Validation of Selection Parameters for Steady State Species for Automatic Reduction of Chemical Mechanisms

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Abstract

In order to define steady state species for the development of automatically reduced chemical mechanisms a reliable and simple selection criteria for steady state species needs to be used. Such a selection criteria can be the chemical lifetime of a species based on the assumption that species with shorter lifetimes than physical processes involved can be set to steady state. Another selection criteria can be a combination of the lifetime with a species sensitivity in order to capture species with overall little importance because of small lifetime and/or a low sensitivity on the desired result thus meaning the species can be computed by approximate means. In this work we have investigated the validity of these selection parameters and their use for selection of steady state species. We find that the error in computation of the species concentration is linearly increasing with lifetime and conclude therefor that a simple first order lifetime measure is a valid and useful selection parameter.

Introduction

The combination of chemical kinetic models with Computational Fluid Dynamics calculations used for prediction of gas flow in combustion chambers provides an efficient tool in terms of time and costs for the investigation of the overall combustion processes.

Often the geometry of the device is very complex, and the performance of commercial software products for combustion optimisation decreases considerably if the number of species exceeds about 10. A detailed chemical mechanism often involves up to one hundred species. Consequently, methods in chemical kinetic modelling are needed to construct a reaction mechanism for a complex fuel and to reduce it to a low number of capable species without a loss of chemical information that is of importance for the accuracy of the calculations.

One well-known method for reducing the chemical mechanism is using Quasi Steady State Approximations (QSSA). For the purpose of determining which parts of a reaction mechanism can be simplified, general mathematical methods are used to discriminate between fast and slow chemical processes. If the species concentrations are also relatively small, the species can be assumed to be in steady state, thus well described by means of (relatively) simple algebraic equations. The conservation equations for the steady state species can be removed from the system of differential equations, keeping the numerical effort low without loss of chemical information. This reduction procedure is very time-consuming when undertaken by hand [1].

Also the compilation of the detailed reaction mechanisms has been a tedious chore. However, software tools for the automatic generation of detailed reaction mechanisms for e.g. complex fuel combustion and pollutant formation have become available [2]. Given the enormous size and complexity of automatically generated mechanisms, it is an awkward business to analyse and reduce these mechanisms of hundreds or thousands of species by the reduction method described above by hand.

In previous publications the authors have presented a method for automatically reducing chemical mechanisms [3][4][5]. A measure of species lifetimes is used alone or is combined with a species sensitivity to represent a level of importance and the species with lifetimes shorter or a level of importance lower than a specified limit are selected for removal. These are assumed to be in steady state, and their concentrations are modelled by means of algebraic equations that are automatically implemented in FORTRAN subroutines

calculating the remaining non-steady-state source terms from reaction rates, besides computing the steady-state concentrations by internal iteration. In order to carry out the procedure for the general case the selection parameter needs to be simple and well defined. As shown in the previous publications the method is proven successful for a variety of chemical mechanisms and physical applications. The results from using the reduced mechanisms lie within acceptable deviations from the result using the detailed mechanism. It is however important to investigate the self-consistency of the method. In this work we investigate the self-consistency of the reduction method using lifetime and level of importance as selection parameters as was done in Løvås et al. [5].

Calculating and Validating the Species Lifetime and Sensitivity Measures

The simulation is performed for a flat laminar premixed stationary methane/air flame without burner stabilisation. The mechanism used for the methane/air kinetics is the well-known methane skeleton mechanism in Peters and Rogg [1] and is also therein validated for this configuration by comparing the estimated flame speed with the experimental values for a range of equivalence ratios. In Løvås et al. the mechanism consisting of 31 species was successfully reduced to only 8 species and the resulting flame speed was deviating less than 2.5% from the flame speed calculated from the detailed mechanism [5]. The species conservation equation for this configuration is given by the well known relation

(1)

$$0 = \frac{\partial}{\partial z}\left(\rho Y_i u_i \right) - W_i \sum_{k=1}^{N_r} \nu_{ik} w_k + \rho u_z \frac{\partial Y_i}{\partial z} .$$

The introduction of the steady state assumption leads to an error in the concentration profiles of the steady state species. In Figure 1 we show the calculated profiles for CH_2O for both the steady state and non-steady state calculations as an example. We obtain the steady state solution by simply setting the convective and diffusive terms equal to zero. That is, we solve numerically the following equation

(2)

$$0 = -W_i \sum_{k=1}^{N_r} \nu_{ik} w_k$$

for the steady state species. It is obvious that the steady state profiles reaches a higher maximum mass fraction and is narrower than the non-steady state profile. This is caused by the missing diffusion terms in equation (2). For simplicity we define the error in the profile assuming steady state by comparing the maximum values, also shown in the Figure 1, by

(3)

$$error = \frac{\left| dY_{\max} \right|}{Y_{\max}} .$$

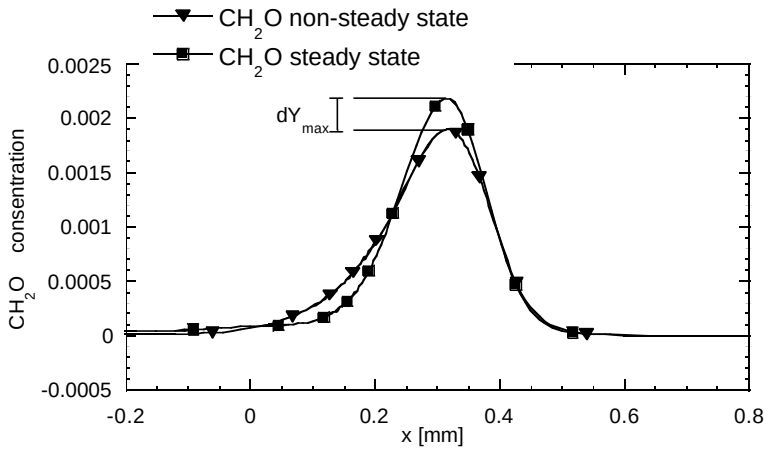

Figure (1) The concentration profiles if CH2O for non-steady and steady state.

Since the steady state species are selected according to their chemical lifetime and species sensitivity the method of calculating the species lifetime becomes crucial for the resulting reduced mechanism. Different ways of defining the chemical liftime has been tested and used to select steady state species. One procedure is to use the species' chemical lifetime given by

(4)

$$t_i^C = -1/\frac{\partial w_i}{\partial c_i} = \frac{c_i}{\sum_{k=1}^{N_R} n'_{ik} r'_k}$$

where subscript i denotes the species, w_i is the species reaction rate and c_i is the species concentration. The chemical lifetime is a measure on how fast the species is consumed after being produced. Taking the different species' diffusion velocities into account, the chemical lifetime is to be weighted to the diffusion of an inert species. In this case that is the N_2 species resulting in a diffusion weighted chemical lifetime

(5)

$$t_i^{CW} = t_i^C \frac{D_i}{D_{N_2}} \cdot$$

If the diffusion weighted lifetime is normalised to the characteristic flame time, the time of passage for a species through the flame, a general measure valid for all flames looks the following

(6)

$$J_i = \frac{t_i^{CW}}{\sqrt{\left(t_i^{CW}\right)^2 + \left(t^F\right)^2}}$$

where $t^F = l_f / u_u$ is the characteristic flame time.

The upper plot in Figure 2 shows the improvements on the error in concentrations by applying a diffusion weighted lifetime instead of the chemical lifetime only for equivalence ratio f=1.0. Species like H and H_2 that diffuse quickly requires as expected with a diffusion weighted lifetime a higher limit in order to be selected as steady state, i.e. they are kept in the mechanism for more crude selection criteria.

The second plot in Figure 2 shows the influence on different equivalence ratios on the error when using the diffusion weighted lifetime. The two cases for φ =1.0 and φ =1.2 shown in the plot have very similar error profiles as expected since the flame speed in both cases are approximately the same. The solution for φ =0.5437 is deviating from the two other solutions mainly because of a longer characteristic flame time.

This motivates the use of the modified lifetime normalised to the characteristic flame time as given in equation (6), and the resulting errors by applying the steady state assumption for all species is shown in the lower plot in Figure 2 for φ =0.5437, φ =1.0 and φ =1.2. As seen in the plot the error increases linearly with increasing lifetime in a narrow band. The lifetime measure as defined above is valid for any general flame. As the lifetime becomes larger also non-linear effects become more significant, especially for the fuel lean flame. This can be seen in the plot in the upper right corner. The plot reveals clearly the main feature with the quasi steady state assumption, namely that by setting species with a modified lifetime shorter than e.g. L=0.004 to steady state means excepting an error in the concentration profiles of 30%.

The main interest is however in how the application of a steady state assumption effects the result of important parameters such as e.g. the calculated flame speed or emission rates. This is possible to investigate through sensitivity analysis. In this case the interesting parameter is the flame speed, and thus the sensitivity of reactions should be investigated to the computed flame speed.

In Løvås et al. [5] the modified lifetime is combined with the species sensitivity and thus the sensitivity of a species is included in the selection procedure for steady state species. The sensitivity of a species i on the reaction rate or the frequency factor for reaction k is given as $S_{ik} = \partial Y_i / \partial w_k$, and the normalised sensitivity of a species i with respect to e.g. species j for all reactions k can be expressed by

$$S_{i,j}^S = \sum_{k=1}^{N_R} \left| \frac{n'_{j,k}}{\left[c_j\right]} \frac{\partial Y_i}{\partial w_k} w_k \right|, i = 1 \ldots N_S \quad \cdot \tag{7}$$

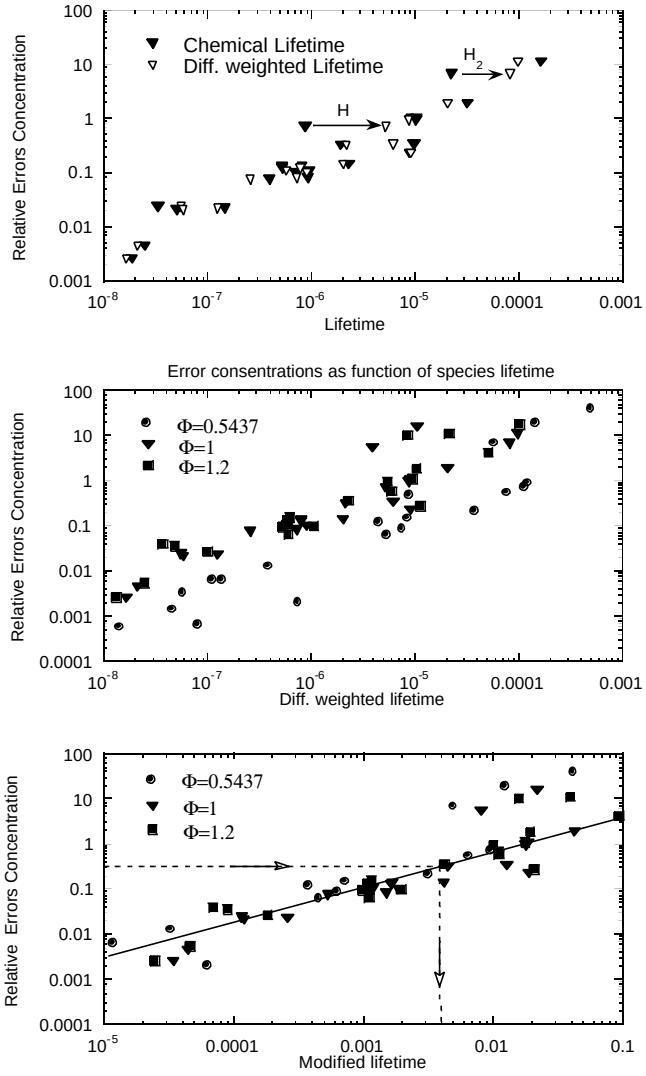

Figure 2: The relative errors in concentration for all species as function of lifetime and equivalence ratio.

The selection parameter for steady state species is in Løvås et al. [5] defined as the *product* of the modified species lifetime and the species sensitivity. In the investigation of the premixed flat flame the level of importance for a species reads the following:

(8)

$$(LOI)_i = S^S_{u_f,i} J_i$$

This selection parameter thus captures species with long lifetimes but with little sensitivity for the desired result and vice versa species with short lifetimes but with high sensitivity will be kept in the mechanism. The relative error for a species j, f_j, calculated from a steady state equilibrium is proportional to J_i, which is also clear from the lower plot in Figure 2:

(9)

$$\frac{f_j}{\left[c_j\right]} \propto J_i \Rightarrow f_j \propto \left[c_j\right] J_i$$

and $S^{S}_{u_f,i}$ represents how the relative error in the species profiles affects the flame velocity υ_f. Strictly speaking the error in calculation of the flame velocity influenced by the error in species *i* is the following

(10)

$$f_{u_f} = \frac{\partial u_f}{\partial [c_i]} f_i .$$

Recognising the first factor on the right hand side as the sensitivity described above and the second factor as proportional to the lifetime proves that LOI is a measure proportional to the error in the flame velocity caused by a steady state assumption.

In Figure 3 the validity of the sensitivity analysis is shown for both 1% change in reaction rates and 10% change in the reaction rates. The most sensitive reaction is the OH and H reaction

[I]

$$H + O_2 = HO + O,$$

and therefore the profiles of O is plotted in Figure 3. As seen in the plot the predicted change in O concentration by 1% change in the reaction rate using sensitivity analysis is very close the calculated result. For a 10% change in the reaction rate the sensitivity analysis predicts a slightly higher change in the concentration profile than the calculated result show. The tendency of a left shifted curve is however clear for both the predicted and the calculated result.

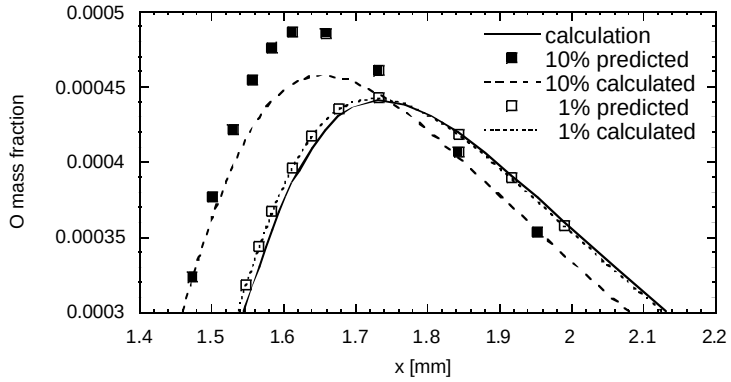

Figure 3: Predicted and calculated change in O concentration profiles by the use of sensitivity analysis.

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