to stress, in closing, that the mechanism M#4 seems a good and affordable candidate to tackle the direct simulation of *n*-heptane combustion.

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