Chemistry Guided Reduction of an Multicomponent Reaction Mechanism

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I. Introduction

The development in computational fluid dynamics and turbulence chemistry interaction modeling in recent years allows for the usage of detailed chemical information for the analyses and optimization of combustion devices. The latest development shows a trend in engineering to replace single component with multi-component reference fuels. This causes reaction mechanisms of increasing sizes, and thereby an increasing demand in mechanism reduction or tabulation techniques.

Mechanism reduction can be performed through lumping, species removal, and quasi steady state or partial equilibrium assumptions. Species removal is frequently performed through directed relation graphs. In [1] we introduced a directed relation graph which used fuel molecules, oxidizer molecules, and sensitive species as seed. Relation graphs were calculated for each atomic flux in the reduction-oxidation system. A reaction sensitivity analysis was performed and the relation graph was initialized for each species by the weighted sensitivity coefficients of all reactions in which the species appeared as reactant. The sensitivity analysis thereby allowed setting targets of the reduced reaction mechanism. Multistep error propagation was calculated from an iterative procedure, which resulted in species weights, which sorted the species according their necessity to be part of the targeted reduced reaction mechanism. We introduced this method as necessity analysis. In [5] we applied the necessity analysis to develop skeleton mechanisms for n-heptane for the full temperature regime and for the high temperature regime only.

Directed relation graph methods cannot reduce mechanisms efficiently which consist of a high number of parallel pathways, with almost equal fluxes. Unfortunately this feature is found in all oxidation mechanisms for larger hydrocarbons. Such mechanisms can be efficiently simplified through chemical lumping, which we applied in [2] as a prestage of the necessity analysis applied in [5]. We introduced a simple rule for the lumping procedure: species of equal size, with the same distance between the same functional groups found at the same carbon classes (primary, secondary, or tertiary carbon) can be lumped. Concentrations of these species are assumed to be equal. This rule allowed to apply chemical lumping during the automated generation of reaction mechanisms [3], [4].

In [1] we assumed that it is necessary to develop reduced reaction mechanisms over the full range of initial conditions, and to define the final set of necessary species by all species with necessity in at least one point of the parameter range. In [5] we identified critical chemical conditions, which are representative for the full parameter range. Since then we apply the method for the critical conditions only, and verify the mechanism thereafter for the full parameter range. Chemistry Guided Reduction (CGR) reduces the development time needed to find an optimum reduced reaction mechanism.

Each reaction in a reaction mechanism has a sensitivity on the performance of the total reaction mechanism. It is not possible to just add submechanisms for different fuel molecules without side effects on the performance of the mechanism for the individual fuel molecules. Each combination of fuel molecules makes a correction of some reaction rate coefficients necessary. In mechanism development these corrections can be performed through automated optimization procedures. On the other hand, the performance of the mechanism will be influenced, if a submechanism for a unused fuel molecule is removed from the reaction mechanism. Again automated optimization can be used to readjust the mechanism. When applying necessity analysis for species removal it is found, that a large number of species can be removed with almost no change of the performance of the reaction mechanism. Species with medium scaled necessity values influence results of the mechanism, and readjustment is necessary if further simplification of the reaction mechanism is wanted. In this presentation we perform CGR for a complex blend of fuel molecules, and demonstrate the performance of strongly simplified chemical systems for low and high temperature combustion.

II. The detailed reaction mechanism

The detailed reaction mechanism consists of 477 species and 4228 reactions. It consists of two larger alkanes: n-heptane and iso-octane. Those reaction models are generated as described in [2] via an semi automatic procedure [4]. The aromatic content is modelled by toluene as described in

[6]. All three submechanisms are based on the same C1-C4 chemistry [7] which was extended by a submechanism for ethanol oxidation.

Calculations for all fuel molecules (n-heptane, iso-octane, toluene and ethanol) show good agreement with the experimental values [8].

III. Reduction procedure

1) Horizontal lumping: The technique of horizontal lumping is applied for the submechanisms for n-heptane and iso-octane [2]. Lumping reduced the mechanism to a size of 400 species and 3988 reactions.

2) Species removal based on necessity analysis: To efficiently remove species with the lowest importance a series of steps were taken. First a set of different constant volume reactors and freely propagating flames is calculated including necessity analysis [1]. The selection of the reactors follow the ideas from [2]. In a second step the probability for species removal is weighted by its necessity value. Species are selected randomly, respectively to their probability for removal. Finally the accuracy of the model and the numerical stiffness is controlled. If the targets of the mechanism are meat the species removal is accepted and the procedure is repeated. Targets can be species concentrations or global parameter such as ignition delay time or laminar flame speed. A skeletal mechanism was generated with 290 species and 3026 reactions. The accuracy of the mechanism after each species removal is compared to the necessity value, which demonstrates the performance of the method.

3) Reaction removal based on sensitivity analysis: A further reduction can be achieved be removing single reactions. To identify those reactions a sensitivity analysis towards various targets such as species, ignition delay time and / or laminar flame speeds is used. The sensitivy coefficient over all cases are normalised and a probability to be removed is assigned to each reaction. This probability density function is used to efficiently decide which reaction to remove while keeping a certain randomness.

4) Species removal and reoptimization: The reduction technique explained before reduced the mechanism to the smallest set of species and reactions within the given accuracy limits. Each further reduction leads to a reaction mechanism which cannot predict the targets of the mechanism with the demanded accuarcy. Nevertheless further reduction is possible when reoptimisation of the Arrhenius coefficients is applied. We apply a genetic optimisation algorithm. The final mechanism for the four component gasoline reference fuel has a size of 205 species and 1460 reactions. The meachnism can be further reduced by the help of time scale analysis or tabulation techniques.

IV. Conclusions

The reduction techniques explained above were applied and the reduced mechanisms is validated against the detailed reaction mechanism. For the laminar flame speed no deviation was observed for the lumped and skeletal mechanisms. Fig. 1 shows that the final mechanism predicts accurately ignition delay times for a wide range of pressures and temperatures. Such mechanisms can be direct input to combustion simulation, or input to further mechanism reduction based on time scale analysis.

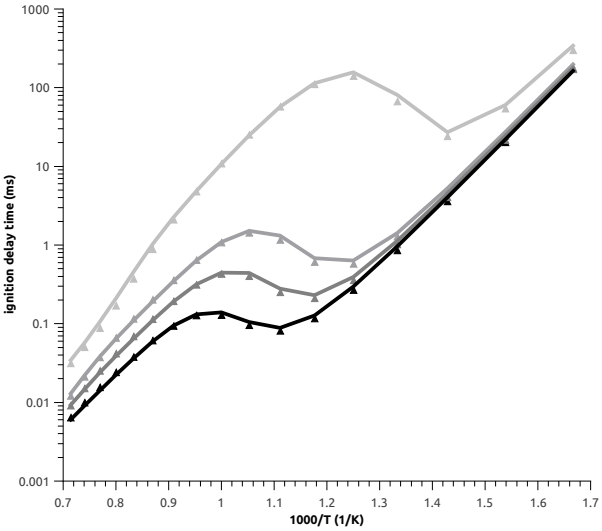

Fig. 1. Simulated ignition delay time for n-heptane at stocheometric conditions. light grey p=3 bar, grey p=27.25 bar, dark grey p=51.5 bar and black p=100 bar. The rectangles represents the lumped mechanism. The line represents the skeletal mechanism after species removal.

All calculations were performed using DARSv2.08.30.

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