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Automated Simulation Error based Reduction of Large Chemical Mechanisms

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Highlights

- Automated simulation error based reduction (ASER) of microkinetic mechanisms is proposed
- ASER is implemented with reaction removal (PCA) and species removal (DRG) techniques
- A combined ASER-DRG followed by ASER-PCA is implemented on several systems
- Extension to homogeneous / heterogeneous mechanism will be demonstrated

1. Introduction

The development of detailed kinetic mechanisms helps improve our understanding of chemically reacting systems. Often, these mechanisms have hundreds of species and reactions. Coupling these large models with transport equations in flow simulations requires significant computational time and in many design and control studies, the model needs to be simulated multiple times. Since only a subset of the full mechanism is sufficient to reproduce the observable features, reduction of detailed models becomes necessary.

The aim of model reduction is to obtain a reduced mechanism that gives identical quantitative response for the important species as the original detailed model. A class of model reduction, called skeletal reduction, focuses on removing redundant reactions or redundant species from the detailed mechanism. A common feature of these methods is that the final mechanism depends on the values of thresholds that govern these reduction methods. These thresholds determine the quantitative response of the reduced model but are not directly related to the observable features (e.g., concentration of important species). Moreover, different threshold values give different reduced mechanisms. The maximum error in the solutions from the full and reduced model indicates the performance of the reduced mechanism and hence, of the threshold.

Thus, simulation error, defined as the normalized difference between the full and reduced mechanisms, becomes an important parameter during reduction. In this work, we design automated algorithm (ASER) that directly uses the simulation error as a criterion for choosing the threshold and determining the reduced mechanism. Both species reduction and reaction reduction based methods are incorporated within the proposed approach. The two reduction methods are implemented independently on gas-phase hydrogen oxidation mechanism involving 47 reactions and 9 species. A combined reduction of DRG followed by PCA using ASER algorithm is also performed. Application to catalytic reaction between NOx and CO (in automotive catalytic convertor) and on chemical vapor deposition will also be presented in the final paper.

2. Methods

Principal component analysis (PCA) using concentration sensitivity [2]: This method relies on developing a concentration sensitivity matrix for all the operating conditions of interest. An eigenvalue decomposition is performed on the sensitivity matrix. Threshold values of eigenvalues and eigenvector components are used to delineate important and redundant reactions of the system.

Directed Relation Graph (DRG) [3]: DRG identifies coupling between various species in a reaction mechanism. The importance index of a species is calculated by the contribution of the species to the production rate of an important species. The species with importance index greater than a threshold are retained, whereas the others are removed as redundant species.

In both these approaches, the final mechanism depends on the choice of threshold values. However, threshold values are not a good predictor of the error in the quantitative response from the full detailed model and the reduced model. Further, implementing of other approximations (such as partial equilibrium or most

abundant surface intermediate) commonly used in reduction of heterogeneous mechanisms require significant human inputs. Nagy and Turányi [5] introduced the concept of simulation error in model reduction. In this work, we adapt the concept of using simulation error and generalize it to species and reaction reduction for homogeneous as well as surface reaction mechanisms.

Automated Simulation Error based Reduction (ASER): Instead of choosing the threshold values (ε), this approach is based on the maximum simulation error (δ_{max}) induced in the reduced mechanism due to the removal of the reactions or species. The important observable species and δ_{max} are identified by the user. Starting with large ε, the reduction procedure is carried out iteratively. The reduced model is obtained at each step, simulations are performed and the simulation errors are calculated. If the maximum of these errors is greater than the user-specified δ_{max}, the threshold is reduced and the process is repeated. The iteration continues until the simulation error falls below the maximum allowable error.

ASER-DRG followed by ASER-PCA: A combined procedure was performed in order to study increase in efficiency of the combined reduction compared to the individual techniques.

3. Results and Discussions

The gas-phase hydrogen oxidation detailed mechanism consists of 47 reactions and 9 species (H_2, O_2, H_2O, H_2O_2, HO_2, H, O, O_3 and OH)[4]. The important species are chosen to be H_2, O_2 and H_2O and δ_{max} as 1%. A stoichiometric reaction mixture was studied with a residence time of 8s in a CSTR at 1500 K. Reduction of the detailed mechanism was performed using ASER-DRG, ASER-PCA and ASER-DRG + ASER-PCA.

Table 1. Performance of the various reduction methods using ASER for 1% maximum error in important species.

	ASER-DRG	**ASER-PCA**	**ASER-DRG + ASER-PCA**
ε	$\varepsilon_{DRG} = 0.9$	$\varepsilon_{\lambda} = 2.03 \times 10^{-3}$	$\varepsilon_{DRG} = 0.9, \varepsilon_{\lambda} = 1.88 \times 10^{-3}$
# species	6	9	6
# reactions	25	22	17
δ_{max}	0.61 %	0.65 %	0.3541 %

The results are summarized in Table 1. Starting with nine species, ASER-DRG identified three species (HO_2, H_2O_2 and O_3) as redundant. In ASER-PCA, 25 reactions were identified to be redundant. ASER-DRG followed by ASER-PCA gave the smallest mechanism of 17 reactions and 6 species and interestingly, smallest error. The results on applying this approach to homogeneous / heterogeneous mechanism and effect of different reactor models such as batch and CSTR will also be presented in the final paper.

4. Conclusion

ASER based algorithm was applied to PCA, DRG and DRG + PCA techniques to identify the thresholds governing the reduction based on simulation error. Reduced mechanisms giving simulation errors less than one percent were obtained for H_2-O_2 mechanism. These results show that simulation error can be used as a criterion for choosing thresholds during reduction and the entire algorithm can be automated. It was also seen that ASER-DRG + ASER PCA gave the smallest mechanism and error compared to the individual methods.

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Keywords
Mechanism reduction; Principal Component Analysis; Directed Relation Graph; Simulation error