Combustion and Flame 156 (2009) 417–428

Contents lists available at ScienceDirect

Combustion and Flame

www.elsevier.com/locate/combustflame

Reduction of very large reaction mechanisms using methods based on simulation error minimization

Tibor Nagy, Tamás Turányi *

Institute of Chemistry, Eötvös University (ELTE), P.O. Box 32, H-1518 Budapest, Hungary

ARTICLE INFO

Article history:
Received 19 March 2008
Received in revised form 31 August 2008
Accepted 3 November 2008
Available online 14 November 2008

Keywords:
Mechanism reduction
Species elimination
Connectivity method
DRG
DRGEP
Principal component analysis

ABSTRACT

A new species reduction method called the Simulation Error Minimization Connectivity Method (SEM-CM) was developed. According to the SEM-CM algorithm, a mechanism building procedure is started from the important species. Strongly connected sets of species, identified on the basis of the normalized Jacobian, are added and several consistent mechanisms are produced. The combustion model is simulated with each of these mechanisms and the mechanism causing the smallest error (i.e. deviation from the model that uses the full mechanism), considering the important species only, is selected. Then, in several steps other strongly connected sets of species are added, the size of the mechanism is gradually increased and the procedure is terminated when the error becomes smaller than the required threshold. A new method for the elimination of redundant reactions is also presented, which is called the Principal Component Analysis of Matrix F with Simulation Error Minimization (SEM-PCAF). According to this method, several reduced mechanisms are produced by using various PCAF thresholds. The reduced mechanism having the least CPU time requirement among the ones having almost the smallest error is selected. Application of SEM-CM and SEM-PCAF together provides a very efficient way to eliminate redundant species and reactions from large mechanisms. The suggested approach was tested on a mechanism containing 6874 irreversible reactions of 345 species that describes methane partial oxidation to high conversion. The aim is to accurately reproduce the concentration–time profiles of 12 major species with less than 5% error at the conditions of an industrial application. The reduced mechanism consists of 246 reactions of 47 species and its simulation is 116 times faster than using the full mechanism. The SEM-CM was found to be more effective than the classic Connectivity Method, and also than the DRG, two-stage DRG, DRGASA, basic DRGEP and extended DRGEP methods.

1. Introduction

One of the consequences of the advancements in gas kinetics is that reaction mechanisms for the combustion of hydrocarbons and other organic compounds are becoming increasingly larger. Especially, models for low temperature combustion and ignition require mechanisms that may contain several hundred or even thousand of species and ten thousands of reactions. Almost all published detailed reaction mechanisms contain redundant species and reactions [1]. One reason for this is that the creators of such mechanisms want to remain on the safe side and tend to include additional species and reactions even if their importance is not certain. Another reason is that detailed reaction mechanisms are usually tested for a wide range, but are utilized at a narrower range of conditions.

The reaction mechanism is utilized as a part of a complex model (e.g. plug-flow, laminar flame or perfectly stirred reactor model). In reaction kinetics simulations, the solutions are determined at selected points of time and/or space. For example, in the case of zero-dimensional non-stationary problems, several time points are selected, while for spatially distributed stationary problems, several spatial points are designated. The aim of mechanism reduction is to obtain almost identical solutions of the complex model for the important species in these points using a smaller mechanism.

Elimination of redundant species and reactions from a large reaction mechanism has several benefits, one of which is that the simulation time may decrease significantly, which is important if the simulation is carried out several thousand or even million times. This is the situation when the mechanism is used for the simulation of a spatially inhomogeneous system or for process control. Also, other mechanism reduction methods, based for example on time scale analysis [2–4] or lumping [5] may be more efficient if the starting mechanism is smaller. Several reviews have dealt with the problem of mechanism reduction [1,6,7].

Frenklach et al. [8] suggested a method for the elimination of species and reactions from a detailed mechanism, when the aim

---

* Corresponding author.
E-mail address: turanyi@chem.elte.hu (T. Turányi).

0010-2180/$ – see front matter © 2008 The Combustion Institute. Published by Elsevier Inc. All rights reserved.
doi:10.1016/j.combustflame.2008.11.001

was the reproduction of ignition delay times and temperature profiles. Those reactions (and the corresponding species) were eliminated that were much slower than the rate determining step(s) and produced much less heat, than the reaction steps having the highest heat production. This approach was extended to laminar premixed flames in a later article [9].

The first general systematic method for species reduction was suggested by Turányi [10] and since then several other methods have been published for this task [11–21]. In the next section, three such methods are reviewed in details.

2. Three methods for species removal

The starting point of all species reduction methods is that the species are usually not equally important. The aim of simulations is to reproduce the concentration profiles of the *important species* or to reproduce some *important features*. In combustion modeling, time-to-ignition and flame velocity are features to be frequently reproduced in simulations. The species reduction methods identify the *redundant species* that can be eliminated from the mechanism (with all their reactions) in such a way that the simulation results for the important species and important features deviate only within small tolerance limits from those of the full mechanism.

An algorithm for the detection of redundant species can be based on the inspection of the Jacobian. An element of the normalized Jacobian of the complex model (see Eq. (1)) provides information about how the time-derivative of the concentration of species j (denoted by f_j) changes, if the concentration of species i (c_i) is perturbed:

$$\tilde{\mathbf{J}}_{ij} = (c_i/f_j)(\partial f_j/\partial c_i). \tag{1}$$

Note that the normalized Jacobian $\tilde{\mathbf{J}}_{ij}$ for constant volume systems is identical to the normalized Jacobian of the system of kinetic differential equations if third body effects are not considered. In constant pressure systems, the volume may change due to the change of the mole numbers, and therefore a species may have an influence on the concentration change of other species even if these species do not have a common reaction. In addition, changing the concentration of a species having a third body weighting factor may influence the rate of the corresponding reactions. If the normalized Jacobian is calculated analytically, these effects have to be taken into account.

The Connectivity Method (CM) [10] uses the following algorithm: The squares of normalized Jacobian elements are summed up for all important species, and the obtained value B_i is used to characterize the strength of the direct link of species i to the group of important species:

$$B_i = \sum_{j \in \text{group}} \tilde{\mathbf{J}}_{ij}^2. \tag{2}$$

Species having high B_i values are closely linked to the important species. Species having the highest B_i values are also included in the summation and the B_i values are recalculated. This procedure is repeated until a gap appears in the series of the ordered B_i values. Species having B_i values above the gap are directly or through other species closely linked to the important species. These are the *necessary species*. In this article, the list of necessary species by definition includes the important species. Because the Jacobian depends on the concentrations, the redundancy of species has to be investigated at several reaction times. Note that the from the point of view of finding strong connections between species, the absolute value of a $\tilde{\mathbf{J}}_{ij}$ element is not relevant. Large value of a $\tilde{\mathbf{J}}_{ij}$ element may be related to a weak connection, while at other circumstances (e.g. in the same system at earlier reaction times) a small value can be related to a strong connection. The Connectivity Method is based on a comparison of $\tilde{\mathbf{J}}_{ij}$ (or B_i) values at the same circumstances.

A species is redundant, if it is redundant at each time investigated. All reactions of the redundant species are then eliminated from the mechanism. More details about the detection of redundant species in this way can be found in articles [22,23]. In the original version of the method, encoded in KINAL [24,25], the user may decide in each step how many species are to be added to the group, using the actual list of B_i values. In a variant of the method always a single species having the highest B_i value is included to the group. This algorithm is encoded as option CONNECT in program KINALC [25].

The Connectivity Method yields only one or few reduced mechanisms, depending on the selected numbers of iterations and the threshold value for B_i. We have found that if there are large number of species in the mechanism, no gap appears in the B_i values for most of the conditions and therefore it is not clear when the iteration should be terminated at each investigated time. Another drawback is that the special role of the important species diminishes rapidly as more and more species are added to the group. Therefore, errors of important species do not necessarily decrease by adding the most connected species to the group.

In this work, an *ad hoc* modification is introduced to the Connectivity Method. Always a single species is included to the group of selected species and the iteration is stopped after n added species. For each reaction time, the list of necessary species was identified for $n = 1, 2, \ldots$. The union of these species at all times provided the list of necessary species, while the other species of the full mechanism were considered redundant. Elimination of the reactions of the redundant species gave a reduced mechanism for each n. A simulation was carried out for each such mechanism. Increasing n, the error tended to decrease and when the error became smaller than a required threshold, the corresponding mechanism was accepted as a recommended reduced one. This is surely not an optimal solution, because the required number of species is usually different at different reaction times, but this modified algorithm proved efficient for the case presented in this paper.

Recently, Lu and Law [15] devised an automatic mechanism reduction procedure based on the theory of directed relation graph (DRG). In later papers, further modifications and improvements were introduced [16–19]. Each vertex in a DRG represents a species in the detailed mechanism, and there exists an edge from vertex A to vertex B if and only if the removal of species B would directly induce significant error to the production rate of species A. This effect is measured by the normalized contribution r_{AB}, defined as

$$r_{\mathrm{AB}} = \sum_{i:\ \mathrm{B\ involved}} |\nu_{\mathrm{A},i} R_i| \Big/ \sum_i |\nu_{\mathrm{A},i} R_i|, \tag{3}$$

where $\nu_{\mathrm{A},i}$ is the stoichiometric coefficient of species A in reaction i, and R_i is the net rate of reversible reaction i, which is difference of the rates of the forward and the backward reactions. Starting from a set of important species, represented by standalone vertexes, and a small user defined threshold $0 < \varepsilon < 1$, a DRG is constructed in an iterative procedure by drawing those edges and the corresponding vertexes for which $r_{\mathrm{AB}} > \varepsilon$. Performance of the DRG can be improved by restarting the procedure, also called "two-stage DRG" [16]. In this case the first stage of DRG reduction is the major reduction stage, while in the second stage DRG is applied for the result of the first stage and this way some further species can be removed.

A major improvement of the DRG method is the DRG-aided sensitivity analysis (DRGASA) [18], when the result of the DRG procedure is improved by identifying those species whose elimination cause only minor increase of the simulation error of the important species or important features. The investigated species were selected on the basis of the DRG results. Also, it was shown [16] that the DRG algorithm can be coded in such a way that the entire reduction can be completed in a time that is linearly proportional to the number of reactions in the mechanism (linear time reduction).

A major drawback of the DRG method is that the value of ε is not directly related to the error of the reduced mechanism. Moreover, it is not guaranteed that decreasing ε results in a monotonically decreasing error of reduction, therefore a bisection (logarithmic) search for the "best" threshold may not always provide the smallest reduced mechanism at a given required simulation error. Also, the DRG method assumes that every selected species is equally important and those species which are strongly coupled to these ones also become selected even though this may not be necessary. This means that species that are in fact redundant may be kept in the reduced mechanism. The algorithm tries to reproduce precisely the fluxes of all selected species even in regions where the corresponding concentrations are negligibly small. Another deficiency is that the DRG method cannot handle the influence of third bodies. In general, it cannot handle the interrelation of species that are arising from non-chemical couplings, like the expansion of a reactive gas mixture at constant pressure due to the change of the total mole numbers.

DRGASA fixed several drawbacks of the original DRG method. Here the error of simulation results is investigated and therefore the simulation error is directly controllable. Also, in DRGASA the error of important species is investigated, and therefore the special role of these species is restored.

Some of the issues discussed above are addressed in the "DRG with Error Propagation" method (DRGEP) [20,21]. A set of primary dependent species can be defined for species A, consisting of those species that appear explicitly in reactions involving A. If species B is not in the primary dependent set of A, then $r_{\mathrm{AB}} = 0$. However, species C interacting with species A through species B is necessary for A only if it is necessary for B and B is necessary for A. This indirect coupling is quantified by path dependent coefficient $r_{\mathrm{AB},i}$, which is the product of the normalized contributions along path i between A and B. The influence of species B on species A is characterized by coefficient R_{AB}, which is the maximum of the path dependent coefficients:

$$r_{\mathrm{AB},i} = \prod_{\mathrm{XY} \in i} r_{\mathrm{XY}}, \tag{4}$$

$$R_{\mathrm{AB}} = \max_{\text{all paths } i} r_{\mathrm{AB},i}. \tag{5}$$

In the DRGEP method, the species selection procedure is based on the R_{AB} values instead of the r_{AB} values like in the DRG method. A connection is considered significant, if its R_{AB} value is larger than threshold ε. In the current version of the DRGEP method [21], r_{AB} is defined differently from the similar quantity in the DRG method (see Eq. (3)). The DRGEP definition for direct couplings is

$$r_{\mathrm{AB}} = \left| \sum_{i:\ \mathrm{B\ involved}} \nu_{\mathrm{A},i} R_i \right| \Big/ \sum_i \max(P_{\mathrm{A}}, C_{\mathrm{A}}), \tag{6}$$

where P_{A} and C_{A} are the formation and consumption rates of species A. The original DRGEP algorithm [20] was amended [21] to improve its performance by new additional features, like scaling, group-based coefficients and integrity check. The DRGEP method fixes the problem that the subsequently selected species are considered as significant as the important species, but shares all other drawbacks of the original DRG method.

In all the three methods discussed above several monitoring points are designated in the time (or space) domain and the procedure is applied to each of these points. The final reduced mechanism is the union of the sets of selected species and their reactions obtained at each sample point. Another common feature of these methods is that the size of the reduced mechanism is controlled by thresholds. The thresholds in the different methods refer to different measures and thus cannot be contrasted directly, but the final results of the methods, i.e. the reduced mechanisms can be compared. Success of a mechanism reduction method can be judged by the size (number of species and reactions) of the reduced mechanism, the decrease of simulation time, and the error of reduction. The latter is based on the comparison of the simulation results at the monitoring points using the full and the reduced mechanisms.

All the three methods above inspect the right-hand side of the ODE and not the simulation results. An advanced mechanism reduction method should use the simulation error as controlling information during the mechanism reduction procedure, and not only for the evaluation of the obtained reduced mechanisms.

Another drawback of these methods is that by increasing the controlling threshold, the obtained smaller reduced mechanism is always a subset of the larger one belonging to a smaller threshold. However, the systems of differential equations used in chemical kinetic simulations are usually highly non-linear, therefore an optimal smaller reduced mechanism is not necessarily a subset of an optimal larger one. The conclusion is that these algorithms are not the best possible.

The three methods discussed above produce a reduced mechanism rapidly. The new Simulation Error Minimization Connectivity Method, to be presented in the next section, generates thousands of candidate reduced mechanisms on the basis of the inspection of the normalized Jacobian and produces a database, in which the errors of simulations using the reduced mechanisms are recorded. Based on this database, an optimal reduced mechanism is selected. This method requires more CPU time than the previous ones, but provides a significantly smaller reduced mechanism for the same allowed simulation error. Also, the thresholds in this method refer directly to the error of reduction.

3. Simulation Error Minimization Connectivity Method (SEM-CM)

3.1. Error measures

Advancement and efficiency of the reduction process is monitored using an error function of the concentrations of the important species. Note, that an important quantitative feature (e.g. ignition delay time) can also be the basis of an error function. Relative error overemphasizes large relative deviations of small concentrations, while absolute errors are sensitive only to the large absolute concentration changes. As a generally applicable measure, a mixed error function can be used. The errors are calculated at several times, which can be distributed logarithmically or linearly equidistant in time as required by the problem. The local error of important species i at time t_j is denoted by $\delta_i(t_j)$ and characterized by the following error function

$$\delta_i(t_j) = 2\frac{c_i^{\mathrm{red}}(t_j) - c_i^{\mathrm{full}}(t_j)}{c_i^{\mathrm{full}}(t_j) + c_{i,\mathrm{MAX}}^{\mathrm{full}}} \approx \begin{cases} \dfrac{c_i^{\mathrm{red}}(t_j) - c_i^{\mathrm{full}}(t_j)}{c_i^{\mathrm{full}}(t_j)} & \text{if } c_i^{\mathrm{full}}(t_j) \sim c_{i,\mathrm{MAX}}^{\mathrm{full}}, \\ \dfrac{c_i^{\mathrm{red}}(t_j) - c_i^{\mathrm{full}}(t_j)}{c_{i,\mathrm{MAX}}^{\mathrm{full}}/2} & \text{if } c_i^{\mathrm{full}}(t_j) \ll c_{i,\mathrm{MAX}}^{\mathrm{full}}, \end{cases} \tag{7}$$

where $c_i^{\mathrm{full}}(t_j)$ and $c_i^{\mathrm{red}}(t_j)$ are the concentrations of species i at time t_j calculated by the full and the reduced mechanisms, respectively, and $c_{i,\mathrm{MAX}}^{\mathrm{full}}$ is the maximum value of the concentration of species i according to the full mechanism over the selected times:

$$c_{i,\mathrm{MAX}}^{\mathrm{full}} = \max_j c_i^{\mathrm{full}}(t_j). \tag{8}$$

This mixed error function ensures that the relative error is examined at concentrations close to the maximum, but its significance is smaller for concentrations much lower than the maximum, where it behaves as a scaled absolute error. Based on the maximum errors of the important species ($\delta_{i,\mathrm{MAX}}$), an overall maximum error (δ_{MAX}) is defined:

$$\delta_{i,\mathrm{MAX}} = \max_j \left|\delta_i(t_j)\right|, \tag{9}$$

$$\delta_{\mathrm{MAX}} = \max_i \delta_{i,\mathrm{MAX}}. \tag{10}$$

Using the root mean square errors of important species ($\delta_{i,\mathrm{RMS}}$), an overall root mean square error (δ_{RMS}) is obtained:

$$\delta_{i,\mathrm{RMS}} = \left(n_t^{-1} \sum_j \delta_i(t_j)^2\right)^{1/2}, \tag{11}$$

$$\delta_{\mathrm{RMS}} = \left(n_{\mathrm{imp}}^{-1} \sum_i \delta_{i,\mathrm{RMS}}^2\right)^{1/2}, \tag{12}$$

where n_t is the number of time points and n_{imp} is the number of important species. Error measures δ_{MAX} and δ_{RMS} refer to maximal and average relative deviations, respectively, between the results obtained from a reduced mechanism and the full mechanism.

This error calculation is appropriate for the general case, but other possible error definitions can also be used. As an example, another appropriate error definition might exclude the error introduced by the time shift, which has a relevance at the simulation of flow reactor experiments with uncertain zero time. Reduced mechanisms should frequently reproduce important features, like time-to-ignition and flame velocity in ignition models and laminar flames, respectively. The error measures above investigate the deviation of the concentration profiles of the original and the reduced mechanisms, but the change of the simulated features could also be monitored in a similar way. The monitored simulation error function may take into account simultaneously the calculated simulation error at very different reaction conditions. This way the obtained reduced reaction mechanism will be applicable at all investigated conditions.

3.2. Building consistent reduced mechanisms

One of the problems with the original CM algorithm is that it identifies the redundant species instead of the redundant reactions. In the CM algorithm, all reactions of redundant species are deleted when the reduced mechanism is produced, which may cause an error. For example, let us consider irreversible reaction $A + B \rightarrow C$ and assume that species A is important. The connectivity method selects species B but not C, since changing the concentration of B changes the production rate of A, but changing the concentration of C has no influence on it. Therefore, according to the algorithm, this reaction is not selected. To avoid this trap, interdependence of the species has to be considered already at the selection of the necessary species. Instead of selecting individual species, combinations of species are identified that results in the selection of at least one new reaction. Therefore, the term complementary set is introduced.

A *complementary set* consists of those species that are not yet selected but would yield at least one additional selected reaction if these were introduced to the current group of selected species. Note that according to this definition, unions of complementary sets are also complementary sets. In the example above, species B alone does not form a complementary set, while species B and C together form one. Inert species should also be considered as single-species complementary sets.

Continuing the previous example, let us consider the following set of reactions: $A + B \rightarrow C$ and $D \rightarrow B$. Assume that the initial concentrations of A and D are non-zero, those of B and C are zero, and species A is an important species. In the first step, species B and C are selected and the corresponding $A + B \rightarrow C$ reaction is also selected. However, in the obtained single step mechanism the concentration of species B is always zero because it has no forming reaction route. To produce a meaningful mechanism, step $D \rightarrow B$ also has to be added. It has to be guaranteed that all species have formation according to the reduced mechanism at the given set of conditions at every stage of the procedure, therefore the terms 'living species' and 'consistent mechanism' are introduced.

A species is designated a *living species* if its initial concentration is non-zero or it has an inflow term (e.g. non-zero inlet concentration in a PSR) or it is formed in chemical reactions. The list of living species depends on the mechanism and also on the initial (or boundary) conditions. A *mechanism* is called *consistent*, if each of its species is living at least at one condition.

The Simulation Error Minimization Connectivity Method (SEM-CM) can be summarized as follows. Starting from the group of n_{imp} important species, complementary sets strongly connected to them are added at each time and the formed reduced mechanisms are made consistent if necessary. The complex model is simulated with each of these mechanisms and their sets of species with their errors are stored in a database. The reduced mechanism that has $n_{\mathrm{imp}} + 1$ species and has the smallest error is identified in the database, and the previous procedure is repeated. If no such a mechanism exists, mechanism with species number $n_{\mathrm{imp}} + 2$, $n_{\mathrm{imp}} + 3$, etc. is looked for. The mechanism building is terminated when the simulation error, using the reduced mechanism, becomes smaller than a required threshold. This way, a series of consistent reduced mechanisms are produced, usually with continuously decreasing error. The flowchart of the algorithm is given in Fig. 1 and the procedure is detailed below.

(i) Initialization

The first step is to carry out simulations using the full mechanism. The concentration sets and the normalized Jacobian matrices belonging to several selected points are saved and the mechanism reduction procedure will be carried out in all these time and/or spatial points. Initially the selected species are the important species.

(ii) Identification of complementary sets of species

Complementary sets of species belonging to the group of n currently selected species are looked for. Such a complementary set can be identified by considering all species of the first reaction and omitting the selected ones. If at least one species remains, then these species form the first complementary set. Going through all reaction steps this way provides a list of the complementary sets of species. Some of these complementary sets can be identical and only the different ones will be investigated further. Note that these sets may contain each other or overlap.

(iii) Ranking the complementary sets

The strength of the direct link of the complementary set k, containing n_k species, to the group of selected species is characterized by the average of the B_i values according to the following equation:

$$C_k = \frac{1}{n_k} \sum_{i \in \mathrm{set}} B_i = \frac{1}{n_k} \sum_{i \in \mathrm{set}} \sum_{j \in \mathrm{group}} \tilde{\mathbf{J}}_{ij}^2. \tag{13}$$

Each complementary set is ranked according to their C_k values. The complementary set obtained from one reaction may be the subset of the complementary set obtained from another reaction. Hence, averaging that is dividing the sum by n_k is needed, otherwise the larger one would always be ranked higher, even if the strong link arises from the reactions related to the smaller complementary set.

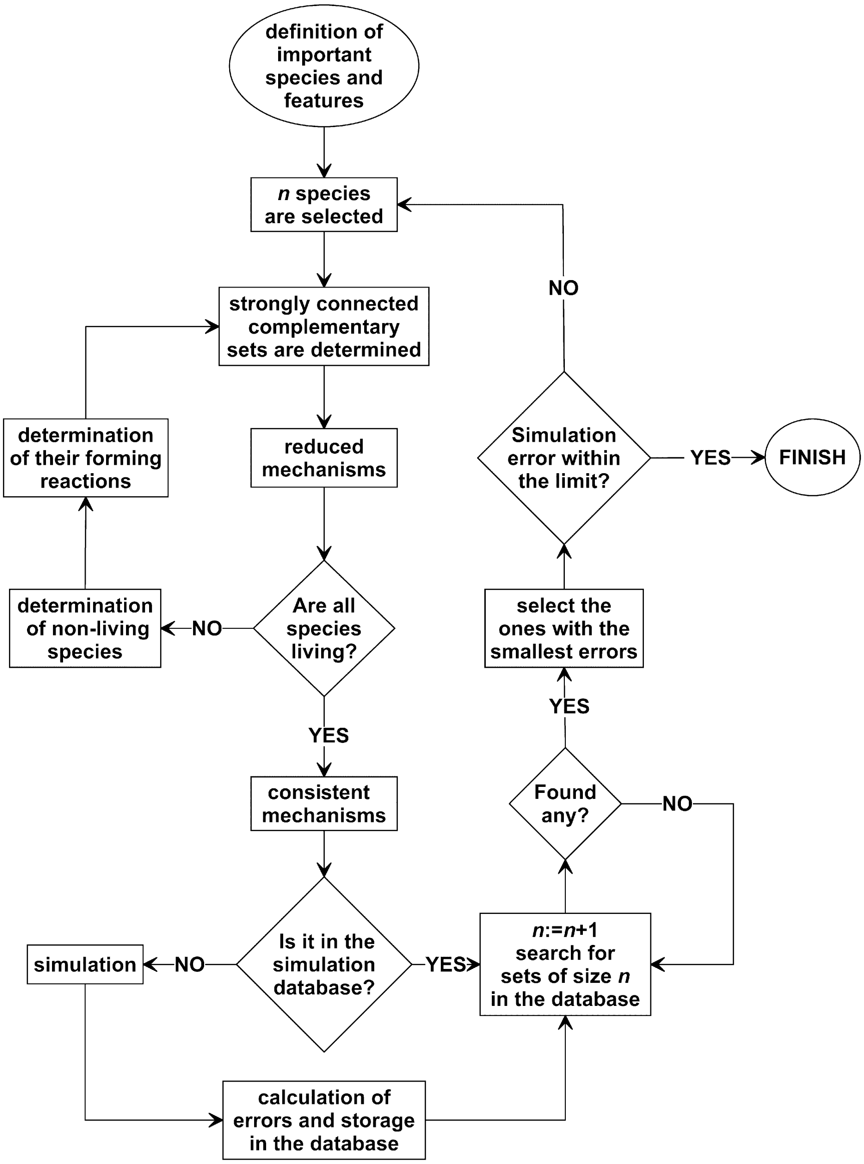


Fig. 1. Flowchart of the SEM-CM algorithm.

This ensures that SEM-CM builds up the mechanisms by adding smaller groups of species.

Handling the inert species as single-species complementary sets allows the investigation if the presence of these species is needed in the simulations through third body or pressure effects. These effects appear in the Jacobian calculation and therefore contribute to measure C_k.

(iv) Generation of extended sets of species

There can be several complementary sets with similarly strong links to the group of selected species, therefore it is reasonable to try more of them to find the optimal way to reduce simulation error. The procedure of building the mechanism to depth level m means the generation of m extended sets of species by adding each complementary set, one by one, from the first rank to the mth rank, to the current group of selected species. This procedure is repeated using the connectivity information at each reaction time t_k. Therefore, the number of the obtained extended sets of species is at most $m \times n_t$, where n_t is the number of times. It can be less, because some of these sets can be identical.

(v) Generation of consistent reduced mechanisms

In the next step, each extended set is checked if all of its constituent species are living. If all species are living, then the reaction steps of the full mechanism that contain only these species form a consistent mechanism. If not, then the reaction steps that produce non-living species are identified and their corresponding complementary sets are determined. A species is living at a given time t_k, if it has been formed from living species in any previous time period. Therefore, the maximum values of $\mathbf{J}_{ij}^2$ up to the actual time t_k are used to calculate values $\bar{C}_k$ to rank the complementary sets:

$$\bar{\mathbf{M}}_{ij}(t_k)^2 = \max_{l \leqslant k} \mathbf{J}_{ij}(t_l)^2, \qquad (14)$$

$$\bar{C}_k = \frac{1}{n_k} \sum_{i \in \text{set}} \bar{B}_i = \frac{1}{n_k} \sum_{i \in \text{set}} \sum_{\substack{j:\ \text{non-living} \\ \text{and selected}}} \bar{\mathbf{M}}_{ij}^2. \qquad (15)$$

Note, that Eq. (15) is similar to Eq. (13), but in the latter the inner summation is carried out for the non-living selected species only. The species belonging to the highest ranked complementary set are added to the group of selected species. This procedure is repeated, until all species become living. In summary, in step (iv) several different species sets are produced and in step (v) consistent mechanisms belonging to them are constructed.

(vi) Simulations and building a database

The efficiency of each reduced mechanism is investigated via a simulation. A database is set up, where each entry contains a species set and the corresponding calculated δ_{MAX} and δ_{RMS} errors. Several loops of steps (ii) to (v) may produce identical sets. For example, the same set having $n+2$ species might have been obtained both from sets with n and $n+1$ species. To avoid duplicated simulations, it is always checked if the investigated species set is already present in the database. If yes, then the corresponding simulation is not repeated.

(vii) Starting a new loop

The smallest mechanisms that have more than n species (usually having $n+1$ species) are looked for in the database, and one or two of them are selected as the starting point of the next loop of the mechanism building procedure.

Our main goal is to reduce error δ_{MAX} during the reaction building procedure, thus it seems reasonable to choose the reduced mechanism with the smallest δ_{MAX} error. However, δ_{MAX} error is sensitive only to those mechanism changes that are significantly affecting the concentration profiles of the important species having errors close to δ_{MAX}. Therefore, δ_{MAX} does not always change by adding new species. Error δ_{RMS} behaves in an opposite way, since it contains the error of all important species at every time, thus it is sensitive to any changes that affect their concentration profiles. A significant decrease in δ_{MAX}, which is our primary aim, is not always accompanied by a significant decrease of δ_{RMS}. This is the case when large δ_{MAX} is originated from a sharp localized deviation of the concentration profile of an important species.

Our experience is that small δ_{MAX} corresponds to the good reproduction of the height and location of the concentration peaks, while small δ_{RMS} corresponds to a good overall agreement between the concentrations calculated from the full and the reduced models. Considering either δ_{RMS} or δ_{MAX} alone was found to be not effective in building the mechanisms.

The species set related to the smallest δ_{RMS} error is utilized as the starting set of selected species in the next loop. If the set related to the smallest δ_{MAX} is a different one, then this set is also used as a starting set. If the smallest δ_{MAX} error is above the required threshold then all steps are repeated from step (ii). If not, then the first part of the mechanism reduction is completed.

The result of steps (i) to (vii) is a database that contains a series of sets of species. To each number of species, the species set with the smallest δ_{MAX} error is identified. It is not guaranteed that this error is a monotonically decreasing function of the number of species, but in our numerical experiments we found that this happens down to small errors.

In the algorithm above, in step (iv), the first m complementary sets are considered. Larger m may result in a reduced mechanism having smaller error after a single cycle, but we found that after several cycles, sets with smaller m may result in a smaller error for the same number of species. If we apply the procedure first with a small depth level m, then with a larger one (e.g. $m+1$, $2m$, $4m$, etc.), we cannot get a worse recommended reduced mechanism having the same number of species, because the database created during all previous runs is also utilized. Thus, this way we may get better and better results by gradually increasing m.

While the procedure described in steps (i) to (vii) effectively reduces the number of species, the reduced mechanisms may still contain redundant reactions.

4. Removal of redundant reactions by the SEM-PCAF method

The procedure above results in a series of consistent reduced mechanisms with different number of necessary species. These mechanisms can be reduced further via the elimination of the redundant reactions. This may lead to a reduced mechanism that can be simulated much faster, while the error of simulation remains essentially the same.

4.1. Identification of redundant reactions

The identification of the redundant reactions is carried out using the principal component analysis (PCA) of the rate sensitivity matrix $\mathbf{F}$ [23,26]. The normalized rate sensitivity matrix is defined as $\bar{\mathbf{F}}_{ij} = (k_i/f_j)(\partial f_j/\partial k_i)$. This method has been encoded as the PCAF option of KINALC [25]. In this program the user has to suggest one or several thresholds for the eigenvalues and the eigenvector elements.

Increasing the threshold values of PCAF in small steps results in the elimination of further reactions, and it causes small, but non-monotonic changes in the error of important species. Therefore, it is impossible to find the optimum threshold values based on a systematic search. Thus, the PCAF procedure is adapted here in such a way, that many different thresholds are tried automatically. Initially, low thresholds for the eigenvalues and eigenvectors are selected, leading to the elimination of few reaction steps. Then, both thresholds are changed independently, resulting in several different, smaller reduced mechanisms. Each of the obtained reduced mechanisms is investigated for consistency. If a mechanism is found not to be consistent, then the corresponding thresholds are considered to be too high, and this mechanism is discarded.

4.2. Finding the fastest reduced mechanism with small simulation error

Simulations are carried out with all consistent mechanisms, and the errors and CPU times are recorded. Many different reduced mechanisms may have an error that is very close to the smallest error found. However, these mechanisms may have significantly different numbers of reactions, thus the required computing times for the simulations may vary considerably. The aim is to find the fastest one among all reduced mechanisms having similarly small errors. Mechanisms having δ_{MAX} errors not more than a few percent higher than the smallest error are investigated further. In our calculations, this threshold was selected to be 2% of the δ_{MAX} error, that is for 5% δ_{MAX} error all reduced mechanisms were also considered up to 5.1% δ_{MAX} error. From all these mechanisms, the one having the smallest CPU time is accepted as the recommended reduced mechanism. In analogy to the naming of SEM-CM, the procedure described in this section is called the Simulation Error Minimization PCAF method or SEM-PCAF method.

Elimination of reaction steps may improve or worsen the agreement of the simulation results with the full mechanism. The SEM procedure allows the selection of those steps, where the elimination leads to simulation results that are closer to the results obtained from the full mechanism. In most cases a slight decrease of the error was observed after the SEM-PCAF reduction.

5. Mechanism reduction exercise: gas-phase chemistry in solid-oxide fuel cells

Solid-oxide fuel cells (SOFCs) could become a power source for electric-driven vehicles. One of the big advantages of them is that they can be operated with hydrocarbon fuels [27,28]. Anthony Dean and his co-workers developed a large elementary reaction mechanism [29] in order to describe the homogeneous gas-phase chemistry in the anode channel of natural gas fueled SOFCs. At the operation of the fuel cell, air is added to the natural gas to prevent deposit formation. Thus, the mechanism has to describe the partial oxidation of methane up to high conversion. This mechanism, due to its large size, cannot be used for computer optimization of fuel cell geometry and operating conditions. Our goal was to produce a reduced mechanism, which reproduces the simulation results of the original mechanism for all large concentration species within a few percent of error. The full reaction mechanism includes 343 reactive species and also species N_2 and Ar. At the conditions of the anode channel of a solid-oxide fuel cell, these latter species do not participate in chemical reactions, but their concentrations affect the concentrations of other species through third-body reactions. The reactive species consist of elements C, O and H. The original full mechanism included 3418 reversible and 38 irreversible reactions. These irreversible reactions did not have a pair in the mechanism, that is the rate of the backward reactions were always considered zero. The reversible reactions were transformed to irreversible ones by program MECHMOD [25]. The "irreversible only" mechanism contains 6874 irreversible reactions.

The operating conditions of a solid-oxide fuel cell can vary across a wide range of conditions, and we selected initial parameters that are representative for the SOFC operation. Therefore, temperature and pressure are chosen to be 900 °C (1173.15 K) and 1 atm (101325 Pa), respectively. The simulations were carried out at isothermal and isobaric conditions. The composition of the initial mixture was 30.0% v/v methane and 70.0% v/v air. The assumed composition of air was 79% v/v nitrogen and 21% v/v oxygen.

The mechanism was provided in Chemkin format. A home-made chemical interpreter called TRANS transformed the mechanism to an internal data representation. This chemical interpreter was able to handle the temperature and pressure dependence of rate coefficients, the third body efficiencies, etc. The mechanism reduction procedure described in this paper was carried out by three Fortran codes. TIBOX may do the simulations alone or as a utility program for the other codes. SEMCM removes the redundant species as described in Section 3. SEMPCAF carries out the simulation speed optimized reaction elimination.

Fortran code DRG was used to make comparisons with mechanism reduction methods DRG and DRGEP. Not only the original DRG method [15] was reproduced, but later improvements like linear time reduction [16], two-stage reduction (restart) [16] and DRGASA [18] were also encoded. The applied DRGEP method included as options scaling and group-based coefficients [21]. Also, integrity could be confirmed during the DRGEP procedure. The Connectivity Method was applied using a modified version of KINALC [25].

Low absolute and relative tolerances (10^{-12} mol cm^{-3} and 10^{-5}, respectively) were applied to the simulations to allow precise error calculations. Local errors were calculated at 121 points equally distributed on a logarithmic time scale between 1 ms and 1000 s, which means 20 points per one order of magnitude. All these points were used in the species and reaction elimination procedures. Those species were considered important, for which the mole fraction exceeded 0.001. These were for the following 12 species: CH_4, N_2, O_2, H_2, H_2O, CH_2O, CO, CO_2, C_2H_2, C_2H_4, C_2H_6, and benzene (C_6H_6).

Reduced mechanisms having very few species result in high δ_{MAX} errors (above 100%), while the original mechanism with 345 species by definition has 0% error. Since the mechanism reduction methods may produce many reduced mechanisms, a plot can be created that shows error δ_{MAX} as a function of the number of species. In general, a mechanism reduction algorithm is more efficient if this curve is running closer to the lower left corner of the plot.

Fig. 2 shows the results of the SEM-CM algorithm as the depth level is changed systematically. Depth levels were increased in steps 1, 4, 16, 64, and 256. Using depth level 1, the error is high as long as the number of species is less than 43, but it decreases sharply by applying more and more species. When the number of species is larger than 60, the error becomes less than 5%. Using together the results of depth level 1 and 4, there is a sharp decrease of errors at 27 species, but this curve reaches 5% error at the same number of species. Using also depth level 16, 5% δ_{MAX} error can be obtained with a reduced mechanism containing 55 species. By increasing the depth level to 256, this δ_{MAX} error can be obtained with 47 species. In this case still only 8% of the total number of possible complementary sets have been considered! Increasing the depth level further, no improvement was obtained.

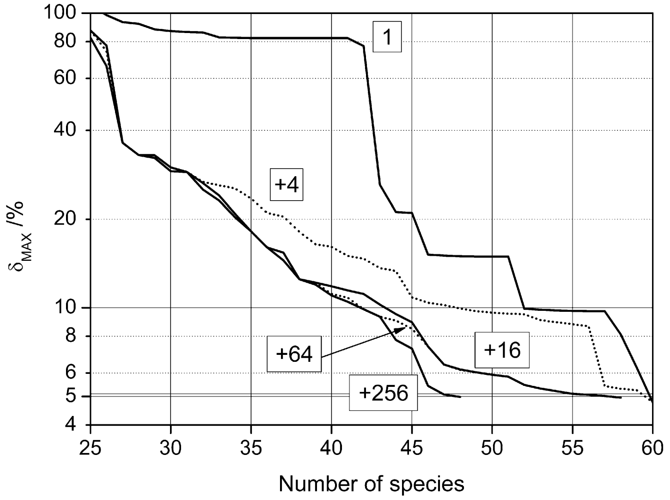


Fig. 2. Maximal simulation errors of the mechanisms as function of species number, obtained by applying the SEM-CM algorithm using depth levels 1, +4, +16, +64, and +256 one after the other.

Table 1
Results of the investigation of the performance of the SEM-CM method. The original full mechanism contained 6874 irreversible reactions of 345 species. Increasing the depth level, the computer time increases (see the discussion in the text). The computer times correspond to a 32 bit AMD Athlon XP 3200+ processor PC.

SEM-CM depth level	1	+4	+16	+64	+256
Additional CPU time (hh:mm:ss)	00:11:58	00:30:36	01:18:17	03:56:10	04:31:41
Cumulated CPU time (hh:mm:ss)	00:11:58	00:42:34	02:00:51	05:57:01	10:28:42
Species	60		55		47
Irrev. reactions	962		823		613
δ_{MAX} (%)	4.77		5.11		5.07
δ_{RMS} (%)	0.922		1.15		1.25

Table 1 shows the results of the investigation of the performance of the SEM-CM algorithm. Increasing the depth level, the computer time increases considerably. Level 1 required 12 min CPU time. Depth level 4 used the database that had been created at level 1, and required additional 31 min (total 43 min). Using also depth level 16 required additional 1 h and 18 min. When depth level 256 was used, the computer time needed was 10 h 29 min altogether. Table 1 shows the efficiency of these strategies by comparing the size of the identified reduced mechanisms for δ_{MAX} error of about 5%. Up to depth level 64, the reduced mechanism consists of 823 irreversible reactions of 55 species. Increasing the depth level to 256, the reduced mechanism consists of 613 irreversible reactions of 47 species. This is the best result of the species elimination step, but the number of reactions can be decreased further using the SEM-PCAF method.

The large computer time demand of the SEM method might be prohibitive when the method is applied to very large mechanisms. In this case, when the number of the recommended reduced mechanisms is very large, it might be practical to decrease

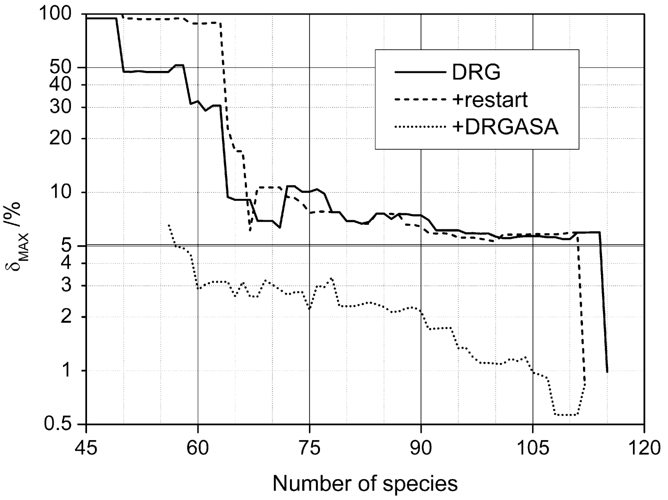


Fig. 3. Maximal simulation errors of the mechanisms as function of species number, obtained by applying the original DRG method and the DRG method with restart and DRGASA extensions.

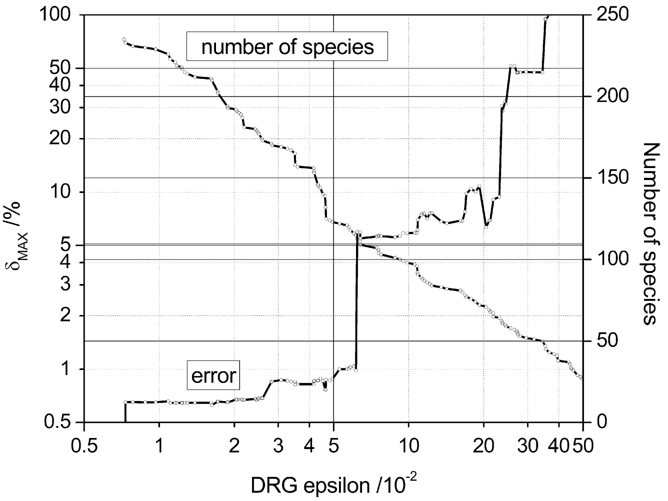


Fig. 4. Maximal simulation error and the number of species as a function of epsilon using the original DRG method.

the number of necessary simulations by using lower depth levels only. Another possibility is to carry out a fast preliminary reduction (e.g. using DRGEP) that results in a small reduction error and then continuing the mechanism reduction using SEM-CM.

Fig. 3 shows the maximum errors (δ_{MAX}) as a function of the number of species when the original DRG method and two improved versions of it are applied. Using the original DRG [15], δ_{MAX} error of 6.3% was achieved already at 71 species. This reduced mechanism could be simulated 8.75 times faster than the full mechanism. Decrease of the error below 5% was obtained only at 115 species. Using "two-stage DRG" [16] or "restart" the results slightly improved, since 6% and 5% was reached at 66 and 112 species, respectively. The best DRG variant is when reduced mechanism with 1% error was achieved using DRG restart, then DRGASA was used and the number of species was gradually decreased with a simultaneous monitoring of the simulation error. This combined method resulted in a mechanism having 57 species.

In the DRG method, it is generally assumed that the simulation error decreases monotonically when threshold ε is lowered, provided that threshold ε is small (e.g. less than 0.2). It is true for the error of flux calculation, but not for the simulation error of the concentration profiles. Fig. 4 shows that by decreasing epsilon the simulation error decreases in large steps and also non-monotonically, while the number of species in the reduced mechanism increases in a monotonic way. The result is that almost the same simulation error can be obtained with mechanisms of very different size using the DRG method. This shows that in the DRG method several epsilon values should be tried and the resulting mechanisms should be checked by simulations.

Table 2

Performance of the original and improved DRG methods. The quoted CPU times include the computer time needed for the simulations and calculation of the simulation error for all suggested reduced mechanisms.

Method	DRG	+ Restart	+ DRGASA
Additional CPU time (hh:mm:ss)	00:01:52	00:01:35	00:06:27
Cumulated CPU time (hh:mm:ss)	00:01:52	00:03:27	00:09:54
Species	115	112	57
Reversible + irreversible reactions	1112 + 9	1059 + 9	407 + 7
Irrev. reactions	2233	2127	821
δ_{MAX} (%)	0.985	0.835	4.99
δ_{RMS} (%)	0.190	0.169	1.39

Table 3

Performance of the original and improved DRGEP methods. The quoted CPU times include the computer time needed for the simulations and calculation of the simulation error for all suggested reduced mechanisms.

Method	Basic method	Group based coefficients	Scaling	Both extra features
CPU time (hh:mm:ss)	00:01:00	00:01:46	00:01:17	00:01:38
Species	80	97	88	93
Reversible + irreversible reactions	582 + 8	807 + 8	744 + 9	756 + 8
Irrev. reactions	1172	1622	1497	1520
δ_{MAX} (%)	5.00	4.79	4.71	4.84
δ_{RMS} (%)	0.988	1.10	1.04	1.18

Table 2 shows the computer time requirement of the various DRG methods. Encoding of the DRG method was based on the "linear time reduction" algorithm [16] for CPU time optimization. The indicated CPU times included the computer time needed for the simulations and the error calculations. In all cases the CPU requirement was below 10 min. The DRG algorithm includes [17] that reversible reactions should be considered, and only those reaction steps can be handled as irreversible, where the rate of the backward step is negligible. For this reason, the original mechanism was used that contains only unpaired irreversible reactions besides the reversible reaction steps. For the comparison of Tables 1 to 4, the number of "irreversible only" reaction steps are also indicated. The smallest reduced mechanism, obtained by DRGASA contains 821 irreversible reactions.

Fig. 5 shows the maximum errors (δ_{MAX}) as a function of the number of species when the basic DRGEP method was applied alone or with extra features. Using the basic DRGEP, δ_{MAX} error of 5% was achieved at 80 species. Using "scaling" or "group based coefficients" slightly improved the algorithm at 7% required error, but made the performance worse at 5% error. Table 3 shows the numerical results for the DRGEP method. DRGEP performed much better than the original DRG and the two-stage DRG, since it produced a smaller mechanism in less time. The CPU requirement was less than 2 min in all cases. The DRGEP method was also applied on the original mechanism containing both reversible and irreversible reaction steps, but for comparisons the numbers of the "irreversible only" reaction steps are also indicated. The smallest reduced mechanism, obtained by DRGEP contains 1172 irreversible reactions.

Fig. 6 compares the best versions of all investigated methods. Considering the maximum errors (δ_{MAX}) as a function of the num-

Table 4

Performance of the mechanisms for the required 5% δ_{MAX} maximum error with the smallest possible number of species that can be achieved by each method.

Method	DRG + restart + DRGASA	DRGEP basic method	CM	SEM-CM depth level 1	SEM-CM depth level $1+\cdots+256$	SEM-PCAF	SEM-PCAF + restart
Time to develop the reduced mechanism (hh:mm:ss)	00:09:50	00:01:00	00:01:05	00:11:58	10:28:42	00:30:11	00:41:57
Size							
Species (originally 345)	57	80	139	60	47	47	47
Irreversible reactions (originally 6874)	821	1172	2494	962	613	297	246
Simulation time (s)	0.720	1.32	4.87	0.875	0.465	0.263	0.233
Speed-up (× times)	37.7	20.5	5.57	31.0	58.4	103	116
δ_{MAX} (%)	4.99	5.01	4.62	4.77	5.07	4.84	4.98
δ_{RMS} (%)	1.39	0.988	0.799	0.922	1.25	1.16	1.16
$\delta_{i,\mathrm{MAX}}$ (%)							
CH_4	0.352	0.658	0.160	0.240	0.759	0.548	0.636
N_2	0.125	0.066	0.068	0.129	0.154	0.166	0.191
O_2	1.52	0.902	0.107	1.20	2.69	1.67	1.62
H_2	1.09	1.10	0.651	0.980	1.57	1.70	2.09
H_2O	1.25	0.818	0.334	1.01	2.19	1.73	1.61
CH_2O	1.91	1.59	0.106	2.07	3.69	3.60	3.52
CO	1.73	0.608	0.723	1.54	2.28	1.47	1.35
CO_2	1.15	0.600	0.368	0.972	1.28	0.752	0.792
C_2H_2	4.99	3.01	4.13	4.35	4.81	4.78	4.24
C_2H_4	4.51	5.01	2.74	2.84	2.84	4.27	4.57
C_2H_6	1.73	1.23	0.321	1.99	5.00	4.49	4.36
C_6H_6	3.90	4.04	4.62	4.77	5.07	4.84	4.98

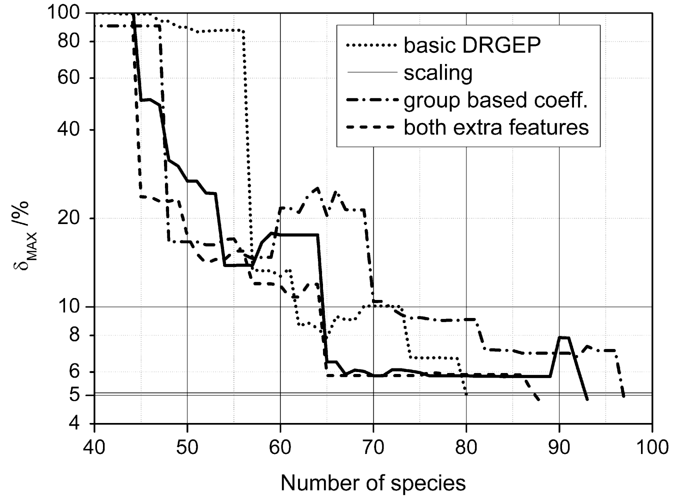


Fig. 5. Maximal simulation errors of the mechanisms as function of species number, obtained by applying the original DRGEP method and the DRGEP method with extensions: (1) scaling, (2) group based coefficients, (3) these two extensions simultaneously.

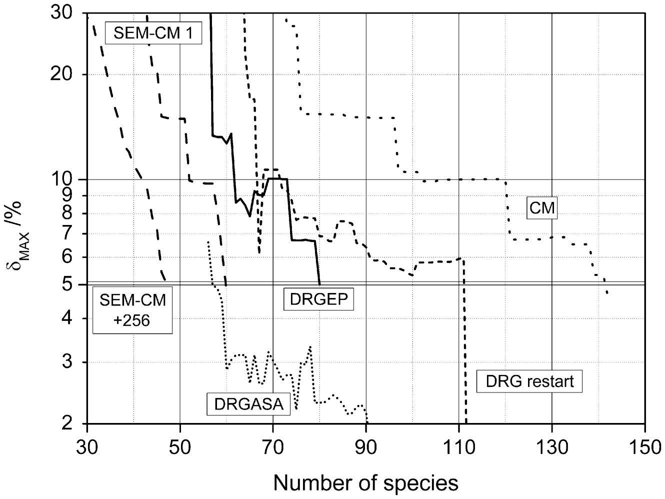
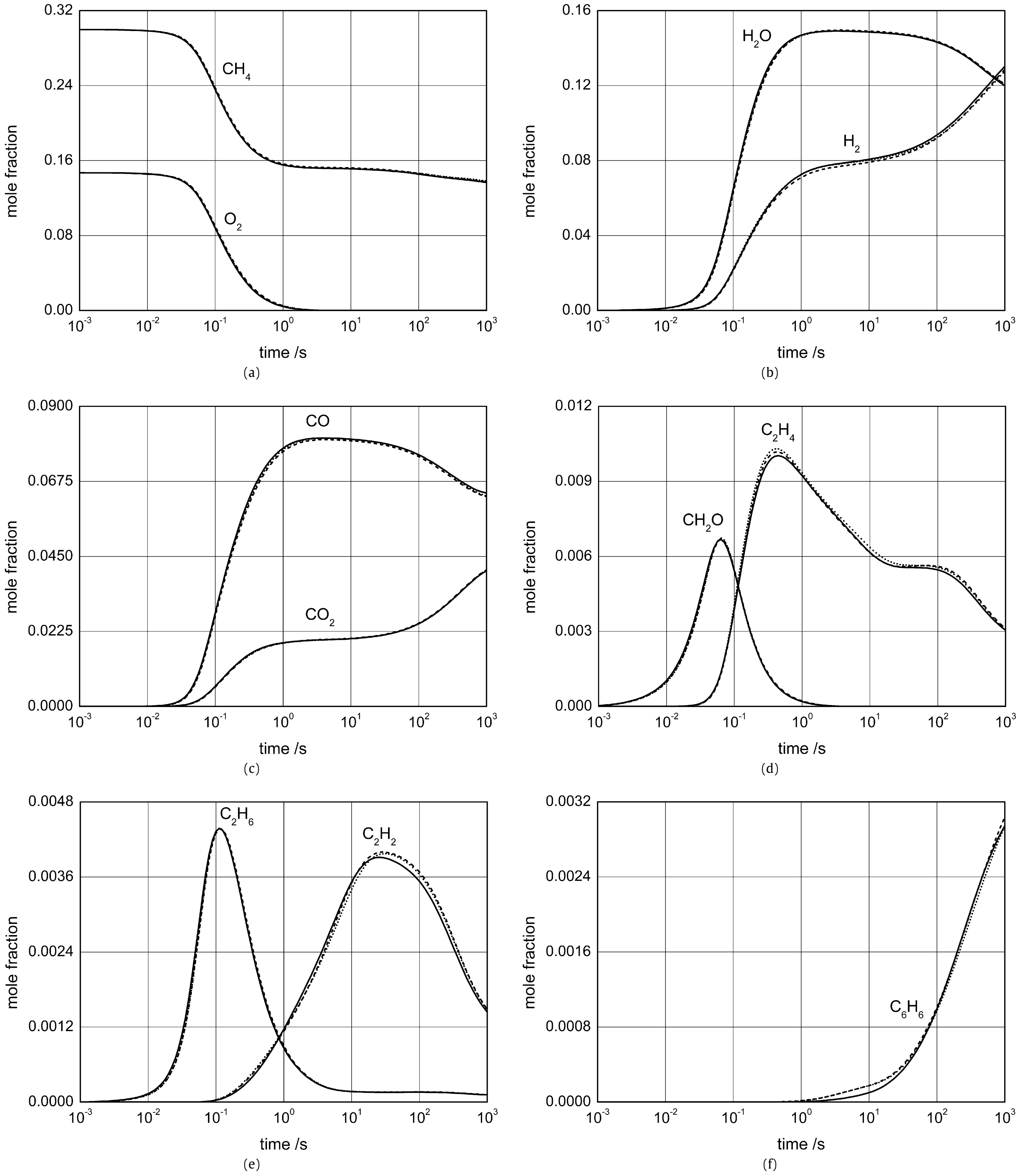


Fig. 6. Maximal simulation errors of the mechanisms as function of species number, obtained by applying the most effective versions of each method. The compared methods are the Connectivity Method (CM), DRG with restart, the basic DRGEP, DRGASA-improved results of the DRG restart method, and SEM-CM (depth level 256).

ber of species, the classic Connectivity Method has the worst performance. At 5% required error, it leaves 139 species in the reduced mechanism by eliminating 206 species. DRGEP is usually better than the two-stage DRG (DRG restart). Using DRGASA, the error is increasing by eliminating more and more species, and this method results in a small mechanism of 57 species at 5% error. SEM-CM using depth level 1 gives a reduced mechanism of similar size. However, SEM-CM using high depth level (in this case depth level 256) is the best of all these methods.

Table 4 shows the numerical results for the best versions of the DRG, DRGEP, CM and SEM-CM methods. DRGEP and CM require about 1 min CPU time. Both DRGASA and SEM-CM (depth level 1) required about 10 min. SEM-CM (depth level +256) required about 10.5 h on a desktop PC, but provided far the smallest reduced mechanism of 47 species and 613 irreversible reactions. When SEM-PCAF was applied on the result of the SEM-CM reduction, the number of irreversible reactions could be reduced to 297.

Table 4 indicates the speed-up of simulations as a result of mechanism reduction. The Connectivity Method provided a reduced mechanism that can be simulated 5.6 times faster. DRGEP and DRG + restart + DRGASA resulted in 20.5 and 37.7 times increase in the simulation speed, respectively. SEM-CM (+256) alone gave 58.4 times speed-up, while the increase of simulation speed is 103 times if the SEM-CM and SEM-PCAF methods are combined. If the SEM-PCAF method is applied again on the mechanism obtained as the result of the combined SEM-CM and SEM-PCAF methods, then an even smaller mechanism is obtained, that consists of 246 reactions. The simulation of the final reduced mechanism is 116 times faster, than that of the initial mechanism. We may call this procedure as ”SEM-PCAF + restart.” The lower part of the table



(a) (b)

(c) (d)

(e) (f)

Fig. 7. Simulation results of the SOFC chemistry example using the full mechanism (6874 reactions of 345 species, solid line), the mechanism obtained by the SEM-CM algorithm (613 reactions of 47 species, dashed line) and after further eliminating the redundant reactions with the SEM-PCAF restart method (246 reactions of 47 species, dotted line). (a) CH_4 and O_2; (b) H_2O and H_2; (c) CO and CO_2; (d) CH_2O and C_2H_4; (e) C_2H_6 and C_2H_2; (f) C_6H_6 concentration–time profiles.

shows that for all mechanism reduction methods for each important species the maximal deviation is less than about 5%.

Fig. 7 shows the simulation results of the SOFC chemistry example using the full mechanism (6874 irreversible reactions of 345 species), the mechanism obtained by the SEM-CM method (613 irreversible reactions of 47 species) and after the further elimination of the redundant reactions by the SEM-PCAF + restart method (246 irreversible reactions of 47 species). The concentration–time profiles of species CH_4, O_2, H_2O, H_2, CO, CO_2, CH_2O, C_2H_4, C_2H_6, C_2H_2, and C_6H_6 are plotted. The figures show that at 5% required error level the reduced mechanism very accurately reproduces the concentration profiles obtained from the full mechanism, even though the simulation is 116 times faster.

6. Conclusion

Previously published methods for species reduction include the Directed Relation Graph (DRG) method [15–19], the DRG with Error Propagation (DRGEP) method [20,21] and the Connectivity Method [10]. These methods investigate the system of kinetic differential equations (or the reaction graph, which is an equivalent form) for the detection of redundant species and reactions in a large reaction mechanism. The size of the obtained reduced mechanism is controlled by a threshold, which cannot be related directly to the error of reduction, that is the deviation between the simulation results obtained by full and the reduced mechanisms. A range of reduced mechanisms can be obtained by systematically changing this threshold.

In the mechanism reduction approach used in this paper, several thousands of reduced mechanisms are produced based on the investigation of the kinetic differential equations. Using the results of simulations, the best one is selected for a given level of error. This approach was implemented for the elimination of both the redundant species (SEM-CM) and the redundant reactions (SEM-PCAF).

Similar approaches have been published in the literature. Turányi [10] recommended the elimination of all consuming reactions of each species, one by one, and considering those species as redundant for which the simulation results of these reduced mechanisms remained within an error limit for the important species and/or important reaction features. This method could not predict the effect of the simultaneous elimination of species groups. Petzold and Zhu [11] generated reduced mechanisms using a nonlinear integer programming approach. The simulation error was calculated and used for the optimization process. The method worked well for few-step mechanisms, but for large mechanisms it was applicable only with many extensions and human decisions, like grouping of the reactions and pre-selection of the most important reactions.

DRGASA [18] also has a similar reduction philosophy. Like in the Simulation Error Minimization Connectivity Method used in this paper, another method (DRG) is used as a guideline, reduced mechanisms are produced, and the final reduced mechanism is selected on the basis of the simulation results. This is the reason why DRGASA performs much better than the other DRG-based methods (see Fig. 6 and Table 4).

According to the Simulation Error Minimization Connectivity Method (SEM-CM), a mechanism building procedure is initiated by creating a small consistent mechanism comprising the important species and their reactions with other species, extracted from the full mechanism on the basis of the normalized Jacobian [10]. A mechanism is called consistent if all of its species have nonzero initial concentration, have an inflow term (e.g. non-zero inlet concentration in a PSR) or are formed by chemical reactions from other species. The procedure is repeated to build up mechanisms of increasing size. Simulations are carried out using all these mechanisms and the mechanism having the smallest error of reduction is selected from several candidates of the same size. This method is basically different from DRGASA, since in the latter method first a midsized reduced mechanism is produced by DRG, and then further species are eliminated one by one based on the results of simulations. The investigated species were selected using the DRG method.

According to the PCAF method with Simulation Error Minimization (SEM-PCAF), several consistent reduced mechanisms are produced using the PCAF method [26] with various thresholds, and simulations are carried out with all the candidate mechanisms. The reduced mechanism having the least CPU time requirement is selected from the ones related to small errors of reduction.

In this paper several methods, namely the original DRG, two-stage DRG, DRGASA, original DRGEP, DRGEP with scaling, DRGEP with group-based coefficients, DRGEP with both features, CM, and the two newly proposed methods (SEM-CM and SEM-PCAF) are compared on the same mechanism reduction task. The chosen numerical example is the reduction of a methane partial oxidation mechanism that has been used for modeling the gas phase reactions in the anode channel of solid oxide fuel cells (SOFCs). This mechanism consists of 6874 irreversible reactions of 345 species and it was tested at the conditions of a typical industrial application. The obtained reduced mechanisms have the following size: DRG: 2233 irreversible reactions of 115 species; DRGASA: 821 irreversible reactions of 57 species; DRGEP: 1172 irreversible reactions of 80 species; CM: 2494 reactions of 139 species; SEM-CM: 613 reactions of 47 species. The increase in the simulation speed is 8.8, 37.7, 20.5, 5.6 and 58.4 times for the DRG, DRGASA, DRGEP, CM and SEM-CM methods, respectively. This shows that the SEM-CM algorithm, introduced in this paper, resulted in the smallest reduced mechanism at a given simulation error and the largest speed-up.

Application of the SEM-PCAF method after the SEM-CM halved the number of reactions and almost doubled the simulation speed. A repeated application of the SEM-PCAF method further decreased the number of reactions in the mechanism. The recommended reduced mechanism (246 reactions of 47 species) allows 116 times faster simulations of the SOFC chemistry, while the concentrations of important species obtained from the reduced mechanism were only slightly different (less than 5%) compared to those of the full mechanism.

Programming considerations

The MEBDFSO Fortran77 code [30] was used for the integration of the kinetic differential equations. The suggested mechanism reduction methods were programmed in Fortran 90 and were made fully automatic, thus these are readily applicable for the reduction of other reaction mechanisms. The code is available from our Web site [25].

Acknowledgments

The authors acknowledge the helpful discussions with Prof. Anthony M. Dean and Dr. Hans-Heinrich Carstensen on the SOFC gas-phase chemistry and with Dr. István Gy. Zsély and Mr. Áron Kramarics on the implementation of the SOFC mechanism. The authors are grateful for the comments of Professors Alison Tomlin, Michael Frenklach, and Jyh-Yuan Chen. We are also grateful for the anonymous reviewers for their very helpful comments. The work was supported by OTKA fund T68256.

References

[1] A.S. Tomlin, T. Turányi, M.J. Pilling, in: M.J. Pilling, G. Hancock (Eds.), Low Temperature Combustion and Autoignition, Elsevier, Amsterdam, 1997, pp. 293–437.
[2] U. Maas, S. Pope, Combust. Flame 88 (1992) 239–264.
[3] T. Turányi, A.S. Tomlin, M.J. Pilling, J. Phys. Chem. 97 (1993) 163–172.
[4] S. Lam, D. Goussis, Int. J. Chem. Kinet. 26 (1994) 461–486.
[5] H. Huang, M. Fairweather, J.F. Griffiths, A.S. Tomlin, R.B. Brad, Proc. Combust. Inst. 30 (2005) 1309–1316.
[6] M.S. Okino, M.L. Mavrovouniotis, Chem. Rev. 98 (1998) 391–408.
[7] C.K. Law, Proc. Combust. Inst. 31 (2007) 1–29.
[8] M. Frenklach, K. Kailasanath, E.S. Oran, Prog. Astronaut. Aeronaut. 105 (2) (1986) 365–376.
[9] H. Wang, M. Frenklach, Combust. Flame 87 (1991) 365–370.
[10] T. Turányi, New J. Chem. 14 (1990) 795–803.
[11] L. Petzold, W.J. Zhu, AIChE J. 45 (4) (1999) 869–886.

[12] H. Soyhan, F. Mauss, C. Sorusbay, Combust. Sci. Technol. 174 (2002) 73–91.

[13] J. Luche, M. Reuillon, J.-C. Boettner, M. Cathonnet, Combust. Sci. Technol. 176 (2004) 1935–1963.

[14] M. Valorani, F. Creta, D. Goussis, J. Lee, H. Najm, Combust. Flame 146 (2006) 29–51.

[15] T. Lu, C.K. Law, Proc. Combust. Inst. 30 (2005) 1333–1341.

[16] T. Lu, C. Law, Combust. Flame 144 (2006) 24–36.

[17] T. Lu, C. Law, Combust. Flame 146 (2006) 472–483.

[18] X.L. Zheng, T.F. Lu, C.K. Law, Proc. Combust. Inst. 31 (2007) 367–375.

[19] T. Lu, C. Law, Combust. Flame 154 (2008) 153–163.

[20] P. Pepiot, H. Pitsch, in: 4th Joint Meeting of the U.S. Sections of the Combustion Institute, Philadelphia, PA, 2005.

[21] P. Pepiot-Desjardins, H. Pitsch, Combust. Flame 154 (2008) 67–81.

[22] A.S. Tomlin, M.J. Pilling, T. Turányi, J.H. Merkin, J. Brindley, Combust. Flame 91 (1992) 107–130.

[23] I.Gy. Zsély, T. Turányi, Phys. Chem. Chem. Phys. 5 (2003) 3622–3631.

[24] T. Turányi, Comput. Chem. 14 (1990) 253–254.

[25] http://garfield.chem.elte.hu/Combustion/Combustion.html.

[26] T. Turányi, T. Bérces, S. Vajda, Int. J. Chem. Kinet. 21 (1989) 83–99.

[27] K.M. Walters, A.M. Dean, H. Zhu, R.J. Kee, J. Power Sources 123 (2003) 182–189.

[28] Ch.Y. Sheng, A.M. Dean, J. Phys. Chem. A 108 (2004) 3772–3783.

[29] G. Gupta, E.S. Hecht, H. Zhu, A.M. Dean, R.J. Kee, J. Power Sources 156 (2006) 434–447.

[30] T.J. Abdulla, J.R. Cash, M.T. Diamantakis, Comput. Math. Appl. 42 (2001) 121–129.