

Using timescale analysis for optimising large chemical mechanisms

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Abstract

A novel chemical kinetic diesel surrogate model is introduced. The model consists of chemistry for each main chemical group in diesel fuel: n-decane, 2,2,4,4,6,8,8-heptamethylnonane, methylcyclohexane, and toluene. Ethanol chemistry is also included should the effect of oxygenates on conventional diesel fuels need to be investigated. This kinetic model is optimised using an automatic optimisation procedure and a novel heuristic for selecting reactions useful in optimisation is introduced. This heuristic combines the Level of Importance (LOI) algorithm and reaction sensitivity analysis to select the most relevant reactions for optimisation, thus including the importance of timescales in optimization, which has previously not been the case. It greatly reduces the time needed to select reactions for optimisation, and furthermore identifies those that would be otherwise ignored. Error analysis is performed on the optimised chemical kinetic mechanism and shows that the optimisation improves its overall response when compared to a wide range of experimental data.

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1 Introduction

As demand for fossil fuels continues to soar, it is important to investigate methods for increased engine efficiency. Hydrocarbon combustion has a wealth of undesirable consequences, including climate change and pollution, which can lead to poor human health [9][25]. It is desired to mitigate these effects by increasing engine efficiency. Computational simulations of engine systems allow researchers to investigate the effects of system changes without performing complex and time-consuming experiments. The chemical kinetics of combustion are of particular importance in these simulations.

Diesel is a common fuel for engine combustion, but its chemical kinetics are notoriously complex due to its high cetane number and wide mix of hydrocarbon species. Diesel engines rely on auto-ignition of the fuel mixture, but this must occur at the correct time in the cycle to provide good fuel efficiency and avoid engine damage. It has not been possible, as yet, to study the most complex aspects of diesel fuel. Diesel fuels have a high carbon number, which makes different experimental setups difficult due to relative resistance to knock when compared to gasoline or jet fuels. There is, however, experimental data measuring ignition delay times for diesel fuel surrogates in shock tubes, and this data has been extensively used throughout this work for model validation purposes.

It is desired to have a chemical kinetic mechanism, such as a diesel surrogate mechanism, model a wide range of combustion criteria. It is not possible to know the exact reaction rate of each elementary reaction. Therefore, the elementary reaction rates within the mechanism are subject to a degree of uncertainty. Some of the more basic reactions have been experimentally investigated and have approximate bounds [10][2]. Others, however, have not been investigated due to experimental constraints, lack of thermochemical data, or otherwise, and therefore have been created based on previous knowledge or thermochemical calculations. It can be considered reasonable and advantageous to alter some of these reaction rates within set limits to improve the model [7] [19].

Recently, several approaches have been proposed in literature, many of which have close resemblances to the presented work [28] [34] [27] [33]. Ziehn and Tomlin [34] present a software package that is able to calculate global sensitivities and their variances (thereby ranking them), whilst You *et al.* [33] focus on identifying difficult experimental data points and incorporating experimental uncertainty into mechanism optimisation. Sheen's papers [27, 28] focus on how uncertainty effects optimisation and how model uncertainty can be minimised during the optimisation process. These techniques mainly focus on model uncertainty rather than model optimisation. Whilst model uncertainty is an important and relevant area of research, this paper focuses on model optimisation; model uncertainty analysis will be the subject of future work.

An important step in those procedures is that of selecting the most influential reactions for optimisation, but none of the previously published works address a general procedure for identifying such influential reactions. We propose that by adequately considering the chemical lifetime of each species within the mechanism, we are able to put forth such a general approach.

In this paper, a method for identifying important reactions for mechanism optimisation is presented and demonstrated in the optimisation of a surrogate diesel fuel mechanism.

The Level of Importance (LOI) technique is proposed to identify the most important, or relevant, species, therefore allowing timescales to be considered in the optimisation process [11]. Reaction sensitivities are performed on reactions containing these species in simulations representative of physical process conditions. It is shown that the reactions that have high sensitivities and important species have a greater impact on the overall system optimisation. This proposed method of reaction selection is therefore general and applicable to different optimisation procedures. As will be discussed, the LOI is a local parameter from which global values are obtained either by integration or use of accumulated maximum values over a given range. Global sensitivity indices, such as those proposed by Ziehn and Tomlin [34], can in principle be applied. One then would not include the chemical timescales explicitly in the optimisation.

A novel four component diesel surrogate fuel is developed and presented; this surrogate is one of the most advanced diesel kinetic mechanisms presently found in literature. Each of the four components (n-decane, methylcyclohexane, heptamethylnonane, and toluene) was chosen to represent a hydrocarbon class typically found in diesel fuels. Optimisation was performed on the reactions selected by the LOI and reaction sensitivity analysis, and an optimised kinetic mechanism was created. This kinetic mechanism was then compared to both experimental data and the original mechanism. Simple error analysis shows that the optimised mechanism more closely matches the experimental data than the non-optimised one. In the present study ignition scenarios are emphasized as this is most relevant condition for the further use of the optimised mechanism. However, it should be noted that the procedure is in principle the same if flame parameters are considered, or even both, in which case integrated or accumulated values of the LOI and sensitivity parameters are to be used [12].

2 Methods

2.1 Level of Importance

The level of importance (LOI) technique is used to identify both important and unimportant species and reaction pathways in large kinetic mechanisms by combining species timescales and sensitivities [12] [11], and thereby rank species according to their relevance. Løvås showed that this ranking is correlated to important reaction paths [11], as will be discussed below.

The LOI for a certain species is defined as [12]:

$$LOI_i^j = S_{ij}\tau_i^C \quad (1)$$

where LOI_i^j is the level of importance of species i with respect to parameter j , S_{ij} is the sensitivity of species i to the perturbation of the parameter, typically the concentration of species j , and τ_i^C is the chemical lifetime of species i .

Sensitivity is described, in its most general form, as the dependence of a particular value c_i on a parameter k_j . The absolute sensitivity used in the LOI calculations in this work is:

$$S_{ij} = \frac{\partial c_i}{\partial c_j} \quad (2)$$

where c_i is concentration of species i , and c_j is the concentration of species j .

The chemical lifetime of a species can be approximated by using the diagonals of the Jacobian matrix for the mathematical system [30] [13]:

$$\tau_i^C = -\frac{1}{J_{ii}} \quad (3)$$

The approximation has been justified by comparing τ_i^C to eigenvalues calculated by rigorous computational singular perturbation (CSP) analysis [13]. It was shown that for a large part of the timescale range, the system is close to linear.

It is important to note that LOI represents a local value, from which a unique global ranking parameter has to be obtained. In the present work, there is adopted an integrated value from the main reaction domain similar to Løvås [11], and also common for obtaining global values from local CSP pointers [17].

2.2 Reaction Sensitivity Analysis

An important species is involved in many reactions, which in turn need to be ranked and sorted. Normalised sensitivity analysis can be performed on reactions as well as on species. In this case, the reaction rate coefficient of an elementary reaction is perturbed instead of species concentration. Therefore, in Equation 2, c_i is the concentration of species i , but k_j is the rate coefficient of reaction j . Furthermore, the relative sensitivity, rather than the absolute sensitivity, is used [31]:

$$S_{\text{OH},j}^r = \frac{k_j}{c_{\text{OH}}} \frac{\partial c_{\text{OH}}}{\partial k_j} \quad (4)$$

where $S_{\text{OH},j}^r$ is the relative sensitivity. In the present work, OH is used as species i , as ignition delay times are defined by the maximum change in OH concentration. Ignition delay times are the central factor in engine knock, a key parameter in engine design and efficiency. Depending on the case of study, the choice of target species can be changed.

It was decided to use this basic definition of reaction sensitivity due to its easy application in a wide range of commercial and open-source software. There are many varieties of sensitivity that can be explored in future work, such as individual or combined Arrhenius parameter sensitivity within a certain rate coefficient.

2.3 Optimisation Procedure

The chemical model was optimised using an automatic optimisation procedure with an objective function at its core. The objective function, based on that found in the paper by

Sheen *et al.* [28], is at the core of this procedure [8]:

$$\Phi_1(x) = \sum_{i=1}^N [\eta_i^{\text{exp}} - \eta_i(x)] \quad (5)$$

where N is the number of experimental data points used in the optimisation, $\eta_i(x)$ is the model response to a set of model parameters x , and η_i^{exp} is the experimental data corresponding to x . In this particular case, η_i^{exp} is the set of shock tube ignition delay times from experiments and $\eta_i(x)$ is the set of ignition delay times as computed by the model. Arrhenius coefficients selected by the method outlined in §3.4 were chosen as the free parameters of the model [4]. This optimisation procedure has been applied in various previous works with a high level of success [24] [3] [18].

By minimising the objective function, the model response becomes closer to the experimental data and the model is thereby optimised. The optimisation procedure allows the modeller to limit the amount that each parameter can be altered, so that an optimum solution that is outside the error bounds is not presented. For most of the reactions considered, for which there is little to no experimental or theoretical investigation, the maximum bounds of error were considered to be one order of magnitude.

Assuming a unique minimum of the objective function, this makes the optimum set of parameters values to defined by:

$$x^* = \arg \min[\Phi_1(x)] \quad (6)$$

A global search for a point near the minimum to this objective function is performed using a low discrepancy sequence. For this work, a Sobol sequence [29] is used to investigate the parameter space. However, other Monte Carlo type approaches are applicable for this purpose.

3 Chemical Kinetic Mechanism

The time needed to optimise a kinetic model is a monochrome increasing function of the number of free parameters chosen. When investigating small systems, the number of possible free parameters is small and manageable. However, when the system gets larger, a selection procedure must be used to find the Arrhenius parameters that will be the most effective when optimising the model.

3.1 Diesel Kinetic Mechanism

A four-component chemical kinetic diesel surrogate fuel model was developed containing n-decane, 2,2,4,4,6,8,8-heptamethylnonane (HMN), methylcyclohexane (MCH), and toluene. The n-decane ($\text{C}_{10}\text{H}_{22}$) kinetic mechanism is a combination of Seiser *et al.*'s n-heptane kinetics, [26] and Westbrook *et al.*'s linear alkane combustion chemistry [32]. HMN ($\text{C}_{16}\text{H}_{34}$, and also known as iso-cetane) from Oehlschlaeger *et al.*'s HMN kinetic mechanism [20] was used to represent the branched alkanes present in diesel fuel. MCH

(C₇H₁₄) from Orme *et al.* [21][23], with toluene sub-mechanism, was used to represent cycloalkanes and aromatic species in the surrogate model. A small sub-mechanism from Marinov [16] was added to the kinetic mechanism to account for the effects of oxygenated species on traditional diesel fuels.

The kinetic mechanism was reduced using the direct relation graphing (DRG) method and species lumping [14][1]. Each sub-mechanism was separately reduced using the DRG, and added together. Duplicate species and reactions were analysed and removed as necessary. Further reduction on this surrogate kinetic mechanism was performed to create the reduced mechanism, containing the 326 species and 2616 reactions. This reduced mechanism was tested against the full one at conditions between 850K and 1400K, as well as between 1 and 15 bar, with only minimal differences being noticed at the lowest temperature and pressure, and none at high temperatures.

3.2 Species Selection

An LOI analysis was performed on n-decane, HMN, and MCH at conditions representative of the temperature, pressure, and composition of an experimental data point. The reactant-specific species with the highest LOI values (*i.e.* the top 10 % of species) were identified. A reactant-specific species is defined as a species that is the product of combustion of one particular species, rather than a general product of combustion of any hydrocarbon.

Table 1: Selection of important non-reactant-specific intermediates as calculated by the LOI

N-Decane	Iso-Cetane (HMN)	Methylcyclohexane
CH ₄	H ₂	CO
CO	CO	H ₂ O
H ₂	CH ₄	H ₂
H	C ₂ H ₂	CH ₄
CH ₂ O	CH ₃	H
C ₂ H ₂	H	O
H ₂ O ₂	OH	H ₂ O ₂

Table 1 shows the species that consistently have high LOI values independent of varying conditions. This table shows that many of the same species are considered important regardless of the starting reactant. All these species are indeed known to be crucial for the correct prediction of important combustion targets, indicating the robustness of the method.

Table 2 presents some of the reactant-specific intermediates with high LOI values. An ‘N’ before or after a species implies that a number of different isomers had a high LOI value, thereby adding complexity. Note that MCH does not appear in the list of reactant-specific intermediates. Further investigation showed that MCH decomposes rapidly at the beginning of the reaction. This table gives a starting point for optimisation, but there is

Table 2: Selection of important reactant-specific intermediates as calculated by the LOI

N-Decane	HMN	Methylcyclohexane
NC₁₀H₂₂	HMN	C ₆ H ₆
C ₁₀ KET-N	AC ₁₀ H ₂₀	C ₆ H ₅ OH
C ₈ O ₃ -N	AC ₉ H ₁₈	Fulvene
C ₇ H ₁₄ O ₁ -3	HMNO ₂ -N	CY ₁₃ PD
C ₁₀ H ₂₀ -N	NC ₁₁ H ₂₂	C ₅ H ₁₀ -1
AC ₈ H ₁₈	NC ₁₅ H ₃₀	IC ₅ H ₈
C ₅ H ₁₀ -1	C ₁₀ KET-N	C ₃ H ₃
C ₈ H ₁₆ -N	JC ₈ H ₁₆	C · OCCCJO
C ₁₀ O ₄ -N	C ₆ H ₁₂ -1	C · CC · CC
C ₈ H ₁₅	C ₅ H ₁₀ -1	
C ₁₀ H ₁₉	C ₇ H ₁₄ O ₁ -3	
C ₉ H ₁₈ -1	AC ₁₂ H ₂₄	
C ₁₀ H ₂₀ -N		

still an abundance of reactions associated with each of these species. Therefore, reaction sensitivity is needed, as will be discussed in §3.3, in order to select the overall most important reactions that can be subject to optimisation.

A problem involving artificially large species lifetimes can arise when the LOI is used on a reduced kinetic mechanism. When a mechanism is reduced using the DRG method, species with low fluxes are removed, along with the reactions in which they participate [14] [15]. This procedure can cause an unphysical build-up of species' concentrations where reaction pathways have been removed.

These large concentrations cause no discernable problems until the LOI is considered, where the chemical lifetimes of these species become unphysically large. Therefore these species have an artificially inflated LOI value. Methods are being tested to automatically identify species with these unphysically large lifetimes.

3.3 Reaction Sensitivity

Whilst the important core reactions for optimisation are well-documented, it is much more difficult to find reactant-specific reactions that can be optimised to improve the kinetic model capabilities. The LOI has indicated which species are involved in these reactions; however, as discussed above, it is necessary to use a selection method, such as that described in §3.4, in order to rank the set of reactions in which the important species interact. These reactions are important for tailoring a multi-component kinetic model, such as the diesel one put forth in this work, to a wide range of different data sets.

The LOI does not provide information about important pathways through each sub-mechanism. However, the reaction sensitivities, as computed by the equation shown in §2.2, can be divided into two separate classes: the core reactions and the reactant-specific reactions. Core reactions contain species with high LOI values, such as the ones seen in Table 1, and

they frequently can be identified through literature searches (*i.e.* by reading Baulch *et al.* [2]).

Hundreds of reaction sensitivities were computed; the selected reactions presented in Figures 1 and 2 are used to help illustrate the new reaction selection technique presented in §3.4.

The reactions presented in Figure 1 are those that contain species with high LOI values. The reactions with the highest sensitivity values were selected to be used in the optimisation procedure.

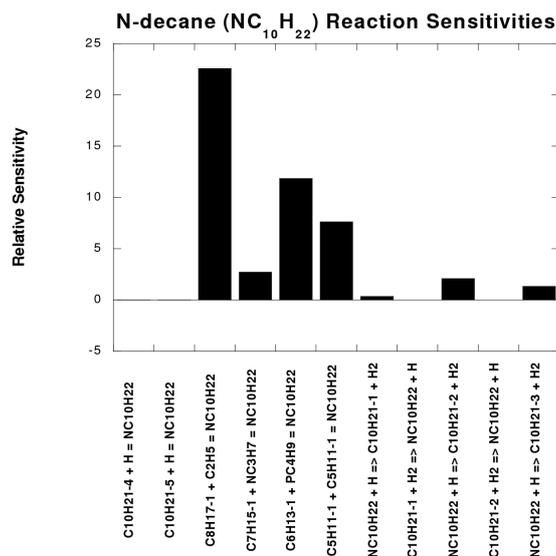


Figure 1: Example reaction sensitivities: *n*-decane

However, the wide range of sensitivity values can also be seen in Figure 2, and each of these reactions contains different numbers of species with high LOI values. This illustrates that a high reaction sensitivity alone is not necessarily sufficient to identify reactions that are useful in the optimisation process which has often been used as a guiding condition. The combination of the two parameters ensures the proper selection and ranking of reactions to optimise as outlined in the following subsection.

3.4 Selection Heuristic

As there may be thousands of reactions that are specific to each sub-mechanism in the kinetic model, a systematic procedure is needed to help identify those reactions that are influential to the model response of interest, *i.e.* those that are ‘optimisable.’ It may not be necessary to alter every optimisable reaction to suitably improve the model response, but a heuristic is necessary nonetheless to identify those that have the most influence. The heuristic presented here combines the the LOI and sensitivity work presented in §3.2 and §3.3.

It is proposed to first investigate reactions containing important reactant-specific intermediates, as seen in Table 2. Sensitivity analysis is performed on these reactions to find those

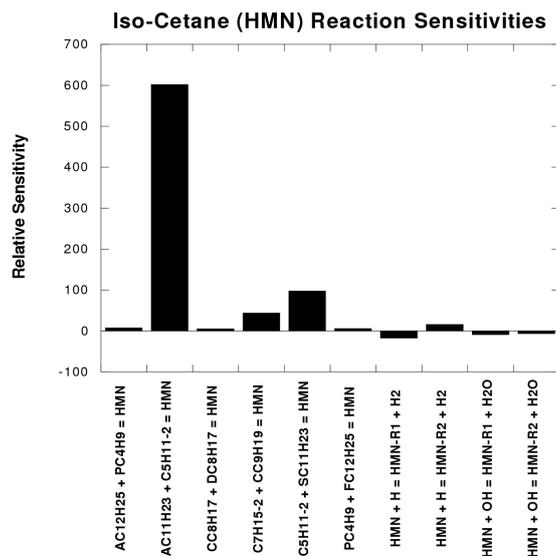


Figure 2: Example reaction sensitivities: HMN

with the highest sensitivity, such as those identified in Figure 2. The reactions with the highest sensitivities, such as reactions 2, 4, and 5 in Figure 2, were selected for potential optimisation. Furthermore, reactions with a majority of species with high LOI values, *i.e.* two out of three or three out of four but lower sensitivities (such as reactions 7–10 in Figure 2), were considered for optimisation. Reactions with either of these characteristics were found to have the greatest effect on optimisation. Such a procedure is easily implementable by automatic means.

4 Optimisation Results and Discussion

Fifteen separate optimisation calculations were performed. Six experimental data sets with 97 data points from three different sources were used [21][22][20]. From these calculations, a set of parameters originally identified by the selection heuristic and shown by the optimisation procedure to be influential to the model optimisation were gathered. The list of optimised reactions is given in Table 3. It can be noted that without the heuristic presented in §3.4 (*i.e.* with sensitivity and timescale analysis combined), the last nine of the reactions in this table would have been overlooked. These reactions were found to be important in low-temperature ignition delay kinetics. Furthermore, it was found that the final reaction in Table 3 has an effect on the combustion of both MCH and toluene. The heuristic has allowed the mechanism to be optimised to a further degree that would have otherwise been impossible without time consuming trial and error based analysis.

4.1 MCH and Toluene results

Figure 3 shows how MCH combustion simulation of the resulting optimised mechanism compares to experimental data at different equivalence ratios and pressures. Improve-

Table 3: Summary of optimised reactions based on LOI and reaction sensitivities

Reaction
$\text{AC}_{11}\text{H}_{23} + \text{C}_5\text{H}_{11-2} \rightleftharpoons \text{HMN}$
$\text{C}_5\text{H}_{11-2} + \text{SC}_{11}\text{H}_{23} \rightleftharpoons \text{HMN}$
$\text{C}_7\text{H}_{15-2} + \text{CC}_9\text{H}_{19} \rightleftharpoons \text{HMN}$
$\text{HMN} + \text{H} \rightleftharpoons \text{HMN-R}_2 + \text{H}_2$
$\text{HMN} + \text{OH} \rightleftharpoons \text{HMN-R}_1 + \text{H}_2\text{O}$
$\text{CO} + \text{H}_2\text{O} \rightarrow \text{HCO} + \text{OH}$
$\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$
$\text{H}_2\text{O}_2 + \text{O}_2 \rightarrow 2\text{HO}_2$
$2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$
$\text{C}_8\text{H}_{17-1} + \text{C}_2\text{H}_5 \rightleftharpoons \text{NC}_{10}\text{H}_{22}$
$\text{C}_6\text{H}_{13-1} + \text{PC}_4\text{H}_9 \rightleftharpoons \text{NC}_{10}\text{H}_{22}$
$\text{NC}_{10}\text{H}_{22} + \text{OH} \rightarrow \text{C}_{10}\text{H}_{21-1} + \text{H}_2\text{O}$
$\text{C}_2\text{H}_4 + \text{C}_8\text{H}_{17-1} \rightleftharpoons \text{C}_{10}\text{H}_{21-1}$
$\text{C}_3\text{H}_6 + \text{C}_7\text{H}_{15-1} \rightleftharpoons \text{C}_{10}\text{H}_{21-2}$
$\text{C}_{10}\text{OOH}_5\text{A} \rightleftharpoons \text{C}_{10}\text{O}_2-5 + \text{OH}$
$\text{C}_{10}\text{OOH}_4\text{B} \rightleftharpoons \text{C}_{10}\text{O}_4-7 + \text{OH}$
$\text{C}_{10}\text{OOH}_5-3\text{O}_2 \rightarrow \text{C}_{10}\text{KET}_5-3 + \text{OH}$
$\text{C}_8\text{OOH}_1-2\text{O}_2 \rightarrow \text{C}_8\text{KET}_1-2 + \text{OH}$
$\text{CH}_3 + \text{HC}_{15}\text{H}_{30} \rightleftharpoons \text{HMN-R}_7$
$\text{CC}_8\text{H}_{17} + \text{JC}_8\text{H}_{16} \rightleftharpoons \text{HMN-R}_5$
$\text{C}_6\text{H}_6 \rightleftharpoons \text{C}_6\text{H}_5 + \text{H}$

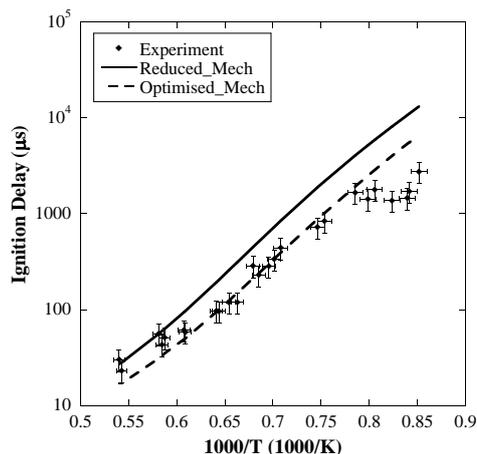
ments on the reduced kinetic mechanism can clearly be seen, especially at lower temperatures.

The optimised kinetic mechanism was tested further against MCH shock tube experiments which were performed at lean and rich conditions. The comparison of both the optimised and reduced kinetic mechanisms can be seen in Figure 4. Subfigure 4a shows that the optimised mechanism matches the experimental data more closely than the unoptimised one. However, subfigure 4b shows that the optimised kinetic mechanism actually performs more poorly than the reduced one in rich conditions. Whilst this is undesirable, it illuminates the importance of the optimisation range selections. The next stage in kinetic mechanism development would involve further optimisation for this range.

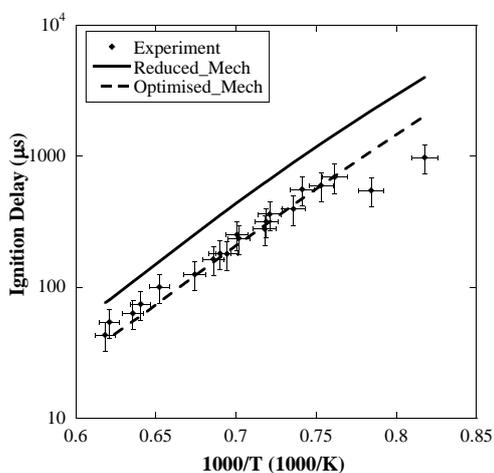
The ‘effectiveness’ of an optimisation can be quantified using error analysis. This can be illustrated by simply comparing each experimental data point value to the value given from the chemical kinetic model using the following equation:

$$\varepsilon = \sum_{n=1}^N \left| \frac{\eta^{\text{exp}} - \eta^{\text{sim}}}{\eta^{\text{exp}}} \right| \quad (7)$$

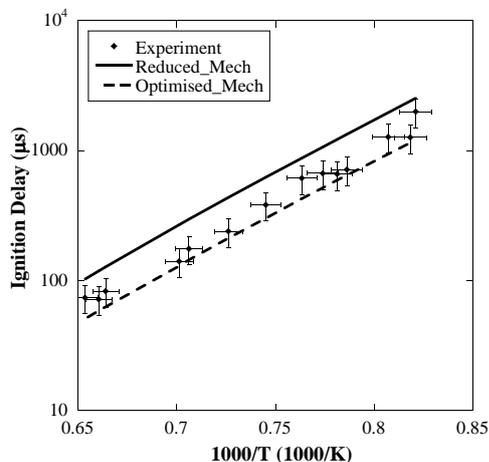
where ε is the defined error quantity. Although derived by basic means, ε is useful for comparing how much the reduced and optimised kinetic mechanisms differ from the ex-



(a) 1 atm



(b) 2 atm



(c) 4 atm

Figure 3: MCH shock tube ignition delay times at $\Phi = 1$ for varying pressures. Experimental data from Orme et al. [21].

perimental data. Table 4 shows that the optimised mechanism is indeed more accurate than the original one when compared to MCH ignition delay time data, even though the optimised mechanism has sacrificed some of the high temperature accuracy for low temperature accuracy instead, even though shock tube experiments are more easily performed at higher temperatures.

The optimisation process was also successful when toluene ignition delay was considered, despite the fact that it was not included in the optimisation procedure itself. Figure 5 and figure 6 show that the optimised mechanism compares better to toluene shock tube data than the reduced mechanism. By identifying sub-mechanisms that are interlinked, it has been possible to minimise the number of optimised reactions whilst still noticing a positive impact on mechanism performance. Further work can still be performed to improve the toluene sub-mechanism response to experimental data.

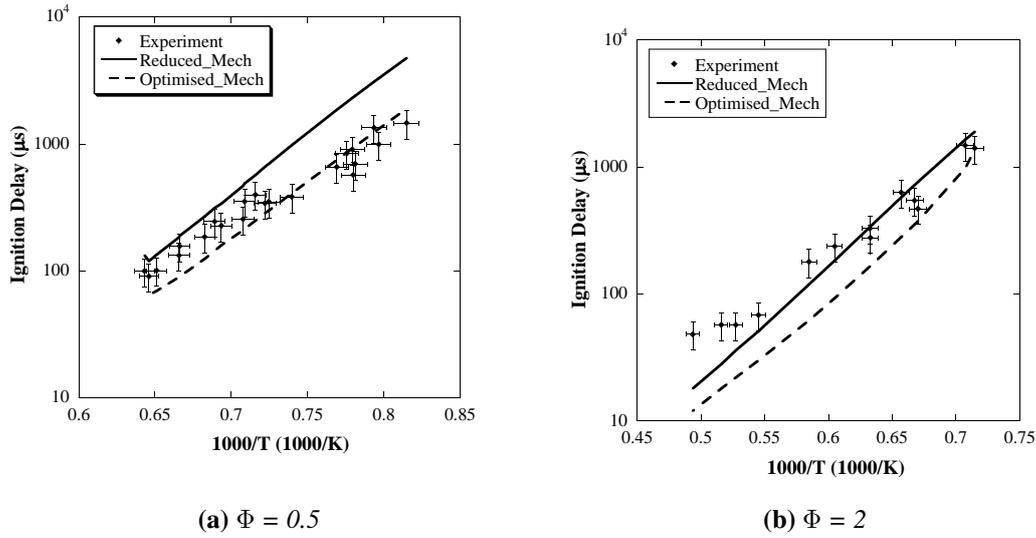


Figure 4: MCH shock tube ignition delay times at 1 atm. Experimental data from Orme et al. [21].

Table 4: Conditions and cumulative error between MCH shock tube experimental data and both the reduced and optimised mechanism

P (bar)	T (K)	Φ	ε —Reduced Mech	ε - Optimised Mech
1.01	1174–1851	1	44.08	13.17
2.03	1223–1617	1	23.10	3.88
4.05	1218–1530	1	9.59	3.51
1.01	1227–1555	0.5	24.83	5.98
1.01	1399–2026	2	4.09	6.23

Table 5: Conditions and cumulative error between toluene shock tube experimental data and both the reduced and optimised mechanism

P (bar)	T (K)	Φ	ε —Reduced Mech	ε - Optimised Mech
3.04	1338–1641	0.33	56.35	29.25
3.04	1358–1758	1	26.37	8.45
15 - 22	971–1173	1	71.98	35.96

It should be noted that medium and low temperature kinetics are emphasized throughout this work. These temperatures have a greater effect on knock and in-cylinder pressure rises when the kinetic mechanism is used in engine simulations and is also considered more challenging with respect to kinetic modelling.

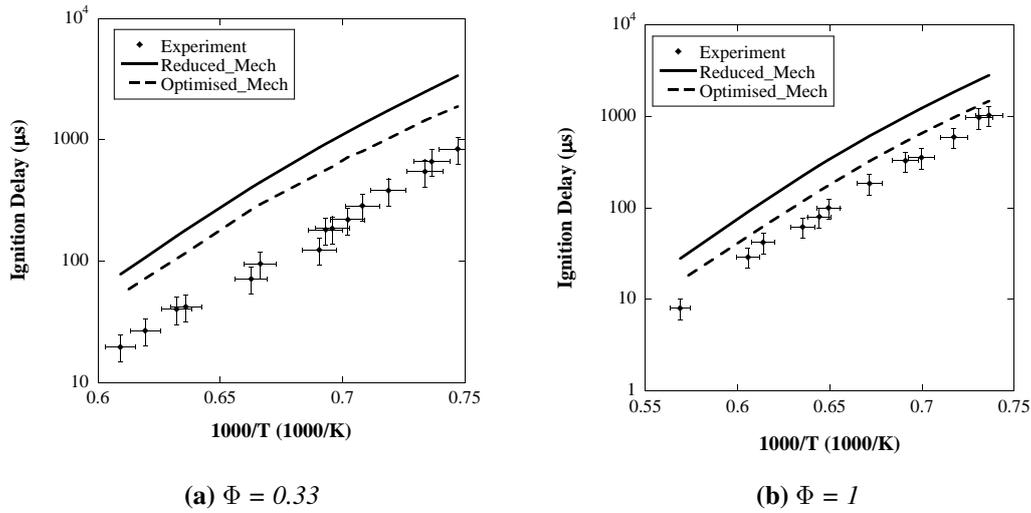


Figure 5: Toluene shock tube ignition delay times at 3 atm and varying Φ . Experimental data from Burcat et al. [5].

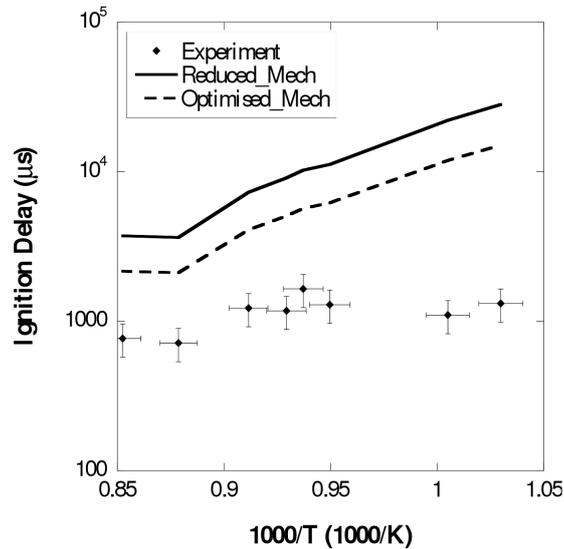
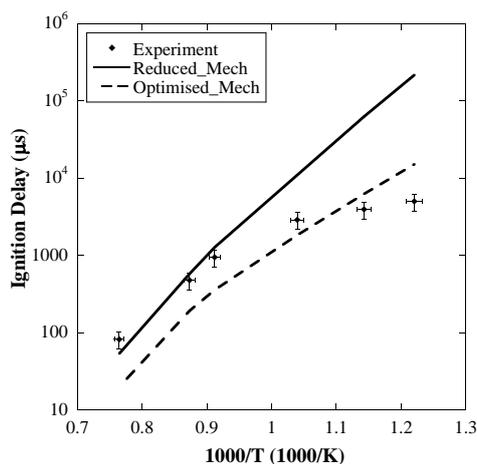


Figure 6: Toluene shock tube ignition delay times at $\Phi = 1$ and $P = 15 - 22$ bar. Experimental data from Davidson et al. [6].

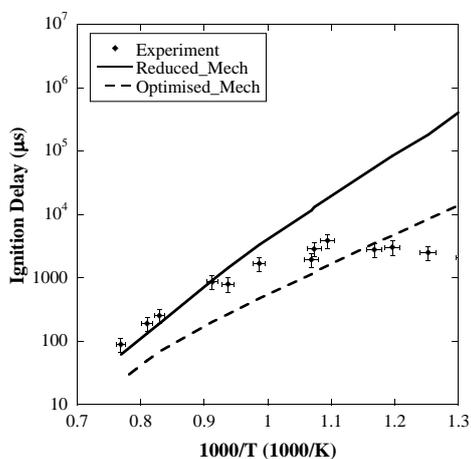
4.2 N-decane results

Figure 7 shows the n-decane combustion at different equivalence ratios and pressures. For n-decane, much more experimental data is available for elevated pressures, which represents an extra challenge for the optimised model. This shows that the optimised kinetic mechanism performs equally well at low equivalence ratios as higher ones. Ignition delay at lower temperatures is greatly improved.

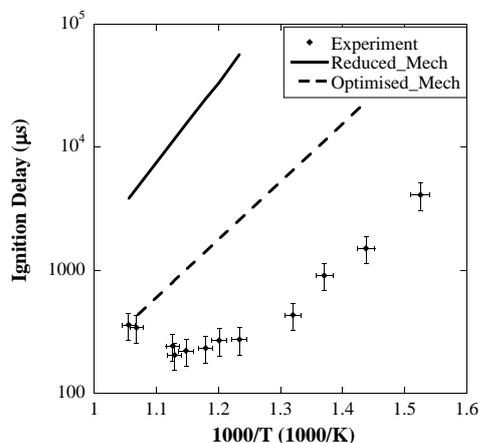
Subfigure 7c shows the improvement of the optimised kinetic mechanism over the reduced one even at high pressures of 50 bar. Whilst the optimised kinetic mechanism still



(a) 15 bar, $\Phi = 0.5$



(b) 15 bar, $\Phi = 1$



(c) 50 bar, $\Phi = 1$

Figure 7: *N*-decane shock tube ignition delay times. Experimental data from Pfahl et al. [22].

gives slow ignition delay times when compared to experimental data, it is a noticeable improvement over the reduced one.

Table 6 shows the difference in ε when both kinetic mechanisms are used to simulate different *n*-decane shock tube experimental data sets; it quantifies the differences seen in Figure 7. This table shows that the optimised kinetic mechanism is an improvement on the reduced one by approximately an order of magnitude for each different data set.

The effect of the reactions selected by the LOI procedure is most noticeable during low temperature *n*-decane combustion. At higher temperatures, *i.e.* above 1000K, reactions 10, 11, and 13–18 in Table 3 were found to have little effect on ignition delay times. However, they have a much greater effect on ignition delay times in low temperature conditions, *i.e.* between 750 and 1000 K. When these reactions were not optimised, it was

Table 6: Conditions and cumulative error between *n*-decane shock tube experimental data and both the reduced and optimised mechanism

P (bar)	T (K)	Φ	ε –Reduced Mech	ε - Optimised Mech
15	819–1308	0.5	57.28	4.61
15	730–1301	1	413.43	25.47
15	743–1275	1	124.10	11.98
50	733–962	0.67	984.69	35.01
50	810–947	1	679.46	28.44
50	827–912	2	211.17	7.08

found that the simulated ignition delay could be increased by nearly 1 ms.

4.3 Iso-cetane results

Finally, optimisation of HMN was performed at a wide range of pressures and equivalence ratios. Figure 8 shows that in this case the optimised mechanism was particularly successful at high pressure and low temperatures. However, overall it can be concluded that also for HMN the optimised model outperforms the original mechanism for all conditions. Error analysis, as shown in Table 7, proves again that this new optimised kinetic mechanism is more accurate than the original reduced one.

Table 7: Conditions and cumulative error between HMN shock tube experimental data and both the reduced and optimised mechanism

P (bar)	T (K)	Φ	ε –Reduced Mech	ε - Optimised Mech
8.1–40.8	1007–1494	0.5	12.48	10.67
9.9–46.9	953–1309	1	31.14	9.41
8.4–47.1	879–1300	1.5	85.88	26.31

5 Conclusions

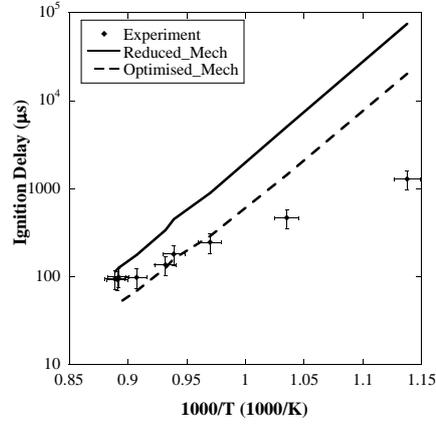
The problem of identifying import reactions for optimisation in large chemical kinetic mechanism (over 2000 reactions) is discussed, and a technique for automatically and reliably identifying reactions important for kinetic mechanism optimisation is presented. This technique is applied to a chemical kinetic surrogate model for diesel fuel containing chemistry for *n*-decane, HMN, MCH, and toluene.

The technique for identifying reactions important for optimisation is a combination of species' importance, as measured by the LOI, and reaction sensitivity. The Level of Importance (LOI) method is used to identify potentially important reactant intermediates by means of timescale analysis. Reactions including the important species are identified.

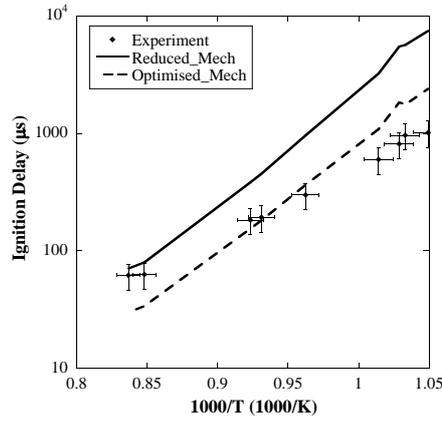
Sensitivity analysis is performed on these reactions. Reactions with either the highest sensitivity values or with the most important species are identified and used for model optimisation. A total of 23 reaction rates were optimised, several of which were identified using the proposed heuristic, and would have otherwise not been considered. The method can be automated and implemented for any type of optimisation tool in hand. The optimised kinetic mechanism was compared against a wide range of shock tube data sets. Error analysis showed the optimised mechanism had better prediction capabilities than the original one.

In future work, it is desired to apply this heuristic to different chemical kinetic mechanisms. Optimisation procedures can aid a modeller to refine individual reaction rates, and by identifying reaction rates that can be optimised, this process can be expedited. It is also desired to investigate the possibility of extending the reaction rate sensitivity capabilities. By introducing either global sensitivity or individual Arrhenius parameter sensitivities, it may be possible to refine the heuristic. If this sensitivity can be linked automatically with the LOI, the optimisation process will be even more quick and intuitive.

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(a) High pressure, $\Phi = 1.5$



(b) High pressure, $\Phi = 1$

Figure 8: Optimisation comparison for iso-cetane shock tube ignition delay times (25-40 bar). Experimental data from Oehlschlaeger et al. [20].

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