

Validation, Reduction and Optimization of Chemical Kinetic Mechanisms for Marine Engine Applications

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Dual fuel marine engines, mainly operated with natural gas, consist a competitive means for meeting the recent emission regulations, which dictate substantially reduced emission limits in specific geographical areas (Emission Control Areas – ECAs). To accurately model combustion and emission formation in dual fuel engines, for example in the context of CFD studies, it is essential to effectively represent the chemistry of methane, the main constituent of natural gas. To this end, detailed chemical kinetic mechanisms should be properly validated and reduced; this yields either skeletal or reduced mechanisms.

The goal of the present study is to derive an optimized skeletal chemical kinetic mechanism for CH₄ combustion, valid in a wide range of conditions relevant for dual fuel engines. This has been performed in five stages, as follows: (a) Validation of the NUIG-NGM detailed mechanism, (b) Sensitivity analysis, (c) Production of a skeletal mechanism by means of the SEM-CM method, (d) Uncertainty analysis of the active rate constants, and (e) Optimization of the skeletal mechanism for the rate constant parameters of the elementary reactions identified by the sensitivity analysis.

The detailed mechanism is validated by comparing simulation results against three sets of indirect experimental data pertinent to the oxidation of CH₄ mixtures, in particular: (i) ignition delay times from shock tube experiments [1-5], (ii) measurements of species profiles in jet-stirred reactors (JSR) [6-8], and (iii) burning velocity measurements [9-10]. These data sets correspond to a wide range of temperatures (900-2100 K), pressures (1-260 atm), and equivalence ratios ($\phi = 0.2-6.0$).

The NUIG-NGM mechanism includes 293 species and 1593 elementary reactions [11]. The results of the validation procedure indicated that the mechanism reproduces a substantial percentage of the experimental data with high accuracy. Representative results regarding ignition delay times, for conditions relevant for dual fuel engine operation, are presented in Fig. 1.

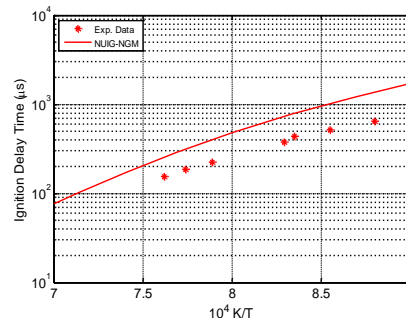


Fig. 1 Ignition delay times versus initial temperature of CH₄-O₂ mixtures at $\phi=0.4$, $P=100$ atm, for experiment [1] and the present computations using a detailed mechanism.

The second stage towards an optimized skeletal mechanism is the local sensitivity analysis. Sensitivity analysis is used to identify the important reactions at representative conditions of

the set of experiments, and thus also the important species, i.e., the ones incorporated in these reactions. This identification of the important reactions is crucial for the computational cost of optimization, since the number of the problem design variables is thus limited to the rate parameters of the important reactions. The identification of important species is of equal significance, as it forms a prerequisite for implementing the chemistry reduction method of the present study. Sensitivity analysis was performed with respect to the pre-exponential factor, A . In the frame of sensitivity analysis, normalized sensitivity coefficients were calculated for conditions corresponding to the three above-mentioned experimental data sets, as follows:

$$\tilde{s}_{ij} = \frac{A_j}{Y_i} \frac{Y_i' - Y_i}{A_j - A_i} \quad (1)$$

where Y_i is the concentration of species i , and A_j is the initial value of the pre-exponential factor of reaction j . Thus, the normalized sensitivity coefficient expresses the variation of a particular species concentration to a small change in the value of pre-exponential factor of a certain reaction. In the present study the CH_4 concentration has been used for calculating normalized sensitivity coefficients. Thus, computed negative values of \tilde{s}_{ij} correspond to enhanced reactivity reactions, while positive values correspond to reactions inhibiting fuel consumption. The outcome of sensitivity analysis in terms of the mechanism important reactions is presented in Table 1.

Important Reactions	
1	$\text{H} + \text{O}_2 \leftrightarrow \text{OH} + \text{O}$
2	$\text{CH}_3 + \text{H} (+\text{M}) \leftrightarrow \text{CH}_4 (+\text{M})$
3	$\text{CH}_4 + \text{OH} \leftrightarrow \text{H}_2\text{O} + \text{CH}_3$
4	$2\text{CH}_3 (+\text{M}) \leftrightarrow \text{C}_2\text{H}_6 (+\text{M})$
5	$\text{HCO} (+\text{M}) \leftrightarrow \text{CO} + \text{H} (+\text{M})$
6	$\text{HCO} + \text{O}_2 \leftrightarrow \text{CO} + \text{HO}_2$
7	$\text{H} + \text{OH} (+\text{M}) \leftrightarrow \text{H}_2\text{O} (+\text{M})$
8	$\text{CH}_3 + \text{O}_2 \leftrightarrow \text{CH}_2\text{O} + \text{OH}$

Table 1. List of important reactions

Further, a skeletal chemical kinetic mechanism was produced by applying the SEM-CM reduction method, developed by the group of Professor T. Turányi at the Eötvös Loránd University of Budapest [12]. The SEM-CM method belongs to the class of reduction methods which do not consider time-scale separation, and is based on the minimization of the rms value of a properly defined error function:

$$\delta_i(t_j) = 2 \frac{C_i^{\text{red}}(t_j) - C_i^{\text{full}}(t_j)}{C_i^{\text{full}}(t_j) + C_i^{\text{full}}_{\text{MAX}}} \quad (2)$$

Where, at time t_j , C_i^{full} denotes the concentration of species i in the detailed mechanism, and C_i^{red} the concentration of the same species i in the skeletal mechanism; $C_i^{\text{full}}_{\text{MAX}}$ is the maximum concentration of species i in time. The procedure is initiated on the set of the important species, as obtained from the sensitivity analysis. This set is then extended by selecting sets of species connected to the important ones, which are selected based on processing values of the normalized Jacobian:

$$B_i = \sum_{j \in \text{important}} J_{ij}^2 \quad (3)$$

where summation is over all important species, j . The index B_i is thus a measure of the effect of variation of the concentration of species i to the concentration of all important species. By including different numbers of species corresponding to high values of the B_i index (and the

corresponding elementary reactions), different sets of connected species and corresponding skeletal mechanisms can thus be produced.

Subsequently, simulations of CH₄ oxidation in JSR were performed, for a wide range of pressure and equivalence ratio of the above mentioned experimental data sets; the skeletal mechanism giving the lowest rms deviation with respect to experiments was selected as a basic reference mechanism. This mechanism was further extended with additional species and corresponding elementary reactions, based on the values of B_i , until a predefined level of the rms deviation was achieved. The final skeletal mechanism consists of 28 species and 119 reactions. Production of the skeletal mechanism has utilized the SEM computational tool developed by the Eötvös Loránd University [13].

Next, uncertainty analysis was performed, in order to determine the boundaries (or uncertainty limits) of the active rate constants. The term ‘active’ refers to the rate constants of the important reactions. Uncertainty analysis restricts the domain of the optimization problem design variables, i.e., the three parameters of the active rate constants, thus resulting in an overall good agreement of chemical kinetics calculations with respect to experiments.

In uncertainty analysis, the uncertainty factor $u_j = \frac{k_j^0}{k_j^{min}} = \frac{k_j^{max}}{k_j^0}$ is first determined. Next, the

boundary limits of the active rate constants are calculated via the uncertainty parameter, f :

$$f_j(T) = \log_{10}(u_j(T)) \quad (4)$$

where k_j^0 is the proposed value of the rate constant of reaction j , k_j^{min} is a possible minimum value of the rate constant of reaction j , and k_j^{max} a possible maximum value.

The acquisition of experimental rate constant values, as well as values calculated via theoretical approaches, is essential for the determination of the k_j boundary limits. In the present study, values of the NIST chemical kinetics database in the temperature range 300-2500 K were used [14], and the boundary limits of k_j were calculated by means of the U-limits computational tool [13].

Finally, the skeletal mechanism was optimized in terms of optimizing rate constant parameters of the important elementary reactions. Here, single-objective optimization was performed in terms of minimizing the following objective function:

$$E(p) = \frac{1}{N} \sum_{i=1}^N \frac{1}{N_i} \sum_{j=1}^{N_i} \left(\frac{Y_{ij}^{mod}(p) - Y_{ij}^{exp}}{\sigma(Y_{ij}^{exp})} \right)^2 \quad (5)$$

where Y_{ij} denotes measured/calculated rate coefficient or measured/calculated concentration of species/ignition time/flame velocity in data point j of data series i , σ denotes the standard deviation of the measured data, N_i is number of data points in data series i , N is the number of data series, and p the vector of design variables. A careful selection among the available experimental data has been performed, and used in calculating values of the objective function $E(p)$.

The boundary limits were incorporated in the optimization process via the covariance matrix [15]. Further, the mean values of the rate constants of the important reactions were utilized, in order to guide optimization towards solutions closer to physically meaningful values of the rate constant parameters. The optimization procedure was terminated when the set of optimal solutions was hardly improved from one optimization cycle to the next one. Optimization has utilized the Flamemaster chemistry solver [16] and the Optima++ optimization code [13].

Finally, the performance of the optimized skeletal mechanism was assessed by comparing computational results for ignition delay times against those of the initial skeletal mechanism, as

well as against the present results using the NUIG-NGM detailed mechanism and experimental data. Results are presented in Fig. 2, illustrating the very good performance of the optimized skeletal mechanism. The present work constitutes a first step towards CFD studies in dual-fuel marine engines.

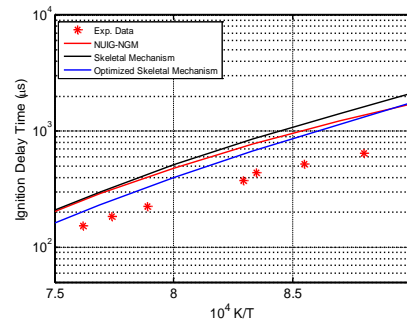


Fig. 2 Ignition delay times versus initial temperature of CH_4-O_2 mixtures at $\phi=0.4$, $P=100$ atm, for experiment [1] and the present computations using different mechanisms.

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