Mechanism Reduction Based on Simulation Error Minimization

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***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 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.**

I. Introduction

Almost all published detailed reaction mechanisms contain redundant species and reactions [1]. Elimination of redundant species and reactions from a large reaction mechanism allows a significant decrease of simulation time. 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 was the reproduction of ignition delay times and temperature profiles. The first general systematic method for species reduction, which is called here the Connectivity Method, was suggested by Turányi [9] and since then several other methods have been published for this task [10-23].

In this paper algorithms Simulation Error Minimization Connectivity Method (SEM-CM) and Principal Component Analysis of Matrix F with Simulation Error Minimization (SEM-PCAF) are described briefly. More details can be found in our recent article [23].

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

A. Definitions

The aim of simulations is to reproduce the concentration profiles of the *important species* or to reproduce some important features. The mechanism reduction methods select further species to the group of important species to ensure the good agreement between the simulation results obtained using the full and the reduced mechanisms. 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.

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 if 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.

B. The algorithm

Connection of a complementary set to the group of currently selected species can be assessed by the following measure:

$$C_{\mathrm{k}} = \frac{1}{n_{\mathrm{k}}} \sum_{\mathrm{i} \in \mathrm{set}} B_{\mathrm{i}} = \frac{1}{n_{\mathrm{k}}} \sum_{\mathrm{i} \in \mathrm{set}} \sum_{\mathrm{j} \in \mathrm{group}} \bar{\mathbf{J}}_{\mathrm{ij}}{}^2 ,$$

where $\bar{\mathbf{J}}_{ij} = \left(c_i / f_j\right)\left(\partial f_j / \partial c_i\right)$ is an element of the normalized Jacobian.

The Simulation Error Minimization Connectivity Method (SEM-CM) can be summarized as follows.

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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. Depth level m means that the first m complementary sets with the highest C_k values are considered. 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 $n_{imp}+1$ 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 $n_{imp}+2$, $n_{imp}+3$, *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.

While the SEM-CM procedure effectively reduces the number of species, the reduced mechanisms may still contain redundant reactions.

III. Principal Component Analysis of Matrix F with Simulation Error Minimization (SEM-PCAF)

A. *The algorithm*

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.

The identification of the redundant reactions is carried out using the principal component analysis (PCA) of the normalized rate sensitivity matrix $\overline{\mathbf{F}}$ [24]. This matrix is defined as $\overline{\mathbf{F}}_{ij} = \left(k_i / f_j\right)\left(\partial f_j / \partial k_i\right)$ 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.

B. *Optimization for simulation time*

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 errors not more than a few percent higher than the smallest error are investigated further. From all these mechanisms, the one having the smallest CPU time is accepted as the recommended reduced mechanism.

IV. Example

Anthony Dean and his co-workers developed a large elementary reaction mechanism [26] in order to describe the homogeneous gas-phase chemistry in the anode channel of natural gas fuelled solid-oxide fuel cells (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. The full reaction mechanism includes 345 species and 6874 irreversible reactions. This mechanism, due to its large size, cannot be used in reacting flow models for the 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 selected initial parameters were representative for the SOFC operation, that is temperature and pressure were 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.

Home-made Fortran codes were developed for the SEM-CM and SEM-PCAF calculations. Another series of Fortran codes were produced for the application of the various DRG and DRGEP methods, including the original DRG method [15], and also later improvements like linear time reduction [16], two-stage reduction (restart) [16] and DRGASA [18]. The applied DRGEP method included as options scaling and group-based coefficients [21]. The Connectivity Method was applied using a modified version of KINALC [25].

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) were considered important. The mole fraction of these species exceeded 0.001 during the 1000 s simulation time.

Fig. 1 compares the best versions of all investigated methods. Considering the maximum errors as a function of the number 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 up to depth level 256) is the best of all these methods, since it provided a 47-species reduced mechanism.

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. 2 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.

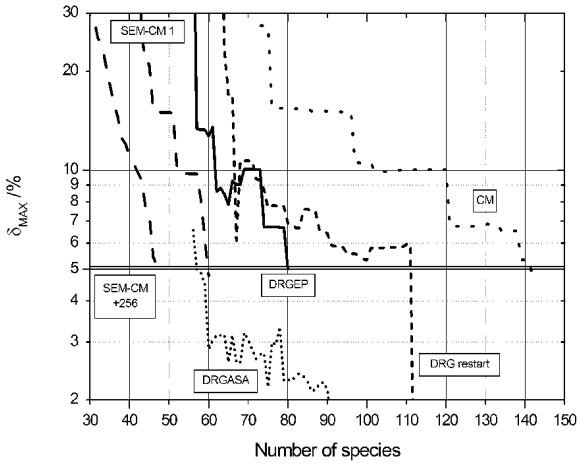

Fig. 1. Maximal simulation errors of the mechanisms as function of species number, obtained by the Connectivity Method (CM), DRG with restart, the basic DRGEP, DRGASA-improved results of the DRG-restart method, and SEM-CM (depth levels 1+4+…+256).

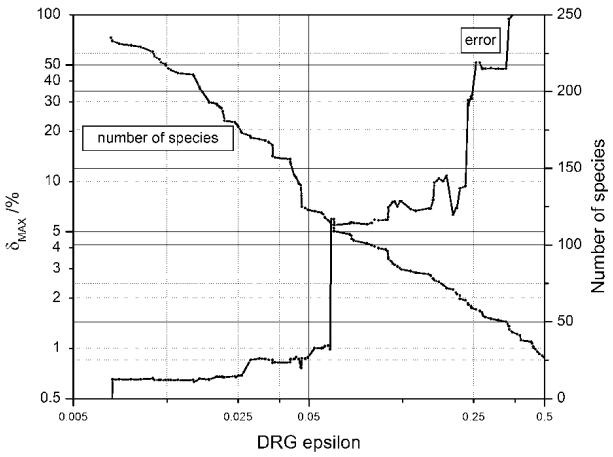

Fig. 2. Maximal simulation error and the number of species as a function of epsilon using the original DRG method.

Table I shows the numerical results for the best versions of the DRG, DRGEP, CM and SEM-CM methods. DRGEP and CM required about 1 minute CPU time. Both DGRDASA and SEM-CM (depth level 1) required about 10 minutes. SEM-CM (depth level 1+4+…+256) required about 10.5 hours 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. 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 Table also indicates the speed-up of simulations as a result of mechanism reduction. SEM-CM (1+4+…+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. The simulation of the final reduced mechanism having 47 species and 246 reactions is 116 times faster, than that of the initial mechanism of 345 species and 6874 reactions.

TABLE I.
PERFORMANCE OF THE MECHANISMS FOR THE REQUIRED 5% 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+4+...+256	+SEM-PCAF	+SEM-PCAF +restart
time to develop the reduced mechanism (hh:mm)		00:10	00:01	01:05	00:12	10:29	+ 00:30	+ 00:42
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

V. DISCUSSION

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 [9]. 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 [9] 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.

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.

According to the PCAF method with Simulation Error Minimization (SEM-PCAF), several consistent reduced mechanisms are produced using the PCAF method [24] with various thresholds; then 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. Application of the SEM-PCAF method after the SEM-CM halved the number of reactions and almost doubled the simulation speed.

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

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