link to published version:

https://doi.org/10.1016/j.cpc.2021.107940

`OptiSMOKE++`: A toolbox for optimization of chemical kinetic mechanisms

Magnus Fürst[a,b,c,*], Andrea Bertolino[a,b,c,], Alberto Cuoci[b,], Tiziano Faravelli[b,], Alessio Frassoldati[b,], Alessandro Parente[a,c,*]

[a] *Université Libre de Bruxelles, Ecole Polytechnique de Bruxelles, Aero-Thermo-Mechanical Laboratory, Avenue F.D Roosevelt, 50 - CP 165/41, 1050 Brussels, Belgium*
[b] *Department of Chemistry, Materials, and Chemical Engineering, Politecnico di Milano, P.zza Leonardo da Vinci, 32, 20133 Milano, Italy*
[c] *Université Libre de Bruxelles and Vrije Universiteit Brussel, Combustion and Robust Optimization Group (BURN), Bruxelles, Belgium*

Abstract

As detailed chemical mechanisms are becoming viable for large scale simulations, knowledge and control of the uncertainty correlated to the kinetic parameters are becoming crucial to ensure accurate numerical predictions. A flexible toolbox for the optimization of chemical kinetics has therefore been developed in this work. The toolbox is able to use different optimization methodologies, as well as it can handle a large amount of uncertain parameters simultaneously. It can also handle experimental targets from different sources: Batch reactors, Plug Flow Reactors, Perfectly Stirred Reactors, Rapid Compression Machines and Laminar Flame Speeds. This work presents the different features of this toolbox together with five different test cases which exemplifies these features.

---

[*] Corresponding authors

Email addresses: `magnus.furst@ulb.be` (Magnus Fürst), `alessandro.parente@ulb.be` (Alessandro Parente)

Manuscript final version (Computer Physics Communications)

Keywords: Optimization, Chemical Kinetics, Combustion

Program summary

Program Title: OptiSMOKE++

CPC Library link to program files: https://doi.org/10.17632/tvjky2n8md.1

Licensing provisions: GPLv3

Programming language: C++

Operating system: Linux/UNIX

Nature of problem: Optimization of uncertain kinetic parameters with respect to experimental data.

Solution method: Using the optimization capabilities of DAKOTA [1], and solving reacting systems with OpenSMOKE++ [2], OptiSMOKE++ determines the optimal combination of specified kinetic parameters, within their uncertainty, and with respect to the experimental data.

References

[1] B. M. Adams, M. S. Ebeida, M. S. Eldred, G. Geraci, J. D. Jakeman, K. A. Maupin, J. A. Monoscheke, L. P. Swiler, J. A. Stephens, D. M. Vigil, T. M. Wildey, W. J. Bohno, K. R. Dalbey, J. P. Eddy, R. W. Hooper, K. T. Hu, P. D. Hough, E. M. Ridgwat, A. Rushdi, Dakota, A Multilevel Parallel Object-Oriented Framework for Design Optimization, Parameter Estimation, Uncertainty Quantification, and Sensitivity Analysis: Version 6.5 User's Manual (2014).

[2] A. Cuoci, A. Frassoldati, T. Faravelli, E. Ranzi, OpenSMOKE++: An object-oriented framework for the numerical modeling of reactive systems with detailed kinetic mechanisms, Computer Physics Communications 192 (2015) 237-264. doi:10.1016/j.cpc.2015.02.014.

1. Introduction

The steady increase in computational power enables us to describe the behavior of complex combustion processes with more detail in Computational Fluid Dynamics (CFD) simulations, thus allowing us to more accurately predict how changes to the system would affect critical parameters, such as emissions, maximum temperature, efficiency, etc. This is crucial in the development of novel technologies, as a more traditional trial-and-error approach for many cases quickly becomes unfeasible, due to both time consumption and costs. The complexity of a combustion simulation can be expressed in many ways, i.e. geometric, flow modeling, chemical mechanism complexity, etc. Only in recent years it became feasible to account for more detailed chemical mechanisms in large scale simulations. This allows to improve the prediction of intermediates and final products of the combustion process significantly, as well as to enhance our fundamental understanding of the complex chemical process occurring in combustion.

A chemical kinetic mechanism is built up from species, thermodynamic and transport data and elementary reactions [1]. Each chemical reaction consists of rate constants (k), which in turn can be expressed as a function of temperature with some parameters (the pre-exponential factor A, the temperature exponent β, and the activation energy E_a) according to the modified Arrhenius' equation ($k = AT^{\beta}exp(-E_a/RT)$, where T is the temperature and R is the ideal gas constant). The definition of these parameters for each reaction in a kinetic mechanism is not straightforward, as they can be based on experimental data and theoretical calculations carried out at different levels of theory [2]. Thus, there is an inherent uncertainty for each of these parameters, and as the size of the mechanism grows, also the number of uncertain parameters increases.

In order to cope with the large amount of uncertain parameters, Uncertainty Quantification (UQ) and Optimization have been increasingly adopted in the process of chemical mechanism development [3]. The widely used GRI mechanisms [4–6] are based on the Bound-To-Bound Data-Collaboration (B2B-DC) [7–10] optimization methodology, where the optimal combination of the kinetic parameters was determined minimizing the distance between measurements and predictions, using surrogate modelling for the selected quantities of interest (ignition delay times, species profiles, and flame speed measurements). Their performance for conventional combustion of natural gas, together with the relatively small size, proved to be an effective combination. In the development of the GRI mechanisms [4–6], especially the pre-exponential factors for the most impactful reactions were optimized.

Wang and co-workers later developed the Method of Uncertainty Minimization using Polynomial Chaos Expansion (MUM-PCE) [11], which again utilizes surrogate modelling for representing the model responses. Then by finding the least-squares point within the parameter space, they determined the optimal mechanism. They used this approach for several different fuels [12–14], and also to develop the Foundational Fuel Chemistry Model (FFCM) [15] for small hydrocarbon fuels. However, in these works [12–16] they only considered the pre-exponential factors and some third body efficiencies as active parameters. A species is considered as a third body if it stays inert though the reaction process, and only transfers/removes energy from the process. Only in a recent study [17], they applied the MUM-PCE approach considering the joint probability distribution of the pre-exponential factors and the activation energies of some reactions.

Cai and Pitsch [18, 19] also used the MUM-PCE [11] methodology, but for the optimization of rate rules instead of specific reactions. Later, they also applied a Bayesian approach for the optimization of rate rules for alkanes [20]. Rate rules are used to derive kinetic parameters for reactions that behave in a similar way. As the determination of one rate rule directly inflicts changes to many reactions, it is a very efficient approach for developing kinetic mechanisms for fuels with larger molecules. Recently, they combined this with the optimization of thermochemical properties in the works of Vom Lehn et al. [21–23], showing a large impact of the thermochemical parameters at especially intermediate temperatures. However, in all these works [18–23], only the pre-exponential factors for the rate rules were considered for the optimization.

The works of Turànyi and co-workers [24–26] have also been focused on the optimization of kinetic mechanisms, but, differently from [4–10, 12–20], they included all three Arrhenius parameters in the optimization, i.e. A, β and E_a, as well as third body collision efficiencies. The approach used in [24–26] is based on using both direct and indirect experimental data, where direct experimental values refers to experimental data of the rate constant k, while the indirect targets consists of concentration profiles, ignition delay times, and laminar burning velocities [24–26]. For some of these targets, they also used response surfaces to predict the effect of changing the kinetic parameters.

The approach based on the use of response surfaces can be highly efficient for mechanism optimization, but, as mentioned by Sikalo et al. [27], the nature of the objective function in mechanism optimization can be highly complex, since it consists of many local minima and maxima. Therefore, Sikalo et al. [27] suggest to use the Genetic Algorithm (GA) global optimization approach, which has been proven to perform very well in these conditions [27–29]. Indeed, Elliott and co-workers have applied GAs for optimizing kinetic mechanism for many different fuels [29–32].

The use of heuristic optimization strategies for solving the problem at hand, i.e. kinetic mechanism optimization, presents an ideal application, and the present work focuses on the development of a flexible toolbox for the optimization of chemical mechanisms. This toolbox, named `OptiSMOKE++`, enables the user to optimize mechanisms performances handling numerous kinetic parameters, under uncertainty. The optimization targets can be experiments from many ideal reactors, considering species concentrations, Ignition Delay Times (IDT) or Laminar Flame Speeds (LFS). The toolbox relies on the `OpenSMOKE++` [33] framework for the numerical simulations of combustion processes, while the `DAKOTA` toolkit [34] is used for the optimization. `DAKOTA` contains many different optimization algorithms, and the user is free to choose any of them. These and more features of `OptiSMOKE++` are demonstrated in this work.

2. Code description

The following section describes the specific functionalities of the `OptiSMOKE++` toolbox, together with some details about the two different codes `OpenSMOKE++` and `DAKOTA`. An overall view of the `OptiSMOKE++` workflow is depicted in Figure 1. The code starts by reading the specified input file, then changes the parameters in the kinetic scheme. The code then double-checks if the rate parameters are within the uncertainty bounds (see Section 2.5), using a non-linear constraint, i.e. $k_{min} \leq k \leq k_{max}$ (provided by the literature). If yes, `OpenSMOKE++` is used for running the simulations, and the results are used to calculate the objective function value. If at least one of the rate parameters are outside of the uncertainty bounds, a penalty function is applied to that evaluation and the simulations are not carried out. This allows for quite a significant computational speed-up, as unnecessary evaluations are avoided. A more thorough explanation regarding the uncertainty bounds can be found in Section 2.5, while the penalty function is discussed further in Section 2.6.

Based on the objective function value, `DAKOTA` suggests a new set of parameter values and the process is repeated until at least one of the stopping criteria has been reached. These stopping criteria can depend on the optimization methodology used, but typical universal ones are: maximum number of evaluations, maximum number of iterations, solution target, and convergence criteria. All the stopping criteria are explained in further detail in the Reference Manual of `DAKOTA` [35].

2.1. OpenSMOKE++

The `OpenSMOKE++` framework [33] was developed specifically for solving reacting systems with thousands of species and reactions. It consists of a series of solvers for 0D reactors (Batch Reactors, Plug Flow Reactors (PFR), Perfectly Stirred Reactors (PSR), Shock-Tube (ST) Reactors, Rapid Compression Machines (RCM)) and 1D laminar premixed and counterflow diffusion flames. The code was written exclusively in object-oriented C++, which

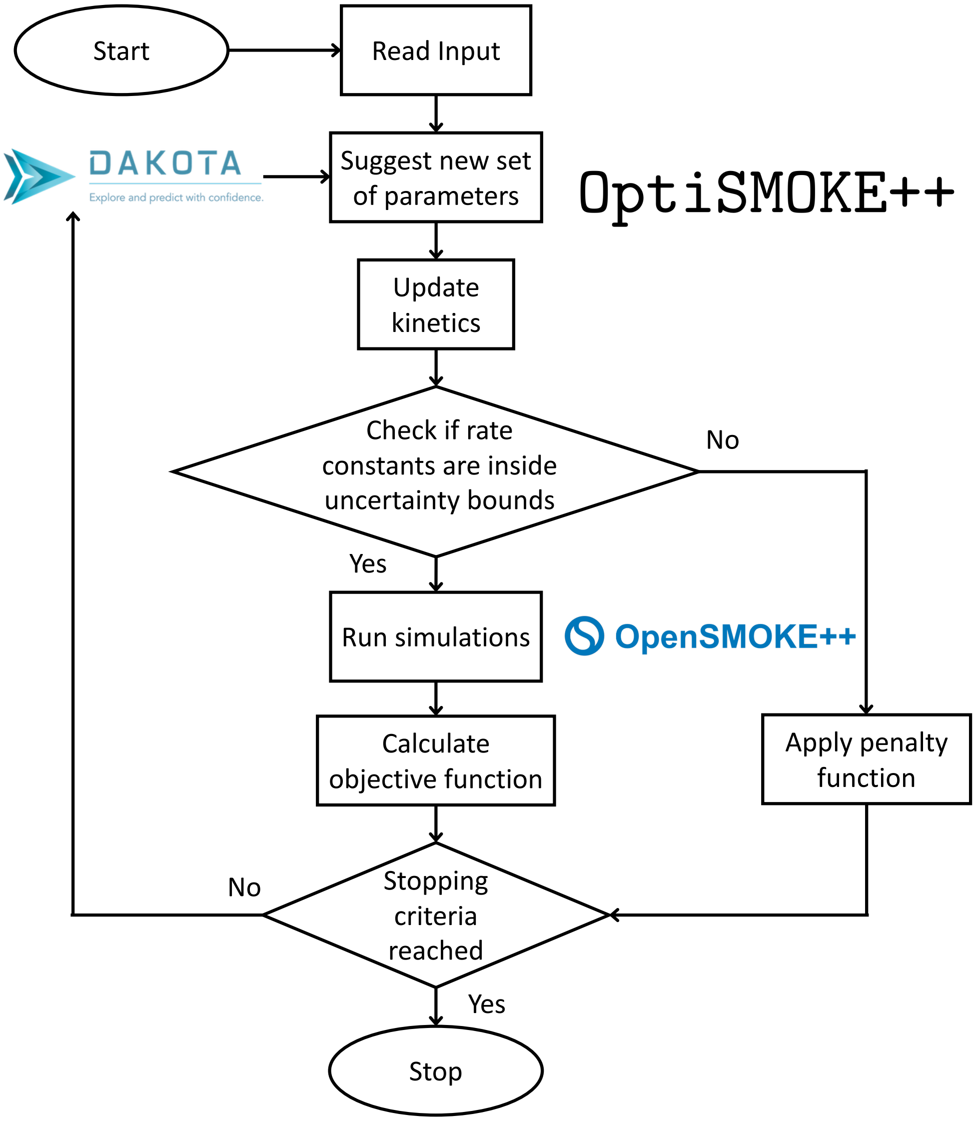


Figure 1: Schematic workflow of `OptiSMOKE++`.

facilitated the coupling with `DAKOTA`, also written in C++. `OpenSMOKE++` utilizes advanced numerical techniques to reduce the computational cost of the simulation, without sacrificing accuracy or robustness. A more extensive description of the code and its utilities can be found in [33].

2.2. `DAKOTA`

`DAKOTA` (Design Analysis Kit for Optimization and Terascale Applications) is a framework developed at and distributed by Sandia National Laboratories [36]. It is a toolkit used for iterative parameter evaluations, such as optimization, sensitivity analysis, uncertainty quantification, etc. The toolkit consists of many different optimization methodologies which can be divided into the following sub-categories: Gradient-Based and Derivative-Free Local Methods and Gradient-Based and Derivative-Free Global Methods.

As `DAKOTA` was intended to be used together with a separate application, it considers the simulation code as a "black box". There exists many cases in literature where `DAKOTA` has been coupled with different simulation software for this purpose [37–39]. `OptiSMOKE++` was written in C++ which allows for a direct and fast communication between `DAKOTA` and `OpenSMOKE++`.

2.2.1. *Optimization algorithms*

The adoption of any optimization methodology in `DAKOTA` is possible with `OptiSMOKE++`. The `DAKOTA` User's Manual [34] provides extensive information regarding the available algorithms. However, due to the problem at hand, i.e. kinetic mechanism optimization, some optimization algorithms are less suited than others. As will be better explained in Section 3, the number of uncertain parameters can range between 7-40 for the simple test cases presented in this work. As many of these uncertain parameters introduce strong non-linearities, the objective function can show a highly irregular behavior.

Due to this, Elliott et al. [29] mentioned that gradient based methodologies are not recommended in this context. For this reason, in this work we adopted four different heuristic derivative-free optimization methodologies. These are the: `coliny_direct` (DIRECT), `mesh_adaptive_search` (MADS), `coliny_solis_wets` (SW) and `coliny_pattern_search` (PS). Detailed information about all these methods can be found in the Reference Manual of `DAKOTA` [35], but a brief description of their working principles is given in the following.

The PS and MADS methods are evolved versions of the most naive approach for optimisation, i.e. the local exhaustive search (ES). Once the constrained parameters hyperspace $\Pi_x \subseteq \mathbb{R}^m$ is defined, the method explores all the possible combinations of the m parameters $\mathbf{x}$. Finally, having examined the entire continuous objective function $f(\mathbf{x}) : \mathbb{R}^m \mapsto \mathbb{R}$ space, it finds the best fitting combination, i.e. $argmin_x\{f(\mathbf{x}) : \mathbf{x} \in \Pi_x\}$. Indeed, this method is not feasible in real applications as it would require infinite computational time. For this reason, more advanced ways of exploring sub-sets of Π_x are adopted. One of them is the Grid Search (GS), which is a global optimisation method, as it discretizes Π_x by defining a m-dimensional grid, made with $p \in N$ equidistant values inside each parameter range. Yet, the number of evaluations E of the objective function f grows exponentially with the number of active variables, i.e. $E = p^m$, making GS extremely inefficient. The Coordinate Search (CS), partially overcomes the problems related to previously analysed methods. In particular, once a step size parameter δ^k is defined, each algorithm iteration k evaluates $2m$ parameters combinations defined as $P^k := \{\mathbf{x}^k \pm \delta^k\}$, where P^k is called the poll set. If one element belonging to the poll set P^k is an optimizer of $\mathbf{x}^k$, then the incumbent solution $\mathbf{x}^{k+1}$, is updated, otherwise $\mathbf{x}^{k+1} = \mathbf{x}^k$ and $\delta^{k+1} = \delta^k/2$. The CS method seeks for an actual local optimizer, meaning it is strongly dependent on the initial guess. For this reason, a Latin Hypercube Sampling (LHS) is initially performed in order to choose a good starting point.

The CS method is the precursor of PS and MADS. In fact, they share the working principle of CS with two major differences:

- the polling set is not just constituted by positive and negative coordinate directions;
- when a descent direction is identified the algorithms extend the radius of the search in that direction, i.e. δ^k can both increase and decrease.

In the PS algorithm, once a grid is initialised in the neighbourhood of the incumbent solution, a polling set is built, with random directions and distances, and evaluated. A mesh size adjustment parameter is introduced, which decreases the step size parameter δ if a mesh optimizer is not found. On the contrary, when a better point $\mathbf{x}^k$ is found, δ is increased to help the algorithm recovering from a bad initial choice of δ^0. In MADS, the only update with respect to PS concerns the mesh. In particular, the frame size parameter Δ^k substitutes the step size parameter in the poll step. This parameter defines a frame of side Δ^k around the incumbent solution. In case of $\mathrm{M} = 2$, the poll set would have 8 different directions. The mesh size parameter $\delta^k \leq \Delta^k$ is used to create a sub-grid internal to the frame to increase the number of possible polling directions. Usually, the ratio δ^k/Δ^k is initialized and kept constant, so that the frame size is the parameter to be decreased/increased in case of unsuccessful/successful evaluations. It has to be pointed out that MADS converge to PS whether $\delta^k/\Delta^k = 1$ is adopted.

The SW method is a local non-gradient based approach, which uses a multivariate normal distribution of the parameters to aid in the randomized search approach. A radius ρ_i around the incumbent solution $\mathbf{x}^k$ is defined, which determines the search space $S_x \subseteq \Pi_x$. If a better solution is found, the radius is increased, and the new search space is determined centred at the new optimal solution. If no better solution is found within this space after a specific number of evaluations, ρ_{i+1} is reduced, restricting the search space. The counter $i = 0, 1, \ldots, n$ keeps track on the number of radius contractions before convergence. The search ends if ρ is smaller than a specified threshold.

The DIRECT methodology is a global non-gradient based optimizer, which starts with a random set of samples and uses these to divide the parameter space Π_x into promising and non-promising search regions. In the promising regions it utilizes fast local optimization approaches, i.e. only changing one parameter at a time, while for the non-promising regions it uses slower global optimization strategies, changing several parameters simultaneously. The regions are then further divided into sub-regions, which are separated into promising and non-promising regions again, and the procedure repeats itself until a stopping criteria has been reached. This balance between local and global search methods has been highly efficient for global optimization problems.

The combination of the different features of these algorithms can even be used in combination, as one methodology can be used to find a good starting point for a subsequent optimization with another methodology. This is in fact what the author of the DIRECT methodology suggest [40]: first find a region in the parameter space with good potential, and then refine the search with a local optimization method.

2.3. Optimization targets

Finding the optimal combination of a set of uncertain kinetic parameters with respect to some experimental targets requires an optimization process typically involving several thousand evaluations. Even if response surface techniques are used, several hundred evaluations are needed initially for creating the response surface. It is therefore important that the numerical simulations are fast and robust, to ensure that the optimization reaches convergence within a reasonable time frame. In the field of kinetic mechanism optimization, it is therefore common to use experimental data from so-called 0D reactors or 1D flames as targets. The present work focuses on the use of the following solvers: Batch Reactor, Plug Flow Reactor (PFR), Perfectly Stirred Reactor (PSR), Rapid Compression Machine (RCM), Shock-Tube (ST) and Laminar Flame Speed (LFS). Experimental data from any of these solver types can therefore be used as targets in the optimization.

2.4. Objective function

In any optimization problem, the optimal solution is always determined based on the objective function (Obj). This is a measure which determines how close the current evaluation (Y^{sim}) is to the experimental targets (Y^{exp}). There exists many different ways to calculate the objective function in an optimization problem, but arguably one of the most common is the L2-norm, also referred to as Least Squares (LS). Here the residual between between the experimental data Y^{exp} and the simulated value Y^{sim}, are squared for each data point (j) in each data set (i):

$$Obj = \sum_{i}^{N} \sum_{j}^{N_i} (Y_{ij}^{exp} - Y_{ij}^{sim})^2 \tag{1}$$

where N refers to the total number of data sets and N_i the number of data points in data set i.

This approach has been used in many works, but this is basically weighing each experimental point equally against each-other. Instead, if an experimental data point has a large uncertainty correlated to it, it would be beneficial to say that this experimental target should have less weight in the objective function, and vice versa for experimental points with small uncertainty. This effect can of course be achieved by a weighted LS definition, and as first introduced in [41], the weight can be directly correlated to the experimental uncertainty by dividing the residual in Eq. 1 with the standard deviation (σ), giving:

$$Obj = \sum_{i}^{N} \sum_{j}^{N_i} \left(\frac{Y_{ij}^{exp} - Y_{ij}^{sim}}{\sigma_{ij}} \right)^2 \tag{2}$$

By weighing the residuals with σ, experimental data with large uncertainty have a lower impact in the overall sum.

In order to avoid that data sets with a large number of data points become overly important, it is also important to weight the objective function based on the number of data points in each data set. The objective function for each data set is therefore divided by the number of data points in each specific data set (N_i), thus removing the bias towards data sets with many experimental targets. Eq. 2 therefore becomes:

$$Obj = \sum_{i}^{N} \frac{1}{N_i} \sum_{j}^{N_i} \left(\frac{Y_{ij}^{exp} - Y_{ij}^{sim}}{\sigma_{ij}} \right)^2 \tag{3}$$

This is the formulation of the objective function that was used for all of the test cases in Section 3.

The determination of the standard deviation is in this approach is crucial for the value of the objective function. As discussed by Olm et al. [26], the standard deviation can be estimated as a combination of the standard deviation based on the reported experimental errors (σ_{exp}) and the standard deviation calculated based on the experimental scatter (σ_{stat}):

$$\sigma = \sqrt{\sigma_{stat}^2 + \sigma_{exp}^2} \tag{4}$$

where σ_{exp} is calculated based on how many standard deviations the experimental error represents, i.e.

$$\sigma_{exp} = \frac{Y^{exp} \cdot \varepsilon}{X} \tag{5}$$

where ε is the reported relative experimental error and X is the number of standard deviations that the experimental error represents. If no specific information regarding how many standard deviations the experimental error represents was given, it was assumed to be 2 standard deviations in this work.

For many cases, only the experimental error is given together with the experimental values. With no repetition of the experimental points, the statistical standard deviation cannot be determined, and the total standard deviation can then be estimated as only the σ_{exp}.

As mentioned in Olm et al. [42], for experimental targets that have a scatter proportional to the experimental value itself (more specifically data such as Ignition Delay Time (IDT)) the objective function should be calculated using the natural logarithm of the experimental and simulated values, i.e. $Y_{ij}^{exp} = ln(y_{ij}^{exp})$ and $Y_{ij}^{sim} = ln(y_{ij}^{sim})$, where y_{ij}^{exp} and y_{ij}^{sim} refers to the absolute experimental/simulated value for data set i and point j. The same applies to σ, i.e. for IDT the natural logarithm of σ_{ij} is used rather than the absolute value. This ensures that the objective function is more evenly distributed between the data points, and it will be easier to achieve overall improvements for each point, rather than only for some. For other experimental targets, such as species concentrations and laminar flame speeds, the objective function is calculated directly based on the absolute value of the experimental and simulated values, i.e. $Y_{ij}^{exp} = y_{ij}^{exp}$ and $Y_{ij}^{sim} = y_{ij}^{sim}$. For the specific cases where $Y^{exp} = 0$, which can occur for species concentrations, the σ_{exp} from Eq. 5 is assumed to be equal to the minimum non-zero value from that data set, in order to avoid numerical issues in Eq. 3.

2.5. Uncertainty range of the kinetic parameters

While performing optimization of kinetic mechanisms, it is very important to consider the limits of the rate constants for each reaction. These limits can be determined based on the so-called uncertainty parameter (f) (or Error limits [43]) as $k_{min} = k_0 \cdot 10^{-f}$ and $k_{max} = k_0 \cdot 10^{f}$, where k_0 is the nominal rate constant. An example of this can be appreciated in Figure 2 where the rate coefficient for reaction 725, from the POLIMI C1C3 V1412 [44] mechanism, is plotted together with k_{min} and k_{max}, considering a constant f of 0.3.

Reversely, f can be determined from the spread of the direct experimental data and theoretical estimations of a specific rate constant ($f = 0.5 \cdot log_{10}(k_{max}/k_{min})$) available in the literature. These limits can also be

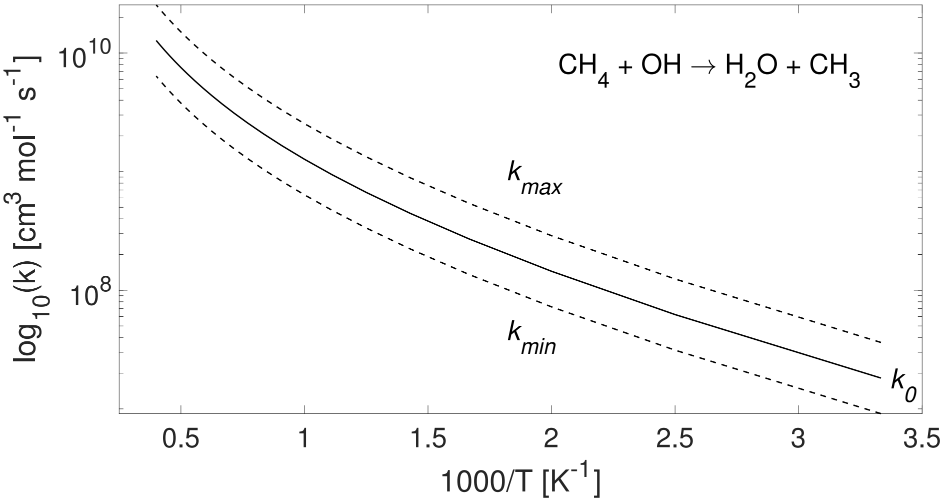


Figure 2: Rate coefficient for reaction 725 from the POLIMI C1C3 V1412 [44] mechanism, with k_0 (—), k_{min} and k_{max} (- -).

used to determine the specific uncertainty range of the kinetic parameter (A, β, and E_a) as done by Fürst et al. [45]. A similar approach was also used by Turànyi and co-workers [46] in their optimization studies. `OptiSMOKE++` uses the approach from [45] to calculate the range of each kinetic parameter, but specific limits can be expressed by the user as well.

In order to reduce CPU-expensive calculations, `OpenSMOKE++` uses the following form of the rate constant k:

$$k = exp\left(ln(A) + \beta \cdot ln(T) - \frac{E}{RT}\right) \tag{6}$$

This is therefore also employed in `OptiSMOKE++`, and $ln(A)$, β, and E_a/R are considered as active parameters for the optimization. Both the low and high pressure limit kinetic parameters from fall-off reactions [47] can be used as uncertain parameters in `OptiSMOKE++`, as well as third body efficiencies.

In this work, the focus is not on the characterization of the distribution of the rate constants. For this reason, the kinetic parameters are considered uniformly distributed within their uncertainty bounds, as discussed by Nagy et al. [46].

2.6. Penalty function

Although the limits of each uncertain kinetic parameter are individually specified with the procedure described above, the non-linear nature of the modified Arrhenius curve does not necessarily ensure that during optimization the rate constant stays within its initially prescribed bounds for the complete temperature span (considered as 300-3000 K to correctly account for realistic temperature conditions in combustion applications). It is therefore important to do a check of the proposed parameter combinations, to see that the rate constants are within the uncertainty limits. The `OptiSMOKE++` code handles this by utilizing a so-called penalty function. Penalty functions can be used for many purposes. For example, Sikalo et al. [27] used a penalty function for keeping the optimized parameters close to the original values. However, in `OptiSMOKE++` the penalty function is implemented to forcefully increase the objective function value for parameter combinations which do not respect the uncertainty limits of the rate constants, for all of the reactions considered. This ensures that the optimizer does not choose a parameter combination which violates this restriction, and finds the optimal combination of parameters which satisfies the constraints. Consequently the use of this penalty function results in quite significant computational savings, as the penalized parameter combinations are not simulated using `OpenSMOKE++`.

The application of this externally defined penalty function allows the users to freely use all the available optimization methodologies available in `DAKOTA`, regardless if they support non-linear constraints or not. In fact, the combination of a penalty function and non-gradient based global optimizers is very efficient for constrained optimization problems such as kinetic mechanism optimization. However, it should be said that for gradient based optimization approaches, penalty functions are not a good choice, as these algorithms depend on the prior evaluations for the estimation of the slope of the objective function. The use of penalty functions disrupts the natural slope of the objective function and gradient based algorithms would then face issues in finding the optimal solution.

3. Test cases

In this section, some test cases will be presented, which illustrates the functionality of the `OptiSMOKE++` toolbox. The different procedures, and the cases, were not necessarily chosen based on efficiency or any specific interests, instead they were chosen in order to show the different features available in the `OptiSMOKE++` toolbox.

3.1. Test case 1: Ignition Delay Time for non-conventional conditions in a Plug Flow Reactor

As a key physico-chemical property of a specific mixture [48], the IDT is an important measure for determining if the kinetic mechanism is accurately predicting the onset of combustion correctly or not. The ignition strongly controls the successive combustion process, which is why it is commonly used as a target for kinetic mechanisms in both validation and optimization.

The experimental target data used in this test case are from Sabia et al. [49], where the ignition delay time of biomass pyrolysis gas (1% C_2H_4, 2% C_2H_6, 10% CH_4, 25% CO, and 62% CO_2) in a PFR was evaluated during Moderate or Intense Low-oxygen Dilution (MILD) conditions, i.e. high inlet temperature and diluted conditions. The IDT was evaluated as the time when the mixture reaches a temperature 10 K higher than the inlet temperature. This experimental data set consists of fuel diluted with nitrogen at different oxygen ratios (Ω) [50]. Ω is defined as the ratio between the amount of oxygen, in both the fuel and oxidizer, and the amount of oxygen required for stoichiometric combustion of the mixture. This is commonly use for fuels which contain partially oxidized compounds (in this case CO). The experimental uncertainty (seen in Figure 3) was evaluated with respect to the displacement of the thermocouples and the inlet velocity from the experimental measurements [49].

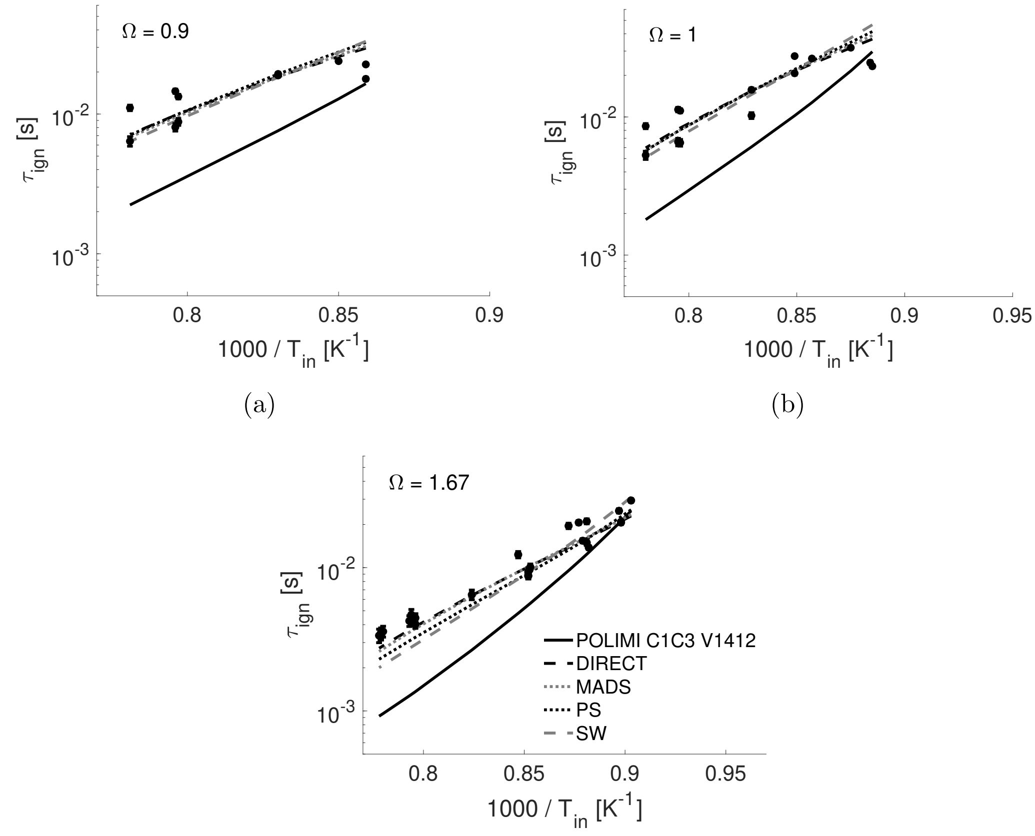
The nominal mechanism used for this test case was the POLIMI C1-C3 V1412 [44] mechanism, consisting of 107 species and 2642 reactions. All the kinetic parameters cannot be optimized for such a large mechanism, which is why an initial study was performed in order to determine the reactions having the largest impact. More details about this can be found in Section S1 in the Supplementary Material. This preliminary analysis selected 11 reactions, and 26 uncertain parameters, which were all handled simultaneously in the optimization study, thus removing necessary intervention by the user. In Table S1 the kinetic parameters considered for this optimization can be found.

This test case was performed using all the different optimization methodologies descried in 2.2.1, namely: `coliny_direct` (DIRECT), `mesh_adaptive_search` (MADS), `coliny_pattern_search` (PS) and `coliny_solis_wets` (SW).

To get a fair comparison between the different optimization methodologies, each method was allowed to run for 10 000 evaluations, and the default settings were used for each methodology. The optimal combination of the uncertain parameters found by each method are presented in Table S5 and the performance of each mechanism can be appreciated in Figure 3. The performance of the different approaches are very similar for the different Ω, with some quite significant improvements compared to the nominal mechanism.

A comparison of the evolution of the minimum of the objective function for the different methods, together with number of evaluations performed, number of penalties and runtime (on one processor) for each method, can all be seen in Figure 4. It should be mentioned that internal stopping criteria for each algorithm are applied, which is why the number of evaluations performed does not strictly correspond to 10 000 for each method.

It can clearly be seen in Figure 4 that the DIRECT methodology is performing overall the best, both in terms of how many evaluations it needs to find good combinations, and in finding the absolute minimum compared to the other methods. However, the runtime is also the second longest compared to the other methods. This is due to the fact that the number of non-penalized evaluations is high for this method. Indeed, only PS shows a lower number of penalties, but also a longer runtime. In fact, the runtime is directly proportional to the number of non-penalized evaluations (# Evaluations $-$ # Penalties) performed, as the application of the penalty function is instantaneous (see Figure 1). It can also be seen that the SW methodology

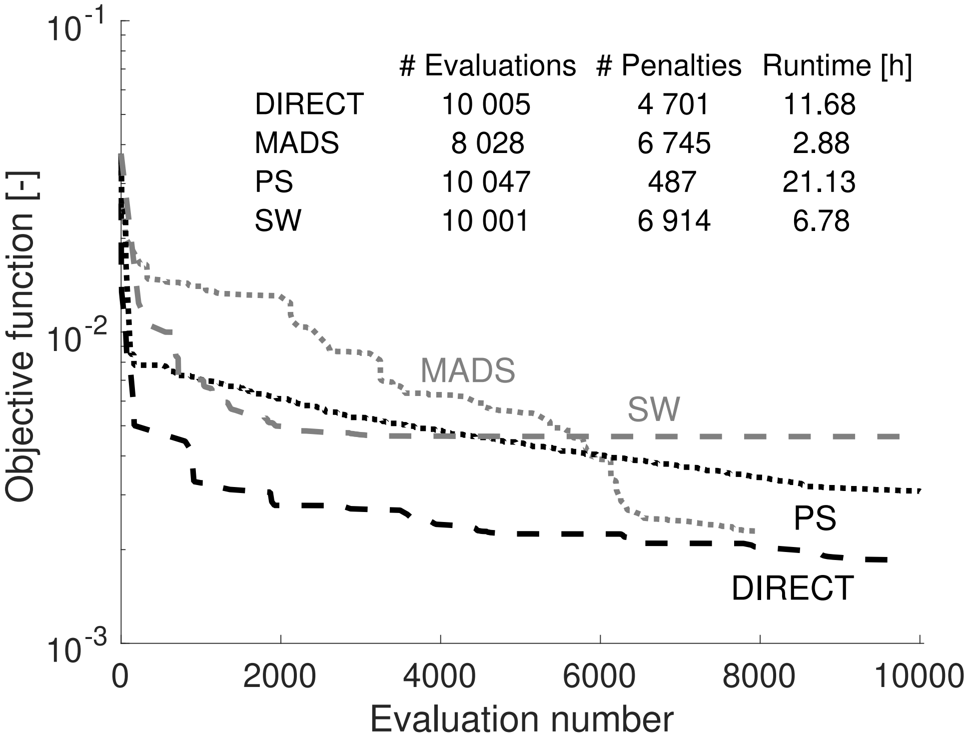


(a) (b)

(c)

Figure 3: Test case 1, IDT for Ω=0.9, 1 and 1.67 at different inlet temperatures, where the experimental data is presented by the black dots with corresponding error bars. The different kinetic mechanisms are represented by the black and grey solid, dashed and dotted lines as follows: POLIMI C1C3 V1412 [44] (—), DIRECT (- -), MADS (···), PS (···) and SW (- -).

quite quickly converges to its optimum. After roughly 3 000 evaluations, no drastic reductions of the objective function is found with the SW methodology. The PS methodology shows a very slow convergence rate with respect to the other methods, which is inherently due to the more local approach of



	# Evaluations	# Penalties	Runtime [h]
DIRECT	10 005	4 701	11.68
MADS	8 028	6 745	2.88
PS	10 047	487	21.13
SW	10 001	6 914	6.78

Figure 4: Evolution of the minimum objective function values, number of evaluations, number of penalties and total runtime on one processor for the different methodologies used in test case 1: DIRECT (- -), MADS (···), PS (···) and SW (- -).

the PS methodology. Finally, the MADS methodology also shows a relatively slow convergence rate with respect to the number of evaluations. However, it also has the largest percentage of penalties with respect to the total number of evaluations. Which consequently results in the fastest runtime out of all the methodologies used.

To further aid the comparison of the different methodologies, the ratio between the explored range and the allowed range of each parameter was evaluated. These values can be found in Table S10 in the Supplementary Material. Based on this evaluations, it can be seen that the DIRECT methodology is evaluating quite a large part of the parameter space, but more importantly, the percentage of the parameter space explored considering only non-penalized evaluations is still very large. Instead, with the MADS methodology, a larger part of the parameter space is explored, but due to the fact that many of the evaluations with the MADS methodology results in penalties, the exploration of the parameter space considering the non-penalized evaluations, is very small for the MADS method. The PS method, similarly as the DIRECT method, shows only a slight reduction of the explored parameter space comparing the complete set of evaluations and the non-penalized evaluations. However, the explored parameter space is quite small for the PS method, which is due to the more local approach employed by the PS methodology. The SW method shows a more sporadic nature in the explored parameter space, considering both the complete set of evaluations and only the non-penalized evaluations.

Considering all this, the DIRECT methodology can be considered to perform best out of these four methodologies, and was therefore used for the remaining test cases.

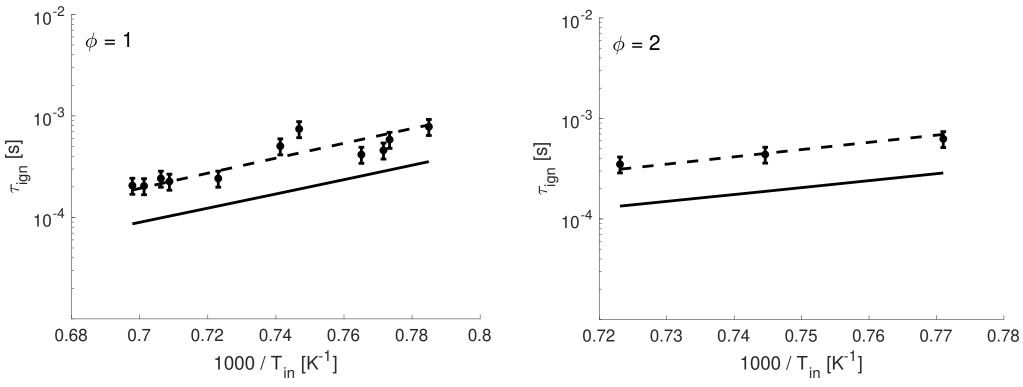
3.2. Test case 2: Ignition Delay Time at high pressures using data from a Shock-Tube

A common approach for measuring the IDT, especially at higher pressures, is either with ST or RCMs. As mentioned in Cuoci et al. [33], the IDT data from both ST and RCMs can be reproduced using a transient closed homogeneous batch reactor simulation, where facility effects can be accounted for using a volume history. This can either be specified using a pressure coefficient that emulates the change in volume and pressure, or by a user defined volume time history profile. `OptiSMOKE++` utilizes these features for the simulation of STs and RCMs.

For this test case, the experimental targets consist of IDT of methane diluted in carbon dioxide in a ST, at high pressures (100 bar) [51]. The IDT was experimentally evaluated at the moment where the maximum change of the exited species OH^* was measured. However, due to the fact that the experiments were performed at very high pressure, the discrepancy between the OH and OH^* profiles were minimal, and the numerical IDT could therefore be evaluated at the moment of maximum change of OH. This was also confirmed by personal communication with the authors of the paper [51]. The experiments were performed at stoichiometric (ϕ=1) and rich (ϕ=2) conditions. The kinetic mechanism used for this case was the GRI 3.0 [6] mechanism, which consists of 53 species and 325 reactions. Similarly to the previous case, an initial study was performed in order to find the most impactful reactions for the different conditions. The 9 reactions and corresponding 20 parameters are reported in Table S2.

The results can be seen in Figure 5, and the nominal and optimized parameter values, together with the objective function values, can be found in Table S6.

It can clearly be seen in Figure 5 that the optimized mechanism is capturing the experimental data very well.



(a)

(b)

Figure 5: Test case 2, IDT for methane at ϕ= 1 and 2, where the experimental data is presented by the black dots with corresponding error bars. The nominal kinetics (GRI 3.0 [6]) is represented by the solid lines (—) and the optimized mechanism by the dashed lines (- -).

3.3. Test case 3: Methanol oxidation in a Jet Stirred Reactor

In this example, the optimization targets consist of species concentrations of methanol (CH_3OH) oxidation at different temperatures in an iso-thermal JSR [52]. A JSR can be modeled as a Perfectly Stirred Reactor (PSR) in experimental studies. Indeed, the injection occurs through jet nozzles with a high velocity, which ensures instantaneous mixing inside the reactor. The species concentrations were measured after a fixed residence time (τ=0.05 s), at atmospheric pressure, and at ϕ=0.5 and 1. The injected mixture consisted of 2000 ppm CH_3OH, 6000/3000 ppm O_2 and was balanced out with N_2. The target species for this study were limited to the major species measured (CH_3OH, O_2, CO, CO_2), but a larger number of species can be handled by `OptiSMOKE++`. The nominal kinetics used for this case was again the POLIMI C1-C3 V1412 [44], and the sensitivity study, for determining which reactions to consider in the optimization, was performed based on each targeted species. This resulted in 7 reactions and 17 kinetic parameters, which are listed in Table S3.

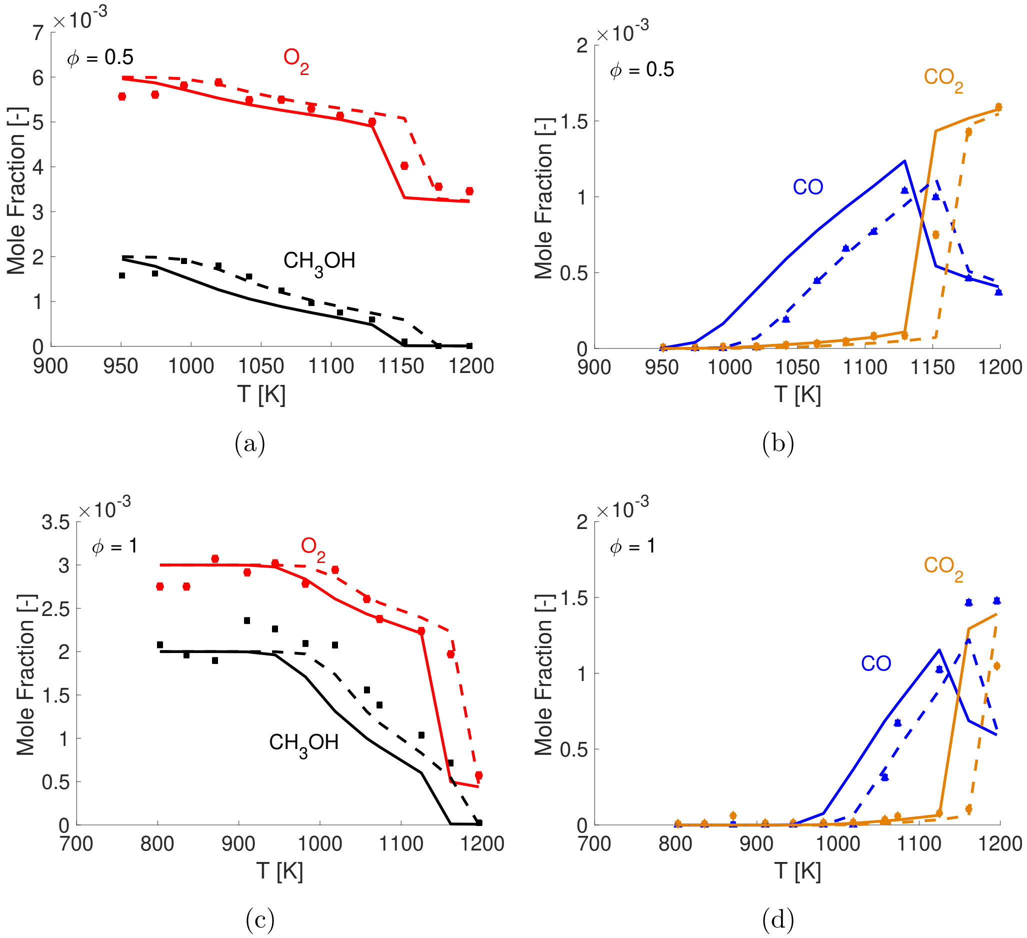
A comparison between the nominal and the optimized mechanism is reported in Figure 6, as well as the parameter values are presented in Table S7. As no experimental uncertainty was reported in [52], a standard uncertainty of 1% of the highest measured concentration of respective species was considered for each point, according to recommendations from Olm et al. [42].

It can clearly be seen that an overall improvement is achieved for each species profile. This can especially be seen for CO and CO_2 in Figures 6b and 6d.

3.4. Test case 4: Combined optimization of IDT and JSR data

In practice, many different targets will be used for optimization, ensuring that the optimized kinetics performs good for a wide range of conditions. The combined optimization of test cases 1 and 3 is therefore used to illustrate this capability of the code. As in test case 1 and 3, the POLIMI C1C3 V1412 [44] mechanism was used. The combination of reactions from Tables S1 and S3 was used in this optimization. The results are presented in Figures 7-8, as well as in Table S8.

Comparing the results from test case 3 (Figure 6) with Figure 8, it can be seen the same improvements were found for the two optimizations. The comparison of the results from test case 1 (Fig. 3) and test case 4 (Fig. 7) shows that the very good agreement obtained in Fig. 3 was not found. Nevertheless, Fig. 7 shows that a substantial improvement with respect to the original kinetic mechanism was achieved for IDT data also in the case of combined optimization.



(a)

(b)

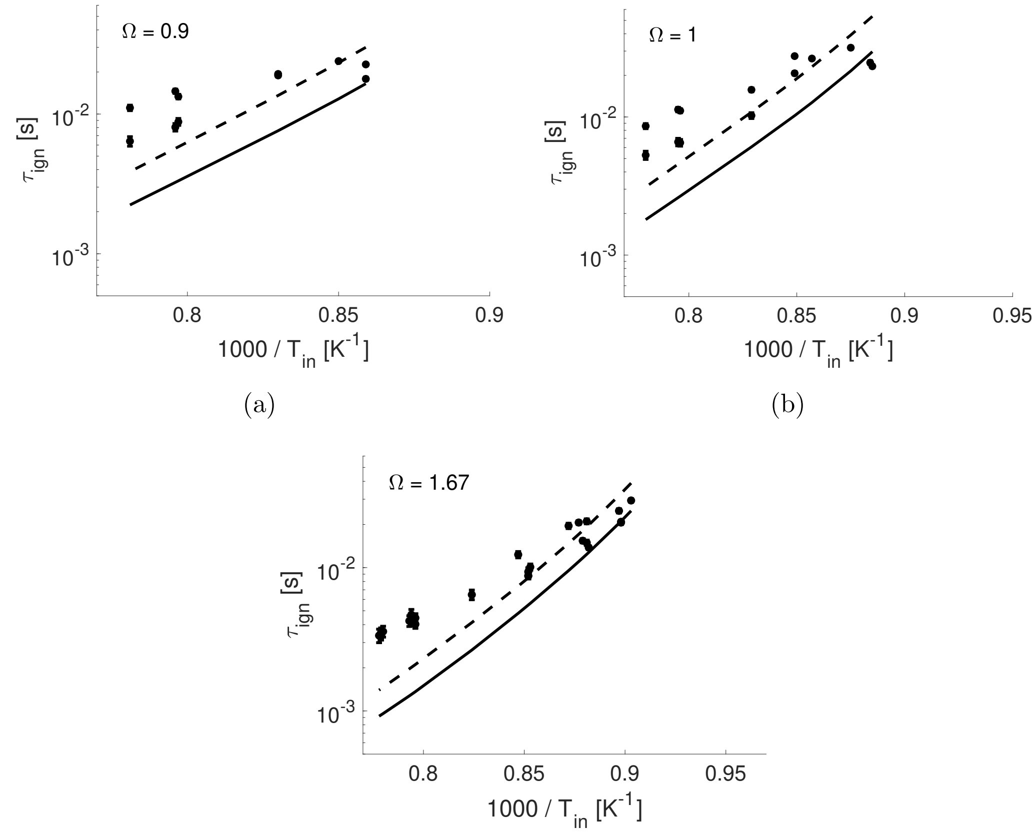
(c)

(d)

Figure 6: Test case 3, oxidation of methanol (CH_3OH) at atmospheric pressure in an isothermal JSR at different temperatures and at ϕ=0.5 and 1. The experimental data is presented by the scatter, with corresponding error bars. The nominal kinetics (POLIMI C1C3 V1412 [44]) is represented by the solid lines (—) and the optimized kinetics by the dashed lines (- -).

3.5. Test case 5: Optimization of Laminar Flame Speed of methanol

As a key quantity for describing the combined effect of a mixtures diffusivity, reactivity and exothermicity [44], the LFS is often used as a target for

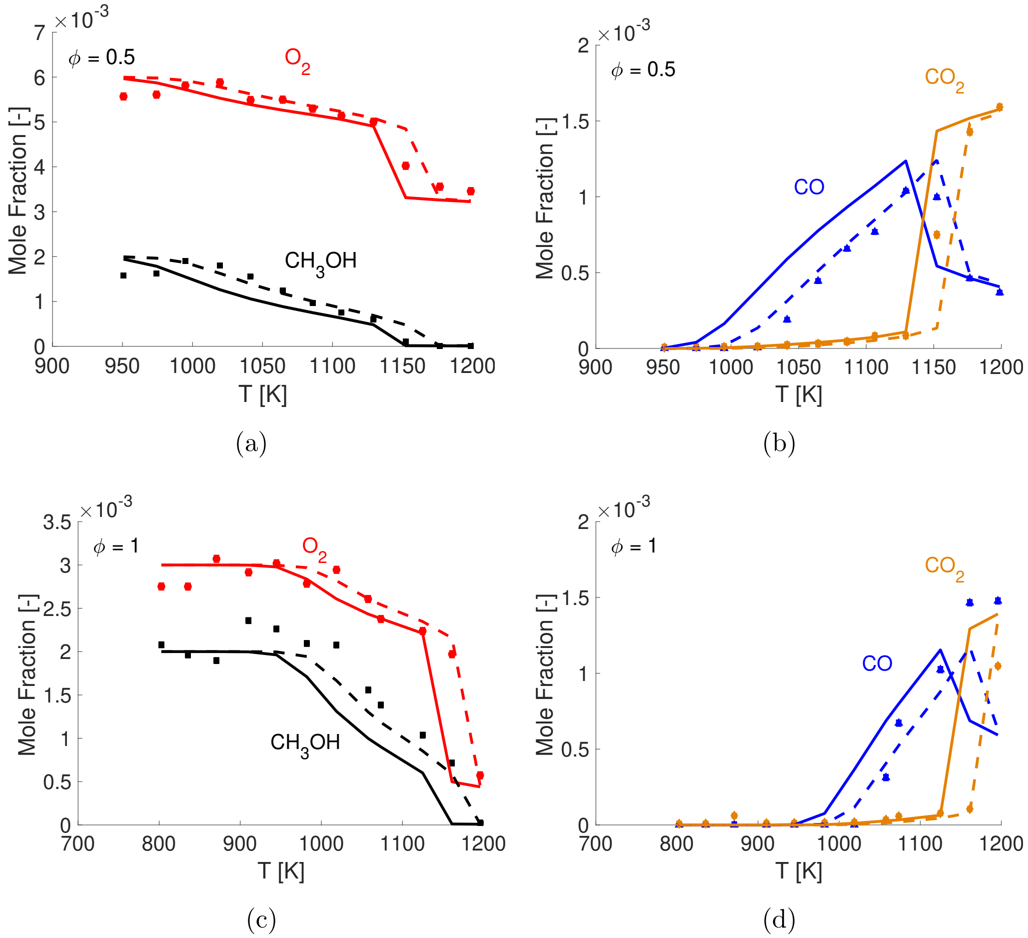


(a) (b)

(c)

Figure 7: Test case 4, IDT for Ω=0.9, 1 and 1.67 at different inlet temperatures, where the experimental data is presented by the black dots with corresponding error bars. The nominal kinetics (POLIMI C1C3 V1412 [44]) is represented by the solid lines (—) and the optimized kinetics by the dashed lines (- -).

the development, validation and optimization of a kinetic mechanism at low temperatures. The LFS describes at which speed the flame front is propagating back towards the unburned gases. When the inlet velocity of the mixture is equal to the LFS, a stable flame front is established. The numerical evaluation of the LFS are mostly done using a 1D premixed flame simulations.



(a)

(b)

(c)

(d)

Figure 8: Test case 4, oxidation of methanol (CH$_3$OH) at atmospheric pressure in an isothermal JSR at different temperatures and at ϕ=0.5 and 1. The experimental data is presented by the scatter, with corresponding error bars. The nominal kinetics (POLIMI C1C3 V1412 [44]) is represented by the solid lines (—) and the optimized kinetics by the dashed lines (- -).

The numerical solution of such a system depends on the inlet mixture composition, kinetic and thermodynamic parameters, as well as the transport properties. `OptiSMOKE++` supports the application of LFS as targets for the optimization by using the premixed laminar flame solver of `OpenSMOKE++`.

The experimental targets used for this test case consists of LFS data of methane/air diluted with 10% CO_2, at 1 bar and an inlet temperature of 473 K [53]. The experimental measurements were performed for an equivalence ratio between 0.7 and 1.2. The kinetic mechanism used for this test case was the GRI 3.0 [6] mechanism and the initial study resulted in determining 3 reactions and 7 kinetic parameters that were used in the optimization study, and are listed in Table S4.

The results of the optimization can be seen in Table S9 and Figure 9.

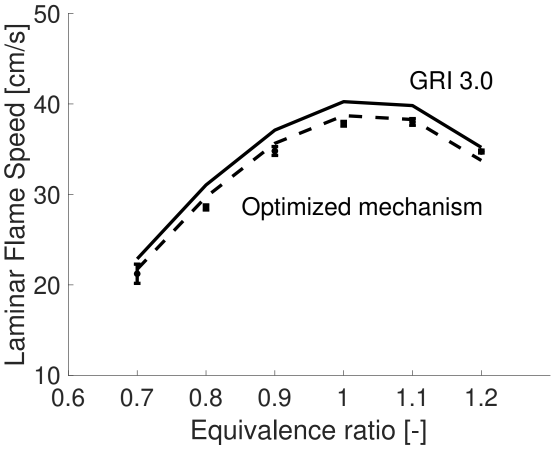


Figure 9: Test case 5, LFS of methane/air diluted with 10% CO_2 at atmospheric pressure and an inlet temperature of 473 K. The experimental data is presented by the black dots with corresponding error bars, and the nominal kinetics (GRI 3.0 [6]) is represented by the solid lines (—) and the optimized mechanism by the dashed lines (- -).

Even though there are only some minor improvements, the optimized mechanism is able to capture the experimental targets very well.

4. Conclusions

This paper describes the different features of `OptiSMOKE++`, a toolbox that couples the optimization toolkit `DAKOTA` and `OpenSMOKE++`, a framework for solving reacting systems with detailed kinetics. `OptiSMOKE++` can be used to optimize kinetic mechanisms with respect to specified experimental targets, to improve the performance of the kinetic mechanism. The toolbox consists of different features, which can be summarized as:

- possibility to use experimental targets from different facilities, i.e. Batch Reactors, PFRs, PSRs, ST, RCMs and 1D flames. Experimental data from different facilities can also be used simultaneously.
- different optimization methodologies, available in the `DAKOTA` toolkit, can be employed.
- in order to produce a feasible optimized kinetic mechanism (i.e. with physically viable kinetic parameters), `OptiSMOKE++` utilizes a penalty function which forcefully increases the objective function value when a set of kinetic parameters gives a rate coefficient outside the uncertainty bounds. This ensures that the optimizer choose an optimal point which still gives physically viable rate coefficient values, as well as it allows for computational savings as penalized parameter combinations are not evaluated using `OpenSMOKE++`.

All these features allows the user to optimize a kinetic mechanism with respect to the targeted experimental conditions in an efficient way.

Acknowledgements

This work has been carried out with the aid of the Short Term Scientific Mission Program of SMARTCATs COST Action (CM1404, www.smartcats.eu), supported by COST (European Cooperation in Science and Technology, www.cost.eu) as well as it has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Sklodowska-Curie grant agreement No 643134, and from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme under grant agreement No 714605. The second Author also acknowledges the support of Funds pour la Recherche Scientifique (FNRS) through a FRIA fellowship of the project "HOPTIMAL: Hierarchical development of OPTimised kinetic Mechanisms for Advanced combustion technoLogies".

References

[1] H. J. Curran, Developing detailed chemical kinetic mechanisms for fuel combustion, Proceedings of the Combustion Institute 37 (1) (2019) 57–81. `doi:10.1016/j.proci.2018.06.054`.

[2] T. Turányi, A. S. Tomlin, Analysis of Kinetic Reaction Mechanisms, Springer, 2015. `doi:10.1007/978-3-662-44562-4`.

[3] H. Wang, D. A. Sheen, Combustion kinetic model uncertainty quantification, propagation and minimization, Progress in Energy and Combustion Science 47 (2015) 1–31. `doi:10.1016/j.pecs.2014.10.002`.

[4] M. Frenklach, H. Wang, C.-L. Yu, M. Goldenberg, C. Bowman, R. Hanson, D. Davidson, E. Chang, G. Smith, D. Golden, W. Gardiner, V. Lissianski, GRI-Mech 1.2.
URL `http://combustion.berkeley.edu/gri-mech/`

[5] C. Bowman, R. Hanson, D. Davidson, W. J. Gardiner, V. Lissianski, G. Smith, D. Golden, M. Frenklach, M. Goldenberg, GRI-Mech 2.11.
URL `http://combustion.berkeley.edu/gri-mech/`

[6] G. P. Smith, D. M. Golden, M. Frenklach, N. W. Moriarty, B. Eiteneer, M. Goldenberg, C. T. Bowman, R. K. Hanson, S. Song, W. C. J. Gardiner, V. V. Lissianski, Z. Qin, GRI-Mech 3.0.
URL `http://combustion.berkeley.edu/gri-mech/`

[7] M. Frenklach, A. Packard, P. Seiler, Prediction uncertainty from models and data, in: Proceedings of the 2002 American Control Conference (IEEE Cat. No.CH37301), Vol. 5, IEEE, 2002, pp. 4135–4140. `doi:10.1109/ACC.2002.1024578`.

[8] P. Seiler, M. Frenklach, A. Packard, R. Feeley, Numerical approaches for collaborative data processing, Optimization and Engineering 7 (4) (2006) 459–478. `doi:10.1007/s11081-006-0350-4`.

[9] R. Feeley, M. Frenklach, M. Onsum, T. Russi, A. Arkin, A. Packard, Model Discrimination Using Data Collaboration †, The Journal of Physical Chemistry A 110 (21) (2006) 6803–6813. `doi:10.1021/jp056309s`.

[10] T. Russi, A. Packard, M. Frenklach, Uncertainty quantification: Mak-

ing predictions of complex reaction systems reliable, Chemical Physics Letters 499 (1-3) (2010) 1–8. `doi:10.1016/j.cplett.2010.09.009`.

[11] D. A. Sheen, H. Wang, The method of uncertainty quantification and minimization using polynomial chaos expansions, Combustion and Flame 158 (12) (2011) 2358–2374. `doi:10.1016/j.combustflame.2011.05.010`.

[12] D. A. Sheen, C. M. Rosado-Reyes, W. Tsang, Kinetics of H atom attack on unsaturated hydrocarbons using spectral uncertainty propagation and minimization techniques, Proceedings of the Combustion Institute 34 (1) (2013) 527–536. `doi:10.1016/j.proci.2012.06.062`.

[13] Y. Xin, D. A. Sheen, H. Wang, C. K. Law, Skeletal reaction model generation, uncertainty quantification and minimization: Combustion of butane, Combustion and Flame 161 (12) (2014) 3031–3039. `doi:10.1016/j.combustflame.2014.07.018`.
URL `http://dx.doi.org/10.1016/j.combustflame.2014.07.018`

[14] O. Park, P. S. Veloo, D. A. Sheen, Y. Tao, F. N. Egolfopoulos, H. Wang, Chemical kinetic model uncertainty minimization through laminar flame speed measurements, Combustion and Flame 172 (2016) 136–152. `doi:10.1016/j.combustflame.2016.07.004`.
URL `http://dx.doi.org/10.1016/j.combustflame.2016.07.004`

[15] G. Smith, Y. Tao, H. Wang, Foundational Fuel Chemistry Model Version 1.0 (FFCM-1) (2016).
URL `http://nanoenergy.stanford.edu/ffcm1`

[16] Y. Tao, G. P. Smith, H. Wang, Critical kinetic uncertainties in modeling hydrogen/carbon monoxide, methane, methanol, formaldehyde, and ethylene combustion, Combustion and Flame 0 (2018) 1–12. `doi:10.1016/j.combustflame.2018.02.006`.

[17] Y. Tao, H. Wang, Joint probability distribution of Arrhenius parameters in reaction model optimization and uncertainty minimization, Proceedings of the Combustion Institute 37 (1) (2019) 817–824. `doi:10.1016/j.proci.2018.08.052`.

[18] L. Cai, H. Pitsch, Mechanism optimization based on reaction rate rules, Combustion and Flame 161 (2) (2014) 405–415. `doi:10.1016/j.combustflame.2013.08.024`.

[19] L. Cai, H. Pitsch, Optimized chemical mechanism for combustion of gasoline surrogate fuels, Combustion and Flame 162 (5) (2015) 1623–1637. `doi:10.1016/j.combustflame.2014.11.018`.

[20] L. Cai, H. Pitsch, S. Y. Mohamed, V. Raman, J. Bugler, H. Curran, S. M. Sarathy, Optimized reaction mechanism rate rules for ignition of normal alkanes, Combustion and Flame 173 (2016) 468–482. `doi:10.1016/j.combustflame.2016.04.022`.

[21] F. vom Lehn, L. Cai, H. Pitsch, Sensitivity analysis, uncertainty quantification, and optimization for thermochemical properties in chemical kinetic combustion models, Proceedings of the Combustion Institute 37 (1) (2019) 771–779. `doi:10.1016/j.proci.2018.06.188`.

[22] F. vom Lehn, L. Cai, H. Pitsch, Impact of thermochemistry on optimized kinetic model predictions: Auto-ignition of diethyl ether, Combustion and Flame 210 (2019) 454–466. `doi:10.1016/j.combustflame.2019.09.011`.

[23] F. vom Lehn, L. Cai, H. Pitsch, Investigating the impacts of thermochemical group additivity values on kinetic model predictions through sensitivity and uncertainty analyses, Combustion and Flame 213 (2020) 394–408. `doi:10.1016/j.combustflame.2019.12.011`.

[24] T. Turányi, T. Nagy, I. G. Zsély, M. Cserháti, T. Varga, B. T. Szabó, I. Sedyó, P. T. Kiss, A. Zempléni, H. J. Curran, Determination of rate parameters based on both direct and indirect measurements, International Journal of Chemical Kinetics 44 (5) (2012) 284–302. `doi:10.1002/kin.20717`.

[25] T. Varga, T. Nagy, C. Olm, I. Zsély, R. Pálvölgyi, É. Valkó, G. Vincze, M. Cserháti, H. Curran, T. Turányi, Optimization of a hydrogen combustion mechanism using both direct and indirect measurements, Proceedings of the Combustion Institute 35 (1) (2015) 589–596. `doi:10.1016/j.proci.2014.06.071`.

[26] C. Olm, T. Varga, É. Valkó, H. J. Curran, T. Turányi, Uncertainty quantification of a newly optimized methanol and formaldehyde combustion mechanism, Combustion and Flame 186 (2017) 45–64. `doi:10.1016/j.combustflame.2017.07.029`.

[27] N. Sikalo, O. Hasemann, C. Schulz, A. Kempf, I. Wlokas, A Genetic

Algorithm-Based Method for the Optimization of Reduced Kinetics Mechanisms, International Journal of Chemical Kinetics 47 (11) (2015) 695–723. `doi:10.1002/kin.20942`.

[28] W. Polifke, W. Geng, K. Döbbeling, Optimization of Rate Coefficients for Simplified Reaction Mechanisms with Genetic Algorithms, Combustion and Flame 113 (1-2) (1998) 119–134. `doi:10.1016/S0010-2180(97)00212-5`.

[29] L. Elliott, D. B. Ingham, A. G. Kyne, N. S. Mera, M. Pourkashanian, C. W. Wilson, Genetic algorithms for optimisation of chemical kinetics reaction mechanisms, Progress in Energy and Combustion Science 30 (2004) 297–328. `doi:10.1016/j.pecs.2004.02.002`.

[30] S. Harris, L. Elliott, D. Ingham, M. Pourkashanian, C. Wilson, The optimisation of reaction rate parameters for chemical kinetic modelling of combustion using genetic algorithms, Computer Methods in Applied Mechanics and Engineering 190 (8-10) (2000) 1065–1090. `doi:10.1016/S0045-7825(99)00466-1`.

[31] L. Elliott, D. B. Ingham, A. G. Kyne, N. S. Mera, M. Pourkashanian, C. W. Wilson, Multiobjective Genetic Algorithm Optimization for Calculating the Reaction Rate Coefficients for Hydrogen Combustion, Industrial & Engineering Chemistry Research (2003) 1215–1224`doi:10.1021/ie020501o`.

[32] L. Elliott, D. Ingham, A. Kyne, N. Mera, M. Pourkashanian, C. W. Wilson, Incorporation of physical bounds on rate parameters for re-

action mechanism optimization using genetic algorithms, Combustion Science and Technology 175 (4) (2003) 619–648. `doi:10.1080/00102200302389`.

[33] A. Cuoci, A. Frassoldati, T. Faravelli, E. Ranzi, OpenSMOKE++: An object-oriented framework for the numerical modeling of reactive systems with detailed kinetic mechanisms, Computer Physics Communications 192 (2015) 237–264. `doi:10.1016/j.cpc.2015.02.014`.

[34] B. M. Adams, M. S. Ebeida, M. S. Eldred, G. Geraci, J. D. Jakeman, K. A. Maupin, J. A. Monschke, L. P. Swiler, J. A. Stephens, D. M. Vigil, T. M. Wildey, W. J. Bohnhoff, K. R. Dalbey, J. P. Eddy, R. W. Hooper, K. T. Hu, P. D. Hough, E. M. Ridgway, A. Rushdi, Dakota, A Multilevel Parallel Object-Oriented Framework for Design Optimization, Parameter Estimation, Uncertainty Quantification, and Sensitivity Analysis: Version 6.5 User's Manual (2014).

[35] B. M. Adams, M. S. Ebeida, M. S. Eldred, G. Geraci, J. D. Jakeman, K. A. Maupin, J. A. Monschke, L. P. Swiler, J. A. Stephens, D. M. Vigil, T. M. Wildey, W. J. Bohnhoff, K. R. Dalbey, J. P. Eddy, R. W. Hooper, K. T. Hu, P. D. Hough, E. M. Ridgway, A. Rushdi, Dakota, A Multilevel Parallel Object-Oriented Framework for Design Optimization, Parameter Estimation, Uncertainty Quantification, and Sensitivity Analysis: Version 6.5 Reference Manual (2014).

[36] The DAKOTA project: Large-scale engineering optimization and uncertainty analysis.
URL `https://dakota.sandia.gov/`

[37] W. R. Elwasif, D. E. Bernholdt, S. Pannala, S. Allu, S. S. Foley, Parameter Sweep and Optimization of Loosely Coupled Simulations Using the DAKOTA Toolkit, in: 2012 IEEE 15th International Conference on Computational Science and Engineering, IEEE, 2012, pp. 102–110. `doi:10.1109/ICCSE.2012.24`.

[38] R. A. Hansel, C. N. Brock, B. C. Paikoff, A. R. Tackett, D. G. Walker, Automated generation of highly accurate , efficient and transferable pseudopotentials, Computer Physics Communications 196 (2015) 267–275. `doi:10.1016/j.cpc.2015.06.014`.

[39] C. N. Brock, B. C. Paikoff, M. I. Sallih, A. R. Tackett, D. G. Walker, Force-based optimization of pseudopotentials for non-equilibrium configurations, Computer Physics Communications 201 (2016) 106–118. `doi:10.1016/j.cpc.2016.01.001`.

[40] D. R. Jones, DIRECT Global Optimization Algorithm, in: C. A. Floudas, P. M. Pardalos (Eds.), Encyclopedia of Optimization, Springer US, Boston, MA, 2009, pp. 431–440. `doi:10.1007/978-0-387-74759-0`.

[41] S. G. Davis, A. V. Joshi, H. Wang, F. Egolfopoulos, An optimized kinetic model of H_2/CO combustion, Proceedings of the Combustion Institute 30 (1) (2005) 1283–1292. `doi:10.1016/j.proci.2004.08.252`.

[42] C. Olm, I. G. Zsély, T. Varga, H. J. Curran, T. Turányi, Comparison of the performance of several recent syngas combustion mechanisms,

Combustion and Flame 162 (5) (2015) 1793–1812. `doi:10.1016/j.combustflame.2014.12.001`.

[43] D. L. Baulch, C. T. Bowman, C. J. Cobos, R. A. Cox, T. Just, J. A. Kerr, M. J. Pilling, D. Stocker, J. Troe, W. Tsang, R. W. Walker, J. Warnatz, Evaluated Kinetic Data for Combustion Modeling: Supplement II, Journal of Physical and Chemical Reference Data 34 (3) (2005) 757–1397. `doi:10.1063/1.1748524`.

[44] E. Ranzi, A. Frassoldati, R. Grana, A. Cuoci, T. Faravelli, A. P. Kelley, C. K. Law, Hierarchical and comparative kinetic modeling of laminar flame speeds of hydrocarbon and oxygenated fuels, Progress in Energy and Combustion Science 38 (4) (2012) 468–501. `doi:10.1016/j.pecs.2012.03.004`.

[45] M. Fürst, P. Sabia, M. Lubrano Lavadera, G. Aversano, M. de Joannon, A. Frassoldati, A. Parente, Optimization of Chemical Kinetics for Methane and Biomass Pyrolysis Products in Moderate or Intense Low-Oxygen Dilution Combustion, Energy & Fuels 32 (10) (2018) 10194–10201. `doi:10.1021/acs.energyfuels.8b01022`.

[46] T. Nagy, É. Valkó, I. Sedyó, I. G. Zsély, M. J. Pilling, T. Turányi, Uncertainty of the rate parameters of several important elementary reactions of the H_2 and syngas combustion systems, Combustion and Flame 162 (5) (2015) 2059–2076. `doi:http://dx.doi.org/10.1016/j.combustflame.2015.01.005`.

[47] R. G. Gilbert, K. Luther, J. Troe, Theory of Thermal Unimolecular Re-

actions in the Fall-off Range. II. Weak Collision Rate Constants, Berichte der Bunsengesellschaft für physikalische Chemie 87 (2) (1983) 169–177. `doi:10.1002/bbpc.19830870218`.

[48] N. V. Petrukhin, N. N. Grishin, S. M. Sergeev, Ignition delay time - an important fuel property, Chemistry and Technology of Fuels and Oils 51 (6) (2016) 581–584. `doi:10.1007/s10553-016-0642-0`.

[49] P. Sabia, M. Lubrano Lavadera, G. Sorrentino, P. Giudicianni, R. Ragucci, M. De Joannon, H_2O and CO_2 Dilution in MILD Combustion of Simple Hydrocarbons, Flow, Turbulence and Combustion 96 (2) (2016) 433–448. `doi:10.1007/s10494-015-9667-4`.

[50] C. J. Mueller, M. P. B. Musculus, M. Lyle, W. J. Pitz, C. K. Westbrook, The Oxygen Ratio : A Fuel-Independent Measure of Mixture Stoichiometry, Tech. rep., Lawrence Livermore National Laboratory (2003).

[51] M. Karimi, B. Ochs, Z. Liu, D. Ranjan, W. Sun, Measurement of methane autoignition delays in carbon dioxide and argon diluents at high pressure conditions, Combustion and Flame 204 (2019) 304–319. `doi:10.1016/j.combustflame.2019.03.020`.

[52] U. Burke, W. K. Metcalfe, S. M. Burke, K. A. Heufer, P. Dagaut, H. J. Curran, A detailed chemical kinetic modeling, ignition delay time and jet-stirred reactor study of methanol oxidation, Combustion and Flame 165 (2016) 125–136. `doi:10.1016/j.combustflame.2015.11.004`.

[53] B. C. Duva, L. E. Chance, E. Toulson, Effect of CO2 Dilution on the Laminar Burning Velocities of Premixed Methane/Air Flames at Ele-

vated Temperature, Journal of Engineering for Gas Turbines and Power 142 (3) (mar 2020). `doi:10.1115/1.4044641`.