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Numerical optimisation for model evaluation in combustion kinetics

M. Fischer *, X. Jiang

Engineering Department, Lancaster University, Lancaster LA1 4YR, UK

HIGHLIGHTS

- An overview of optimisation in combustion chemical kinetics is presented.
- Four optimisation methods were implemented and validated.
- Four mechanisms could not initially capture profiles related to ethane and methyl.
- GRI-mechanism 3.0 was optimised in that respect.

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ABSTRACT

Numerical optimisation related to the estimation of kinetic parameters and model evaluation is playing an increasing role in combustion as well as in other areas of applied energy research. The present work aims at presenting the current probability-based approaches along applications to real problems of combustion chemical kinetics. The main methods related to model and parameter evaluation have been explicated. An in-house program for the systematic adjustment of kinetic parameters to experimental measurements has been described and numerically validated. The GRI (Gas research institute) mechanism (version 3.0) has been shown to initially lead to results which are greatly at variance with experimental data concerning the combustion of CH_3 and C_2H_6. A thorough optimisation of all parameters has been performed with respect to these profiles. A considerable improvement could be reached and the new predictions appear to be compatible with the measurement uncertainties. It was also found that neither GRI 3.0 nor three other reaction mechanisms considered during the present work should be employed (without prior far-reaching optimisation) for numerical simulations of combustors and engines where CH_3 and C_2H_6 play an important role. Overall, this study illustrates the link between optimisation methods and model evaluation in the field of combustion chemical kinetics.

1. Introduction

The use of numerical methods for parameter estimation has become widespread in fields related to applied energy research. Amongst many other applications, they have been used for the development of a non-linear model describing a wind turbine [1] and modelling a fuel-cell [2], the heat dynamics of a building [3], and a hydraulic turbine [4], to name but a few of them. They are also increasingly employed for the development and evaluation of combustion models [5–8]. Computational Fluid Dynamics (CFD) simulation has become an essential ingredient for the optimal utilisation of complex power generation systems based on combustion [9–11]. Reliable computational predictions require the presence of an accurate chemical kinetic model which is generated from the reduction of a complex reaction mechanism [12,13]. Since the reduction process lowers almost inevitably the accuracy of the kinetic description of the combustion [14], the detailed reaction mechanism must reach a high level of trustworthiness for allowing realistic CFD simulations of complex systems such as, say, internal combustion engines or gas turbines. The uncertainties of kinetic coefficients can lead to large prediction errors with respect to the release of pollutants and important combustion features such as ignition delay times or flame velocities because the parameter imprecisions get propagated towards all results [15,16]. Hence, a good understanding of combustion kinetics has become vital for the optimal and sustainable utilisation of fossil and renewable fuels [10,17,18] and the use of new fuels such as synthetic ones. It is universally recognised amongst researchers that the development of micro-kinetic detailed reaction mechanisms has been a great step forward for both the chemical understanding and the predictability of combustion processes.

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* Corresponding author. Tel.: + 44 1524 594645.
E-mail address: m.fischer@lancaster.ac.uk (M. Fischer).

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Such reaction mechanisms include all possible elementary reactions that can occur under a wide variety of conditions. They allow a detailed description of the chemical processes taking place on a molecular level. The determination of parameters corresponding to the real chemistry is a complex task. Traditionally, it has been achieved in three different manners.

- By designing experiments isolating some reactions in such a way that the model variables corresponding to the measurements can be expressed analytically as a function of parameters of interest. The optimal values can then be identified mathematically through a least-square regression.
- By using methods from theoretical chemistry such as Density Functional Theory calculations [19] coupled with Transition State Theory. Depending on the involved assumptions and simplifications, some methods, especially semi-empirical techniques, can lead to great uncertainties with respect to the evaluated parameters.
- By analogy with similar reactions with known rate coefficients. An unknown uncertainty is also introduced by this approach.

If the mechanism contains all possible reactions playing a role in the experiments at hand and enough profiles are available for an unambiguous estimation of all active parameters, the first method is the most promising one for obtaining values with great accuracy. Nevertheless, most chemical kinetic descriptions cannot be sufficiently simplified to provide analytical expressions precise enough for parameter estimation. In such a case, an optimisation method minimising the distance $d(p)$ between experimental results and model predictions must be utilised. The determination of optimal coefficients is itself closely related to model evaluation which consists of assessing how well a reaction mechanism can match a set of measurements.

The present article concerns the use of numerical optimisation methods for the evaluation of models used to describe combustion chemical kinetics such as those applied to the CFD simulation of power generation. It has been organised in such a way to remain relevant for model evaluation in other fields of applied energy. In Section 2, different approaches to the evaluation of kinetic models are presented and examined. In Section 3, the optimisation program Kinefit [14] is presented and validated. In Section 4, Kinefit is applied to the combustion of ethane and the methyl free radical. Finally, in Section 5, the conclusion of this work and future outlook are given.

2. Methodologies for model evaluation in chemical kinetics

2.1. Frequentist and Bayesian approaches

Frequentism and Bayesianism [20] are currently the main approaches utilised for the evaluation of predictive models. While confronted with the problem of estimating parameters out of a set of experimental data, both frequentists and Bayesians view a measurement (which might be a concentration, an ignition delay time, a flame velocity and so on.) as composed of three terms:

$$m = m_t + m_s + m' \tag{1}$$

where m_t is its true value, m_s its systematic error and m' a random fluctuation around $m_t + m_s$. The systemic error is always an unknown term which would be otherwise corrected. For the sake of parameter estimation, one has to suppose it is negligible and set it to zero. It is an assumption which might be well founded in cases where the measurement method has been independently validated. It can be more problematic otherwise, in situations where the measurement technique has not been well assessed. Let N be the number of measured profiles, n_i the number of measurements for the i-th profile with $i \in \{1 \ldots N\}$ whereas $m_{i,j}$ and $e_{i,j}$ designate the model and experimental values, respectively. Let $\sigma_{i,j}$ denote the standard deviations corresponding to the experimental values. The chi-squared norm is defined as

$$d = X^2 = \sum_{i=1}^{N} \sum_{j=1}^{n_i} \left(\frac{m_{i,j} - e_{i,j}}{\sigma_{i,j}} \right)^2. \tag{2}$$

Since the standard deviations are frequently unknown, they are often pragmatically approximated as being proportional to the measurements $\sigma_{i,j} = \epsilon e_{i,j}$ whereby measurements equal to zero are not considered in the sum of Eq. (2). Following this rule, the relative distance or relative least-square can be defined as

$$d = X^2 = \sum_{i=1}^{N} \sum_{j=1}^{n_i} \left(\frac{m_{i,j} - e_{i,j}}{e_{i,j}} \right)^2. \tag{3}$$

Under the assumption that the measurement errors are normally distributed, the probability that the experimental values would obtain if model M is correct $p(E \mid M)$ can be computed [8]. If $\upsilon = N_{data} - N_{parameters}$ is large then

$$p(E|M(k)) = p(X^2) = \frac{\Gamma\left(\frac{\upsilon}{2}, \frac{X^2}{2}\right)}{\frac{\Gamma}{2}} \tag{4}$$

whereby k represents the ensemble of uncertain parameters taking on some value ranges [8].

It is at the next stage that Bayesians and frequentists part ways. While the former use this value and a prior probability distribution of the parameter space for computing a posterior distribution via Bayes' theorem (with problems discussed in Section 2.2), the latter do not consider that model M has a probability of being true. Instead, they judge it according to its agreement with the experimental data represented by $p(E \mid M(k))$ which should be below a given threshold (there are no universal rules for determining such limits). If the model cannot reproduce the measurements within their uncertainties, it is rejected, otherwise it is deemed worthy of further considerations. It is worth noting that the truth of a model is indicated solely by its ability to correctly reproduce the set of experimental data while *all other possible alternatives* fail to do so [21]. The remainder of this subsection focuses on the frequentist approach to model evaluation.

If the parameters of a reaction mechanism could only take on one set of precise values known beforehand, the whole modelling enterprise in chemical kinetics would merely consist of comparing the performances of different models. In practice, this is never the case. A priori, parameters can have any of the values included within so-called feasible sets accounting for theoretical and experimental constraints. The parameters must then be optimised within this domain so as to minimise $X^2(k)$ and hence also maximise $p(E \mid M(k))$ according to the spirit of Maximum Likelihood Estimation [22]. The most widespread form of such feasible sets consists of hypercubes where all parameters are included between a lower and an upper bounds, that is $l_i \leqslant p_i \leqslant u_i$. The problem of this representation lies in the fact that parameters are very often tightly correlated with respect to their accounting for experimental data. Consequently, the feasible set is frequently spanned up by a complex geometry (which may not even be continuous). Frenklach [23] emphasised the need to consider the *whole* ensemble of available measurements for fitting kinetic parameters while determining a feasible set defined as all physically possible parameter values compatible with the experimental data and their uncertainties. In this way, the size of the feasible set (i.e. the imprecision of the parameter set) diminishes as new measurements come in.

There is another way optimisation methods can be applied to chemical kinetic problems. Let us suppose that a reaction mechanism leads to considerable discrepancies with experiments it should reproduce. For many practitioners, this means that the reaction pathways themselves should be modified or improved. However, as Singer et al. [8] pointed out, this conclusion is only warranted if the set of parameter values used for the simulation is already optimal. Such a situation calls for an optimisation of the model using all influential parameters. While a successful adjustment of the parameters to the measurements does not prove the model's accuracy, the presence of significant discrepancies for their optimal values shows that it should be probably rejected or changed. A new form of sensitivity analysis called *reaction significance analysis* has been developed to that end [14]. Let us consider a parameter q comprised in the interval $[q_l; q_u]$. Its reaction significance is defined as

$$S = max\{d(q), q \in [q_l; q_u]\} - min\{d(q), q \in [q_l; q_u]\}. \qquad (5)$$

It is a natural measure of the influence of q on the overall distance d between model predictions and measurements. Afterwards, reaction parameters are sorted out according to their significance coefficients. A thorough global optimisation gathering all parameters having a noticeable influence on d is then performed. The lowest distance d_{min} is then utilised for computing the probability defined in Eq. (4) for $\nu = N_{data}$. While high probability values consistent with the measurements (within their uncertainties) are *no* confirmation of the model, low values are a strong indication it cannot account for the experiments at hand [14]. An example of such a procedure is given in Section 4. In the next subsection, the reasons why Bayesian methods have not been considered for this study are explicated.

2.2. Problems with the classical Bayesian methodology

While many kineticists and modellers need not be concerned about the theoretical bases of methods they use in order to perform successful studies, we deemed it necessary to briefly go into more foundational issues at this place. In the last years and decades, Bayesian methods have been increasingly employed for problems related to the estimation of kinetic parameters [16,24–28]. Single-value (traditional) Bayesianism [29] is the view that convictions or beliefs in propositions (including the values of model parameters) come in numerical degrees behaving like probabilities (i.e. following the Kolmogorov axioms). Its name stems from the fact that upon seeing new evidence, probabilities are updated according to Bayes' theorem. Whilst traditional Bayesianism has been extremely successful in a great number of situations [30], it also suffers from problems which cast real doubts on its *universal* applicability [31]. The choice of prior probabilities necessary for starting the calculation chain is viewed as particularly problematic [32].

As a simple illustrating example, let us first consider the case of a coin we do not know anything about. We are interested in its probability of landing heads while being tossed at random. According to the *Principle Of Indifference* applied to single probabilities [33], we are to consider that both possible outcomes are equally probable so that $p = 0.5$. However this immediately leads to a problem. This value is exactly the same we would assign to the event if we knew (through a long series of trials or a physical analysis) that the coin is equally poised. This has led Salmon [34] to conclude that the principle of indifference tries to generate a specific knowledge out of the absence of knowledge and any information. In a situation of complete ignorance about the coin, there is indeed no more reason to assign to its landing heads a probability of 0.5 than one of 0.3, 0.7 or 0.86 [35]. Under such circumstances, it seems far more meaningful to consider this probability as unknown or even undefined [33].

Let us now turn our attention to a simple chemical kinetic problem which illustrates a different (albeit related) concern. We want to evaluate the value of a pre-exponential factor A (mol cm^{-3}) and we only know that it is included within the interval $[10^{10}; 10^{16}]$. According to the principle of indifference, we ought to represent our lack of knowledge through a uniform probability distribution such that all intervals having the same size are equally likely to contain the true value of the parameter. That is $p(A \leqslant a) = (a - 10^{10})/(10^{16} - 10^{10})$ as shown in Fig. 1. The probability that p is contained within the interval $[10^{12}; 10^{14}]$ is given by $p_1 = (10^{14} - 10^{12})/(10^{16} - 10^{10}) = 0.0099$. Let us now consider the logarithmic form of the parameter $l = log(A) \in [10; 16]$. Given the fact we are equally ignorant about the shape of its initial probability distribution, we should also attribute it a uniform one. Therefore, the probability that it is included within the interval $[12; 14]$ is $p_2 = (14 - 12)/(16 - 10) = 0.33333$. Nevertheless p_2 must also be the probability that $A \in [10^{12}; 10^{14}]$ (through a straightforward application of the operator 10^x). However $p_2 > p_1$ by a factor of 33.67. Considering other mathematical reformulation of the unknown parameter leads to an endless number of such paradoxes [33]. Following Norton [33], this shows that a state of complete ignorance cannot be represented through a unique probability distribution. Choosing to uniformly distribute A leads to a strongly non-uniform (and hence necessarily non-neutral) distribution of $log(A)$ and vice versa. Owing to these two reasons, it is increasingly recognised that uniform prior probabilities represent a precise knowledge instead of a neutral state of ignorance [31,35,36].

This has led an increasing number of researchers to develop other probabilistic frameworks which can be gathered under the name of *imprecise probability* [37–39]. These approaches amount to representing one's confidence in a theory or model (in our case a reaction mechanism with given parameter values) through a probability interval [*Lower value*; *Upper value*] rather than through a single real number. In the lack of information, indifference is represented through the interval $[0; 1]$ which would be attributed to the probability of the coin landing heads and that of its landing tails. In the case of the kinetic pre-exponential parameter, the probability of A being included in any interval $[A_1; A_2]$ (with $A_2 > A_1$) is described by the interval $[0; 1]$. It must be emphasised that proponents of this paradigm view it as an extended form of Bayesianism rather than as a departure from it. In the last several years, imprecise probability notions have been applied to a considerable number of cases in diverse fields such

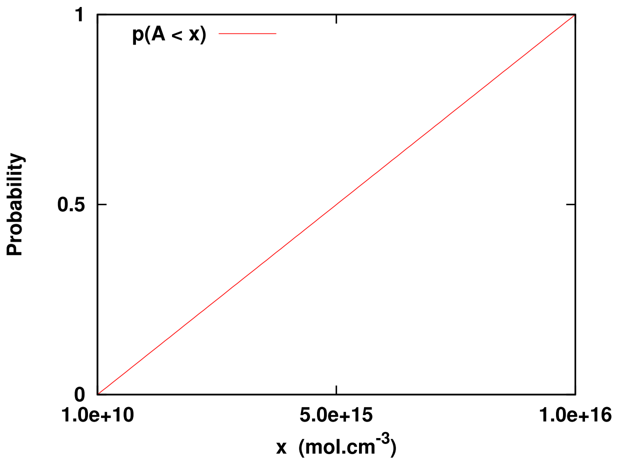


Fig. 1. Prior probability distribution for the pre-exponential factor A mol cm^{-3}.

as climate change [40,41], and engineering [42–44]. Reichert [45] argued for their usefulness for parameter estimation problems where prior knowledge is either very limited or absent altogether. Wang [46] applied them to chemical kinetical Monte Carlo simulations. To the best of our knowledge, there has not yet been any application to the estimation of kinetic parameters itself. From a theoretical standpoint, they could turn out to be largely superior to traditional Bayesian techniques owing to their preserving the distinction between lack of information and justified knowledge. However, from a computational viewpoint they might also prove too expensive. Hence, the use of frequentist methods may be an efficient and sound alternative to all Bayesian techniques which have been presented here.

3. The program Kinefit for the optimisation of kinetic parameters

3.1. Optimisation methods

Kinefit [14] is a program developed in C++ by the author which allows one to match kinetic parameters to a set of experimental data. It relies on the software Homrea [47] for the chemical kinetics simulation of homogeneous systems where everything depends on the reaction time. Four optimisation methods have been implemented in Kinefit for finding the global minimum of the distance between measurements and the results of the model: an adaptive Random Search, a Genetic Algorithm and two algorithms which mimic quasi-Newton methods through the indirect estimation of derivatives, namely Bobyqa [48] and Condor [49]. They all rely on computing the function $d(p)$ by solving the differential equation system for different parameter values. Box constraints on each parameter are often not sufficient if several parameters of the same reaction are optimised simultaneously. Consequently, penalty terms have been implemented in order to put constraints on the whole reaction rate coefficient governed by the Arrhenius law. Upon convergence to a local minimum of the parameter space, a random restart is performed for all approaches except the genetic algorithm.

It is worth mentioning that such a technique cannot be employed for the overall optimisation of large reaction mechanisms such as the GRI-mechanism through the use of a wide set of experimental data. Solving the numerous systems of differential equations involved in that case is unmanageable for most currently available computers. In this situation, methods based on surface mapping must be used [5]. They consist of expressing algebraically every single variable of interest as a function of specific active parameters which exert a non-negligible influence on it. With a successful mapping, it becomes computationally much easier to minimise the distance $d(p)$ considering the surrogate algebraic models instead of the differential equations. While this technique is currently indispensable for the large-scale optimisation of reaction mechanisms (and the reduction of the size of the feasible set as explained in Section 2.1), such surrogate models may produce deviations from the original model and involve a very large number of trials for their construction [14]. Consequently, for the optimisation of a reasonably small number of parameters using a reasonably small number of experiments, methods directly solving the differential equation systems in a stepwise fashion might prove more efficient and accurate. This is the reason why they have been chosen for the present work.

3.2. Validation of Kinefit

Numerical tests were performed for validating the optimisation methods. A detailed description of the process can be found in Fischer (2011) [14]. They are all based on the H_2–O_2 sub-mechanism of the GRI-mechanism 3.0 [50]. Computationally generated experimental profiles were created using all initial values of the reaction parameters. Optimisation problems based on six experiments with three temporal profiles (OH,H_2O, and H_2O_2, respectively) were constructed. The most influential parameters were then identified and *modified* in such a way to introduce great discrepancies with the experimental profiles. Often, it can be observed that the distance $d(p)$ oscillates (or fluctuates) as function of its parameter values (as illustrated in Fig. 2), thereby producing suboptimal local minima. In this example, the relative distance defined in Eq. (3) has been employed. One cause of the oscillations of the distance as function of separately varied parameters was identified: it was related to the exponential decrease and increase of concentrations due to self-ignition. A set of greatly diverse numerical experiments was then considered for validating the four methods of Kinefit. It could be shown that the methods are reliable for retrieving an optimal solution in parameter spaces far larger than what can be realistically expected. As an illustration, Fig. 3 shows results of the first numerical validation test, “Ini” and “Fit” referring to the unoptimised and optimised profiles, respectively.

4. Optimisation of the GRI-mechanism with respect to the combustion of C_2H_6 and CH_3

As was mentioned in the introduction, a reliable and useful CFD simulation of power generation through combustion necessitates a correct understanding of the underlying detailed chemical kinetics. Capturing the kinetics of ethane combustion and the related one of the methyl free radical is important for two reasons. On the one hand, C_2H_6 is the second most abundant constituent in natural gas [51,52] so that it can significantly influence the combustion characteristics [53,54]. On the other hand, the correct description of its combustion is made necessary by the hierarchical nature of reaction mechanisms of higher-order hydrocarbon fuels which naturally leads to the formation of C_2–C_3 species and radicals [55–57]. The reactions it undergoes may also be fairly similar to those of diesel fuels which are mostly constituted of alcanes [58]. What is more, in a recent study [59] concerning the combustion of biogas (mostly composed of methane and carbon dioxide), the recombination reaction $2CH_3 + M \rightarrow C_2H_6 + M$ has been demonstrated to play a vital (inhibitive) role in the formation of the pollutants CO and NO which have well-known detrimental effects on

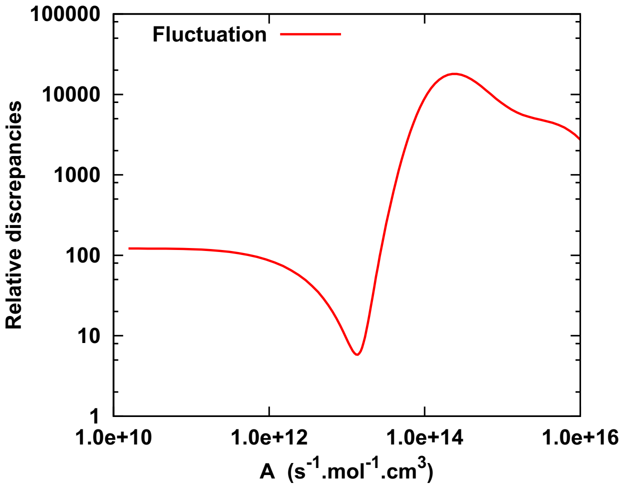
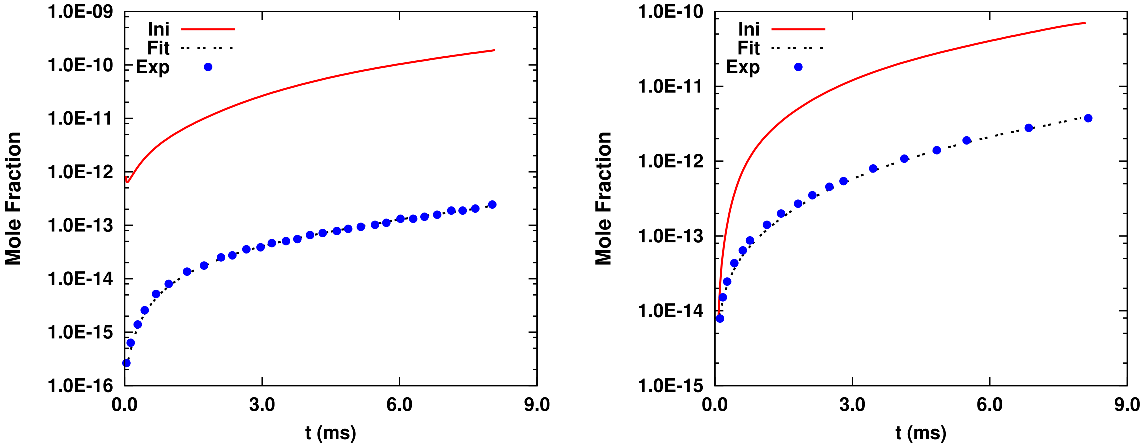


Fig. 2. Example of oscillation [14].



(a) Experiment 1, OH.

(b) Experiment 4, H_2O_2.

Fig. 3. Numerical validation of Kinefit.

humans and the environment. In addition, CH_3 level has been shown to have a considerable influence on the formation of soot particles and their noxious precursors PAH (Polycyclic Aromatic Hydrocarbons) [60]. Thus, the correctness of parameter values pertaining to the chemistry of ethane and methyl (and its transfer to reduced kinetic models) can have a great impact on the prediction accuracy of the pollutant levels and power generation efficiency of an industrial combustor by a CFD simulation. For all these reasons, correctly capturing the kinetics of $CH_3—C_2H_6$ is of great relevance to the optimal use of combustion technologies.

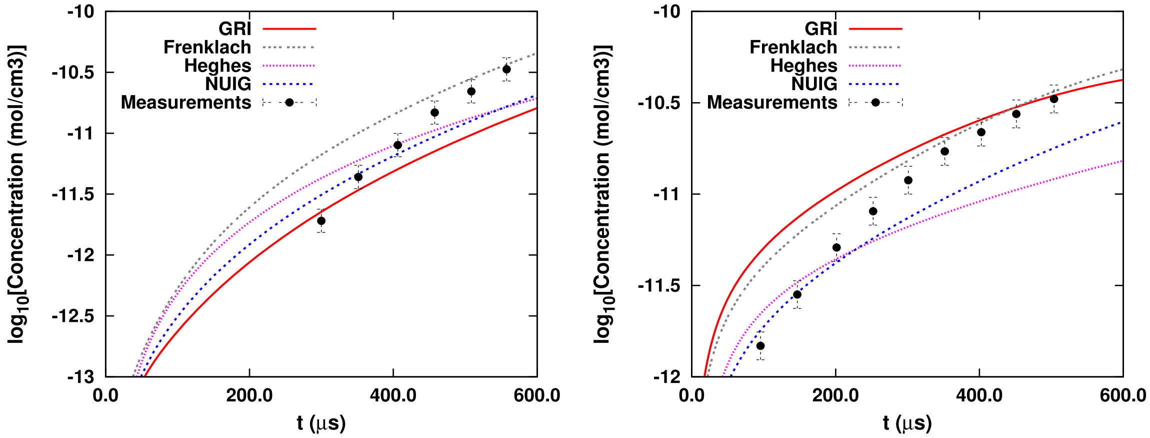
Saito et al. [61] have conducted experiments specifically tailored to investigating the chemistry of C_2H_6 and CH_3 combustion. Their results consist of temporal profiles of O and H free radicals measured during the oxidation of C_2H_6 and CH_3 using atomic resonance absorption spectroscopy (ARAS).

The experimental conditions are reported in Table 1. Four detailed reaction mechanisms have been considered for their simulations. The Gas Research Institute (GRI) mechanism 3.0 [50] is a model for the simulation of methane combustion which was developed through the systematic optimisation of the kinetic and thermo-chemical parameters with the Surface Mapping method (allowing the use of a great number of measurements for the parameter estimation [15,62]). Its performance with respect to the combustion of carbon monoxide and hydrogen are also satisfactory. It consists of 325 elementary reactions and encompasses 53 species which accounts for the combustion of H_2 ,CO, CH_4, N_2 (NOx formation) as well as reactions between the nitrogen and the hydrocarbons. Heghes developed a reaction mechanism [47] for $C_1—C_4$ hydrocarbons which was validated with respect to laminar flame speeds and ignition delay times in shock tubes. It was tested with respect to the stoichiometric/ fuel-lean burning of H_2 , $H_2—CO, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}$. Overall it produced a satisfying agreement with the measurements except for acetylene. The mechanism consists of 412 elementary reactions and 61 species and is based on a rate-data compilation by Baulch et al. [63] grounded on kinetic experiments, quantum chemical computations and analogies with well-known reactions. Heghes adjusted the coefficients within their uncertainty intervals to the experiments she considered. It contains all reactions of the GRI-mechanism except those involving N_2 which always remains inert in this model. In addition, it also includes all steps required for describing the combustion of the $C_2—C_4$ compounds under lean and stoichiometric conditions. Frenklach et al. [64,65] developed a reaction mechanism accounting for the formation of Polycyclic Aromatic Hydrocarbons (PAH) under rich and pyrolytic conditions. It is based on the GRI-mechanism (version 1.2) complemented by steps describing the formation of ever growing carbonaceous species which are the precursors of the first soot particles. It could reasonably well predict diverse profiles of aromatic species and their intermediates in laminar flames. The NUIG (National University of Ireland in Galway) mechanism is a $C_0—C_5$ reaction mechanism resulting from a long-term endeavour aiming at determining a reaction mechanism capable of describing the combustion of various hydrocarbons under a wide range of conditions. It has a hierarchical structure and includes $H_2—O_2, CO—CH_4, C_2, C_3, C_4$ and now C_5 submechanisms [66–69].

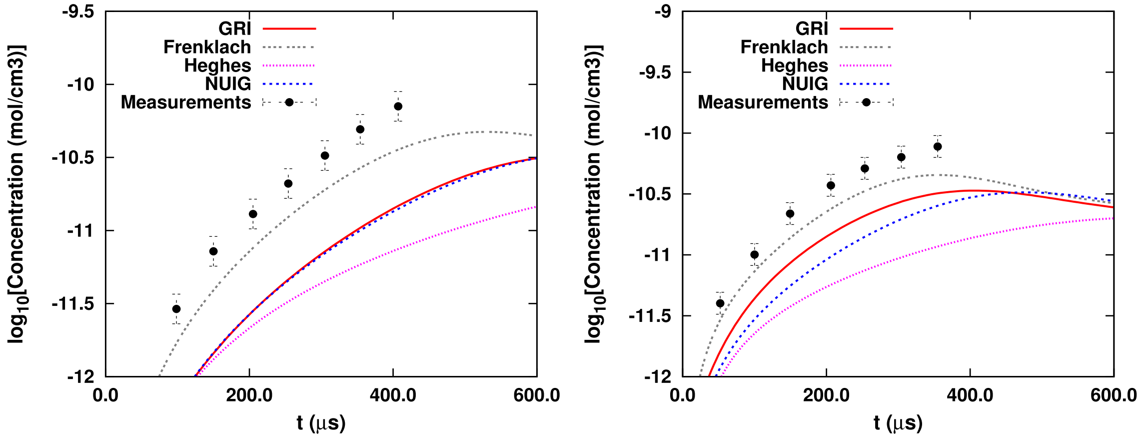
Table 1
Experimental conditions of Saito et al. [61].

Experiment	X_{CH_3I} (ppm)	$X_{C_2H_6}$ (ppm)	X_{O_2} (ppm)	*T* (K)	*p* (bar)	Measured
1	0	20	1000	1520.000	1.580	H
2	20	0	1000	1550.000	1.611	H
3	0	10	2000	1620.000	1.724	H
4	0	10	2000	1660.000	1.767	O
5	10	0	2000	1700.000	1.767	O
6	0	10	2000	1740.000	1.852	H
7	0	10	2000	1750.000	1.862	O
8	20	0	1000	1800.000	1.871	O
9	10	0	2000	1930.000	2.006	H
10	20	0	1000	1940.000	2.016	H
11	10	0	2000	2000.000	2.079	O
12	10	0	2000	2150.000	2.235	O

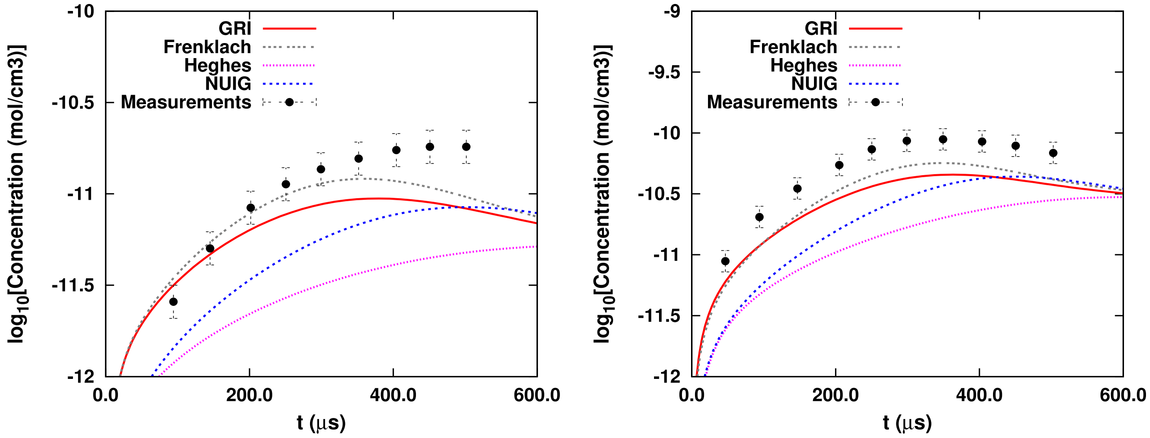
The four mechanisms lead to predictions which are at strong variance with the measurements of Saito et al. [61] as can be seen in Figs. 4-5. Since the GRI-mechanism 3.0. is widely used and is the simplest of all four mechanisms, we considered here the question of its compatibility with the experimental data at hand employing the methodology described in Section 2.1 Following the error-statistical (frequentist) paradigm [21], a given result R is a *severe test* of a hypothesis H if its probability given the falsehood of H $p(R \mid \neg H)$ is very low in comparison to $p(R \mid H)$. If H is the hypothesis "the GRI mechanism cannot account for the data of Saito et al.", a severe test would consist of performing a thorough optimisation using all sensitive parameters under generously large variation intervals. Indeed, the likelihood that such an optimisation would fail given the sufficiency of the GRI-mechanism is fairly small. Consequently, a reaction significance analysis was carried out. It led to the identification of 30 sets of Arrhenius parameters (A, n, Ea) for normal and pressure-dependent reactions which are reproduced here.



(a) First experiment (b) Second experiment

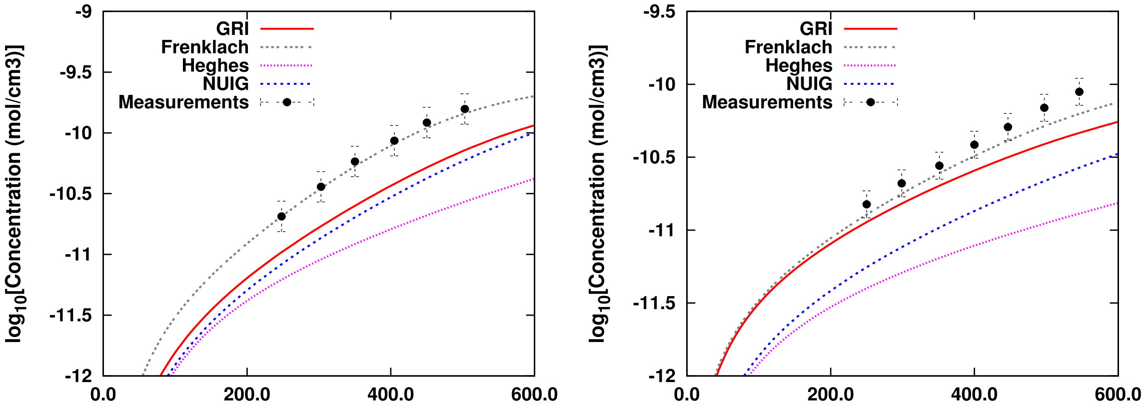


(c) Third experiment (d) Sixth experiment



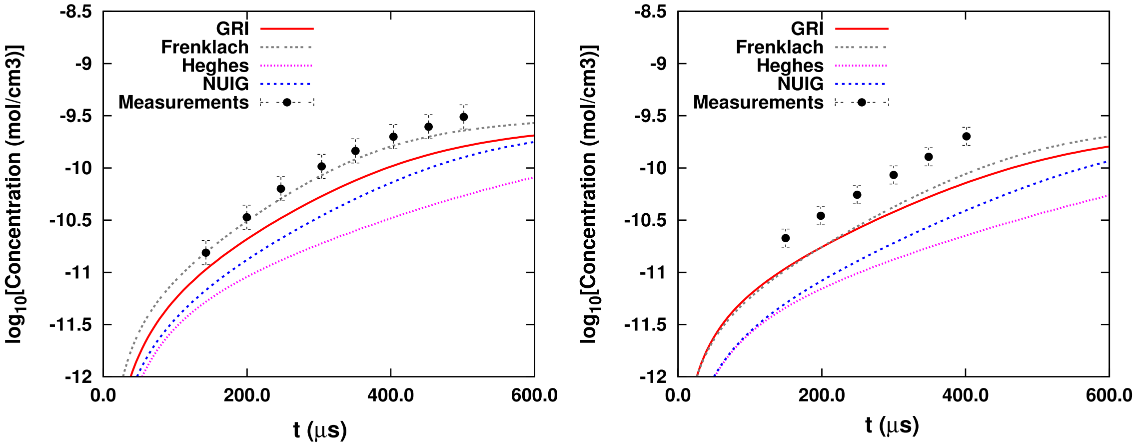
(e) Ninth experiment (f) Tenth experiment

Fig. 4. Initial predictions of H-profiles [61].



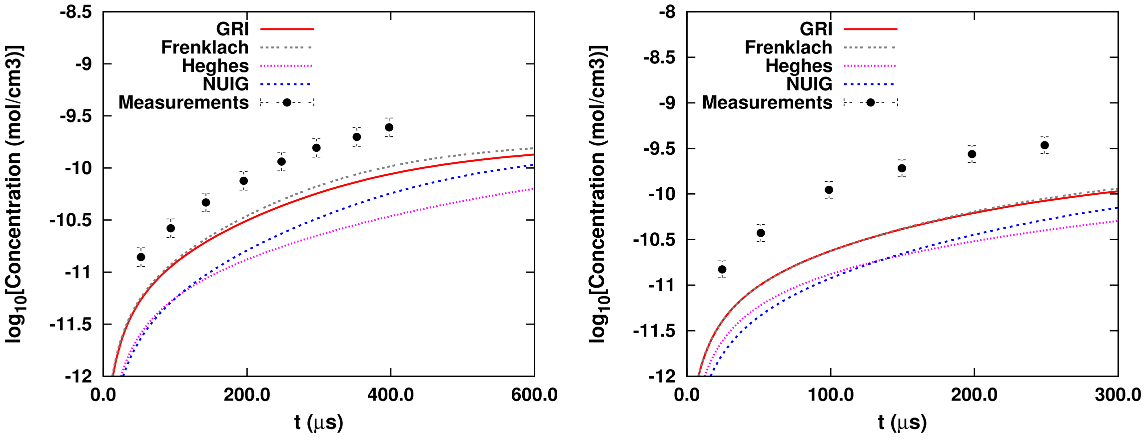
(a) Fourth experiment

(b) Fifth experiment



(c) Seventh experiment

(d) Eighth experiment



(e) Eleventh experiment

(f) Twelfth experiment

Fig. 5. Initial predictions of O-profiles [61].

$$O + CH_3 \leftrightarrows H + CH_2O$$

$$O + CH_2O \leftrightarrows OH + HCO$$

$$O + C_2H_6 \leftrightarrows OH + C_2H_5$$

$$O_2 + CH_2O \leftrightarrows HO_2 + HCO$$

$$H + CH_2O \leftrightarrows HCO + H_2$$

$$H + CH_2OH \leftrightarrows OH + CH_3$$

$$OH + CH_3 \leftrightarrows CH_2 + H_2O$$

$$OH + CH_3 \leftrightarrows CH_2(S) + H_2O$$

$$OH + CH_2O \leftrightarrows HCO + H_2O$$

$$OH + C_2H_6 \leftrightarrows C_2H_5 + H_2O$$

$$CH_2 + O_2 \rightarrow OH + H + CO$$

$$CH_2 + CH_4 \leftrightarrows CH_3 + CH_3$$

$$CH_2(S) + O_2 \leftrightarrows CO + H_2O$$

$$CH_2(S) + CH_4 \leftrightarrows CH_3 + CH_3$$

$$CH_3 + O_2 \leftrightarrows O + CH_3O$$

$$CH_3 + O_2 \leftrightarrows OH + CH_2O$$

$$CH_3 + CH_3 \leftrightarrows H + C_2H_5$$

$$CH_3 + CH_2O \leftrightarrows HCO + CH_4$$

$$CH_3 + C_2H_6 \leftrightarrows C_2H_5 + CH_4$$

$$O + CH_3 \rightarrow H + H_2 + CO$$

$$OH + CH_3 \rightarrow H_2 + CH_2O$$

$$CH_2 + O_2 \rightarrow H + H + CO_2$$

$$CH_2 + O_2 \leftrightarrows O + CH_2O$$

$$H + CH_2 + M \leftrightarrows CH_3 + M \quad (\mathrm{LOW})$$

$$H + CH_3 + M \leftrightarrows CH_4 + M \quad (\mathrm{LOW})$$

$$H + HCO + M \leftrightarrows CH_2O + M \quad (\mathrm{LOW})$$

$$H + C_2H_5 + M \leftrightarrows C_2H_6 + M \quad (\mathrm{LOW})$$

$$CH_3 + CH_3 + M \leftrightarrows C_2H_6 + M$$

$$CH_3 + CH_3 + M \leftrightarrows C_2H_6 + M$$

$$CH + H_2 + M \leftrightarrows CH_3 + M \quad (\mathrm{LOW})$$

LOW indicates the low-pressure coefficients of a reaction involving a third body M. Most elementary steps involve methyl and its derivatives which confirms the fact that not capturing these measurements might amount to a poor description of their chemistry. The pre-exponential factors, temperature coefficients and activation energies of the reactions were optimised between the following bounds:

$$\frac{A_0}{20} \leqslant A \leqslant 20A_0,$$

$$n_0 - 0.8 \leqslant n \leqslant n_0 + 0.8,$$

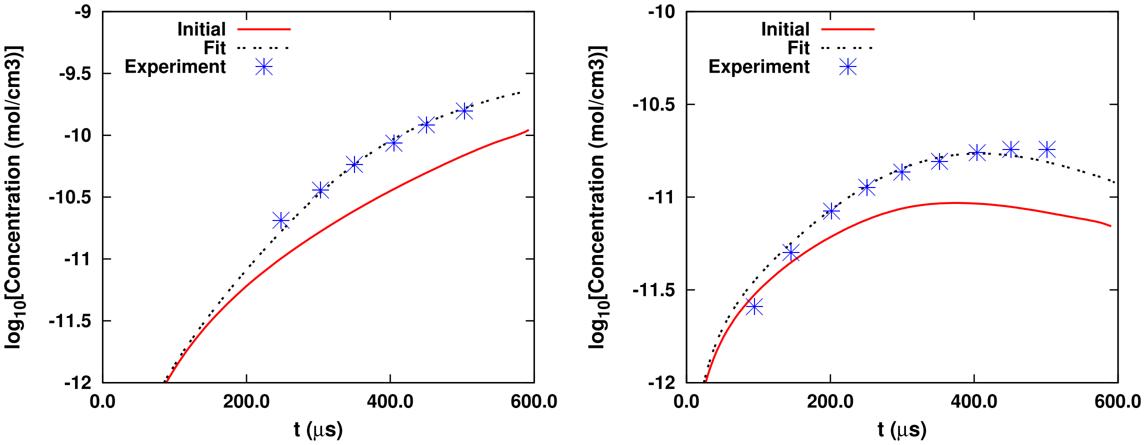
$$E_{a,0} - 0.8 \leqslant E_a \leqslant E_{a,0} + 0.8, \text{ and}$$

$$\frac{k_0}{20} \leqslant k \leqslant 20k_0.$$

The initial pressures (p_1 to p_{12}) were also optimised within their uncertainty limits. Further details can be found in Fischer [14]. Two adjusted profiles are shown in Fig. 6 as an illustration. A significant improvement is clearly recognisable as can be seen in Table 2 reporting the relative distance d. The total relative distance is approximately $d = 3.212$. If one assumes (as a first approximation) that the standard deviation is the same for all experimental concentrations (e.g. 10%of the value), the chi-squares norm can be employed according to the Equation:

$$X^2 = \frac{1}{\upsilon_{dev}^2} d \tag{6}$$

whereby υ_{dev} is the Relative Standard Deviation (RSD) such as $\sigma_{i,j} = \upsilon_{dev} e_{i,j}$. It is then possible to deduce the likelihood that model and experiments are consistent with each other



(a) Experiment 4, O.

(b) Experiment 9, H.

Fig. 6. Results of the optimisation.

Table 2
Experimental uncertainties and relative discrepancies with the optimised model.

Experiment	*d* (Initial GRI)	*d* (Optimised GRI)	Sigma	RSD (Saito et al. [61])
1 (H)	1.00587	0.470034	1.62566005383362E−012	0.2053665627
2 (H)	10.4447	0.141941	8.83656410747787E−013	0.1748169072
3 (H)	4.38189	1.46446	4.68996753233265E−012	0.2260840041
4 (O)	1.85252	0.0662706	1.00846073651306E−011	0.2859295192
5 (O)	0.804567	0.0414185	7.87604939142709E−012	0.2060669917
6 (H)	2.56961	0.218659	7.40568905996078E−012	0.1996942103
7 (O)	1.68681	0.0871119	2.85021920261905E−011	0.2748452665
8 (O)	1.86445	0.0552085	1.06422663063066E−011	0.1917053011
9 (H)	1.22014	0.270206	2.24545528842395E−012	0.2032845683
10 (H)	2.19984	0.217566	6.70332761593378E−012	0.1974196808
11 (O)	3.14536	0.0855826	1.54455867778865E−011	0.2062074785
12 (O)	3.50812	0.0938258	2.30360721969696E−011	0.2090250957

$$Pr_0(X^2) = \frac{\Gamma\left(\frac{n_e}{2}, \frac{X^2}{2}\right)}{\Gamma\left(\frac{n_e}{2}\right)}. \tag{7}$$

For RSD values greater than 20%, the probability of consistency becomes superior to 75%, thereby indicating that the reaction mechanism is in good agreement with the experiments [8]. At first sight, such a large measurement error does not seem unlikely for the state of the ARAS method at the time of the study of Saito et al. [61] and this was the initial conclusion of Fischer (2011) [14]. A later consideration of the absorption curves of H and O given by Saito et al. [61] seems to show a different picture. The oscillations of the absorption intensity (in comparison to the average values) appear to indicate that for H the relative standard deviations can be at most 17% and for O at most 6%. Most of the time, the fluctuations are much smaller than those values. However, Saito et al. [61] gave themselves uncertainty bounds on their measurements based upon repeating their experiments under similar circumstances. Their values have been extracted from their profiles and are reported in Table 2.

According to such results, the relative standard deviations are fairly high and are included in the interval [0.1748; 0.2748]. This suggests that the discrepancies between the results of the optimised GRI 3.0 and the measurements might reasonably fall within their uncertainty ranges. The situation is ambiguous so that it does not appear possible to draw the strong conclusion that the GRI-mechanism stands in conflict with this series of measurements. The determination of valid kinetic coefficients for ethane-sensitive and methyl-sensitive reactions must involve a large-scale optimisation also including all methane experiments used to develop the GRI-mechanism. For leaving them unconsidered makes it very likely that parameter values optimised in relation to ethane and methyl would no longer be compatible with the combustion of methane [5]. Owing to the enormous size of the differential equation systems involved here, such an optimisation can only be managed through the production of surrogate algebraic models via techniques such as the Surface Mapping method [6].

It is worth noting that all of the four reaction mechanisms considered here lead to initial results which are greatly at variance with these measurements highly dependent on methyl chemistry. These strong discrepancies may indicate that the chemistry of ethane and methyl is not optimally captured by the models so that they should not be used (without a preceding thorough large-scale optimisation) to simulate combustors or internal combustion engines where the CH_3 level is expected to play an important role in determining thermal efficiency and pollutant formation.

5. Conclusion

At the beginning of chemical kinetics, the analytical estimation of chemical kinetic parameters from empirical data was a feasible technique. With the inexorable grow in complexity of reaction mechanisms, experimental data sets and theoretical constraints, this simple approach has proved unreliable as a *systematic* procedure [5]. Today, it is increasingly recognised that the complex states of affairs prevailing in the chemical kinetics of combustion necessitate the use of numerical optimisation methods [7,8,15]. The importance of numerical optimisation for model evaluation is also being recognised in other research areas concerning applied energy, e.g. [1–4].

The first objective of this work was to provide a short but useful overview of the related methods and their underlying foundations. The more theoretical Section 2 can also be directly applied to model evaluation problems in other domains of applied energy research. The two main paradigms aiming at such parameter estimations are Bayesianism and frequentism as presented in Section 2.1. Classical Bayesian techniques assigning a single probability to models have the considerable drawback of blurring the distinction between knowledge and ignorance, as explained in Section 2.2. Imprecise Bayesian approaches using probability intervals circumvent this problem and may be theoretically promising. However they can be very demanding from a computational standpoint. Consequently, frequentist methods have been retained for the present work. Their applications are twofold. On the one hand, they can be used to systematically update parameter *feasible sets* defined as the ensemble of physically possible values compatible with all available measurements given their uncertainties [6]. On the other hand, they can also be employed to demonstrate, through a thorough optimisation, that a reaction mechanism stands in conflict with a set of experiments [8].

The program Kinefit for the optimisation of kinetic parameters has been developed by the author and validated numerically. It has then been applied to the optimisation of the GRI-mechanism 3.0 with respect to experiments related to the combustion of ethane and the methyl free radical. A considerable improvement has been reached and the adjusted model predictions seem compatible with the experimental uncertainties. An optimisation of GRI 3.0. in relation to these profiles for determining reliable kinetic coefficients is a long-term enterprise which must include the large experimental set previously used for constructing and optimising this mechanism [50]. Neither the unoptimised GRI 3.0 nor the unoptimised mechanisms of Frenklach, Heghes and NUIG presented in Section 4 should be employed for simulating combustors or engines where the chemistry of methyl and ethane can be expected to play an important role.

Overall, the present study demonstrates the relevance of numerical optimisation methods for the evaluation of chemical kinetic models. It seems likely they will become increasingly important for combustion research in the future, especially in relation to new fuels including blends.

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