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Systematic procedure for reduction of kinetic mechanisms of complex chemical processes and its software implementation

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Abstract Feasibility of multidimensional hydrodynamic modeling depends critically on the availability of accurate reduced kinetic mechanisms of physical and chemical processes taking place in the system. Such mechanisms should describe the processes under consideration within a specified error tolerance in the range of initial conditions of interest while keeping the number of species and reactions as small as possible. We have developed an advanced tool for reduction of detailed kinetic mechanisms with a minimal human effort. The tool includes 10 reduction and 2 analysis methods which are based on the results of zero-dimensional modeling. The methods can be combined and applied in sequence. The reduction tool has been implemented as a part the Chemical Workbench computational package and has been tested for a number of large kinetic mechanisms of gas-phase processes. Using this tool, we reduced the mechanism of tar gasification from 177 species and 879 reversible reactions to only 83 species and 278 reactions, while the mechanism of methane combustion initially involving 127 species and 1,206 reactions was reduced to 42 species and 173 reactions.

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Introduction

Detailed kinetic mechanisms describing complex chemical processes, such as hydrocarbon oxidation, can consist of hundreds of species and thousands of elementary reactions [1,2]. Kinetic modeling based on detailed mechanisms provides a precise description of behavior of concentrations of species and thermodynamic parameters with respect to time. Obtaining the solution for the mechanisms of such a complexity in homogenous systems is a matter of seconds for modern computers. However, multidimensional simulations of reacting flows involving chemical transformations in such a detail is still not possible due to the extreme computational complexity [2,3]. For this reason, development of different approaches to reduce kinetic mechanisms is a necessary step for taking advantage of detailed chemical information in multidimensional hydrodynamic modeling of complex processes and devices [2,3]. Reduced mechanisms usually describe processes with a lower precision and are applicable in a narrower range of initial conditions than detailed mechanisms. However, such reduced mechanisms make 3D computational fluid dynamics (CFD) simulations feasible.

A mechanism can be simplified separately from CFD simulations in a common zero-dimensional reactor. This approach makes possible a systematic reduction of an arbitrary chemical mechanism. Another way to incorporate complex chemistry into CFD simulations is to approximate the solution by polynomial functions with locally defined coefficients [4–6].

A large number of methods [7–10] for systematic reduction of kinetic mechanisms have been suggested. Some of them exclude reactions and species that can be disregarded under particular conditions [8,9]. As a result, a skeletal mechanism is obtained. Such a mechanism includes only a minimal set of reactions and species that are important for the description of the system. Thus, in a skeletal mechanism, reactions are elementary physical and chemical processes that actually occur in the system under the conditions considered. Each mathematical algorithm of this kind has a set of method-specific parameters that determine which species and reactions should be neglected. In this work they are referred to as controlling parameters. The accuracy of the skeletal mechanism can be controlled by varying values of the controlling parameters [7,8,12,13].

If the number of species and reactions in the skeletal mechanism in not small enough for CFD simulations, a global mechanism should be developed. Such a mechanism consists of overall reactions [2] with the rates calculated on the basis of elementary reactions [11]. In this case, the reactions in the mechanism do not correspond to any real elementary processes and the reaction rates are approximations that do not generally follow Arrhenius form.

The accuracy of description of physical and chemical variables (concentrations of species, temperature, and pressure) by the mechanism can be validated against experimental data as well as the data obtained using the detailed mechanism [12]. In latter case, it is assumed that the detailed mechanism is already validated against experimental data.

Algorithms for elimination of unimportant species and reactions can be divided into three groups: (1) sensitivity analysis and derivatives [9], (2) rates of production analysis and derivatives [8], and (3) time-scale analysis and derivatives [11,14,15]. There is a number of ways to combine these approaches [1,10,16]. In some combinations, methods are applied successively [1,16]. In this case, species and reactions are removed if any of the reduction methods marks them as unimportant. There can also be combinations in which reactions and species are removed only if all the methods mark them as unimportant [10].

In the present paper, a software tool for mechanism reduction is developed. The tool allows a construction of skeletal mechanisms using any combination of 10 mechanism reduction methods. Although there are other reduction tools already available [3,17], some of them are coupled with CFD codes and reduce mechanisms only with respect to specific CFD models [3], while the others [17] include only mechanism analysis methods and do not provide means to automatically produce reduced mechanisms. As opposed to these approaches, the advanced tool developed in the present study provides the means to automatically reduce and validate kinetic schemes prior to using them in CFD simulations.

The paper is organized as follows. In Sect. 1 general structure of the mechanism reduction module is presented. In Sect. 2 the graphical user interface is described. In Sect. 3 algorithms of methods are given in detail. In Sect. 4 results obtained with the module are discussed.

1 Mechanism reduction module

The software module is integrated into the Chemical Workbench software package (CWB, http://www.kintechlab.com/products/chemical-workbench/) for physical and chemical modeling and solving of systems of stiff ordinary differential equations [18]. This module is able to analyze and reduce mechanisms of chemical processes simulated in the Calorimetric Bomb Reactor (CBR), CBR with Sensitivity (CBRS), and other zero-dimensional models. Reactor models and the reduction module are integrated into a single environment so that results of kinetic calculations or series of calculations can be passed to the reduction module and then the reduced mechanism developed can be passed back to the reactor considered. The results of kinetic calculations can include the following data:

1. The solution of the set of kinetic equations determined by the mechanism in a certain range of initial conditions. The solution includes concentrations of all species, rates of all reactions, and thermodynamic parameters at each value of the argument, i.e. time or length in case of the plug flow reactor model.

2. The sensitivity matrix including sensitivity of concentrations of species to rate parameters of reactions at specified values of the argument. These data are generated only in the kinetic reactor models with sensitivity.

3. The Jacobean matrix. These data are also generated only in the kinetic reactor models with the sensitivity CBRS model at specified values of the argument.

In addition to the results of calculation, each method requires specification of the reduction parameters. These reduction parameters include (1) the method parameter which controls the number of species and reactions to be eliminated, (2) the set of most

important species, which determines what species should be correctly described by the reduced mechanism, and (3) the set of argument values at which the solution is to be analyzed. It should be noted that some algorithms have several method parameters.

In total, 10 mechanism reduction and 2 mechanism analysis methods are implemented within the mechanism reduction module.

The mechanism reduction methods include:

1.   Direct Sensitivity Analysis (DSA) [18].
2.   Principal Component Analysis (PCA) [9,20].
3.   Normalized Rate Sensitivity Coefficients (NRSC) [20].
4.   Overall Normalized Species Sensitivity Coefficients (OSS) [21].
5.   Detailed Reduction Method (DR) [23].
6.   Rate of Production Index Analysis (ROP Index) [12,24].
7.   Directed relation graph (DRG) [25].
8.   Directed relation graph with error propagation(DRGEP) [8].
9.   Path Flux Analysis (PFA) [13].
10.   Computational Singular Perturbation method (CSP) [7,12,15,16,26,27].

The mechanism analysis methods include:

1.   Quasi Steady State Index (QSSI) [28].
2.   Rate of production analysis [24].

All algorithms for the reduction are implemented as individual modules with a unified software interface. Each algorithm returns a vector including computed values of importance index of species. If a method analyzes importance of reactions, the corresponding vector is also returned. Values written to these vectors are compared to the value of the method parameter, which works as a threshold separating important species and reactions from unimportant ones. The important reaction and species determined in this way are marked with ticks in the graphical user interface. Resulting mechanisms of important species and reactions can be saved to the Chemical Workbench project and further used in physical and chemical simulations. The reduction methods implemented in the mechanism reduction module differ in the algorithm of importance evaluation. This approach simplifies the addition of new methods. In the case when the reduction methods are applied in combination, reactions and species marked as important by any algorithm are considered to be important and stay in the mechanism. The operations of union and intersection of resulting sets of important species and reactions generated by different methods can be controlled by the user in the general part of the graphical user interface, as described in Sect. 4.

The procedure for systematic simplification of kinetic mechanisms is fully integrated in the CWB software. The generation of required input data for the mechanism reduction module and the evaluation of the accuracy of reduced mechanisms are carried out in the CWB. Results of physical and chemical simulations performed using CWB are stored in several binary files. The mechanism reduction module reads all the necessary information about the results of simulations from these files. The reduced mechanism obtained is saved to the Chemical Workbench project, replacing the initial mechanism in the considered calculation. Thus, the same simulations can be repeated with the newly obtained reduced mechanism. If the comparison of simulations results
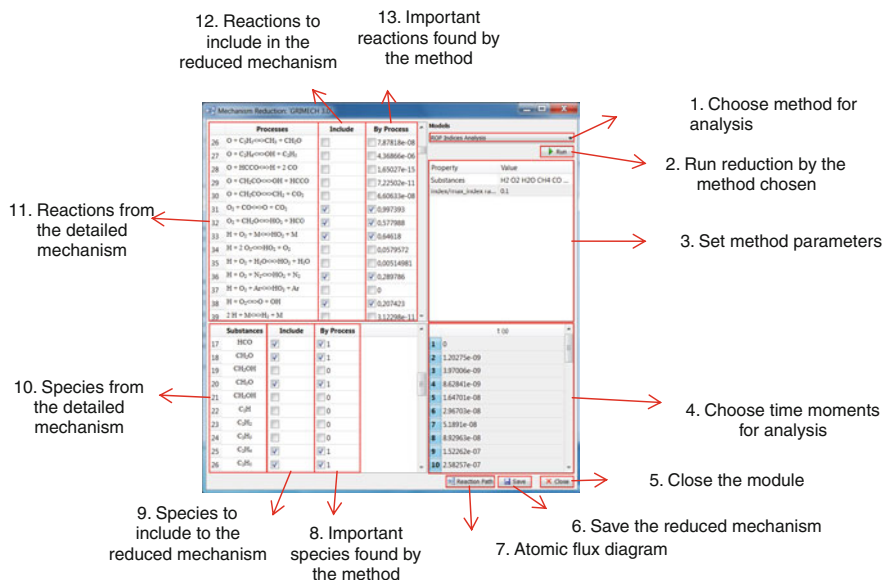
Fig. 1 Graphical user interface of the mechanism reduction module

shows that the reduced mechanism satisfies the error tolerance, the mechanism reduction module can be called again for further reduction. Otherwise, the reduced mechanism can be replaced by the detailed mechanism in the considered CWB calculation and the reduction can be restarted.

2 Graphical user interface

The graphical user interface (GUI) of mechanism reduction module is presented in Fig. 1

The graphical interface is divided in two parts. On the right hand side, there are the controls:

1. Choice of the method.
2. Running the method chosen.
3. Setting parameters of the method and target species.
4. Choice of time moments for analysis.
5. Closing the module without saving results.
6. Saving the simplified mechanism.
7. Calling diagram illustrating fluxes of atoms and reaction pathways. On the left hand side, the results of analysis are illustrated:
8. Important species according to the method considered.
9. Species to be included in the reduced mechanism.
10. List of species in the detailed mechanism.
11. List of reactions in the detailed mechanism.
12. Reactions to be included in the reduced mechanism.

13.　Important reactions according to the method considered.

The initial detailed mechanism which is being analyzed and reduced is represented by list of species (10) and reactions (11). The argument values at which the analysis should be performed can be chosen in panel (4). The vectors of reaction and species importance index values returned by the reduction methods are given in columns (8) and (13), respectively. Species and reactions marked as important by any of the reduction methods applied in combination for at least one argument value are shown in columns (9) and (12), respectively, and are included in the reduced mechanism when the saving button (6) is pressed. The marks in columns (9) and (12) can also be edited by the user, providing the possibility of manual modification of the reduced mechanism. The methods using the sensitivity or Jacobean matrices can reduce mechanisms only at argument values for which the corresponding data were generated.

A reduced mechanism obtained at particular initial conditions is generally applicable only at these initial conditions. In order to obtain a reduced mechanism applicable in a range of initial conditions, several reduced mechanisms for different initial conditions should be united. The Chemical Workbench environment and the mechanism reduction module are able to generate results for several sets of initial conditions and to analyze them simultaneously, thus producing the reduced mechanism applicable in the required range of initial conditions.If results of a series of simulations are transfered to the mechanism reduction module as input data, all these calculations are available for the analysis and are represented in panel (4). An example of working with calculations performed at different initial temperatures is shown in Fig. 2. The reduced mechanism is constructed for each row of panel (4) and then unified. Thus, the mechanism reduction module can be used to obtain reduced mechanisms applicable to as many sets of initial conditions as available in the simulation results supplied.

3 Algorithms of methods of mechanism reduction and mechanism analysis

In this section, we describe the methods implemented within the mechanism reduction module. The description of each of these methods consists of a block diagram illustrating the algorithm, list of the input parameters, and explanation of the diagram. The following notations are used:

t—Time,

$\vec{c}$—Vector of species concentrations,

$\vec{R}$—Vector of rates of species transformations,

$\vec{I}$—Vector of importance index values of species or reactions (depending on the method),

S—Sensitivity matrix of species concentrations to reactions rate constants,

$\vec{w}$—Vector of rates of elementary reactions,

ν—Stoichiometric matrix of the system,

Ω—List of target species,

Threshold—threshold value for the importance index (controlling parameter),

J—Jacobean matrix of system,

$\frac{d\vec{c}(\vec{k},t)}{dt} = \vec{R}(\vec{k}, \vec{c}(\vec{k}, t))$—Set of kinetic equations.

	Temperature (Stream 1	t (s)
140	1200	0.00353039
141	1200	0.00566926
142	1200	0.0094738
143	1200	0.0193351
144	1200	0.110088
145	1200	1
146	1400	0
147	1400	8.5911e-10
148	1400	9.86963e-09
149	1400	1.97308e-08
150	1400	4.68089e-08
151	1400	1.1141e-07

Fig. 2 Analysis of the mechanism in a range of initial conditions

Target species in each method are those species which concentrations should be accurately described by the simplified mechanism. They include products, reagents, and most important intermediates.

3.1 Methods of sensitivity analysis

There are several types of sensitivity matrix: a concentration sensitivity matrix, a rate sensitivity matrix, and a Jacobian matrix. Concentration sensitivity matrix is the sensitivity of species concentrations with respect to reaction rate constants. The components of the concentration sensitivity matrix $\widehat{\mathbf{S}}$ and of the normalized concentration sensitivity matrix $\mathbf{S}$ are given by

$$\widehat{S}_{ij} = \frac{\partial c_i}{\partial k_j},$$

$$S_{ij} = \frac{k_j}{c_i}\widehat{S}_{ij} = \frac{k_j}{c_i}\frac{\partial c_i}{\partial k_j}$$

The value of the sensitivity coefficient of substance i to the rate constant of reaction j corresponds to the variation of the concentration of species i at a small change of the rate constant of reaction j. Therefore, the reaction j should be considered to as important if at least one of the important species has a large sensitivity with respect to this reaction.

Rate sensitivity matrix is the sensitivity of rates of species transformations with respect to rate constants. The components of the rate sensitivity matrix $\widehat{\mathbf{F}}$ and of the normalized rate sensitivity matrix $\mathbf{F}$ are defined as

$$\widehat{F}_{ij} = \frac{\partial R_i}{\partial k_j},$$

$$F_{ij} = \frac{k_j}{R_i}\widehat{F}_{ij} = \frac{k_j}{R_i}\frac{\partial R_i}{\partial k_j}.$$

In this case, the value of the sensitivity coefficient of substance i with respect to rate constant of reaction j corresponds to the variation of the transformation rate of species i at a small change of the rate constant of reaction j. The same as in the case of the concentration sensitivity matrix, the reaction j can be considered as important if at least one of the important species has a large sensitivity to with respect to it.

Jacobian matrix is the sensitivity of rates of species transformations to species concentrations. The components of the Jacobian matrix $\widehat{\mathbf{J}}$ and the normalized Jacobian matrix $\mathbf{J}$ correspond to:

$$\widehat{J}_{ij} = \frac{\partial R_i}{\partial c_j},$$

$$J_{ij} = \frac{c_j}{R_i}\widehat{J}_{ij} = \frac{c_j}{R_i}\frac{\partial R_i}{\partial c_j}.$$

In the case of the Jacobian matrix, the value of the sensitivity coefficient of substance i with respect to substance j shows the variation of the transformation rate of species i at a small change of the concentration of species j. The sensitivity coefficient of species i with respect to itself corresponds to the timescale of its transformation. The species j can be considered as important if at least one of the important species has a large sensitivity with respect to it.

The sensitivity matrices can be differential or integral. The components of differential sensitivity matrices are determined by the derivatives at a single moment of time. The components of integral sensitivity matrices are averaged over a period of time $\widehat{S}_{ij}^{int} = \frac{1}{T}\int_T \frac{\partial c_i}{\partial k_j}dt$. All the methods of sensitivity analysis described in this section are applicable both in the cases of integral and differential sensitivity. In the Chemical Workbench computational package, the differential and integral sensitivities are considered in the reactor models with Sensitivity and with Deviation, respectively.

3.1.1 Direct sensitivity analysis (DSA)

In the DSA method, the maximum value of the concentration sensitivity to each reaction is calculated and compared with the threshold value [18]. The method parameters are:

– Threshold (controlling parameter). The reactions with all sensitivity coefficients smaller than the threshold value are excluded from the mechanism.

The input of the method consists of the sensitivity matrix $S_{ij} = \frac{k_j}{c_i}\frac{\partial c_i}{\partial k_j} = \frac{\partial \ln c_i}{\partial \ln k_j}$ computed in the CWB calculation and the threshold value determining which reactions should be excluded (Fig. 3). The importance index I_i of the reaction i is equal to
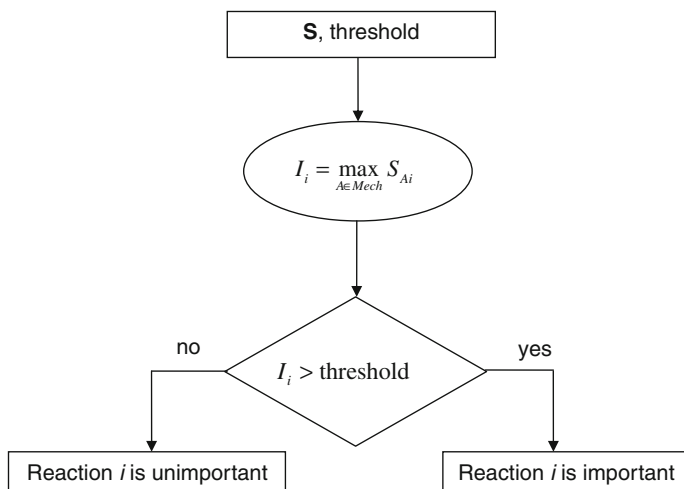
Fig. 3 Scheme of the method of direct Sensitivity Analysis (*DSA*). **S** is the sensitivity matrix, the threshold is the value defining important reactions, i denotes the reaction under analysis, A corresponds to species from the mechanism, and I_i is the importance index of reaction i

the maximum of absolute values of sensitivity coefficients S_{Ai} among all the species. The index I_i is not normalized and can take any value greater than zero. Once found, importance index values of all reactions are compared with the threshold value. By default, the threshold equals to 1 and can be varied in the graphical user interface.

If the index I_i is greater than the threshold, the reaction i is considered to be important. Otherwise, the reaction is considered as unimportant. The skeletal mechanism is derived from the detailed mechanism by keeping only important reactions.

3.1.2 Principal component analysis (PCA)

The PCA method is based on the calculation of eigenvectors and eigenvalues of the sensitivity matrix [9,20]. The groups of reactions having large weights in different eigenvectors are called principal components of the sensitivity matrix. The reactions that have significant weights in the principal components with large eigenvalues are included in the simplified mechanism.

The method parameters are:

– Eigenvalue threshold (the first controlling parameter). The reactions included only in the principal components with eigenvalues below this threshold are excluded.
– Eigenvector threshold (the second controlling parameter). This parameter determines the minimum weight of reactions in eigenvectors above which the reactions are included in the principal components.
– Target group of species, i.e. the set of important species that should be described accurately by the reduced mechanism.

The input of the PCA method consists of the concentration sensitivity matrix, the two threshold values and the list of important species. The reactions are grouped by their
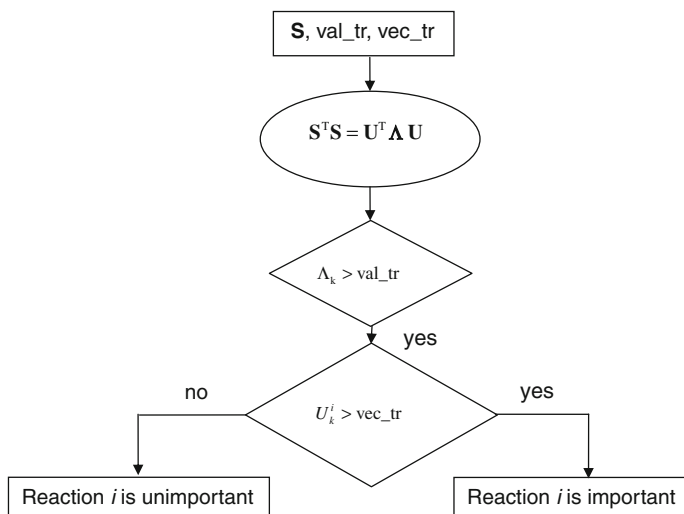
Fig. 4 Scheme of the method of principal component analysis (*PCA*). **S** is the sensitivity matrix, val_tr is the eigenvalue threshold, vec_tr is the eigenvector threshold, Λ is a diagonal matrix with the elements corresponding to the eigenvalues of the sensitivity matrix, **U** is the matrix with the columns corresponding to the eigenvectors of the sensitivity matrix

relevance to the description of a specified set of species. This is done by the eigenvalue and eigenvector decomposition of the sensitivity matrix. Only sensitivity coefficients of the important species are analyzed.

The PCA algorithm scheme is presented in Fig. 4. In order to find eigenvalues and eigenvectors of the matrix **S** it is transformed to the symmetric square matrix $\mathbf{S^T S} = \mathbf{U^T \Lambda U}$. The number of columns and rows in the matrix $\mathbf{S^T S}$ equals to the number of reactions in detailed mechanism. The columns of the matrix **U** represent eigenvectors. The groups of reactions that contribute the most to these eigenvectors are determined and referred to as principal components. The matrix $\mathbf{\Lambda}$ is diagonal, with the elements equal to eigenvalues of the sensitivity matrix **S**. The largest eigenvalues correspond to the principal components which are the most relevant to the description of selected important species.

Each principal component has as many elements as there are reactions in the detailed mechanism with a nonzero weight in the corresponding eigenvector. The weights can take values from 0 to 1. In order to find the most important reactions in each principal component the weights are compared with the eigenvector threshold. The default value of the eigenvector threshold is 0.2. A reaction is excluded from the principal component if its weight in this component is lower than this threshold. The reaction is considered as included in the principal component if its weight is greater than the eigenvector threshold. Each reaction can be included in several principal components. Each component is characterized by its eigenvalue. Only components with eigenvalues greater than the eigenvalue threshold are considered important for the description of the selected species. The default value of the eigenvalue threshold is 1. Only reactions included in the important principal components are kept in the reduced mechanism.
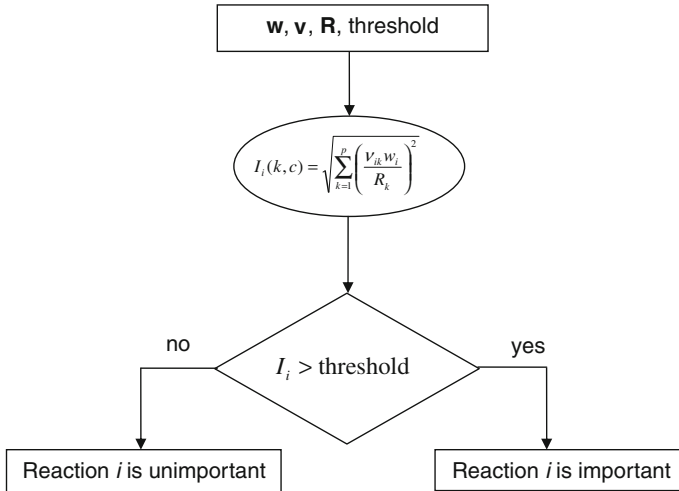
Fig. 5 Scheme of the method of normalized reaction sensitivity coefficients (*NRSC*). The vector $\vec{\mathbf{w}}$ corresponds to the reactions rates, the vector $\boldsymbol{v}$ corresponds to the stoichiometric coefficients, the vector $\vec{\mathbf{R}}$ corresponds to the rates of total changes in the species concentrations, the threshold is used to determine the important reactions

The PCA algorithm is more complex than the DSA algorithm. However, the PCA method generally produces smaller mechanisms with the same accuracy.

3.1.3 Normalized rate sensitivity coefficients (NRSC)

In the NRSC method, the most important reactions are determined by the analysis of coefficients of the rate sensitivity matrix [20]

$$F_{ij} = \frac{k_j}{R_i} \frac{\partial R_i}{\partial k_j} = \frac{\partial \ln R_i}{\partial \ln k_j} \quad .$$

The method parameters are:

– Target group of species, i.e the set of important species that should be described accurately by the reduced mechanism.
– Threshold (controlling parameter). The reactions with all sensitivity coefficients smaller than the threshold value are excluded from the mechanism.

Unlike the two previous methods (DSA and PCA), in the NRSC method, the different sensitivity matrix is considered and the use of sophisticated reactor models in CWB simulations is not required. The matrix $\mathbf{F}$ can be generated from results of any CWB calculation.

The NRSC algorithm is presented in Fig. 5. The input of this method consists of the data on reaction rates $\vec{\mathbf{w}}$, stoichiometric coefficients of species in reactions $\boldsymbol{v}$, rates of species transformation $\vec{\mathbf{R}}(R_i = \sum_j v_{ij} w_j)$, and the threshold value. The importance index of reaction j is calculated as

$$I_j(k, c) = \sqrt{\sum_{i=1}^{p} \left(\frac{\partial \ln R_i(k, c)}{\partial \ln k_j} \right)^2} = \sqrt{\sum_{i=1}^{p} \left(\frac{v_{ij} w_j}{R_i} \right)^2}.$$

Thus, the importance index of each reaction equals to the root-mean-square of ratios of sensitivity coefficients of all important species to the reaction rates. The index is not normalized and takes any non-negative value. The importance index of each reaction is compared with the threshold value. The reduced mechanism is composed of those reactions which importance index exceeds the threshold.

3.1.4 Overall normalized species sensitivity coefficients (ONSS)

In the ONSS method, the sensitivity matrix of transformation rate of important species to concentrations of all other species is analyzed [21,22]

$$J_{ij} = \frac{\partial R_i}{\partial c_j}.$$

The method parameters are:

- Target group of species, i.e the set of species that should be described accurately by the reduced mechanism. List of important species initially consists only of these species..
- Threshold (controlling parameter). The species for which the sensitivity coefficients are all smaller than the threshold value are excluded from the mechanism.

The ONSS algorithm is presented in Fig. 6. The input consists of the rates of species transformations $\vec{R}$, concentrations of all species $\vec{c}$, the list of important species Ω, and the threshold value of the importance index.

The importance index values of the species not present in Ω are found as

$$I_j = \sum_{i \in \Omega} \frac{c_j}{R_i(k, c)} \frac{\partial R_i(k, c)}{\partial c_j} = \sum_{i \in \Omega} \frac{\partial \ln R_i(k, c)}{\partial \ln c_j} = \sum_{i \in \Omega} \frac{c_j}{R_i(k, c)} J_{ij}$$

The index is not normalized and can take any nonnegative values The importance index values of initial target species are not calculated and are taken equal to -1. By default, the threshold equals 1. If the importance index of a species j exceeds the threshold value, the species j is added to the list of important species Ω. As any species is added to the list Ω, a new iteration of the importance analysis is required. The calculation of the importance index is repeated until no additional species need to be added to the list Ω or all of species are already included in this list. Finally, the reduced mechanism is composed of species added to the list Ω and the reactions involving only species from the list Ω.
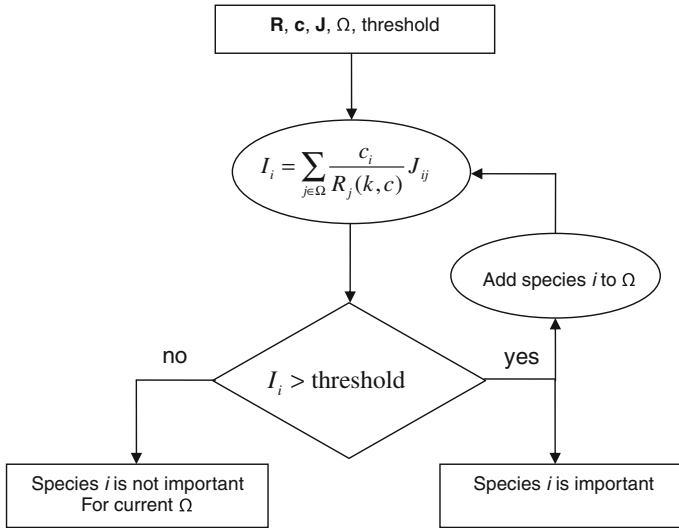
Fig. 6 Scheme of the method of overall normalized species sensitivity coefficients (*ONSS*). The vector $\vec{c}$ corresponds to the species concentrations, the vector $\vec{R}$ corresponds to the rates of total changes in the species concentrations, **J** is the Jacobian matrix, the threshold value is used to determine the important species

3.2 Methods of rate of production analysis

In this section, methods based on the analysis of rates of species production are described. These methods require only the knowledge of solution of the set of kinetic equations and, hence, can be applied to results of simulations in any reactor model.

3.2.1 Detailed reduction method (DR)

The DR method is the simplest approach for measuring importance of reactions by their rates [23]. The reactions are sorted by the rate of species production and consumption or the heat dissipation rate. The reactions with the rates below the threshold are excluded.

The method parameters are:

– Threshold type, i.e. the type of rate to be analyzed (rate value, heat generation rate, relative rate compared to a specific reaction).
– Threshold (controlling parameter). The reactions with the rates below the threshold are excluded from the mechanism.
– Threshold process. The reactions slower than the threshold process are excluded from the mechanism.

The DR algorithm is shown in Fig. 7. The input consists of reactions rates w and the threshold value. When the reactions rates are analyzed, the default threshold value is 10^{21} $\frac{1}{cm^3 \times s}$. If the heat generation is considered, then the threshold process must be specified and all reactions producing less heat than this threshold process are excluded
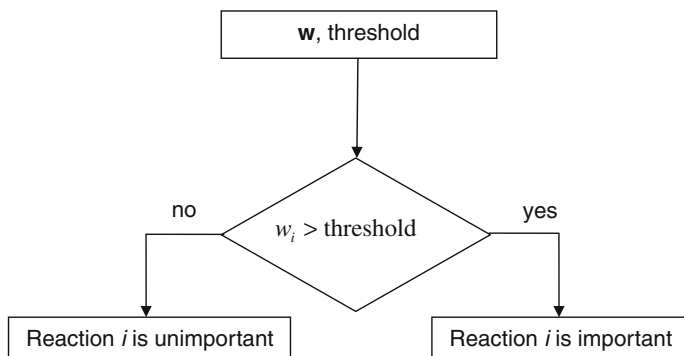
Fig. 7 Scheme of the detailed reduction (DR) method. The vector $\vec{\mathbf{w}}$ corresponds to the reactions rates, the threshold value is used to determine the important reactions

from the mechanism. If the relative rates compared to a specific reaction are analyzed, then the threshold process should be specified as well and all reactions slower than this process are excluded from the mechanism.

3.2.2 Rate of production index analysis (ROP Index)

The ROP index method is based on the iterative analysis of species production and consumption rates and finding the reactions that contribute the most to the transformation of target species [12,24].

The method parameters include:

– Target group of species, i.e the set of important species that should be described accurately by the reduced mechanism.
– Threshold (controlling parameter). The reactions with the importance index values below the threshold are excluded from the mechanism.

The ROP index algorithm is shown in Fig. 8. The input consists of the reactions rates $\vec{\mathbf{w}}$, the stoichiometric coefficients $\boldsymbol{v}$, the list of target species Ω, and the threshold value. The importance index of the reaction j for transformation of the important species i is calculated according to the formula

$$I_{ij} = \frac{v_{ij}\left(|\vec{w}_j| + |\overleftarrow{w}_j|\right)}{\sum_k v_{ik}\left(|\vec{w}_k| + |\overleftarrow{w}_k|\right)},$$

where $\vec{w}_j$ is the rate of the reaction j, $\overleftarrow{w}_j$ is the rate of the reaction reverse to the reaction j. The summation in the denominator is performed over all reactions involving the species i.

The importance index is normalized and can take values from 0 to 1. The default threshold value is 0.1. The number of importance index values calculated for any reaction equals to the number of items in the list of target species. Among these
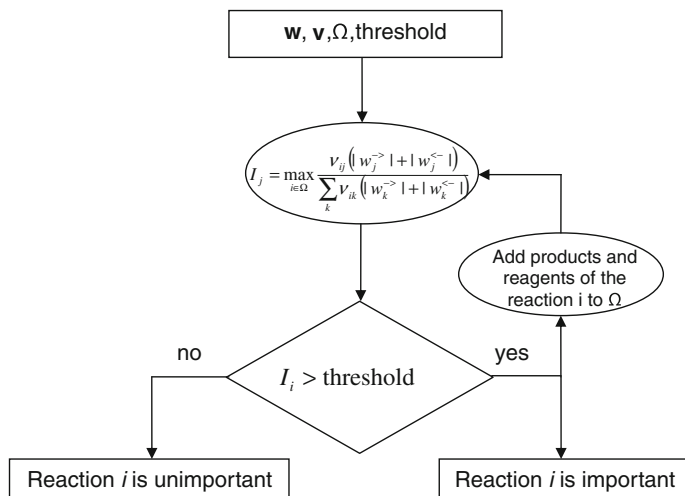
Fig. 8 Scheme of the method of rate of production (*ROP*) index. The vector $\vec{\mathbf{w}}$ includes the reactions rates, the vector $\mathbf{v}$ corresponds to the stoichiometric coefficients, Ω is the set of target species, the threshold is used to determine important reactions

index values, the greatest corresponds to the overall importance of the reaction for the mechanism. If the overall importance of the reaction is greater than the threshold, the reaction is kept in the mechanism, and all of its reagents and products are added to the list Ω of important species. As any species is added to Ω, a new iteration of the rate of production analysis is performed. The values of importance index are recalculated for all the reactions that are considered as unimportant. If some of these reactions turn out to be important for the newly added species, they are also added to the reduced mechanism, as well as their reagents and products. The rate of production procedure is repeated until no new species need to be added to the list Ω or all the species in the system are already included in this list. In the end, all the reactions considered to be important at some stage of the analysis and the species included in the list Ω of target species form the skeletal mechanism.

3.2.3 Directed relation graph (DRG)

The DRG method is a modification of the previous approach. In this method, the importance of all the non-target species for description of the target species is determined by the analysis of the rates of transformations between them [25].

The method parameters are:

– Target group of species, i.e the set of important species that should be described accurately by the reduced mechanism.
– Threshold (controlling parameter). The species with the importance index values below the threshold are excluded from the mechanism.

The DRG algorithm is illustrated in Fig. 9. The input of the method consists of the reactions rates $\vec{\mathbf{w}}$, the stoichiometric coefficients $\mathbf{v}$, the list Ω of target species, and the
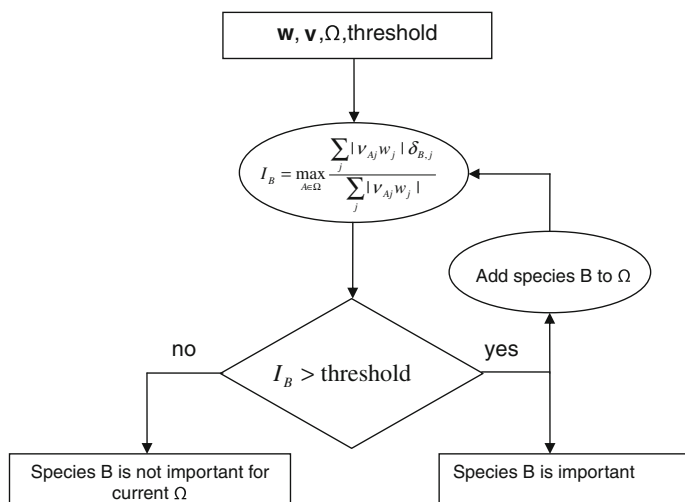
Fig. 9 Scheme of the directed relation graph (*DRG*) method. The vector $\vec{\mathbf{w}}$ corresponds to the reactions rates, the vector $\boldsymbol{v}$ corresponds to the stoichiometric coefficients, Ω is the set of target species, the threshold is used to determine which species are important

threshold value. The importance index of the non-target species B with respect to the target species A is evaluated according to the formula

$$
I_{AB} = \frac{\sum_j |v_{Aj} w_j| \delta_{B,j}}{\sum_j |v_{Aj} w_j|}
$$

where v_{Aj} is the stoichiometric coefficient of the substance A in the reaction j, w_j is the rate of the reaction j (the difference between the rates of the forward and reverse reactions), $\delta_{B,j}$ is the coefficient that is equal to unity if the reaction j involves the species B and to zero otherwise. The summation in the denominator is performed over all reactions involving the target species A. The index is normalized and can take the values in range from 0 to 1. The default threshold value is 0.1.

For each non-target species B, the number of evaluated importance index values equals the number of target species in the list Ω. The maximum of these values corresponds to the overall importance of the species B for the mechanism. If the overall importance is greater than the threshold, then species B is considered important and added to the list Ω. As any species is added to the list Ω, a new iteration of the importance analysis is required. The calculation of the importance index for each non-target species is repeated until no additional species need to be added to the list Ω or all of species are already included in this list. Finally, the reduced mechanism is composed of species added to the list Ω and the reactions involving only species from the list Ω. The DRG method, as opposed to the ROP index method, operates with species rather than reactions and therefore can directly exclude species from the mechanism.

3.2.4 Directed relation graph with error propagation (DRGEP)

The DRGEP method is an extension of the directed relation graph method. In order to reduce the number of species in the final simplified mechanism in the DRGEP method, indirect relations between species are taken into account [8].

The method parameters are:

– Target group of species, i.e the set of important species that should be described accurately by the reduced mechanism.
– Threshold (controlling parameter). The species with the importance index values below the threshold are excluded from the mechanism.

The difference between the DRG and DRGEP methods can be explained by example of the mechanism presented in Fig. 10. Let A be one of the target species and let the species importance threshold be 0.3. According to the DRG method,

$$\tilde{I}_{AB} = \frac{w_{AB}}{w_{AB} + w_{AC}} = 0.2 < 0.3,$$
$$\tilde{I}_{AC} = \frac{w_{AC}}{w_{AB} + w_{AC}} = 0.8 > 0.3.$$

Hence, the species C is important for the species A and the species B is not. Therefore, the species C should be added to the list of target species. The values of importance index of the remaining non-target species (B and D) for the species C are given by

$$\tilde{I}_{CB} = \frac{w_{CB}}{w_{CB} + w_{CD}} = 0.33 > 0.3$$
$$\tilde{I}_{CD} = \frac{w_{CB}}{w_{CB} + w_{CD}} = 0.67 > 0.3$$

Thus, all the species should be added to the reduced mechanism and the mechanism cannot be reduced. The DRG method does not take into account that the species B and D are not as important for the initial target species A as they are for the species C since they influence the species A indirectly through C. The DRGEP method differs from the DRG in the indirect influence index. The values of indirect influence index of the species B and D on the species A through the species C are calculated as follows

$$I_{AB} = \tilde{I}_{AC} \times \tilde{I}_{CB} = 0.8 \times 0.33 = 0.26 < 0.3,$$
$$I_{AD} = \tilde{I}_{AC} \times \tilde{I}_{CD} = 0.8 \times 0.67 = 0.54 > 0.3.$$

Since the species D can influence the species A only indirectly, its importance index with respect to A is 0.54. This is greater than the threshold value and the species D is included in the reduced mechanism. The influence of the species B on the species A is obtained as the maximum between the values of direct and indirect influence indices. Therefore, the overall importance of the species B is found to be 0.26. This is less than the threshold and, thus, the species B is excluded from the mechanism.

The DRGEP algorithm is shown in Fig. 11. The input consists of the reactions rates w, the stoichiometric coefficients ν, the list of target species Ω, and threshold value.
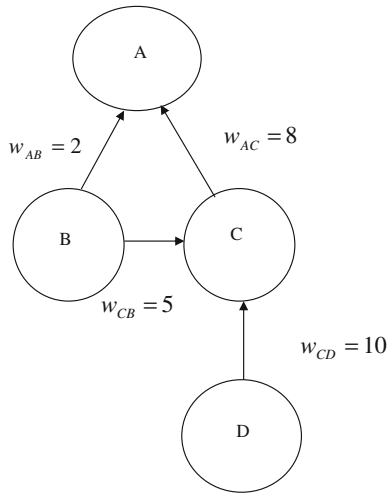
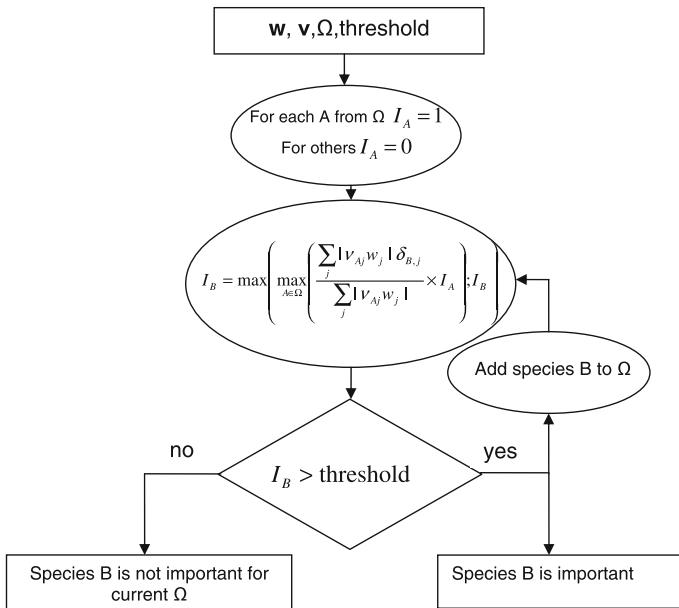**Fig. 10** Example of a chain of species transformations

Fig. 11 Scheme of the method of directed relation graph with error propagation (*DRGEP*). The vector $\vec{\mathbf{w}}$ corresponds to the reactions rates, the vector $\boldsymbol{v}$ corresponds to the stoichiometric coefficients, Ω is the set of target species, the threshold is used to determine the important species

The importance index of the non-target species B for the description of the target species A is calculated as

$$I_{AB} = \frac{\sum_j |v_{Aj} w_j| \delta_{B,j}}{\sum_j |v_{Aj} w_j|} \times I_A$$

where ν_{Aj} is the stoichiometric coefficient of the species B in the reaction j, w_j is the rate of the reaction j (the difference between the rates of the forwards and reverse reactions), $\delta_{B,j}$ is the coefficient that is equal to unity if the reaction j involves the species B and to zero otherwise. The summation in the both cases is performed over the reactions involving the species A. The importance index is normalized and can take values in the range from 0 to 1. The default threshold value is 0.1. For the initial target species, the importance index is not calculated and is assigned to 1.

For each non-target species B, the number of calculated importance indices equals the number of target species in the list Ω. The maximum among these values corresponds to the overall importance of the species B for the mechanism. If the overall importance is greater than the threshold, the species B is considered as important and is added to the list Ω. If any species is added to the list Ω, another iteration of the importance analysis is performed. The calculation of the importance index for each non-target species is repeated until no additional species need to be added to the list Ω or all the species are already in this list. Finally, the reduced mechanism consists of the species added to the list Ω and the reactions involving only species from the list Ω.

It should be noted that the importance index of any non-target species B is multiplied by the importance index of the target species A. If A is among the initially target species, this factor equals 1 and the importance index of the non-target species B is not changed. If the species A is added to Ω during the analysis, the factor is lower than 1. Therefore, the importance index of the species B is reduced, thus taking into account that the species B influences the initial target species indirectly, through the species A. It should also be mentioned that in the case when the importance index of the species B is lower than the threshold, no indirect influence through this species need to be investigated. This is because all importance indices are lower or equal to 1. Thus, any indirect influence index values with respect to the initial target species calculated through the species B are lower or equal to the importance index of the species B, which is lower than the threshold.

3.2.5 Path flux analysis (PFA)

The PFA method is based on the separate calculation of production and consumption of species and the analysis of their mean values. Thus, the channels of production and consumption are both found for each species in the reduced mechanism [13].

The method parameters are:

–   Target group of species, i.e the set of important species that should be described accurately by the reduced mechanism.
–   Threshold (controlling parameter). The species with the importance index values below the threshold are excluded from the mechanism.

The PFA algorithm is shown in Fig. 12. The input consists of the reactions rates $\vec{w}$, the stoichiometric coefficients ν, the list of target species Ω, and the threshold value. The importance index is normalized and can take values from 0 to 1. By default, the threshold equals to 0.1.
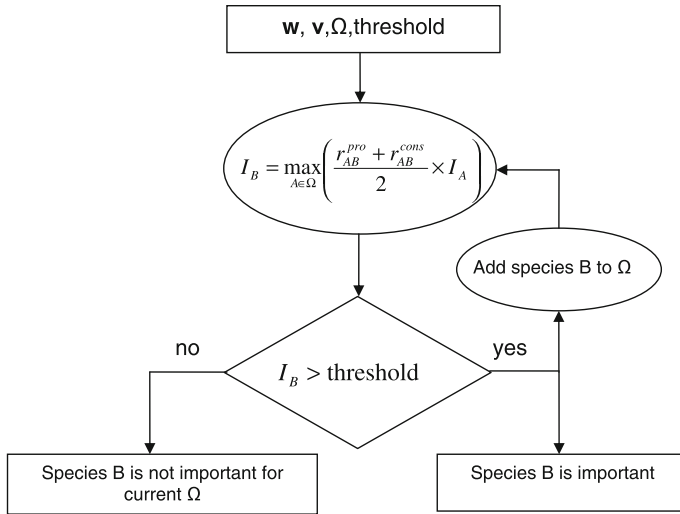
Fig. 12 Scheme of the method of path flux analysis (*PFA*). The vector $\vec{w}$ corresponds to the reactions rates, the vector v corresponds to the stoichiometric coefficients, Ω is the set of target species, the threshold is used to determine the important reactions

The production flux for each target species $A \in \Omega$ equals

$$P_A = \sum_k \max(\nu_{Ak} w_k, 0).$$

The consumption flux of the species A is given by

$$C_A = \sum_k \max(-\nu_{Ak} w_k, 0)$$

The contribution of the non-target species B in the production of the species A is found as

$$r_{AB}^{pro} = \frac{P_{AB}}{\max(P_A, C_A)},$$

where

$$P_{AB} = \sum_k \max(\nu_{Ak} w_k \delta_B^k, 0),$$

$$\delta_B^k = \begin{cases} 1, & \nu_{Bk} \neq 0 \\ 0, & \nu_{Bk} = 0 \end{cases}.$$

The contribution of the non-target species B to the consumption of the species A is evaluated as

$$r_{AB}^{cons} = \frac{C_{AB}}{\max(P_A, C_A)},$$

$$C_{AB} = \sum_k \max(-\nu_{Ak} w_k \delta_B^k, 0).$$

The importance indexof the species B is determined by

$$I_B = \max_{A \in \Omega} \left(\frac{r_{AB}^{pro} + r_{AB}^{cons}}{2} \times I_A \right).$$

The species B is added to the list Ω of target species if the importance index I_B exceeds the threshold. The procedure is repeated for each new set of target species. As no more species can be added to the list Ω, the final set of the important species is found. All the species present in the initial list of target species are assigned importance index values $I_A = 1$. Finally, the reduced mechanism consists of the species added to the list Ω and the reactions involving only the species from the list Ω.

3.3 Methods of time-scale analysis

The analysis of time scales is based on the analysis of the Jacobian matrix. The elements of the Jacobian matrix are in the units of frequency $(\frac{1}{\sec})$ and the diagonal elements correspond to the frequencies of species transformations. The eigenvectors and eigenvalues of the matrix correspond to the linear combinations of species which transformations are coupled (eigenvectors) and corresponding time scales (reciprocal eigenvalues). Therefore, the analysis of the Jacobian matrix allows finding quasi-steady-state species and dividing species into "fast" and "slow" subdomains. Fast time scales correspond to small transformation times and high frequencies. Slow time scales correspond to large transformation times and low frequencies.

The most well-known method of time-scale analysis is the quasi-steady state assumption for species concentrations. According to this method, the species with the fastest time scales of transformation achieve the quasi-steady state faster than the process as a whole and, thus, can be considered as slowly changing. Hence, the differential equation for evolution of the concentration of such species can be replaced by an algebraic constraint on the species concentrations. From this constraint, the concentration of one of the species can be expressed as an algebraic function of the other concentrations and eliminated from the mechanism. The drawback of this method is that the rates of transformations of other species depend on the quasi-steady concentrations of the species in the quasi-static state. In order to eliminate these concentrations, a nonlinear algebraic equations system needs to be solved, which is often more complicated than solving the complete set of differential equations.

3.3.1 Computational singular perturbation method (CSP)

In this method contribution of reactions to "slow" and "fast" sub domains is treated separately and most important for each sub domain form the skeletal mechanism [7,12,15,16,26,27]. In order to separate sub domains the Jacobian matrix is used.

The method parameters are:

– Threshold value. Primary controlling parameter. Reactions corresponding to importance index values below the threshold are excluded from the mechanism.
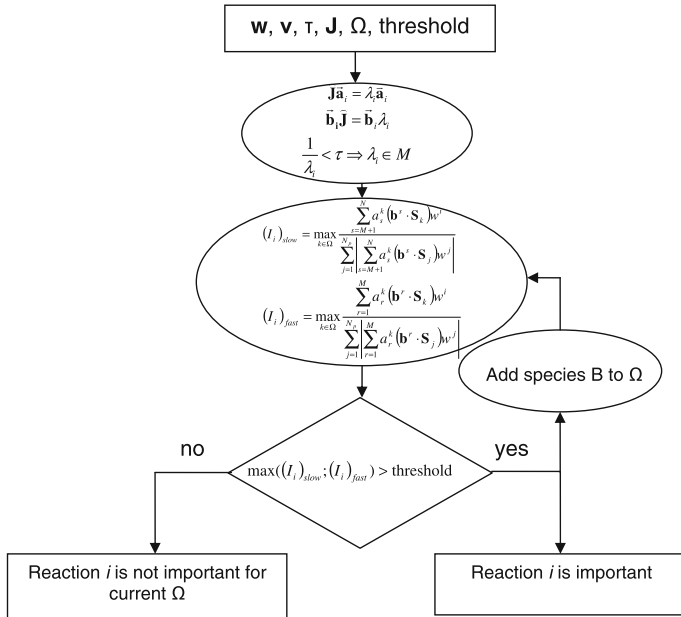
Fig. 13 The vector $\vec{\mathbf{w}}$ corresponds to the reactions rates, the vector $\boldsymbol{v}$ corresponds to the stoichiometric coefficients, Ω is the set of target species, $\mathbf{J}$ corresponds to Jacobian matrix, τ corresponds to critical timescale defining fast and slow processes, the threshold is used to determine the important reactions

– Time scale. Additional controlling parameter. Time scale that separates fast and slow sub domains.

In contrast to the quasi-steady-state analysis, linear combinations of species are investigated for quasi-steady state rather than individual species. Thus, all of the quasi-steady states in the system can be found. Groups of coupled species are found by the eigenvalue and eigenvector decomposition of the Jacobian matrix.

The algorithm of the method is illustrated in Fig. 13. The input consists of the reactions rates $\vec{\mathbf{w}}$, the stoichiometric coefficients $\boldsymbol{v}$, the critical time scale separating "fast" and "slow" slow sub domains τ, the Jacobian matrix $\mathbf{J}$, the list of target species Ω, and the threshold value. The importance index is normalized and can take values in range from 0 to 1. The default threshold value is equal to 0,1. The time scale parameter (τ) is specified by the user, can take any nonnegative value, and has the default value of 10^{-5}.

The Jacobian matrix is not symmetric. Hence, each eigenvalue corresponds to the pair of vectors: the column vector—$\mathbf{J}\vec{\mathbf{a}}_i = \lambda_i \vec{\mathbf{a}}_i$, and the row vector—$\vec{\mathbf{b}}_i \mathbf{J} = \vec{\mathbf{b}}_i \lambda_i$. If $\frac{1}{\lambda_i} < \tau$, where τ is the critical time scale, the pair of vectors corresponds to the fast subsystem, otherwise the pair of vectors corresponds to the slow subsystem. The transition matrix from the species to the independent linear combinations of species is given by the row vectors ($\mathbf{b}$). The inverse transformation is given by the column vectors ($\mathbf{a}$). The importance index of the reaction k influencing the target species i in the slow and the fast sub domains is computed as follows:

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

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

where w^k is the rate of reaction k, $\mathbf{S}_k$ is the stoichiometric vector corresponding to reaction k, $(\mathbf{b}^s \cdot \mathbf{S}_k)$ is the scalar product of two vectors giving the stoichiometric coefficient of the group of species in the reaction k, N is the number of time scales, M is the number of fast timescales, N_p is the number of reactions in mechanism.

The number of the timescales is equal to the number of the species. For each reaction and each important species two values of the importance indices are calculated. Thus, the number of the importance index values calculated for each reaction is twice the number of the target species. The greatest among the index values represents the overall importance of the reaction for the mechanism. If the overall importance is greater than the threshold, the reaction is considered as important. All the reactants and products of the reaction are added to the list of target species Ω.

If any of the species were added to Ω, the new iteration of the importance analysis is required. The values of the importance index are recalculated for all reactions that were considered unimportant. If some of them turn out to be important for the newly added species, they are added to the reduced mechanism, as well as their reagents and products. The iterations of the procedure is repeated until no new species need to be added to the list Ω, all the species in the system are already included in this list. Finally, all the reactions considered to be important at some stage of the reduction procedure and species included to the list Ω of important species form skeletal mechanism.

3.4 Auxiliary methods for mechanism analysis

Methods of mechanism analysis presented in this group are not created for the mechanism reduction but rather for understanding of the most important reactions and species and determining optimal values for the input parameters of other methods.

3.4.1 Species quasi steady state index (QSSI)

In this algorithm calculates best candidates to quasi steady state species are found based on analysis of atomic fluxes [28].

The method parameters are:

– Atom. Type of atoms used for calculation of fluxes.
– Threshold value. Species corresponding to index values greater than the threshold can be considered as quasi steady state species.

The algorithm of the method is shown in Fig. 14. The input consists of the reactions rates $\vec{\mathbf{w}}$, the stoichiometric coefficients ν, the type of atoms A for fluxes calculation, and the threshold value. The index can take values in range from 0 to 1. The default
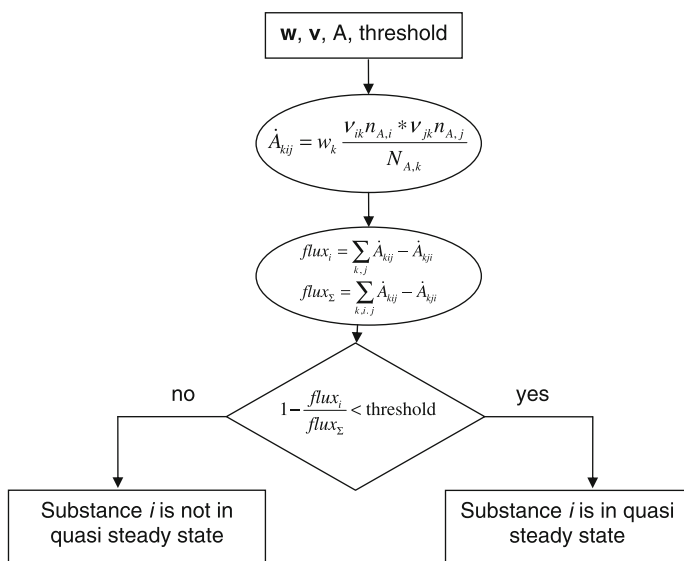
Fig. 14 Scheme of Species Quasi State Index method, The vector $\vec{\mathbf{w}}$ corresponds to the reactions rates, the vector $\mathbf{v}$ corresponds to the stoichiometric coefficients, n is the number of atoms in species, the threshold is used to determine the important reactions, A corresponds to the type of atoms to be used to calculate the fluxes

value of the threshold is 0,1. The default value for A is hydrogen atom. The flux of the atom A in the reaction k from the reagent i to the product j is calculated as follows:

$$\dot{A}_{kij} = w_k \frac{v_{ik} n_{A,i} * v_{jk} n_{A,j}}{N_{A,k}}$$

where w_k is the rate of the reaction k, the number of atoms of the type A in the species i and j are $n_{A,i}$ and $n_{A,j}$ respectively. v_{ik}, v_{jk} are the stoichiometric coefficients of the species i, j in in the reaction k. $N_{A,k}$ is the total number of atoms of the type A in all the species participating to reaction k with stoichiometric coefficients taken into account.

The flux of atom A through each substance is calculated as follows:

$$flux_i = \sum_{k,j} (\dot{A}_{kij} - \dot{A}_{kji})$$

The total flux of atom A through all the species and reactions:

$$flux_\Sigma = \sum_{k,i.j} (\dot{A}_{kij} - \dot{A}_{kji})$$

The value of the quasi steady state index for the species i is $1 - \frac{flux_i}{flux_\Sigma}$. If this value is greater than the threshold, species i can be considered to be in the quasi steady state. This method allows tracing of the fluxes of each type of atom in the mechanism.
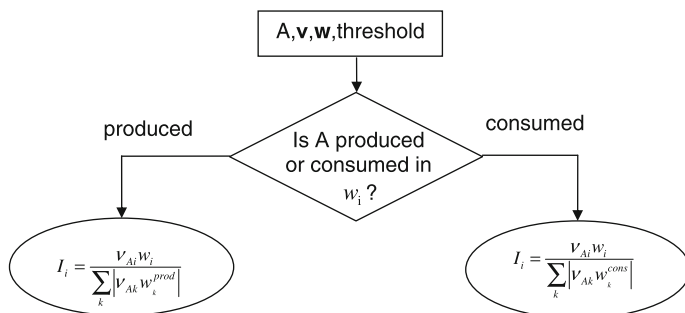
Fig. 15 Scheme of Rate of Production Index method, A corresponds target species, the vector $\vec{w}$ corresponds reactions rates, v is matrix of stoichiometric coefficients

3.4.2 Rate of production

In this method the contributions of the reactions to the production of the selected species are analyzed [24].

The method parameters are:

– Substance. Choice of species for analysis.

The algorithm of the method is shown in Fig. 15. The input consists of the reactions rates $\vec{w}$, the stoichiometric coefficients v, and the target species A. By default A is the first species in the mechanism.

Participation of each reaction to the production and consumption of a chosen target species is analyzed. Rate of each reaction is the difference between forward and reverse rates. If this difference is positive, the species on the left hand side of the chemical reaction equation are considered to be consumed and the species on the right hand side are considered to be produced. It the difference is negative, things are other way around. If the target species is consumed in reaction i, the consumption index is calculated for it:

$$I_i = \frac{v_{Ai} w_i}{\sum_k \left| v_{Ak} w_k^{cons} \right|}$$

The consumption index has negative value since either v_{Ai} or w_i is negative, but not both at the same time. Possible values that the consumption index can take are from -1 to 0.

If the target species is produced in reaction i, the production index is calculated for it:

$$I_i = \frac{v_{Ai} w_i}{\sum_k \left| v_{Ak} w_k^{prod} \right|}$$

The production index is positive since both v_{Ai} and w_i are positive or negative at the same time. Possible values that the production index can take are from 0 to 1.

Table 1 Comparison of reduced mechanisms obtained with different methods combinations

Combination	Species	Reactions
DRG followed by rate of production	90	220
Rate of production followed by DRG	91	206
Number of common species and reactions in mechanisms	82	173

This method is helpful in identifying the main channels of the production and consumption of individual species.

4 Results

4.1 Optimal sequence of methods

An ability to apply the methods in sequence allows creating combinations of methods within the reduction module. In order to improve efficiency of the reduction it is necessary to understand which methods should be combined and in what order. The results of the reduction of the tar gasification mechanism, which is described in more detail in the next section, performed by the combination of methods DRG and Rate Of Production Index applied in different order are presented in Table 1. According to the table, the number of reactions and species in simplified mechanism changes slightly when the techniques are applied in different order, but nevertheless the lists of reactions in these cases are different. As the difference in the number of reactions and species between different combinations is minor, other considerations should be taken into account. Among them are the reduction priorities and computational efficiency.

An optimal sequence of methods for the reduction of the mechanisms was found in our previous work [30]. The combination consists of the DRG, CSP, and DSA applied in sequence. Simplification of the mechanism by the chain of these methods consists of the following steps:

1. The detailed mechanism is simplified by the DRG, and a first preliminary mechanism is obtained. Kinetic simulations results are recalculated with this mechanism.
2. The first preliminary mechanism and the new calculation results are passed to the CSP method. Thus, a second preliminary mechanism is obtained. Kinetic simulations results are recalculated with this mechanism.
3. The second preliminary mechanism is passed to the DSA, and a final skeletal mechanism is obtained.

Since reduction of the number of species is the main objective of the mechanism simplification,, the first method to apply should be the method eliminating species directly. Reduction of the number of reactions and additional species not participating to the remaining reactions is of secondary importance. Hence, the DRG should be applied first as the most effective method of species elimination. After that the most effective method for the reactions elimination should be applied, which is the CSP. The third method is mostly required for eliminating any redundant species without the
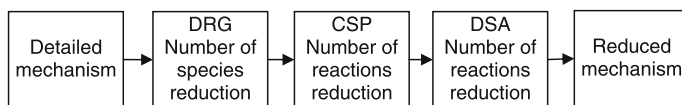
Fig. 16 Sequence of reduction methods

consumption or production channels, and any reduction method can be used for this purpose with the small value of the controlling parameter. The most simple of them is the DSA or DR, but others, like the DRG, may also be used.

On the other hand, there are also considerations of computational efficiency. Methods of sensitivity analysis require the sensitivity matrix of dimensionality $M \times M$, where M—number of reactions, to be generated. Similarly, the timescale analysis requires Jacobian matrix of dimension $N \times N$, where N—number of species, to be computed. Thus, the dimensionality of matrices and amount of the computation to be performed depends on the number of species and reactions in the mechanism by a power law.. Hence, the sensitivity analysis of extremely large mechanisms is time consuming as well as the timescale analysis. The selected order of methods simplifies the use of the CSP and the DSA techniques. It is presented on Fig. 16. The number of species is reduced by the DRG prior to the CSP analysis. The number of reactions is reduced by the CSP prior to the DSA.

4.2 Tar gasification mechanism simplification

The mechanism reduction module and the optimal combination of methods were used for the reduction of the tar gasification mechanism. This mechanism describes the transformation of the volatile compounds released from the coal after a rapid heating into the synthesis gas. The synthesis gas is a fuel consisting primarily of CO and H_2. The tar is reacting with the oxygen and the water at the high temperature ($\sim$1,200 K) and pressure ($\sim$10–30 atm.). The kinetic model of the process assumes that the main component of the tar is an aromatic compound called dimethylnaphtalene. The gasification takes place in the mixture rich with water (50 %). Water is almost not being consumed during the process due to the high concentration. The conversion time is the period of time from the beginning of the process until the products concentrations have achieved the equilibrium. The conversion time was chosen to be the target parameter, which must be correctly described by the reduced mechanism. The detailed mechanism consists of 879 reversible reactions and 177 species. The final skeletal mechanism consists of 278 irreversible reactions and 83 species.

Simulations with the mechanism were performed in the calorimetric bomb reactor model with constant pressure and temperature (CBR-PT). The temperature of the process was varied in range 1,200–3,000 K, the pressure was fixed to 20 atm, the initial mixture in all simulations was the following: 3.68 % CO; 2.94 % CH_4; 57.2 % H_2O; 1.77 % CO_2; 1.52 % C_4H_8; 29.4 % O_2; 1.77 % N_2; 1.7 % dimethylnaphtalene ($CH_3C_{10}H_6CH_3$). Such an initial mixture is emulating the initial mixture of the tar gasification process. Description of the products final concentrations and the conversion time with the accuracy of 10 % was the criterion for the simplification. Compari-
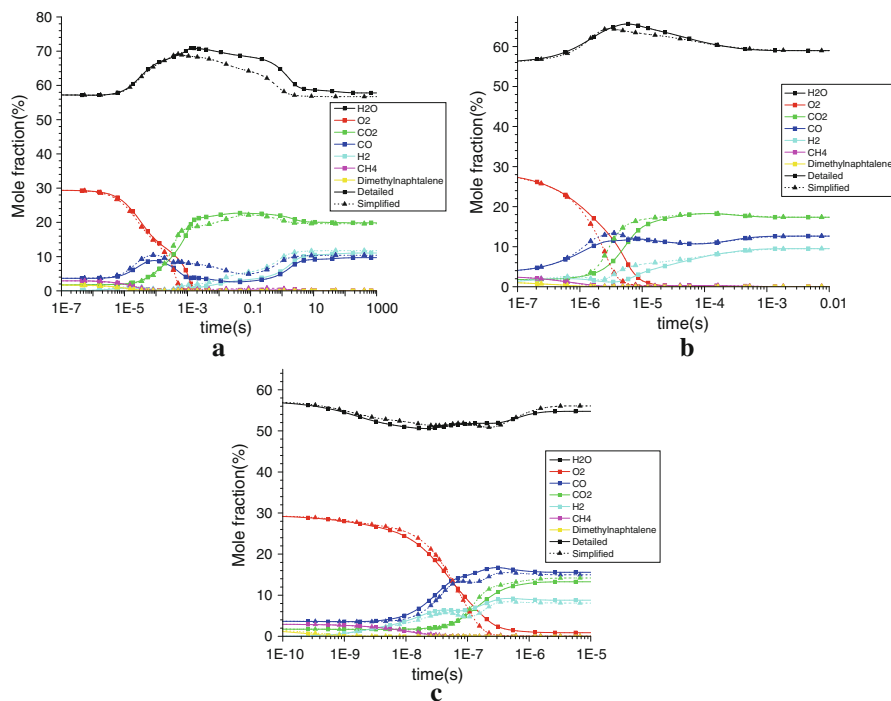
Fig. 17 Concentrations profiles of products and reagents in tar gasification process in isothermal conditions at temperatures **a** 1,500 K, **b** 2,000 K, **c** 3,000 K

son of the concentration profiles of the most important species is presented in Fig. 17. According to the graphs, the conversion time is described within the specified margins of error by the simplified mechanism.

The detailed mechanism of the tar gasification includes both reversible and irreversible elementary reactions. The rates of reversible reactions are usually significantly lower than the rates of irreversible reactions since any reversible reaction can be separated into a pair of irreversible ones. Total rate of a reversible reaction is equal to the balance between rates of these irreversible reactions. The difference between the rates of reversible and irreversible reactions may reach several orders of magnitude making them incommensurable. Therefore all of the reactions should be expressed in a single form. Either a reversed process should be added to each irreversible reaction or the reversible reactions should be divided into the pairs of irreversible reactions. The second way was chosen in this work as the simpler one. The disadvantage of this approach is that if only one irreversible reaction from the pair is excluded, the thermodynamic equilibrium of the individual reversible elementary stage is broken. Thus, errors in the description of the final concentrations of the species may arise. Nevertheless, since the 10 % error in final concentrations was allowed, the reduction was performed in this manner and significant simplification has been achieved.

In Fig. 18 the reduced mechanism accuracy versus number of reactions in the mechanism at the temperature of 1,200 K is presented. The Y axis on the graph corresponds
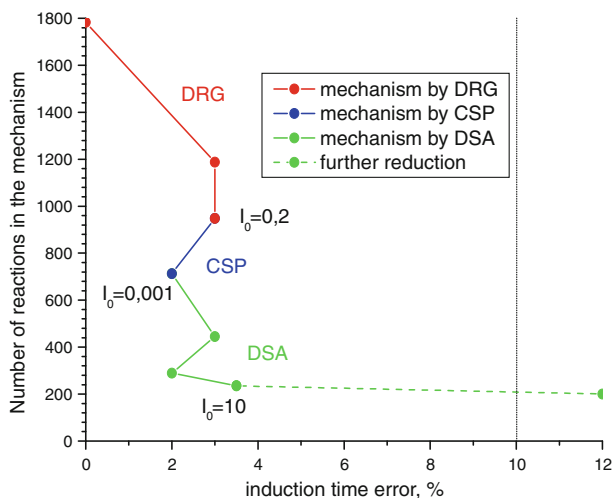
Fig. 18 Dependence of accuracy of reduced mechanism as a function of reduction degree at 1,200 K

to the relative H_2 conversion time error with respect to the detailed mechanism. The X axis corresponds to the number of reactions. Intermediate simplified mechanisms obtained by different methods are represented by the points on the graph. The methods correspond to following colors:—the DRG is red, the CSP is blue, the DSA is green. The values of the threshold parameters corresponding to the smallest mechanisms achieved by each method are presented. The line corresponding to the DSA method shows a characteristic feature of the mechanism reduction: the error increases abruptly as the controlling parameter exceeds the critical value. At this moment a qualitative change in the description of the process due to the exclusion of the important reactions and species from the mechanism occurs. In order to achieve better reduction the error tolerances have to be greater than the small error oscillations that occur during the reduction.

At the temperature of 1,200 K the following reduction parameters values were used:

DRG: The threshold value was set to 0.2. The set of target species included products: CO, H_2, CO_2, H_2O, CH_4, C_4H_8, dimethylnaphtalene ($CH_3C_{10}H_6CH_3$), C_9H_9, $C_6H_5C_2H_2$, O_2, N_2. All the time points of the solution were analyzed. The simplified mechanism, elaborated by the DRG consists of 86 species and 948 reactions.

CSP: The critical time scale was set to 1 s. The threshold value was set to 0.001. The same target species set as in the DRG was used. The simplified mechanism, obtained after the CSP, consists of 86 species and 713 reactions. The number of species was not reduced since the elimination of species was disabled in the implementation of the program and replaced by the output of species transformation timescales.

DSA: The threshold value was set to 10. The simplified mechanism obtained after the DSA consists of 83 species and 235 reactions.

The Jacobian matrix and the concentration sensitivity matrix were analyzed at the following points of time: 10^{-2}, 1, 10, 3×10^4, and 10^5. Finally, the mechanism consisting of 83 species and 235 reactions was obtained.
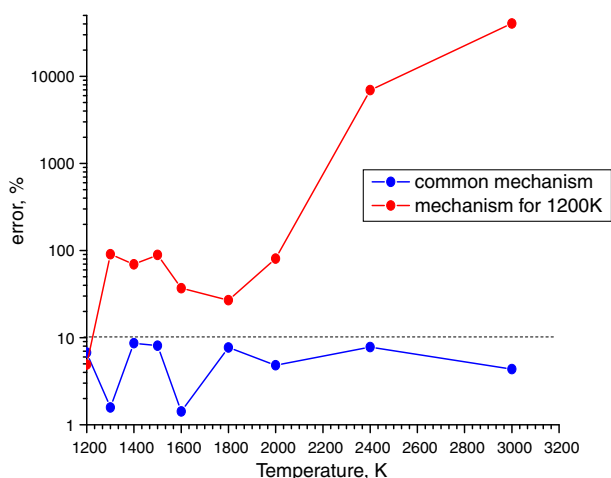
Fig. 19 Errors of reduced mechanisms at different temperatures

In order to obtain the mechanism for the temperatures in range 1,200–3,000 K the high temperature reduced mechanism was obtained in similar manner at 3,000 K. The high temperature reduced mechanism consists of 57 species and 153 reactions. The number of the common species and reactions between the high temperature mechanism and the low temperature mechanism is 43 species and 111 reactions. Several reactions from the high temperature mechanism were added to the low-temperature mechanism to form the general reduced mechanism. Specifically, those reactions involving only the common species between the two mechanisms and absent in the low temperature mechanism were added. The resulting general mechanism consists of 83 species and 278 reactions. The high temperature mechanism and the low temperature mechanism could also be merged however this would lead to a larger general mechanism. Comparison of the low-temperature with the general reduced mechanism is presented in Fig. 19. According to the graphs the process is described correctly by the low-temperature reduced mechanism only at 1,200 K. On the other hand the process is described correctly by the general reduced mechanism within the whole temperature domain.

4.3 Reduction of methane combustion mechanism

The mechanism reduction was used for the reduction of the Konnov methane combustion mechanism [33]. The Konnov methane combustion mechanism was reduced from 127 species and 1206 reactions to 41 species and 173 reactions. The criterion for the reduction was to reproduce the solution of the detailed mechanism at the initial temperature 1,200 K. The maximum error tolerance for each target species transformation timescale and the temperature change timescale was 1 %. The maximum error tolerance for the final concentrations of the target species and the final temperature was 1 %. The process was simulated in the stoichiometric methane–air mixture

$CH_4:O_2:N_2 = 1:2:4$ at $p = 1$ atm in the calorimetric bomb reactor with constant volume and no heat exchange with the external medium (CBR-VQ reactor model). The Jacobian matrix was calculated in Calorimetric Bomb Reactor with Sensitivity (CRS-VQ) reactor model.

At the temperature 1,200 K following reduction parameters values were used:

DRG: The threshold value was chosen to be 0.2. The set of target species was chosen to be: CO_2 H_2O CH_4 O_2 CO H_2 NO N_2O. All the time points of the solution were analyzed. The simplified mechanism, elaborated by the DRG consists of 52 species and 507 reactions.

CSP: The critical time scale was chosen to be 0.001 s. The threshold value was chosen to be 0.0001. The same target species set as in the DRG was used. The simplified mechanism, obtained after the CSP, consists of 52 species and 181 reactions. The number of species was not reduced since the elimination of species was disabled in the implementation of the program and replaced by output of species transformation timescales.

DRG: The threshold value was chosen to be 0.1. The same target species set as in the DRG was used. The simplified mechanism obtained after the second DRG consists of 41 species and 173 reactions.

The Jacobian matrix was analyzed in the CSP at the following points of time: 10^{-7}, 10^{-6}, 10^{-5}, 10^{-4}, 2×10^{-4}, 3×10^{-4}, 7×10^{-4}, 10^{-3}, 3×10^{-3}, 4×10^{-3}, 5×10^{-3}, 6×10^{-3}, 7×10^{-3}, 8×10^{-3}, 9×10^{-3}, 10^{-2}, 1.2×10^{-2}, 2×10^{-2}, 5×10^{-2}, 10^{-1}. Finally, the mechanism consisting of 83 species and 235 reactions was obtained.

The resulting reduced mechanism accurately describes the induction time at the temperatures 1,000–2,000 K and the pressure 1 atm in the stoichiometric methane–air mixture $CH_4:O_2:N_2 = 1:2:4$. The time profiles of the temperature and the target species are also described accurately. It should be noticed that the methane combustion is accurately described in the whole range of initial temperatures of 1,000–2,000 K by the single mechanism obtained at the initial temperature value of 1,200 K in the CBR-VQ reactor model.

The time profiles of the target species concentrations obtained on the different stages of the reduction at the initial temperature 1,200 K are presented on the Fig. 20. Figure 20a gives the comparison of the simulations results obtained with the first preliminary mechanism (DRG1) with the results obtained with the detailed mechanism. In the same manner comparison of the results obtained with the second preliminary mechanism (CSP) and the final reduced mechanism (DRG2) with the results obtained using the detailed mechanism is presented in Fig. 20b, c. According to the graphs final concentrations of the target species are described exactly at each stage. The timescales of the key concentrations change are described well on each stage of the reduction and fit into the 1 % error tolerance compared to the detailed mechanism.

The temperature profiles at different initial temperatures are presented in Fig. 21a, b, c. Comparison of the temperature time profiles corresponding to the mechanisms obtained on each stage of the reduction with the temperature profiles obtained with the detailed mechanism is given. The dotted lines correspond to the detailed mechanism; the reduced mechanism corresponds to the solid lines. According to the graphs,
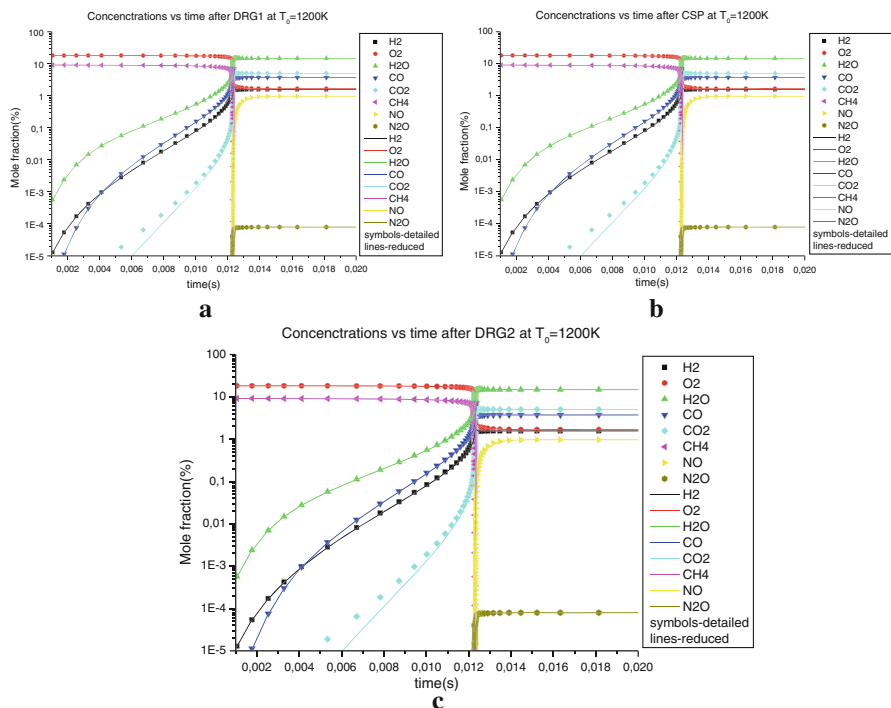
Fig. 20 Concentrations profiles of key species at initial temperature 1,200 K at different stages of the reduction: **a** DRG1, **b** CSP, **c** DRG2

final temperature is described exactly by each reduced mechanism. Despite the minor discrepancies, the induction time according to the temperature time-derivative maximum is described well by the final reduced mechanism and fits into the specified 1 % error.

Figure 22 presents temperature dependence of the induction time calculated at different stages of the reduction. According to this picture, the induction time is described within 1 % error by each reduced mechanism throughout the whole temperature range 1,000–2,000 K. Despite the minor discrepancies at high temperatures, the temperature change timescale is described well by the final reduced mechanism (DRG2) and fits into the specified error margin.

Summary of the results is presented in Table 2 and Table 3 given in supplementary electronic materials (Online resource 1). Table 2 presents the initial set of species in the detailed mechanism and their presence or absence in the reduced mechanism at each stage by "+" or "−" sign correspondingly. Summary of the reaction list is presented in Table 3.

5 Conclusions

The module for kinetic mechanisms reduction was elaborated in this work and integrated into the Chemical Workbench environment for physical and chemical modeling. Systematical approach to the development of simplified kinetic models by means of
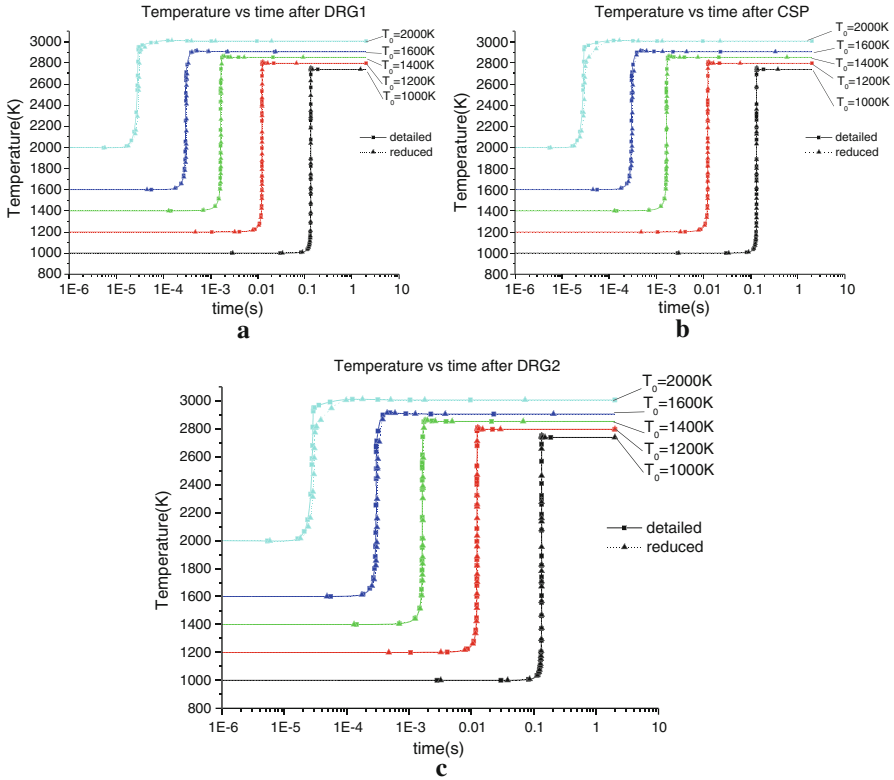
Fig. 21 Temperature profiles at different initial temperatures and different stages of the reduction: **a** DRG1, **b** CSP, **c** DRG2
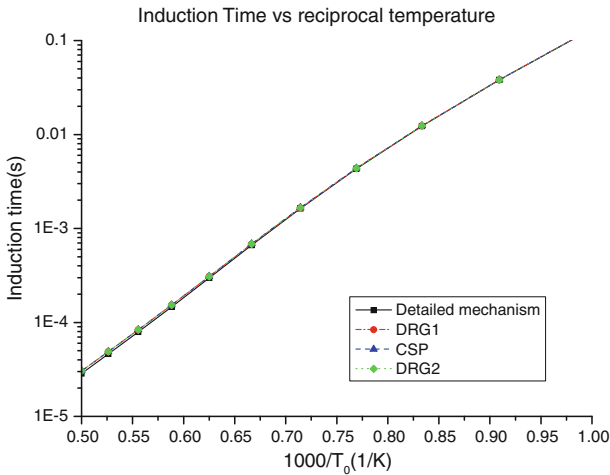

Fig. 22 Induction time versus initial temperature at different stages of the reduction

10 reduction techniques was developed. The module allows simplification of kinetic mechanisms by combinations of methods. The results of kinetic simulations obtained with the detailed mechanism are used for the reduction. Kinetic simulations can be reproduced with the reduced mechanism and compared with the results obtained with the detailed mechanism.

The next step in the automation of the mechanisms reduction will be the automatic choice of methods for the reduction and automatic selection of the controlling parameters values of the methods based on the definition of physical reduction criteria given by the user. The physical reduction criteria could include error tolerances for the induction time, final concentrations of the important species, the final temperature. The module should automatically call the kinetic calculations in CWB and compare the accuracy of the reduced mechanism against the detailed one.

References

1. A.G. Xia, D.V. Michelangeli, Atmos. Chem. Phys. **9**, 4341 (2009)
2. M.I. Strelkova, A.A. Safonov, Combust. Sci. Tech. **180**, 1788 (2008)
3. M.A. Cremer, C.J. Montgomery, D.H. Wang, M.P. Heap, J.-Y. Chen, Proc. Combust. Inst. **28**, 2427 (2000)
4. J.A. Shorter, P.C. Ip, J. Phys. Chem. **103**, 7192 (1999)
5. S. Singh, J.M. Powers, S. Paolucci, J. Chem. Phys. **117**, 1482 (2002)
6. S.B. Pope, Combust. Theory Model. **1**, 41 (1997)
7. M. Valorani, F. Creta, F. Donato, H.N. Najm, D.A. Goussis, Proc. Combust. Inst. **31**, 483 (2007)
8. P. Pepiot-Desjardins, H. Pitsch, Combust. Flame **154**, 67 (2008)
9. S. Vajda, P. Valkó, T. Turányi, Int. J. Chem. Kinet. **17**, 55 (1985)
10. J.-Y. Chen, Transact. Aeronaut. Astronaut. Soc. Rep. China **33**, 59–67 (2001)
11. D.A. Goussis, J. Comput. Phys. **128**, 261 (1996)
12. M. Valorani, F. Creta, Combust. Flame **146**, 29 (2006)
13. W. Sun, Z. Chen, Combust. Flame **157**, 1298 (2010)
14. A. Massias, D. Diamantis, Combust. Flame **117**, 685 (1999)
15. T. Lu, Y. Ju, C.K. Law, Combust. Flame **126**, 1445 (2001)
16. Y. Shi, H.-W. Ge, J.L. Brakora, R.D. Reitz, Energy Fuels **24**, 1646 (2010)
17. T. Turanyi, Comp. Chem. **14**, 253 (1990)
18. M. Deminsky, V. Chorkov, G. Belov, I. Cheshigin, A. Knizhnik, E. Shulakova, M. Shulakov, I. Iskandarova, V. Alexandrov, A. Petrusev, I. Kirillov, M. Strelkova, S. Umanski, B. Potapkin, Comput. Mater. Sci. **28**, 169 (2003)
19. R.P. Dickinson, R.J. Gelinas, J. Comput. Phys. **21**, 123 (1976)
20. T. Turányi, T. Bérces, S. Vajda, Int. J. Chem. Kinet. **21**, 83 (1989)
21. L.E. Whitehouse, A.S. Tomlin, Atmos. Chem. Phys. **4**, 2057 (2004)
22. T. Turanyi, New J. Chem. **14**, 795 (1990)
23. E.E. Brocka, Ph.E. Savage, Chem. Eng. Sci. **53**, 857 (1998)
24. P. Glarborg, J.A. Miller, Combust. Flame **65**, 177 (1986)
25. T. Lu, C.K. Law, Proc. Combust. Inst. **30**, 1333 (2005)
26. A. Kazakov, M. Chaos, J. Phys. Chem. **110**, 7003 (2006)
27. S.H. Lam, D.A. Goussis, Int. J. Chem. Kinet. **26**, 461 (1994)
28. J. Revel, J.C. Boettner, J. Chim. Phys. Phys. Chim. Biol. **91**, 365 (1994)
29. N.J. Brown, G. Li, Int. J. Chem. Kinet. **29**, 393 (1997)
30. A.V. Lebedev, M.V. Okun, Systematic procedure for simplification of kinetic mechanisms of chemical processes (Phys. Chem. Kinet. In Gas Dyn. 10 (2010)), http://www.chemphys.edu.ru/pdf/2010-09-06-001.pdf. Accessed 3 May 2012

31. I.Gy. Zsély, I. Virág, T. Turányi, in *Proceedings of the 4th Mediterranean Combustion Symposium*, ed. by F. Beretta, N. Selçuk, M.S. Mansour. (Lisbon, Portugal, 2005), paper IX. 4
32. A.S. Tomlin, T. Turányi, M.J. Pilling, in *Low temperature combustion and autoignition*, ed. By M.J. Pilling, G. Hancock. (Elsevier, Amsterdam, 1997), pp. 293–437
33. A.A. Konnov, Combust. Flame **156**, 2093 (2009)