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Mechanism optimization based on reaction rate rules

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ABSTRACT

Accurate chemistry models form the backbone of detailed computational fluid dynamics (CFD) tools used for simulating complex combustion devices. Combustion chemistry is often very complex and chemical mechanisms generally involve more than one hundred species and one thousand reactions. In the derivation of these large chemical mechanisms, typically a large number of reactions appears, for which rate data are not available from experiment or theory. Rate data for these reactions are then often assigned using so-called reaction classes. This method categorizes all possible fuel-specific reactions as classes of reactions with prescribed rules for the rate constants. This ensures consistency in the chemical mechanism. In rate parameter optimizations found in the published literature, rate constants of single elementary reactions are usually systematically optimized to achieve good agreement between model performance and experimental measurements. However, it is not kinetically reasonable to modify the rate parameters of single reactions, because this will violate consistency of rate parameters of kinetically similar reactions. In this work, the rate rules, that determine the rates for reaction classes are calibrated instead of the rates of single elementary reactions leading to a chemically more consistent model optimization. This is demonstrated by optimizing an *n*-pentane combustion mechanism. The rate rules are studied with respect to reaction classes, abstracting species, broken C–H bonds, and ring strain energy barriers. Furthermore, the uncertainties of the rate rules and model predictions are minimized and the pressure dependence of reaction classes dominating low temperature oxidation is optimized.

1. Introduction

Chemical kinetic mechanisms play a significant role in CFD modeling of combustion. For simple species (e.g. H_2) or engine relevant fuels (e.g. *n*-heptane), well-validated models can be found in the literature [1–3]. However, limited kinetic information is found for the combustion of emerging alternative fuels. In order to simulate the combustion of such fuels, the development of accurate kinetic models is of particular importance.

A typical model development process is composed of several steps. First, a kinetic mechanism including C_0–C_4 chemistry is chosen as base mechanism. The C_0–C_4 mechanism has a great influence on the combustion of hydrocarbon species and therefore many of the reaction rates specified for those reactions have been intensively investigated from direct experimental measurements or quantum chemical calculations [4–6]. Based on the C_0–C_4 mechanism, the fuel specific chemistry is then derived using prior knowledge of similar molecules and their reaction classes, which describe the possible oxidation steps of the fuel. All possible reactions occurring in each oxidation step are categorized as a class of reactions with the assigned rate constant expressions. The rate constants of several important reactions could be determined from quantum chemistry calculations [7–13] or experimental measurements [14–16]. However, it is computationally and experimentally difficult to determine the rate constants of all involved reactions due to the large number of intermediate species and reactions during oxidation. One strategy to determine the missing reaction rate coefficients is to use rate rules that are defined as rate constants for certain reaction classes [3,17,18].

Subsequently, additional experimental or computational data are used to tune these rate parameters [19]. Typically, sensitivity analyses of rate parameters are performed at the experimental conditions of interest to choose the important rate constants which are needed to be tuned. The deviations between model and experiment can be minimized by tuning these important reaction rate coefficients. In principle, that is done by perfecting the rate parameters iteratively and comparing the results with experimental observations [20]. An adapted set of rate constants is reached after several iterations of this procedure and good agreement between model results and experiments can be obtained.

Recently, several automatic frameworks were developed and implemented successfully to replace this process [21–24]. The idea is to quantify the relation between model response [25] and uncertain parameters and thus apply a minimization algorithm to fit the parameters for a good agreement between model response and

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experimental measurement, which is called solution mapping by Frenklach [22]. In addition, the so-called uncertainty quantification (UQ) process has been applied to chemical models allowing the possibility to estimate uncertainties of rate parameters and model results [26–28]. While some UQ approaches explicitly propagate the experimental uncertainty into parameter uncertainties and thus reproduce the experimental uncertainty in the modeling process [21,29], other approaches such as the full Bayesian technique [30,31], estimate the uncertainty based on probability theory.

However, the above mentioned automatic frameworks focus on the calibration of individual reactions. As described, the reaction constants of most derived reactions in a kinetic model are obtained using rate rules and a rule can be used for few to dozens of reactions in a mechanism. Therefore, in the common reaction class based way of mechanism construction, rate constants of reaction classes and rate rules should be modified, not individual reactions belonging to a reaction class. Thus, kinetically similar reactions are treated equally, which ensures model consistency. Ideally, every reaction rate in a mechanism should be determined individually and with high accuracy, which is unfortunately not the case for the most reaction mechanisms. If no information on a particular reaction is available from experimental measurements or ab initio calculations, it is kinetically not reasonable to modify a rate of just a single reaction of a reaction class, only because this reaction shows a higher sensitivity than other reactions of the same class. Instead, the rate for the associated class should be optimized.

In this study, the goal is to develop and demonstrate amore appropriate method for automatic calibration of chemical kinetic models, which can be used when specific information of particular elementary reactions is lacking, by performing optimization of reaction rate rules. The methodology is demonstrated here by optimizing an *n*-pentane combustion model. A chemical model is generated based on a well-validated base mechanism for C_0–C_4 chemistry. The fuel specific chemistry is derived using reaction classes and rate rules. Accurate rate parameters determined individually from computational chemistry and experimental measurements are incorporated in the reaction mechanism whenever available. For a better agreement with the measured data, the rate rules for reaction classes are then subjected to an automatic calibration process. The base mechanism and all well-studied rate parameters are exempted from calibration, as their rate uncertainties are relatively small. Only the reactions that have not been studied in detail, here especially the important reaction classes involving fuel-peroxy and -peroxide species in the low temperature regime, are considered in the calibration procedure.

While ignition delays at high temperature are usually sensitive to only a few reactions, many reactions play a significant role for low temperature ignition. The rate coefficients of these reactions will generally be considered as uncertain parameters in the model calibration. This large number of uncertain parameters leads to an unfeasible optimization process concerning computational cost. This might be one reason why no studies on automatic calibration of low temperature chemistry are found in the published literature. The calibration of rate rules provides the possibility to reduce the number of uncertain parameters by using rate rules that categorize the chemically similar and sensitive reactions into a class. In this study, the ignition delay times at low temperatures are incorporated in the calibration process. Thereby, previous calibration approaches [53,29,22,32] are extended to the engine relevant low temperature chemistry.

Note that for most of the published calibration methodologies the assumption is made that the chemistry model is perfect [22,32,33,29]. In other words, if one could obtain data with zero errors, the assumption states that the parameters could be fitted perfectly and the model will be able to predict any other experiment exactly. Thus, the calibration framework is employed as a pure numerical tool to fit the rates and optimize the model predictions. The modification of the set of the chemical reactions is typically not considered in the calibration. This issue will also be explored in this work. The pressure dependence of low temperature chemistry will be studied in parallel to the calibration process in order to obtain a better model.

The temperature dependence of the set of the chemical reactions is assumed to be correct in this study. In general, if the temperature dependence in terms of the activation energy is considered in the optimization process, it is expected that better agreement can be obtained for a wide range of conditions as the number of uncertain parameters is doubled. However, this increase in the number could lead to a much higher computational expense, which makes it again difficult to calibrate the low temperature ignition. For each experimental condition considered in the calibration, $(2n+1)^2$ numerical simulations are required to generate the model response surface for n uncertain parameters [25]. More importantly, however, the constraint of both frequency factors and activation energies of reactions is not trivial, because uncertainties of reactions found in the literature [7,8] are given for rate constants k and not for pre-exponential factors A and activation energies E separately. A method for dealing with this has to be developed.

The presentation of the study is organized as follows. In the first part, the reaction classes and the rate rules, as well as the optimization methodology, are introduced. The second part provides details of the development of an *n*-pentane mechanism and the computational information. Following this, the calibration approach is first applied for high temperature combustion and then extended to the complex low temperature chemistry. The mechanism is further improved through the incorporation of pressure dependent rules.

2. Methodology

2.1. Reaction classes and rate rules

Recently, a number of kinetic mechanisms were built in a systematic way for components of interest for transportation fuel surrogates [3,17,18,34,19]. Curran et al. [3] proposed a kinetic mechanism for *n*-heptane combustion using the methodology of reaction class and rate rule. This methodology was further successfully applied to build kinetic models for the combustion of iso-octane [17], *n*-alkane hydrocarbons [18], 2-methylalkanes [19] and some oxygenated fuels [34,35]. In the currently common approach, 30 reaction classes listed in Table 1 are used to build up a reaction mechanism. The first ten reaction classes are used to describe high temperature oxidation of the fuel, while classes 11–30 are needed to describe the complicated low temperature combustion. As mentioned earlier, the rate rules for each class are generated based on available chemical kinetic knowledge [3,19].

As an example, the rate rules for class 15, the alkyl peroxy radical isomerization ($RO_2 \rightarrow QOOH$), from Sarathy et al. [19] are shown in Table 2. The alkyl peroxy radical isomerization plays a significant role in the low temperature regime. With the subsequent O_2 addition, isomerization, and formation of the carbonylhydroperoxide, two OH radicals are produced, which lead to low temperature chain branching. If inaccurate rates are employed, a large modeling error can be introduced. The reaction rules for alkyl peroxy radical isomerization, as shown in Table 2, depend on the ring strain energy barrier and on the nature of the broken C–H bond. In this study, one set of Arrhenius coefficients is treated as one rule and thus one potential calibration object of the model optimization. Therefore, twelve rate rules are prescribed for the alkyl peroxy radical isomerization class. If a rate rule is calibrated,