

Systematic Reduction of Large Chemical Mechanisms

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Abstract

The directed relation graph method with error propagation (DRGEP) is proposed as a new method for the systematic reduction of large chemical detailed mechanisms. The method is based on the directed relation graph (DRG) approach, but uses generalized coupling coefficients based on error propagations. A skeletal mechanism consisting of the lowest possible number of species and reactions, which reproduces selected targets such as species concentrations, ignition delay times or laminar burning velocities with a given accuracy, is automatically generated. The method has been successfully applied in the reduction of large mechanisms for n-heptane and primary reference fuel oxidation, achieving typical reduction ratios of 2.5 for the number of species and 5 for the number of reactions while keeping the errors on ignition delay time and main species concentrations below 10%. Compared with the DRG method, DRGEP provides significantly improved accuracy of the resulting reduced mechanism, if the same number of species is kept. Comparison with an existing manually reduced mechanism shows the potential of an additional automatic lumping procedure to obtain short skeletal mechanisms that can be directly used in more complex simulations.

Keywords: Systematic reduction of kinetic mechanisms, Autoignition, Heptane, Primary Reference Fuel

1. Introduction

Reactive flow computations such as simulations of engine combustion chambers, require the accurate prediction of chemical features like heat release, ignition delay time, consumption and production of main reactants and products or pollutant formation. Detailed kinetic mechanisms are now available for a large number of hydrocarbon fuels. However, these mechanisms are usually designed to model accurately fuel oxidation or auto-ignition over a large domain in temperature, pressure and initial concentration space and can include thousands of reactions and up to one thousand species, which prohibits their direct implementation in flow simulations. Mechanism reduction aims to reduce those mechanisms to the smallest possible size, which still leads to an accurate prediction of a number of chosen targets over the domain of interest. The first major step of a reduction process identifies all species and reactions, which have little or no influence on the targets and removes them definitively from the mechanism. It reduces the number of differential equations that have to be solved by reducing the number of species and accelerates the computation of source terms by removing unimportant reactions. The second step reduces further the number of differential equations by replacing some of them by algebraic relations through quasi-steady-state assumption [1] or species

lumping [2]. This paper focuses on the systematic reduction of detailed mechanisms to a skeletal level.

As most of the computational savings comes from the reduction of the number of differential equations to be solved, it is essential to be able to correctly identify species that do not play an important role during the chemical processes. To gain insight into the complex chemical dynamics, Bendtsen et al. [3] introduced a reaction matrix \underline{P} defined at any time t , whose elements P_{ij} correspond to the production of species j from all reactions involving species i as reactant at that time t . This matrix quantifies the interactions existing between species and is used to iteratively select important species. The selection process starts with a set of major products or reactants. Species that contribute more than a certain percentage to the overall removal or production of any of these important species are included in the set. This procedure is repeated until no more species is included. The results were used to generate pathway plots at several times showing graphically the conversion of fuel into main intermediates, and then main products.

Tham et al. [4] used the same reaction matrix to select an initial pool of species: for each of the major product or reactant, an additional set of important species is selected by going through the reaction matrix following the path that connects one species to another one that is most strongly coupled with it. A second step selects for each of those species a subset of

reactions such that a certain percentage of the total formation or destruction of that species is kept in the skeletal mechanism. Any additional species appearing in the kept reactions are then added to the list of important species and this last step is repeated until no more species are added. Reactions involving large heat release are also added to the mechanism. No threshold is needed for the selection of the initial set of species. This method is efficient in selecting important reactions, but tends to retain a large number of species for a given accuracy.

Recently, Lu et al. [5] used a species selection procedure similar to the one proposed by Bendtson et al. [3], but applied it to the automatic generation of skeletal mechanisms with various complexities and domains of applicability. Given a threshold parameter ϵ , a directed relation graph (DRG) is constructed, whose nodes correspond to species present in the mechanism. There exists a directed edge from species A to species B only if the normalized interaction coefficient r_{AB} that quantifies the dependance of species A on species B , is greater than ϵ . The interaction coefficient is defined as :

$$r_{AB} \equiv \frac{\sum_{i=1,I} |\nu_{A,i} \omega_i \delta_{Bi}|}{\sum_{i=1,I} |\nu_{A,i} \omega_i|} \quad (1)$$

where the subscript i designates the i^{th} elementary reaction, $\nu_{A,i}$ the stoichiometric coefficient of species A in reaction i , ω_i the production rate of species A for the reaction i and δ_{Bi} is the Kronecker symbol:

$$\delta_{Bi} = \begin{cases} 1, & \text{if the } i^{\text{th}} \text{ reaction involves species B} \\ 0, & \text{otherwise} \end{cases}$$

If A is to be kept, then B has to be kept too. To initiate the selection process, the user has to specify a set of starting species, that may be just a single species, namely the fuel. Species kept are those that are reachable from species included in the initial set.

This method was applied to auto-ignition and PSR simulations. The pre-defined domain of applicability of the skeletal mechanism to be generated is densely sampled in pressure, equivalence ratio, temperature and time. The DRG selection method is applied to each of those points and the final resulting skeletal mechanism is the union of the set of species obtained at each sample point. The selection process is fast, requires a single evaluation of the solution using the detailed mechanism and depends on one unique user-defined parameter. However, a major drawback of this method is that the value of ϵ is not directly related to an error measure. One value for ϵ applied to different mechanisms will return disparate species reduction ratios and accuracies. Moreover, it assumes that every species selected is equally important and that the set of strongly coupled species to which it belongs has to be kept entirely, which may not be necessary. These questions are addressed in the following sections, where a modified version of the DRG method is proposed and evaluated.

2. Directed Relation Graph with Error Propagation (DRGEP)

For each species A present in a kinetic mechanism, a set of primary dependant species can be defined, consisting of those species that appear explicitly in reactions involving A . The strength of the interaction between A and each species of this primary dependant set is defined by the interaction coefficient r_{AB} defined in Eq. 1. A directed relation graph can be constructed as stated by Lu et al. [5] using $\epsilon = 0$. It should be

noted that if a species B is not in the primary dependant set of A , then $r_{AB} = 0$.

It can easily be seen that a species A will depend on the species contained in its primary dependant set, but also on all species directly related to them and so on. However, a species C interacting with species A through a third species B is important for A only if it is important for B and if B is important for A .

To quantify this more complex coupling, we define a path-dependant coefficient $r_{AB,i}$ on path i from A to B as being the product of each primary interaction coefficient encountered on the path. On Fig 1, for example, if path #1 is $A \rightarrow B \rightarrow D$, the coupling coefficient between A and D is:

$$r_{AD,1} = r_{AB} \cdot r_{BD}$$

If an error is made on D , it propagates through B and the larger the coupling coefficient between A and D is, the bigger impact this error will have on A . Finally, we define the generalized interaction coefficient of species A with species B as the maximum path-dependant coefficient between A and B :

$$R_{AB} \equiv \max_{\text{all paths } i} \{r_{AB,i}\}$$

For example, on Fig 1, A depends on C with coefficient

$$R_{AC} = \max \{r_{AB} \cdot r_{BC}, r_{AC}\}$$

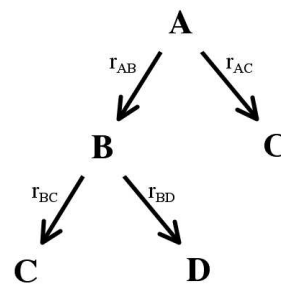


Fig. 1: Interaction graph between four species; coefficients r correspond to primary interactions. Species A depends on species C and D through its interaction with species B

Each species is associated with a subset of species that is sorted by order of importance of the coupling existing between them. For any species A , a subset of the most important species with respect to some threshold value ϵ can be formed by keeping in the set only the species i for which:

$$R_{AB} \geq \epsilon$$

The smaller ϵ is, the more species are included in the set, so that species A can be predicted more accurately.

The skeletal mechanism corresponding to one particular value of ϵ is then generated as follows. First, a set of target species is defined. This set includes the species whose evolution should be accurately described by the skeletal mechanism, usually the major reactants and products, NO and NO₂ if we are interested in NO_x formation and any additional species of special interest. Then defining some threshold ϵ , a subset of important species for each of the target is automatically selected following the procedure described above. The complete set of species to be kept is the union of all these subsets. Any elementary reaction containing a species that has not been selected is removed from the mechanism.

The major difference of this new selection method compared to the DRG theory is that it allows a finer selection of species as it really focuses on how the error made on a species will propagate to the targets. Selected species are not equally important anymore, as those that are farther from the targets are comparatively more important for the species they are related to than those directly linked to the targets. As a consequence, the choice of the targets must be made carefully since only the targets will be guaranteed to be described accurately. The level of accuracy of any other species will be adjusted dynamically according to the target selection and the adequation between skeletal and detailed mechanism may be quite poor for those species. This is not a problem as long as the user keeps in mind the conditions for which the skeletal mechanism has been developed.

To illustrate the difference between the DRG method [5] and this new DRGEP method, the extreme case with all primary interaction coefficients equal is considered, as shown in Fig 2. The target in this case will be the species *A*. Depending on the value of ϵ , different species will be selected. For $\epsilon > \alpha$, no additional species will be selected in both methods as the primary interaction coefficient from *A* to *B* is too small. However, when $\epsilon \leq \alpha$, we have different behaviors. Using primary interactions only, we see that if *B* is selected, *C* and *D* are automatically selected. There are only two different subsets available, one with all four species, the other with the target alone. On the other hand, *B* can be selected independently of *C* and *D* when generalized coefficients are used, as *C* and *D* are selected only if ϵ is smaller than α^2 , but are eliminated otherwise. This allows three different subsets containing one, two or four species. This overly simple case shows that in the context of a real chemical mechanism, where interactions between species are infinitely more complex, the DRGEP method will be able to provide more feasible subsets of species, that is, subsets whose corresponding skeletal mechanism satisfies the error requirements, and thus may lead to smaller subsets than using the primary interactions alone.

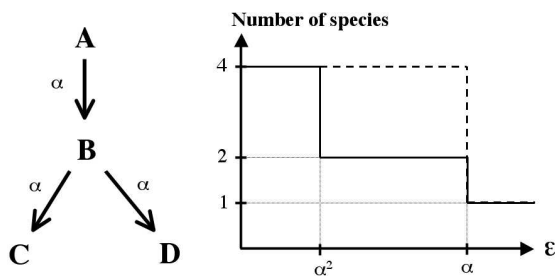


Fig. 2: Example of species selection using DRG (dashed line) and DRGEP (solid line)

The DRGEP method identifies unimportant species and removes them from the skeletal mechanism. This insures that the most important steps, assumed to be associated with the most important species are retained. However, not every reaction step involving important species is important. A second level of reduction identifies those unimportant steps and removes them. If a step does not contribute a lot to the production or consumption rate of each species that appear in it, it can safely be removed, provided that the overall production and consumption rates of each of those species remain close to the original ones. Assuming that the first step kept all necessary species needed to reproduce the detailed mechanism results to a given accuracy, removing extra unimportant reactions should

leave the number of species unchanged. That is why the following procedure is applied to each and every species selected by the first step. Considering forward and backward reactions separately, normalized production and consumption rates of a species *i* with respect to a reaction *j* are defined by:

$$P_{ij} = \frac{|\max(0, \nu_{ij})\omega_j|}{\sum_k |\max(0, \nu_{ik})\omega_k|}$$

$$C_{ij} = \frac{|\min(0, \nu_{ij})\omega_j|}{\sum_k |\min(0, \nu_{ik})\omega_k|}$$

For each species *i* that has been kept, both normalized production and consumption rates for each irreversible reaction involving that species are sorted by increasing value. For one threshold δ , there exists an index *J* such that:

$$\frac{\sum_{j=1}^J (P_{ij})}{\sum_{\text{all } j} P_{ij}} > \delta \quad \text{and} \quad \frac{\sum_{j=1}^J (C_{ij})}{\sum_{\text{all } j} C_{ij}} > \delta$$

Only reactions from 1 to *J* are included in the subset of reactions. The final subset of reactions is the union of each species' subset.

3. Reduction Process

The previous section explained how a skeletal mechanism can be generated for a given ϵ and δ . A certain number of questions remains unanswered, namely, what data to use to select species and reactions, how to measure the error between skeletal and detailed mechanism and what values should ϵ and δ have to obtain the best reduction possible.

3.1. Space Sampling

Detailed mechanisms are generally valid over a much wider domain in pressure, temperature and concentration than needed in practical applications. A skeletal mechanism will be constructed to match the detailed one only over well-defined regions. Several points which are characteristic of this restricted domain are selected, on which the skeletal mechanism will be required to satisfy a certain accuracy. If those points are well-chosen, it is expected that the reduced mechanism will remain valid inside the region mapped by them. These points can include auto-ignition of homogeneous systems, diffusion or premixed flames at various pressures, temperatures and equivalence ratios. Then it is well-known that in auto-ignition calculations for example, the chemistry taking place before ignition is totally different to what happens after ignition, and the evolution of species frequently involves different time scales. NO_x formation will be much slower than O_2 consumption. To take everything into account, a few characteristic times are selected and the species and reaction selection is done using integrated reaction rates up to those times.

3.2. Error Evaluation

The most accurate way to evaluate the error introduced in the skeletal mechanism is to actually compute the solution using the reduced mechanism. This will be done here. At each sample point, depending on the kind of simulation done, an error is computed for temperature, ignition delay time, laminar burning velocity and concentrations of the targets, scaled to be between 0 and 1. Errors on concentrations or temperature are evaluated using the following formula:

$$\Delta X = \frac{\int_{\mathcal{D}_X} |X_{det} - X_{red}|}{\int_{\mathcal{D}_X} |X_{det}|}$$

where \mathcal{D}_X refers to the interval in time relevant for species X , that is, when most changes occur for that species. Those intervals are determined automatically at the beginning of the reduction process. For instance, \mathcal{D}_{Fuel} in auto-ignition goes from 0 to shortly after ignition whereas \mathcal{D}_{CO_2} will start shortly before ignition and stops when CO_2 has reached its equilibrium value.

The global errors are the maximum errors of all sample points, and each of them has to satisfy the corresponding accuracy requirement for the skeletal mechanism to be valid.

3.3. Iterative Process

It will be shown in the next section that in most cases, this method removes species so that the global error increases as the number of species decreases in a monotonic and relatively smooth way. This allows a search for the optimal skeletal mechanism through a bisection algorithm. Starting from two values of ϵ , the first one, ϵ_{max} , associated with an unacceptable error, the second one, ϵ_{min} , with an error within the tolerances, a new ϵ is chosen equidistant to ϵ_{min} and ϵ_{max} and the corresponding skeletal mechanism is constructed and evaluated. Depending on the quality of this new mechanism, either ϵ_{min} or ϵ_{max} is replaced by this new value and the procedure is repeated until the best acceptable mechanism is found.

It must be emphasized that even if the optimal value for ϵ is different from one mechanism to another, the order of magnitude usually remains the same. The initial boundary values for ϵ can be chosen accordingly and the whole procedure converges only in a few iterations. Moreover, evaluating the solution on a reduced mechanism is much cheaper than on the detailed one, and solutions for too large values of ϵ are seldomly evaluated entirely, as the skeletal mechanism is rejected as soon as the solution at one point exceeds the tolerated error.

4. Numerical Results

Two large kinetic mechanisms have been selected to validate the DRGEP method proposed above, namely a mechanism for heptane oxidation and a mechanism for primary reference fuel (PRF) oxidation.

4.1. Reduction of a large Heptane Mechanism

A detailed chemical kinetic mechanism for n-Heptane oxidation [6] has been chosen to validate the above systematic reduction procedure. This mechanism consists of 557 species among 2540 reversible reactions (which corresponds to a total of 5077 reactions if backward and forward reactions are counted separately).

To evaluate the capabilities of both species selection procedures described above, skeletal mechanisms obtained using DRG and DRGEP are generated for a large number of values of the threshold coefficient ϵ on a restricted domain. Only auto-ignition of a stoichiometric mixture of n-Heptane and air is considered here. Sample points include two pressures, 1 and 13.5 bars and five temperatures between 600K and 1700K. Four different points in time are considered, namely $t = 0.5\tau_{ign}$, τ_{ign} , $1.3\tau_{ign}$ and $10\tau_{ign}$. The target species are n-Heptane, O_2 , H_2O , CO , CO_2 and H_2 . Maximum errors on ignition delay times and species concentrations are shown in Fig 3.

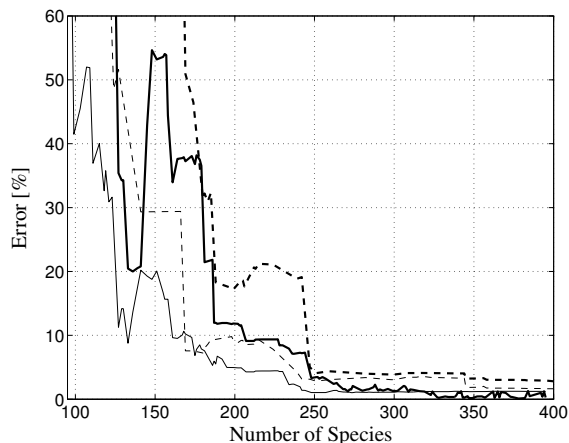


Fig. 3: Reduction of n-heptane mechanism - Maximum error on main species concentrations (bold lines) and on ignition delay time (thin lines) as a function of the number of species kept in the skeletal mechanism; Species selection done using DRG method (dashed lines) and DRGEP method (solid lines).

It can be noted that for both methods, the error is mostly a decreasing function of the number of species and that it remains small and nearly constant when there are more than 250 species in the skeletal mechanism. This indicates that the selection of the less important species that should be eliminated first is efficient, as it achieves a reduction ratio of more than 2 without introducing much error in the prediction of target species concentrations and ignition delay times. However, for a same number of species kept in the skeletal mechanism, the error introduced by using the generalized interaction coefficients in the DRG method is 2 to 10 times smaller compared to the one obtained using DRGEP. Giving each species a weight that depends on how much they propagate errors to the targets helps identifying species that have no influence on the error by eliminating them at once, whereas they may remain in the mechanism when every kept species is considered as equally important.

Another major difference is the smoothness of the curves. Both of the curves have jumps when a species or a group of species is eliminated, that is comparatively more important than what has already been removed. This occurs for example around 250 species, but the amplitude of the jump is much larger for the DRG method compared to DRGEP, bringing the maximum error on concentration beyond 15%, which is not acceptable in most applications. The number of species cannot be reduced further using this approach, a species or group of species essential to the prediction of one of the targets, in this case, the consumption of the fuel at high temperature, has been removed. With a smaller jump and a smoother slope, DRGEP keeps the maximum error in the target species below 10% and the error on ignition delay time below 5% while removing another 50 species.

This mechanism is then reduced automatically for a wider range of conditions by applying the DRGEP method as described above. Both auto-ignition and plug flow reactor (PFR) simulations are used, with pressure varying between 1 and 50 bars, temperature between 600K and 1700K, equivalence ratios between 0.5 and 2.5. Plug flow reactors simulations are done with nitrogen diluent of 98%. Targets species are the same as above. Concentrations of targets species have a 10% allowed error while ignition delay time and temperature have

a 5% allowed error. After the first stage of reduction, only 246 species and 2140 reactions are kept in the mechanism. An additional set of reactions are then removed using the production/consumption rates criterion. In the present configurations, it can be noted that the cut-off value δ that is used to separate reactions that have to be kept from unimportant ones, is close to unity and small variations of this parameter have a large impact on the number of reactions of the resulting mechanism. After this second stage of reduction, the final skeletal mechanism obtained consists of 246 species and only 1462 reactions, that is a reduction ratio of 2.2 for the species and nearly 3.5 for the reactions. This final skeletal mechanism will be compared in the following with the detailed mechanism from which it has been generated and a very short skeletal mechanism derived previously [7] that consists in 54 species only.

Ignition delay times obtained using the detailed, skeletal and short skeletal mechanisms for different pressures are shown in Fig 4. The automatically generated mechanism produces ignition delay times in really good agreement with those from the detailed mechanism. The 54 species mechanism has been derived for high pressures and compares well for pressures higher than 3 bars, but underpredicts ignition delay times at very high temperatures.

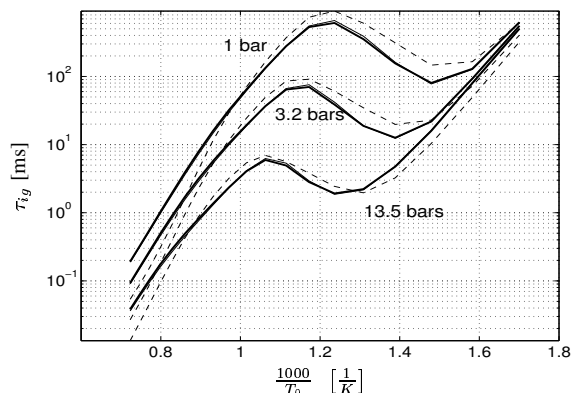


Fig. 4: Reduction of n-heptane mechanism - Comparison of ignition delay times for various pressures; Detailed mechanism (solid bold lines), Skeletal mechanism obtained by automatic reduction (solid thin lines), Short skeletal mechanism [7] (dashed lines)

The early development of the main species in highly diluted lean and rich n-heptane/air mixtures in PFR simulations are shown in Figs. 5 and 6. The 246 species mechanism leads to a slightly faster fuel consumption and CO production, but the equilibrium values predicted by each mechanism are the same. The overall agreement between these mechanisms is good and the required tolerances are satisfied.

The good performance of the short skeletal mechanism for ignition delay time prediction is noteworthy, given the number of species kept in the system. Such a reduction ratio (about 10 for the number of species) cannot be achieved using the present method only. As seen in Fig. 3, keeping less than 200 species leads to huge errors for both concentrations and ignition delay times. The mixture n-heptane/air does not ignite anymore when less than 100 species are kept. All species that have been kept in the short skeletal mechanism are kept in the 246 species skeletal mechanism. However, a major difference can be found in the treatment of isomers, such as alkylperoxy radicals. They appear to have the same relative importance in fuel consumption and thus, form a group that is kept or removed as a whole. In the short skeletal mechanism, these

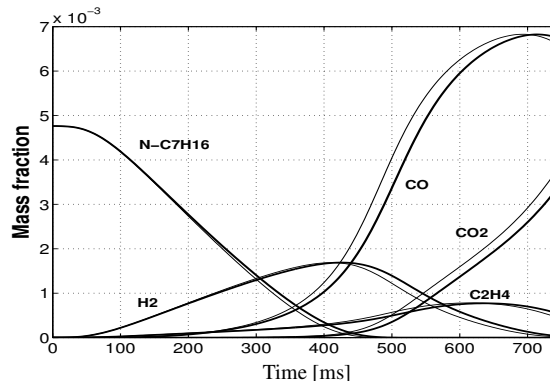


Fig. 5: Reduction of n-heptane - Species development for lean n-heptane oxidation ($\phi = 0.79$) in PFR at a pressure of 3 bars given by the skeletal n-heptane mechanism obtained by automatic reduction (solid thin lines) compared with results from detailed mechanism (solid bold lines)

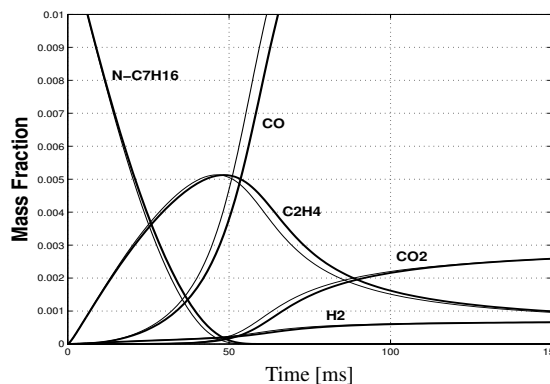


Fig. 6: Reduction of n-heptane - Species development for rich n-heptane oxidation ($\phi = 2.27$) in PFR at a pressure of 3 bars given by the skeletal n-heptane mechanism obtained by automatic reduction (solid thin lines) compared with results from detailed mechanism (solid bold lines)

isomers have been lumped into a single average species while the reactions rates associated with those isomers have been adapted. This lumping can save here more than 60 species and has to be considered as an efficient option for further reduction.

4.2. Reduction of Primary Reference Fuels Mechanism

To evaluate the capability of the reduction procedure to handle very large mechanisms, the DRGEP method has been applied in the reduction of a detailed chemical kinetic mechanism compiled for the primary reference fuel (PRF) consisting of n-heptane and iso-octane. The PRF is used to define the octane reference scale for fully blended gasolines [8]. This mechanism consists of 990 different chemical species and 4060 reversible elementary reactions (8476 reactions if backward and forward reactions are considered separately). The target species are n-heptane and iso-octane, O_2 , H_2O , CO , CO_2 and H_2 . The species concentrations and ignition delay time have a 10% allowed error. Sample points have a pressure of 40 bars and include three temperatures between 750K and 1100K. Only auto-ignition is considered here for three differ-

ent stoichiometric mixtures of n-heptane and iso-octane of octane numbers 0, 80 and 100 respectively. As for the n-heptane reduction, four different points in time are considered, namely $t = 0.5\tau_{ign}, \tau_{ign}, 1.3\tau_{ign}$ and $10\tau_{ign}$. The automatically generated skeletal mechanism consists of 374 species and 1772 reactions. Figure 7 shows comparison of ignition delay times from the skeletal and the detailed mechanisms.

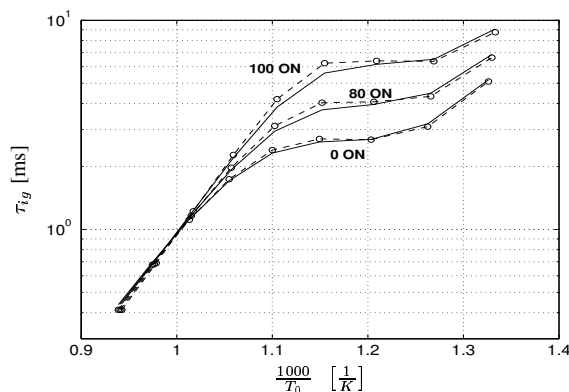


Fig. 7: Reduction of Primary Reference fuels mechanism - Comparison of ignition delay times at 40 bars; Detailed mechanism (solid lines), Skeletal mechanism obtained by automatic reduction (open circles)

Whereas the skeletal mechanism predicts n-heptane ignition quite well, the reduced mechanism becomes less accurate as the octane number increases. This can be explained by the lower reactivity of iso-octane compared to n-heptane. Iso-octane is the limiting factor in this reduction. The threshold parameters ϵ and δ used in the reduction are based on the performance of iso-octane ignition alone, forcing the algorithm to keep more species than necessary to predict the n-heptane behavior to the required accuracy. Thus, a possible improvement of this method could consist in 'differential' reduction for multi-component mechanism, where each component could be reduced to a level independent of the others, that still leads to acceptable errors for the mixture.

5. Conclusion

In the present work, we have proposed and evaluated a directed relation graph method with error propagation for the automatic generation of skeletal mechanisms. These mechanisms are guaranteed to match results obtained using detailed chemistry within a user-defined accuracy for any specified target. Through the definition of generalized coupling coefficients, error propagation is analysed. This allows an efficient selection of the species and reactions that can safely be removed. A bisection search is then applied to determine the optimal skeletal mechanism. The DRGEP method has been successfully applied to the reduction of very large detailed kinetic mechanisms, for which high reduction ratios were achieved while keeping the errors below 10%. Although the measure of the error requires the computation of the solution, a few iterations are usually sufficient and the largest kinetic mechanisms can be reduced in a couple of hours on a typical PC. Comparison with an existing manually reduced mechanism shows the potential of an additional automatic lumping procedure to obtain short skeletal mechanisms that can be directly used in more complex simulations.

Acknowledgments

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