Optimized rate rules and kinetic models for large normal and *neo*alkenes

Pengzhi Wang^a, Tibor Nagy^{b,*}, Sirio Brunialti^c, Máté Papp^d, Hossein S. Saraee^a, Colin Banyon^a, S. Mani Sarathy^c, Tamás Turányi^d, Henry J. Curran^{a,*}

^aCCC, School of Biological and Chemical Sciences, Ryan Institute, MaREI, University of Galway, Galway, Ireland ^bIMEC, HUN-REN Research Centre for Natural Sciences, Budapest, Hungary ^cCCRC, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia ^dInstitute of Chemistry, Eötvös Loránd University (ELTE), Budapest, Hungary

Abstract

A consistent set of rate rules for the reactions of large alkanes involving primary and secondary carbons is optimized based on *n*- and *neo*pentane, *n*- and *neo*hexane, and *n*-heptane chemistry. The initial mechanism of these fuels is autogenerated by a suitably modified version of MAMOX++ based on the central Arrhenius curve of their prior uncertainty range, which was determined by a review of theoretical studies of alkanes. The Reduction Assisted Parameter Optimization and Mechanism Development (RAPOD) approach was used to accelerate the optimization, so an accurate reduced mechanism was developed using the DRGEP method, by which the number of species and reactions were reduced from 4432 species and 16778 reactions to 1754 and 8380, respectively. The GalwayMech1.0 served as a core mechanism, and the thermodynamic data were taken from a high-level calculation study, in case of unavailability, the group additivity method trained on the previously published data was employed for the estimation. As optimization targets, we collected 68, 57, and 166 measurements of these target fuels in shock tubes, rapid compression machines, and jet-stirred reactors, respectively. 116 important rate rules out of 187 rate rules were identified by the PCA-SUE method, and their A, n, E Arrhenius parameters were optimized within their prior uncertainty range using the Optima++ code. In addition, the thermodynamic data (heat of formation and entropy) of RH, R, RO₂, QOOH, and O₂QOOH were optimized within a carefully evaluated uncertainty range of each species. The two-step optimization reveals a generally good performance for these target fuels compared to the other mechanism. As a validation of the optimized rate rules, mechanisms were generated for 2,2- and 3,3dimethyl pentane, *n*-octane, *n*-nonane and *n*-decane fuels and tested against experiments. The optimized rate rules provide a significantly improved description of the ignition delays of these fuels compared to the initial rate rules, demonstrating their universality and transferability.

Keywords: combustion mechanism, parameter optimization, Optima++, mechanism generation, MAMOX++

*<u>nagy.tibor@ttk.hu</u>, <u>henry.curran@universityofgalway.ie</u>

11. Introduction

2 The large alkanes are important components in 3 practical fuels and are usually used as surrogate fuels 4 [1]. Therefore, it is important to build a model 5 including various large alkanes for mixture 6 simulation, which helps explore advanced fuels and 7 develop advanced combustion strategies and devices. 8 The performance of the large-alkanes mechanism is 9 affected by the thermochemistry and core mechanism 10 (C $_0$ -C $_4$). The core mechanism was recently developed 11 as part of the C3MechV4.0 mechanism [2], in which 12 the C₀–C₄ sub-mechanisms were comprehensively 13 refined based on literature experiments. The 14 thermochemistry data of combustion intermediates of 15 alkanes (e.g. alkyl radicals, alkyl-peroxy radicals, etc) 16 have also been updated recently by Elliot et al. [3, 4] 17 using a very high-level theory and sophisticated error 18 cancellation strategies. Based on the results of these 19 accurate calculations, Ghosh et al. [5, 6] improved the 20 group additivity values for thermochemistry data by 21 refining the values of the main groups and by adding 22 some new correction terms. The thermochemistry 23 estimated based on the improved group additivity 24 values was shown to be more accurate relative to the 25 high-level accuracy calculations compared to the 26 group additivity estimates by the RMG [7] and Burke 27 et al. [8].

The fuel-specific sub-model is usually developed 28 29 using rate rules in which the rate constant of each 30 reaction class with certain types of reaction is 31 determined. Bugler et al. [8] established alkane rate 32 rules targeting three pentane isomers and built a 33 pentane mechanism with a global good performance 34 on ignition delay times (IDTs). Zhang et al. [9] further 35 updated the alkane rate rules by considering five 36 hexane isomers with more complex structures. Cai et 37 al. [10] established a consistent set of rate rules for 38 linear alkanes from C_7 to C_{11} . Due to the updated core 39 chemistry and the accurate thermochemistry data, 40 these rate rules for large alkanes need to be updated to 41 improve the quality of the constructed mechanisms. 42 Wang et al. [11] and Heng et al. [12] updated the rate 43 rules of alkanes by targeting the extended 44 experimental data of *iso*-octane and its isomers with 45 the latest core chemistry and thermochemistry data. 46 However, due to the limited diversity of the structures, 47 their rate rules are still not accurate enough to employ 48 them reliably to the other alkanes.

49 Due to the diversity and commonality of chemical 50 environments and chemical pathways for large 51 alkanes, it is necessary to consider multiple fuels 52 simultaneously in rate rule development studies to get 53 a universally applicable, consistent set of rate rules. 54 For example, pentane isomers, hexane isomers, n-55 heptane, *iso*-octane, and the larger n-alkanes should 56 be investigated at once. Due to the large size of the 57 models for such large alkanes, the construction and 58 parameter tuning of these models cannot be done 59 manually without errors in a reasonable time. 60 MAMOX++ [13-15] code is an effective tool for auto61 generating combustion kinetic mechanisms based on 62 a set of rate rules. Optima++ [16-18] is a highly 63 effective, robust kinetic model optimization software 64 which has been recently extended to the rate rule 65 optimization, and was employed to successfully 66 optimize a reaction mechanism autogenerated for 67 pentane isomers by MAMOX++ [19]. The optimized 68 model showed a significant and comprehensive 69 improvement compared to Bugler's model [20]. The 70 combined application of MAMOX++ and Optima++ 71 has been proven to be an efficient way of model 72 development based on rate rules.

In this work, as the first part of our comprehensive 73 74 studies of alkane rate rules, we focus only on primary 75 and secondary carbon rate rules, that is classes of 76 reactions that take place on or between primary and 77 secondary carbon atoms. To establish these rate rules, 78 we generated mechanisms for *n*-pentane, *neo*pentane, 79 *n*-hexane, *neo*hexane, and *n*-heptane, reduced them 80 using DRGEP, and after merging, we optimized them 81 using Optima++. Subsequently, as a validation of the 82 optimized rate rules, mechanisms for 2,2-dimethyl 83 pentane (22DMP), 3,3-dimethyl pentane (33DMP), n-84 octane, *n*-nonane, and *n*-decane were generated using 85 MAMOX++, which then were tested against 86 experiments. Due to the experimental studies of 87 22DMP and 33DMP being rare, IDTs of them were 88 measured in a rapid compression machine (RCM). 89 providing essential experimental data for validating 90 alkane rate rules involving quaternary carbons. 91 Additionally, to evaluate the reactivity trend of n-92 pentane, *n*-hexane, and *n*-heptane, this study extends 93 ignition delay time measurements for *n*-hexane using 94 a shock tube (ST).

96 2. New experiments and literature data

In the present study, ignition delay times of 97 98 22DMP, 33DMP and *n*-hexane are measured in ST 99 and RCM at the University of Galway. Both facilities 100 are introduced in detail in our previous studies [21, 101 22]. The uncertainty of reflected shock temperature in 102 the ST and compression temperature in RCM are ± 20 103 K and ± 15 K, which lead to approximately $\pm 20\%$ 104 uncertainty in ignition delay times in both facilities, 105 as discussed in Li et al. [23]. Table 1 summarizes the 106 experimental conditions used in the present study. The 107 IDTs of 22DMP and 33DMP were measured in RCM 108 at $\varphi = 0.5$ and p = 20 atm, while *n*-hexane experiments 109 were conducted in ST at $\varphi = 1.0$ and p = 30 atm. These 110 experiments were done in air and covered the negative 111 temperature coefficient (NTC) regime of the three 112 fuels.

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Condition of	present ex	periments
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fuel	<i>T</i> (K)	p (atm)	φ	x			facility
				fuel	O_2	N_2	
<i>n</i> -hexane	700-1300	30.0	1.0	2.16	20.6	77.3	HPST
22DMP	680–955	20.0	0.5	1.87	20.6	77.5	RCM
33DMP	680–960	20.0	0.5	1.87	20.6	77.5	RCM

Several experimental and modelling studies of n-1 2 pentane, neopentane, n-hexane, neohexane, and n-3 heptane have been conducted over the past decades. 4 Based on a literature survey, we have collected 1489 5 experimental measurements altogether including our 6 present measurements. To accelerate the optimization 7 task, a carefully selected subset containing only 157 8 measurements was utilized. The selected experiments 9 were chosen to ensure coverage of a wide range of 10 temperatures, pressures, and equivalence ratios, 11 providing a comprehensive dataset for optimization. 12 For instance, from each data series, at least one IDT 13 experiment was selected in the low-, the intermediate-14, and the high-temperature regimes, while jet-stirred 15 reactor (JSR) experiments were selected to capture 16 inflection points in species concentration curves. The 17 covered conditions and literature references are 18 shown on the poster. 19

20 3. Methodology

The flow chart is shown in Error! Reference 21 22 source not found. In the present work, the optimized 23 thermodynamic data, updated core chemistry, and 24 initial rate rules were employed in MAMOX++ to 25 generate an initial mechanism. The initial rate rules in 26 the present work were taken by the central rate 27 constant of the prior uncertainty range which was 28 determined by reviewing the literature studies 29 following the same procedure presented in Wang et 30 al. [19] based on the theory proposed by Nagy et al. 31 [24, 25]. The mechanism generated for n- and 32 neopentane, n- and neohexane, and n-heptane 33 combustion, contained 5743 species and 18761 34 reactions, which is too large for direct optimization 35 even if well-scaling solvers, Zero-RK [26, 27] is used 36 within Optima++. To accelerate the optimization of 37 large combustion mechanisms, Nagy and coworkers 38 proposed the Reduction-Assisted Parameter 39 Optimization and Mechanism Development 40 (RAPOD) procedure [28]. We employed the RAPOD 41 approach using DRGEP mechanism reduction method 42 [29, 30] to reduce the autogenerated detailed model. 43 which thereby could be reduced to 2000 species and 44 9167 reactions and made the optimization task 45 feasible. Then, the rate constants in rate rules format 46 from the reduced mechanism are optimized within 47 their determined uncertainty range using Optima++ 48 and Zero-RK solver [26, 27] on the selected 157 49 RCM, ST, and JSR experiments. As a validation, the 50 optimized rate rules were employed to generate 51 mechanisms of *n*-octane, *n*-nonane, *n*-decane, 52 22DMP, and 33DMP, which were tested against 53 experiments to test the transferability and universality 54 of alkane rate rules. Chemkin-Pro [31] is used for 55 simulating these data.

The performance of a combustion kinetic model 57 can be characterized by an error function, which 58 quantifies the deviation of the simulation results from 59 the experimental data. In Optima++ the following



Fig. 1. Flow chart of rate rule optimization

60 experimental uncertainty normalized mean square 61 error function is used:

$$E(P) = \frac{1}{N} \sum_{f=1}^{N_f} \sum_{s=1}^{N_{fs}} \frac{w_{fs}}{N_{fsd}} \sum_{d=1}^{N_{fsd}} \left(\frac{Y_{fsd}^{sim}(P) - Y_{fsd}^{exp}}{\sigma(Y_{fsd}^{exp})} \right)^2.$$
(1)

Parameters N, Nf, Nfs, Nfsd are the number of data 62 63 series in all data files, the number of files, the number 64 of series in the f^{th} file, the number of data in the s^{th} 65 series of the f^{th} file, respectively. Y_{fsd}^{exp} and $\sigma(Y_{fsd}^{\text{exp}})$ 66 are the d^{th} experimental data in the s^{th} series of the f^{th} 67 file and its one standard deviation uncertainty, 68 respectively. $Y_{fsd}^{sim}(P)$ is the corresponding simulated 69 value with the investigated kinetic model at parameter 70 values **P**. For ignition delays, transformation $Y=\ln$ 71 IDT was applied, and relative error was interpreted as 72 an absolute error in natural logarithmic scale. The 73 Optima++ code minimizes this error function by using 74 the very robust FOCTOPUS algorithm [32]. The error 75 function can be evaluated only for a part of the data 76 collection, for example only for IDT or concentrations 77 measured in JSR. The value of the error function has 78 an absolute meaning, as \sqrt{E} measures the uncertainty 79 normalized root-mean-square deviation (RMSD) 80 between the model and the experimental results, thus st for the perfect model $\sqrt{E} \le 1$, and if $\sqrt{E} \sim 2$ is usually 82 considered as a great model, and we typically 83 considered a model satisfactorily predictive if $\sqrt{E} < 3$. 84 In the following, we analyse performance 85 improvements in terms RMSD error.

86 Uncertainty limits of rate coefficients were 87 determined by considering all previous theoretical and 88 experimental determination for a given rate rule and 89 assuming a factor 2 uncertainty around them. The 90 average curve of the upper and lower boundaries of 91 the unified uncertainty band is fitted with the 92 Arrhenius equation and taken as the central rate rule 93 and was used for the generation of the initial kinetic

Table 2
Molecular size dependent 2σ uncertainties of NASA polynomial coefficientsCoeff.Total uncertainty for GA values α_6 $2\sigma_6 = \left(61.27 + \frac{M}{0.7617\frac{g}{mol}}\right)K$ $2\sigma_6 = \left(-417.8 + \frac{M}{0.1255\frac{g}{mol}}\right)K$ $\sigma_{6,tot} = \sqrt{\sigma_{6,S1D}^2 + \sigma_{6,GA}^2}$ a_7 $2\sigma_7 = 0.2697 + \frac{M}{348.1\frac{g}{mol}}$ $2\sigma_7 = -0.5050 + \frac{M}{79.30\frac{g}{mol}}$ $\sigma_{7,tot} = \sqrt{\sigma_{7,S1D}^2 + \sigma_{7,GA}^2}$

1 model. The symmetrized boundaries around this 2 central curve were stored in the form of covariance 3 matrix [24]. The Arrhenius curve of each important 4 rate rule was optimized within this uncertainty band 5 (checked within 500-2500 K). As the uncertainty 6 ranges determined by this procedure are usually wide, 7 they allow significant, even unphysical changes in the 8 shape (E: slope and n: curvature and slope) of the 9 Arrhenius curves. Therefore, in addition to the 10 constraints in the rate coefficients, we introduced ± 1 11 kcal/mol and ± 1 constraints for the *E* and *n* Arrhenius 12 parameters, respectively to preserve the physical 13 character of the initial central Arrhenius curve during 14 optimization. In the case of PLOG reactions and rate 15 rules that are defined with varying *E* and *n* values (i.e. 16 depending on the heat of reactions), the Arrhenius 17 curves were modified by a common tuning factor with 18 Arrhenius type temperature dependence to maintain 19 their consistency during optimization [19].

The important kinetic parameters of the model, 21 called active parameters, were identified using the 22 PCA-SUE method [33], which is based on the 23 principal component analysis of the experimental data 24 uncertainty normalized and parameter uncertainty 25 scaled local sensitivity matrix.

Significant developments have been made to the 26 27 Optima++ code with this study, as now it allows 28 optimization of thermodynamic data, more 29 specifically the a_6 and a_7 NASA polynomial 30 coefficients, through which thermodynamic 31 functions: enthalpy H(T) and entropy S(T), 32 respectively, can be shifted. These changes affect two 33 things in the model: the reaction enthalpies and the 34 reaction free energies can be changed, the latter of 35 which is used (together with the forward rate 36 coefficient) to calculate the rate coefficient of the 37 backward reaction. Therefore, this development 38 allows the tuning of the backward rate coefficients of 39 important reactions independently from the forward 40 rate coefficients. The molecular size dependent 41 uncertainty ranges of NASA polynomial coefficients 42 a6 and a7 of relevant species: RH, R, RO2, QOOH, and 43 O₂QOOH were determined with carefully evaluation 44 of the error analysis of the STAR-1D protocol [3, 4] 45 and the group additivity (GA) based estimations 46 thermodynamic data estimate [5, 6]. The following 47 Table summarizes the molecular size dependence of 48 the uncertainties of a_6 and a_7 coefficients separately 49 for the STAR-1D method, the GA fit to the STAR-1D 50 results, and the total GA based estimations. 51

The NASA polynomial coefficients were 53 optimized within $\pm 2\sigma$ uncertainty range. It is expected 54 that the errors of the estimated thermodynamic data of 55 isomers, and thereby those of the a_6 and a_7 parameters 56 are strongly correlated, therefore, similarly to the rate 57 rules the a_6 and a_7 parameters of different isomers 58 were shifted together during optimization.

However, simultaneous optimization of rate rules 60 alongside thermodynamic data makes the rate rules 61 non-universal as the tuned thermodynamic data is 62 specific to species of the training system and non-63 transferable to other fuels. Consequently, we carried 64 out the optimization in two steps: first only the rate 65 rules were optimized, thus they are expected to be 66 transferable; second, the beside the optimized rate 67 rules, the a_6 and a_7 coefficients were optimized to 68 develop an even more accurate mechanism for the 69 investigated species.

71 4. Results

72 *4.1 Evaluation of the optimized models*

Figure 2 illustrates the improvements of species rs concentration achieved by optimizing either only rate r6 constants or both rate constants and thermodynamic r7 data. Optimizing only the rate constants generally r8 enhances the model, although some error values r9 remain notably high (>3), such as C6H10OOH2-4, 80 C7H14-1, and C7H14-2. The most significant 81 improvements are observed in cyclic ethers. For 82 instance, the RMSD error value of C6H12OOH2-3 83 concentration has decreased significantly from 12.3 to



Fig. 2. Improvement in the experimental uncertaintynormalized RMSD error for species concentrations between the initial mechanism and after optimization of the rate rules, and subsequent thermodynamic data optimization.



Fig. 3. Improvement in experimental uncertainty-normalized RMSD error for the 1st-stage and final-stage ignition delay times between the initial mechanism, after optimization of the rate rules, and subsequent thermodynamic data optimization.

1 1.57 upon optimization. However, concentration 2 errors of olefins, such as C5H10-1, C7H14-1, and 3 C7H14-2 showed limited improvement.

4 Figure 3 shows the improvements in 1st-stage and 5 total ignition delay times. The model optimized for 6 rate constants alone shows substantial overall 7 enhancement but performs worse for the 1st-stage 8 ignition of compounds like *neo*pentane and *n*-heptane. 9 This is likely because most reactions influencing the 10 1st-stage ignition also affect the total ignition, 11 indicating that optimizing rate constants alone cannot 12 resolve the compromise issue.

13 In addition to optimizing rate constants, this work 14 further refines thermodynamic data. Fig. 2 15 demonstrate that the additional optimization of 16 thermochemistry significantly improved the 17 concentration predictions for species, such as 18 C6H12O2-4, C7H14-1, and C7H14-2, which showed 19 only minor error reduction by rate rule optimization 20 alone. Moreover, thermodynamic data optimization 21 significantly improved the prediction of 1st-stage 22 IDTs, and also provided slight improvements in total 23 stage IDTs. Fig. 4 presents the validation of the 24 optimized model against ignition delay times 25 measured in ST and RCM for n-pentane, n-hexane,



Fig. 4. Validation of the optimized model against the IDTs of *n*-pentane, *n*-hexane, and *n*-heptane. Experimental data were obtained from Refs. [20, 34] and the present study.

26 and *n*-heptane at p = 30 atm and $\varphi = 1.0$. An evident 27 trend is observed in reactivity: *n*-pentane < *n*-hexane 28 < *n*-heptane. However, no clear trend emerges for the 29 1st-stage IDT. The 1st-stage ignition of *n*-pentane is 30 noticeably slower than that of *n*-hexane, which closely 31 resembles the 1st-stage IDT of *n*-heptane. The present 32 model exhibits slightly too fast reactivity in the NTC 33 region for *n*-hexane, nevertheless, it effectively 34 predicts both total and 1st-stage IDT for these fuels.

Fig. 5 provides a comprehensive comparison 36 between the present optimized model and 13 literature 37 models. The error values are calculated based on 38 selected data points. For IDTs, the error values of the 39 present model are all below 3, indicating that it can 40 predict IDTs within the error bars on average. While 41 the present model shows slightly higher error values 42 for JSR concentrations in the case of *n*-pentane, *n*-43 hexane, and *neo*hexane, its performance is still 44 superior to other models.

For *n*-pentane and *neo*pentane, the most recently 46 updated model by Wang et al. [19] (Wang_2024) 47 exhibits IDT RMSD error values around 3 in shock 48 tube and RCM experiments, while its JSR RMSD



Fig. 5. Experimental uncertainty-scaled RMSD errors of ignition delays of the initial mechanism, the rate rule + thermodynamic data optimized model and 13 literature models.



Fig. 6. Validation against *n*-pentane ignition delay times from Bugler et al. [20].

Fig. 7. Validation against *neo*pentane ignition delay time from Bugler et al. [20].

1 error values are higher (5.3 for *n*-pentane and 4.3 for 2 neopentane). By optimizing the thermodynamic data, 3 the present study achieves improved results, reducing 4 IDT RMSD errors for *n*-pentane and *neo*pentane to 5 approximately 2. For *n*-hexane and *neo*hexane, 6 Zhang's model [35] (Zhang_2019) was initially 7 developed for five hexane isomers and later updated 8 in C3MechV3.3 [36] and C3MechV4.0 [2]. The IDT 9 error values for these models are comparable to those 10 of the optimized model; however, our model 11 demonstrates better performance in predicting the JSR 12 data for neohexane. For n-heptane, most models 13 accurately predict IDTs in shock tube experiments. 14 However, only the present model, along with 15 C3MechV3.3 and C3MechV4.0, can capture the 16 RCM data reliably. Chang et al.'s model [37] 17 (Chang_2022), which is a skeletal mechanism, is



Fig. 8. Validation against *n*-hexane and *neo*hexane ignition delay times from Chen et al. [38] and Zhang et al. [9], respectively

Fig. 9. Validation against n-heptane ignition delay times from refs. [34, 35, 39-41].

18 noteworthy for its ability to predict IDTs from shock 19 tube and JSR experiments for *n*-pentane, *n*-hexane, 20 and *n*-heptane, which is relatively rare. Figures 6-9 21 show the validation of the present model against the 22 literature data over a wide range of conditions. The 23 present model basically predicts the experiments well. 24

25 4.2 Application of optimized rate rules to 26 mechanism generation for other alkanes

The current rate rules were developed using n-28 pentane, *neo*pentane, *n*-hexane, *neo*hexane, and n-29 heptane. In this section, these rate rules are applied to 30 generate combustion kinetic models for 22DMP, 31 33DMP, *n*-octane, *n*-nonane, and *n*-decane using 32 MAMOX++. As shown in Fig. 10, the initial rate rules 33 generally underestimated the IDTs of these fuels in 34 the NTC region. Using the optimized rate rules, a



Fig. 10. Validating optimized rate rules in other alkanes: 22DMP, 33DMP, *n*-octane, *n*-nonane, and *n*-decane. The experiments are taken from the present study and refs. [42-44].

1 significantly improved description is obtained both 2 qualitatively and quantitatively.

45. Conclusion

The primary and secondary alkane rate rules in 5 6 mechanisms (autogenerated by MAMOX++ and 7 reduced by DRGEP) were optimized using the 8 Optima++ code to fit experimental data from n-9 pentane, neopentane, n-hexane, neohexane, and n-10 heptane IDT and JSR concentration measurements. 11 After the optimization of Arrhenius parameters, 12 thermodynamic data of important species were 13 optimized (via a₆ and a₇ NASA coefficients). Both 14 optimizations enhanced model performance greatly.

15 Using MAMOX++, the optimized rate rules were 16 utilized to generate mechanisms for other large 17 alkanes: 22DMP, 33DMP, n-octane, n-nonane, and n-18 decane. To address gaps in experimental data, ignition 19 delay times for *n*-hexane, 22DMP, and 33DMP were 20 measured in the shock tube and RCM, covering the 21 NTC temperature regime. The auto-generated models 22 accurately predicted the experimental results, 23 demonstrating of the universality and transferability 24 of the optimized rate rules for reactions taking place 25 on primary and secondary carbons in the combustion 26 of larger alkanes.

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