Final report of ERA Chemistry / OTKA project NN100523
entitled: “Development of accurate reaction mechanisms”
(“Pontos reakciókinetikai mechanizmusok kifejlesztése”)
1 October 2011 – 30 September, 2015

Summary

Methanol is an alternative automotive fuel that may replace gasoline. A significant part of worldwide electricity production is based on the combustion of natural gas, which is mainly methane. The aim of the project was to develop accurate reaction mechanisms for the combustion of methanol and methane using mechanism optimization. This means that large amount of published experimental data was collected and parameters of mechanisms were fitted to provide the best agreement with the experiments. The goal was to obtain rate parameters that correspond to the physics and chemistry of the important elementary reactions. Therefore, experimental data related to ethanol and ethane combustion were also collected and utilized. As a result of the work, improved reaction mechanisms were obtained that describe methanol, ethanol and methane combustion using several diluent gases (*e.g.* N_2, Ar, He) at a wide range of fuel–oxygen ratio, temperature and pressure. Comparison with the simulation results of existing recently published mechanisms indicated that these new mechanisms are currently the most accurate ones. Since the efficient combustion of these fuels with low pollutant emission is an important aim, the new mechanisms may be utilized in several development projects related to environment protection.

Összefoglalás

A metanol egy lehetséges alternatív üzemanyag, amely kiválthatja a benzint. Az elektromos áram termelése világszerte jelentős mértékben a földgáz égésén alapul, amely nagyrészt metánból all. A kutatás célja az volt, hogy a mechanizmusoptimalizálás módszerével pontos reakciókinetikai mechanizmusokat dolgozzunk ki a metanol és a metán égésének leírására. Nagy mennyiségű, irodalomban közölt kísérleti adatot gyűjtöttünk össze, és a mechanizmusok paramétereit úgy illesztettük, hogy azok jól leírják a kísérleteket. Arra törekedtünk, hogy olyan sebességi paramétereket kapjunk, amelyek a fontos elemi reakciók fizikai és kémiai folyamataira vonatkoznak, emiatt etanol és etán égésére vonatkozó kísérleti adatokat is gyűjtöttünk és felhasználtunk. A munka eredményeképpen új reakciómechanizmusokat kaptunk, amelyek leírják a metanol, etanol és metán égését többféle hígítógáz (pl. N_2, Ar, He) alkalmazásánál, széles tüzelőanyag–oxigén aránynál, tág hőmérséklet- és nyomástartományban. Az új mechanizmusokkal kapott eredményeket összehasonlítottuk az utóbbi években közölt korábbi reakciómechanizmusokkal, és az új mechanizmusok a legjobbnak bizonyultak. Fontos cél ezeknek a tüzelőanyagoknak a hatékony égetése alacsony szennyezőanyag kibocsátás mellett, emiatt az új reakciómechanizmusokat várhatóan több környezetvédelmi célú kutatásban és fejlesztésben fel fogják használni.

Participants in the project

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Introduction

OTKA project NN100523 is an ERA Chemistry collaboration project with the group of Prof. Henry J. Curran (NUIG, Galway, Ireland). The aims of the project covered the following main areas:

i) Elaboration of new tools for the development of accurate reaction mechanisms. This includes suggestion of an improved data format for the storage of experimental data and development of new methods for the comparison and optimization of large reaction mechanisms. The methodical development included the elaboration of new algorithms and protocols, and writing and testing new software tools. This part of the work was also a part of OTKA project K84054. The differences between the two projects are that in OTKA project K84054 the investigated chemistry is the combustion of hydrogen and syngas. Also, since the chemical systems studied in project NN100523 are much larger and more complex, therefore extra tools and methods had to be developed.

ii) Investigation of C1 hydrocarbon and alcohol combustion chemistry systems. Such systems are the combustion of methanol and the combustion of lean methane–oxygen–diluent mixtures.

iii) If the concentration of methane is high in the methane–oxygen–diluent mixture (it is also true for stoichiometric mixtures), then large amount of ethane is produced during combustion in elementary reaction 2 $CH_3 \rightarrow C_2H_6$. Therefore, the mechanism for the combustion of stoichiometric and rich methane–oxygen–diluent mixtures has to include the relevant elementary reactions of C2 species. This chemistry was investigated in the following systems: ethanol combustion, ethane combustion, methane combustion in a wide range of equivalence ratios, and ultra-rich combustion of methane.

The results of the project are discussed according to the topic areas above.

1) Elaboration of tools for the development of accurate reaction mechanisms

In this project accurate reaction mechanisms were developed by mechanism optimization. This term refers to a systematic search of parameter values (typically rate parameters, but possibly also thermodynamic properties or transport data) of a combustion model within their physically realistic domain of uncertainty in order to achieve the best possible reproduction of selected experimental results.

Combustion related experiments include measurements of ignition delay times, laminar flame velocities and species profile determinations in flames and reactors. Such measurements are called bulk or indirect ones, since the results are not directly related to the rate coefficients of a single elementary reaction in a mechanism. These experimental results can be interpreted via comparison with simulation results using complete detailed mechanisms. The aims of the direct experiments are the determination of rate coefficients of elementary reactions at a given temperature, pressure and bath gas. However, the obtained rate coefficient values usually have a high uncertainty and therefore the detailed reaction mechanisms based on direct measurements only cannot reproduce well the results of indirect measurements.

The use of mechanism optimization techniques to improve detailed combustion models follows the initial ideas of Frenklach and Miller [1-3]; an algorithm was formulated later by Frenklach, Wang, and Rabinowitz [4]. Frenklach *et al.* further developed the mechanism optimization approach towards data collaboration [5-9]. Another series of mechanism optimization papers was published by Wang and co-workers [10-14].

In these optimization methods typically a small number of optimization targets based on representative indirect measurement data were defined, and the most influential rate parameters at these conditions (called "active parameters") were identified using local sensitivity analysis. Active parameters included *A*-factors of the rate expressions, third body collision efficiency parameters, and selected enthalpies of formation. The authors created polynomial surrogate models (so called "response surfaces") for each optimization target. After the optimization many of the obtained *A*-factors were found to be at the edges of their assigned uncertainty intervals. To address this issue, the objective function was modified in more recent works so that deviations of the *A*-factors from their initial values were penalized [9, 13-15].

An alternative optimization methodology was developed in our group [16, 17], which differs from the above methods as follows: (i) a much larger number of indirect and direct experimental data are used as optimization targets, (ii) all Arrhenius parameters (*A*, *n*, *E*) of the important reactions are optimized instead of *A*-factors only, (iii) response surfaces are utilized to replace flame calculations only; the more accurate direct integration is used for the spatially homogeneous simulations, (iv) new algorithms are used for the generation of response surfaces and for the global parameter estimation and (v) the temperature-dependent uncertainties of the optimized rate coefficients are estimated. Instead of penalizing the deviation of the optimized rate coefficients from the recommended values, direct measurements of rate coefficients are included as optimization targets.

The optimal set of parameters was obtained by the minimization of the following objective function:

$$E(\mathbf{p}) = \frac{1}{N}\sum_{\mathrm{i}=1}^{N}\frac{1}{N_{\mathrm{i}}}\sum_{\mathrm{j}=1}^{N_i}\left(\frac{Y_{\mathrm{ij}}^{\mathrm{mod}}(\mathbf{p}) - Y_{\mathrm{ij}}^{\mathrm{exp}}}{\sigma(Y_{\mathrm{ij}}^{\mathrm{exp}})}\right)^2 , \qquad (1)$$

where

$$Y_{\mathrm{ij}} = \begin{cases} y_{\mathrm{ij}} & \text{if } \sigma(y_{\mathrm{ij}}^{\mathrm{exp}}) \approx \text{constant} \\ \ln y_{\mathrm{ij}} & \text{if } \sigma(\ln y_{\mathrm{ij}}^{\mathrm{exp}}) \approx \text{constant} \end{cases} .$$

Here N is the number of datasets and N_i is the number of data points in the *i*-th dataset. The value y_{ij}^{exp} is the *j*-th measured data point in the *i*-th dataset. For the indirect measurement data, the modelled value is y_{ij}^{mod}, obtained from a simulation using an appropriate detailed mechanism, which belongs to a given set of rate parameters **p**. For direct measurement data, y_{ij}^{mod} corresponds to the calculated rate coefficient at a given temperature, pressure and diluent composition. During the global minimum search, multiple random parameter sets **p** are created, and the corresponding *E*(**p**) values are evaluated. The exact algorithm has been described in detail in article [16].

The posterior covariance matrix $\mathbf{\Sigma}_\mathbf{p}$ of the optimized parameters can be estimated using the following equation [16]:

$$\mathbf{\Sigma}_\mathbf{p} = \left[\left(\mathbf{J}_\mathrm{o}^\mathrm{T} \mathbf{W} \mathbf{\Sigma}_\mathbf{Y}^{-1} \mathbf{J}_\mathrm{o} \right)^{-1} \mathbf{J}_\mathrm{o}^\mathrm{T} \mathbf{W} \mathbf{\Sigma}_\mathbf{Y}^{-1} \right] \left(\mathbf{\Sigma}_\mathbf{Y} + \mathbf{\Sigma}_\Delta \right) \left[\left(\mathbf{J}_\mathrm{o}^\mathrm{T} \mathbf{W} \mathbf{\Sigma}_\mathbf{Y}^{-1} \mathbf{J}_\mathrm{o} \right)^{-1} \mathbf{J}_\mathrm{o}^\mathrm{T} \mathbf{W} \mathbf{\Sigma}_\mathbf{Y}^{-1} \right]^\mathrm{T} \tag{2}$$

Here, the matrices $\mathbf{\Sigma}_\mathbf{Y}$ and $\mathbf{\Sigma}_\Delta$ contain the estimated statistical and systematic errors of the experimental results, respectively. $\mathbf{W}$ is the matrix of weights of the individual data points, and $\mathbf{J}_\mathrm{o}$ is the first derivative matrix of the model results according to the optimized parameters at the optimal parameter set.

The evaluation of the error function requires simulations of the experiments. The appropriate simulation programs (SENKIN [18] for shock tube and flow reactor calculations, PSR [19] for perfectly stirred reactor calculations and PREMIX [20] for premixed laminar flames) of the CHEMKIN-II package [21] were used. SENKIN and PSR are fast and numerically stable codes, while PREMIX works well for the simulation of small mechanisms only. Therefore, several flame simulations were carried out using the FlameMaster [22] and OpenSMOKE [23] codes instead of PREMIX.

All experimental data were encoded in a well-defined XML data format. This format is based on the PrIMe data format of Michael Frenklach [24], but it was further developed and we call this extended version the ReSpecTh data format [25, 26]. The Optima code, used for the optimization and mechanism comparison calculations, is able to read the ReSpecTh data format files.

The methodology was described in a series of publications. In a part of these articles hydrogen or syngas combustion was investigated, but these publications also include the description of the newly elaborated methods and tools. In a series of book chapters, the newly introduced tools are discussed together with a review of the various related methods of other authors.

Related publications:

T. Turányi, T. Nagy, I. Gy. Zsély, M. Cserháti, T. Varga, B. T. Szabó, I. Sedyó, P. T. Kiss, A. Zempléni, H. J. Curran:
Determination of rate parameters based on both direct and indirect measurements
Int. J. Chem. Kinet., **44**, 284–302, (2012)

C. Olm, I. Gy. Zsély, T. Varga, T. Nagy, T. Turányi:
Comparison of the performance of several recent wet CO combustion mechanisms,
Proceedings of the European Combustion Meeting 2013, Paper P5-2.
ISBN 978-91-637-2151-9., 2013

I.Gy. Zsély, C. Olm, R. Pálvölgyi, T. Varga, T. Nagy, T. Turányi:
Comparison of the performance of several recent hydrogen combustion mechanisms,
Proceedings of the European Combustion Meeting 2013, Paper P4-13.
ISBN 978-91-637-2151-9., 2013

T. Nagy, C. Olm, I. Gy. Zsély, T. Varga, R. Pálvölgyi, É. Valkó, G. Vincze, T. Turányi:
Optimisation of a hydrogen combustion mechanism,
Proceedings of the European Combustion Meeting 2013, Paper P4-14.
ISBN 978-91-637-2151-9., 2013

C. Olm, I. Gy. Zsély, R. Pálvölgyi, T. Varga, T. Nagy, H. J. Curran, T. Turányi:
Comparison of the performance of several recent hydrogen combustion mechanisms,
Combustion and Flame, **161**, 2219-2234 (2014)

C. Olm, I. Gy. Zsély, T. Varga, H. J. Curran, T. Turányi:
Comparison of the performance of several recent syngas combustion mechanisms,
Combustion and Flame, **162**, 1793-1812, (2015)

T. Varga, C. Olm, T. Nagy, I. Gy. Zsély, É. Valkó, R. Pálvölgyi, H. J. Curran, T. Turányi: Development of a joint hydrogen and syngas combustion mechanism based on an optimization approach, *Int. J. Chem. Kinetics*, submitted, 2015

T. Varga, T. Nagy, C. Olm, I.Gy. Zsély, R. Pálvölgyi, É. Valkó, G. Vincze, M. Cserháti, H.J. Curran, T. Turányi: Optimization of a hydrogen combustion mechanism using both direct and indirect measurements, *Proc. Combust. Inst.*, **35**, 589-596 (2015)

A.S. Tomlin, T. Turányi:
Investigation and improvement of reaction mechanisms using sensitivity analysis and optimization, Chapter 16 in: Development of detailed chemical kinetic models for cleaner combustion, eds: F. Battin-Leclerc, E. Blurock, J. Simmie, pp. 411-445, Springer, 2013

A.S. Tomlin, T. Turányi:
Mechanism reduction to skeletal form and species lumping, Chapter 17 in: Development of detailed chemical kinetic models for cleaner combustion, eds.: F. Battin-Leclerc, E. Blurock, J. Simmie, pp. 447-466, Springer, 2013

T. Turányi, A.S. Tomlin:
Storage of chemical kinetic information, Chapter 19 in: Development of detailed chemical kinetic models for cleaner combustion, eds.: F. Battin-Leclerc, E. Blurock, J. Simmie,
pp. 485-512, Springer, 2013

2) Methanol combustion

Methanol is widely used as an alternative fuel and feedstock in various industrial processes. Even though substantial efforts have been made to understand its combustion characteristics, large differences in reactivity predictions of various methanol reaction mechanisms can be observed. A lack of agreement between experimental data and simulation results using detailed kinetic mechanisms was identified in the first stage of this sub-project, which motivated us to develop a new, systematically optimized methanol combustion mechanism.

The collection of experimental data includes measurements of fundamental combustion properties (so called "indirect measurements") such as homogenous ignition delays, laminar burning velocities and concentration profiles measured in various types of facilities. Altogether 4340 data points in 224 datasets were collected. All data were stored in XML files adhering to the ReSpecTh Kinetics Data format specification [25, 26].

Several mechanisms developed for the modelling of the combustion of methanol were also collected. The mechanisms of Zabetta and Hupa (2008, "AAU-2008") [27], Alzueta *et al.* (2001) [28], Hamdane *et al.* (2012) [29], Johnson *et al.* (2009, developed for propanol) [30], Kathrotia (2011, C_1–C_4 hydrocarbons) [31], Klippenstein (2011) [32], Konnov 2009 (C_2/C_3 hydrocarbons and oxygenates) [33], Li *et al.* (2007) [34], Rasmussen *et al.* (2008) [35], the 2014 San Diego mechanism [36] as well an ethanol mechanism of the same group (Saxena and Williams, 2007) [37] have been investigated. Simulations were carried out at the conditions of the collected indirect experiments using solvers of the CHEMKIN-II package [21]. Table 1 shows the average error function values for these 11 mechanisms, calculated using a sum-of-squares error function (Equation 1) that provides a quantitative description of the agreement of experimental and simulation data; lower numbers represent a better agreement.

Based on the results of this mechanism testing, the mechanism of Li *et al.* [34] was found to be a good candidate for further improvement by means of optimization. An initial mechanism for subsequent optimization was developed using this mechanism as a starting point. Some modifications were carried out to ensure that the mechanism contains all species and reactions that are chemically relevant in the combustion of methanol and formaldehyde. The H_2/CO sub-mechanism was replaced by our previously optimized joint hydrogen and syngas mechanism [38] that also features excited OH radical reactions. Noble gases Kr and Ne were added to the mechanism as possible third body collision partners as they were used in some experimental studies. Thermochemical data of the species not appearing in the H_2/CO sub-mechanism were updated with the values of Burke *et al.* [39] and Goos *et al.* [40]. An additional pathway of the reaction of CH_3OH with HO_2 yielding CH_3O and H_2O_2 was added to the mechanism, using the rate coefficient recommended by Klippenstein *et al.* [32]. After all modifications, the initial mechanism for optimization consisted of 24 species and 102 reactions, which is not much larger than the original mechanism of Li et al. (21 species/ 93 reactions).

Sensitivity analysis was carried out at the conditions of the collected indirect experiments, with respect to the *A* factors of each reaction in the initial model, including low pressure *A* factors for pressure dependent reactions. Based on the results of this analysis, 45 rate parameters of 15 reactions important in methanol and formaldehyde combustion (oxidation and pyrolysis) were selected for optimization. Apart from these 15 reactions, some H_2/CO reactions that were optimized in the study of Varga *et al.* [38] were also found to be sensitive, but these were not selected for optimization as they had already been optimized previously.

The selected reactions are summarized in Table 2. All three Arrhenius parameters (*A*, *n* and *E*) were optimized for all reactions. In one case (R77, $OH + CH_3 + M = CH_3OH + M$), both the high- and low-pressure limit rate parameters were selected for optimization. For the selected reactions, direct rate coefficient measurements were collected from the literature and were also encoded in the ReSpecTh format [25, 26]. In total 660 direct measurement data points were used for 14 of the 15 reactions. Following the method described by Nagy *et al.* [41], temperature-dependent uncertainty limits were calculated from direct rate coefficient measurements and theoretical studies for the rate coefficients of each selected reaction. This method provides the prior uncertainty limits which represent the range in which the rate coefficient can still be considered physically meaningful. Therefore, these uncertainty limits can be used as boundaries for the optimization method while ensuring that only physically feasible random parameter sets are tested.

A pre-selection of the data was carried out before optimization. Experimental data that could not be reproduced within 3σ of their experimental scatter by any of the mechanisms and data generated using outdated experimental techniques were excluded from the evaluation of the error function, both for comparing the performance of the mechanisms and for optimization. For laminar burning velocity data, 91 of 778 collected data points were affected by this selection. From the 687 flames that remained in the comparison, 345 (~50%) were used as optimization targets, 146 of these via polynomial surrogate models (“response surfaces”) and 199 via direct calculations.

Table 1 shows that our optimized mechanism performs better than the 11 mechanisms collected from the literature, both overall and separately for each type of data. While this new mechanism is only slightly better than our initial mechanism for laminar burning velocity simulations, its major strength is its improved accuracy in 0D simulations, since ignition delay times and particularly concentration profiles are predicted much more accurately.

The covariance matrix of the optimized parameters was also calculated (Equation 2), from which the temperature-dependent uncertainty of the optimal rate coefficients can be obtained. These posterior uncertainty limits represent how precisely the rate coefficients can be determined from the available indirect and direct measurement data. They can only be considered meaningful in the temperature range for which combustion data were included in the optimization (roughly 750 – 2400 K). If at the extremes of this range none of the experimental data is closely related to the parameters of the certain reaction, the posterior uncertainty limits can be wider than the prior ones. With the exception of reaction R42 ($CH_2O + HO_2 = HCO + H_2O_2$), all posterior uncertainty limits are, however, considerably narrower than the respective prior limits (see Fig. 1 and also the corresponding f values in Table 2). As it has been discussed earlier, the prior uncertainty limits were determined using direct measurements and theoretical determinations available from literature. The optimized rate parameters of these 14 (out of 15) reactions can be considered the best representation of the kinetic information that can be extracted from the utilized experimental results. The $f_{\mathrm{posterior}}$ values of R42 are much higher than the f_{prior} values at 500 K (0.88 vs. 0.21), while they are roughly in the same order of magnitude at 2500 K (1.07 vs. 0.91). This means that although reaction R42 is an important one, its rate parameters cannot be accurately determined from the available experimental data.

Results on the comparison of the performance of several methanol combustion mechanisms have been presented on a poster in the International Symposium on Combustion. The manuscript about the development of the new methanol combustion mechanism will be submitted for publication in this year.

Related publication:

C. Olm, R. Pálvölgyi, T. Varga, É. Valkó, H. J. Curran, T. Turányi:
Investigation of the performance of several methanol combustion mechanisms
35th International Symposium on Combustion San Francisco, 3-8 August, 2014, 2014
(conference abstract and presented poster)

Table 1. Methanol combustion: comparison of error function values calculated for the optimized mechanism and the mechanisms collected from the literature. The values are averaged over each experimental category, and the overall value is the average of the values for the individual experimental categories, weighted by the number of datasets within each category.

		Average error function value					
Mechanism	Ref.	Ignition delay times		Laminar burning velocities	Concentration profiles		**Overall**
		CH_3OH	CH_2O		CH_3OH	CH_2O	
AAU-2008	[27]	14.5	2.4	no transport data	68.3	96.9	**–**
Alzueta-2001	[28]	30.2	10.3	no transport data	158.1	24.9	**–**
Li-2007	[34]	12.6	3.2	5.7	34.9	77.9	**18.0**
SaxenaWilliams-2007*	[37]	48.2	1.5	5.9	42.1	105.2	**31.9**
Klippenstein-2011	[32]	71.0	3.2	5.1	40.1	77.9	**36.6**
Johnson-2009*	[30]	19.4	9.9	28.9	81.0	88.3	**39.8**
Rasmussen-2008	[35]	62.4	4.9	19.2	193.7	65.4	**71.2**
Kathrotia-2011*	[31]	15.9	7.4	[6.7]	185.7	656.0	**[84.8]**
Konnov-2009*	[33]	72.1	6.8	[114.0]	139.8	48.0	**[99.5]**
Hamdane-2012	[29]	354.2	5.9	(106.8)	73.2	375.9	**(187.3)**
SanDiego-2014*	[36]	27.5	1.5	46.1	1495.5	503.6	**369.8**
Initial mechanism	This work	13.4	2.1	3.7	36.5	74.4	17.6
Optimized mechanism		11.6	1.8	3.6	23.7	39.5	**12.3**
No. of datasets		**68**	**7**	**89**	**47**	**13**	**224**
No. of data points		**443**	**99**	**687**	**2649**	**462**	**4340**

* Not primarily developed for methanol, but larger fuels, including oxygenates

() Flame simulations were carried out using the FlameMaster software [22]

[] Flame simulations were carried out using the OpenSMOKE software [23]

The other flame simulations used CHEMKIN-II PREMIX [20]

Table 2. Methanol combustion: the reactions selected for optimization, prior and posterior uncertainty limits and the optimized reaction rate parameters. HPL and LPL indicate rate parameters belonging to high- and low-pressure limit, respectively. Units are in cm mol s and K.

Optimized subset of reactions		Uncertainty limits		Optimized parameters		
		f_{prior}	$f_{\text{posterior}}$	ln *A*	*n*	*E*/*R*
R37 LPL	$CH_2O + M = CO + H_2 + M$	1.50	0.22–0.42	160.01	−14.86	54832.3
R38	$CH_2O + H = HCO + H_2$	0.26–0.71	0.11-0.15	16.87	1.87	1026.9
R40	$CH_2O + OH = HCO + H_2O$	0.25–0.79	0.07–0.18	24.80	0.76	−77.4
R41	$CH_2O + O_2 = HCO + HO_2$	1.4	0.29–0.37	25.17	1.55	26128.8
R42	$CH_2O + HO_2 = HCO + H_2O_2$	0.21–0.91	0.88–1.07	−1.39	4.06	3902.2
R47	$CH_3 + HO_2 = CH_3O + OH$	0.8	0.39–0.48	18.44	1.69	−1004.7
R53	$CH_3 + HO_2 = CH_4 + O_2$	1	0.24–0.58	42.80	−1.93	459.0
R60	$CH_2OH + O_2 = CH_2O + HO_2$	0.7	0.37–0.52	47.06	−1.82	3563.5
R67 LPL	$CH_3O + M = CH_2O + H + M$	0.49–1.35	0.17–0.38	40.82	−1.35	6852.9
R77 HPL	$OH + CH_3 + M = CH_3OH + M$	0.68–0.79	0.24–0.37	36.60	−0.72	357.4
R77 LPL	$OH + CH_3 + M = CH_3OH + M$	1.2	0.08–0.42	128.18	−11.45	5076.3
R80	$CH_3OH + H = CH_2OH + H_2$	0.34–0.92	0.27–0.58	35.18	−0.54	3905.3
R83	$CH_3OH + OH = CH_3O + H_2O$	1	0.16–0.44	−11.49	5.44	−967.6
R84	$CH_3OH + OH = CH_2OH + H_2O$	0.50–0.97	0.12–0.31	24.40	0.63	271.0
R87	$CH_3OH + HO_2 = CH_2OH + H_2O_2$	1	0.12–0.39	4.59	3.57	8181.4

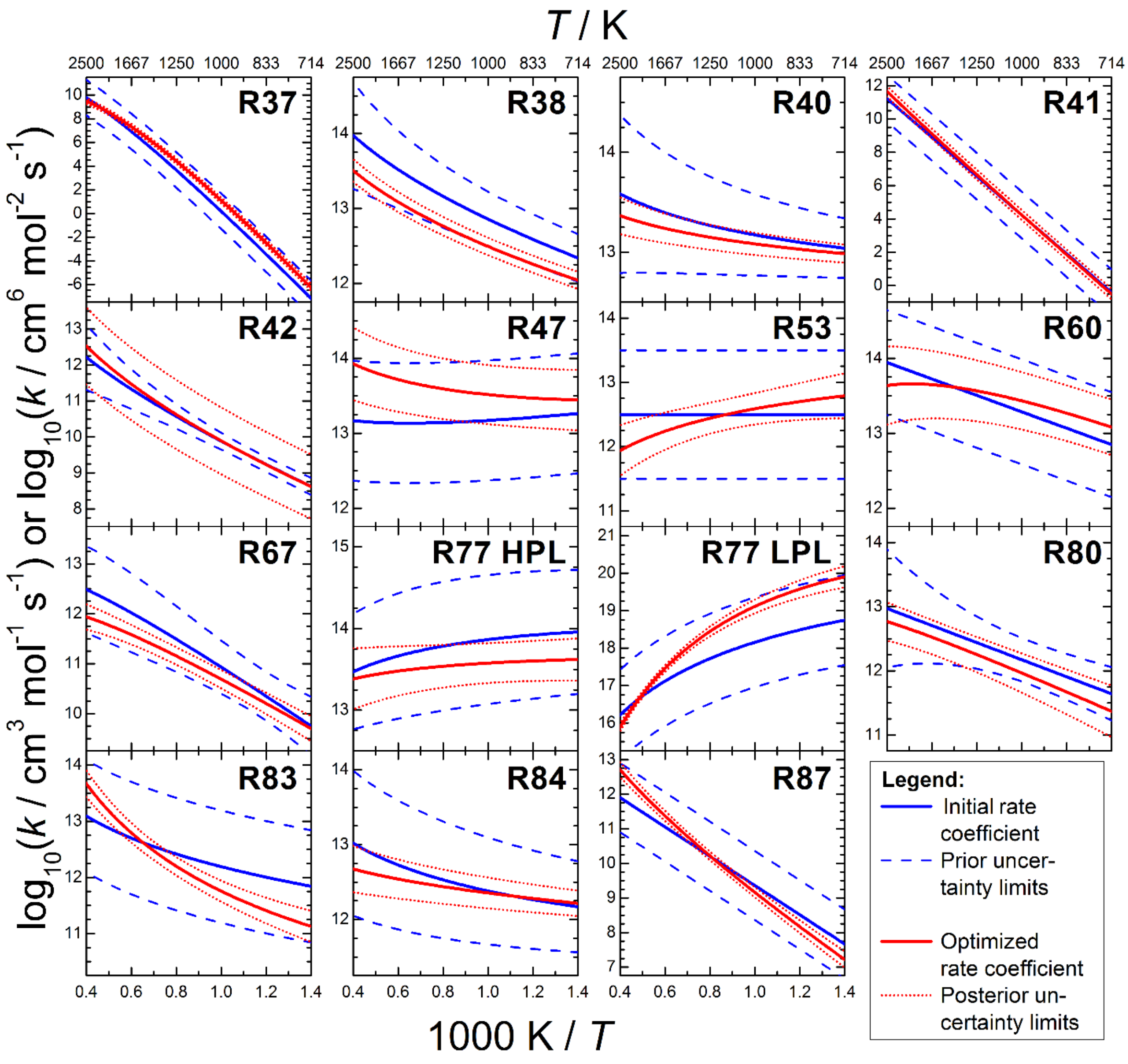

Fig. 1. Arrhenius plots of the initial and optimized rate coefficients with their prior and posterior uncertainty ranges for the 15 optimized reactions. The unit of the rate coefficient of R77 at the low-pressure limit (LPL) is cm^6 mol^{-2} s^{-1}, and it is cm^3 mol^{-1} s^{-1} for the other reactions.

3) Ethanol combustion

A detailed reaction mechanism for ethanol combustion was developed for describing ignition, flame propagation and species concentration profiles with high accuracy. Starting from a modified version of the ethanol combustion mechanism of Saxena and Williams [37] and adopting the H_2/CO base chemistry from the joint optimized hydrogen and syngas combustion mechanism of Varga *et al.* [38], an optimization of 44 Arrhenius parameters of 14 important elementary C1/C2 reactions using several thousand direct and indirect measurement data points was performed. The final optimized mechanism was compared to 14 reaction mechanisms (see Table 3) that have been used for the simulation of ethanol combustion with respect to the accuracy in reproducing the available experimental data, including measurements of ignition delay times in shock tubes (444 data points in 39 datasets) and rapid compression machines (20/3), laminar burning velocity measurements (991/122), and species profiles measured using flow reactors (1816/24), jet stirred reactors (561/9) and shock tubes (8871/14). In addition to providing best fitted values for 44 Arrhenius parameters (see Table 4), the covariance matrix of the optimized parameters was calculated, which provides a description of the temperature-dependent ranges of uncertainty for each of the 14 optimized rate coefficients.

The results have been published in the 6-page conference paper of the European Combustion Meeting 2015, and a more detailed manuscript has been submitted to the International Journal of Chemical Kinetics.

Related publications:

C. Olm, T. Varga, É. Valkó, S. Hartl, C. Hasse, T. Turányi:
Development of an ethanol combustion mechanism based on a hierarchical optimization approach, *Proceedings of the European Combustion Meeting 2015*, Paper P1-35,
ISBN 978-963-12-1257-0, 2015

C. Olm, T. Varga, É. Valkó, S. Hartl, C. Hasse, T. Turányi:
Development of an ethanol combustion mechanism based on a hierarchical optimization approach, *Int. J. Chem. Kinetics*, submitted, 2015

Table 3. Comparison of error function values by experiment type and overall between 14 recently published mechanisms, the initial mechanism for optimization (see text) and the new optimized mechanism. The corresponding numbers of datasets and data points for each column are denoted below the double solid line.

Mechanism ID	Ref.	Ignition delay times	Laminar burning velocities	Major species profiles*	**Overall**
Kathrotia-2011**	[31]	193.5	–	356.9	**–**
Konnov-2009	[33]	82.0	–	1185.7	**–**
Leplat-2010	[42]	38.0	5.5	114.7	**36.3**
Marinov-1999	[43]	61.8	7.1	114.2	**41.9**
RDmech-2009	[44]	58.0	32.3	1291.1	**317.8**
RöhlPeters-2009	[45]	59.9	7.4	108.6	**40.4**
SanDiego-2014	[46]	20.2	44.9	5039.0	**1152.4**
SaxenaWilliams-2007	[37]	48.4	16.8	261.1	**77.5**
Zaragoza-2011	[47]	44.2	no transport data	128.7	**–**
DagautTogbé-2012	[48]	43.9	–	73.2	**–**
Johnson-2009	[30]	32.2	no transport data	96.1	**–**
Ogura-2007	[49]	67.8	no transport data	109.3	**–**
UCL44f-2013	[50]	51.9	–	219.5	**–**
ZhongZheng-2013***	[51]	97.0	6.9	914.3	**226.9**
Initial mechanism	This	40.1	9.2	156.0	**48.0**
Optimized mechanism	work	9.8	5.4	44.6	**15.0**
No. of datasets		**42**	**122**	**47**	**211**
No. of data points		**464**	**991**	**11248**	**12703**

* Major species are: C_2H_5OH, O_2, CO, CO_2, H_2, H_2O, CH_4, C_2H_2, $m/z = 28$ (*i.e.* a superposition of CO and C_2H_4) [52], and C_2H_n [53].

**(*) For premixed flame simulations, all species with ≥ 4 C (**) atoms or ≥ 6 C atoms (***) were removed from the mechanisms, together with all reactions in which they participate.

– Some simulation results could not be obtained. In this case, overall results were not indicated.

Table 4. Reactions selected for optimization, the rate parameters in the initial mechanism and the optimized values of the parameters. Units are in cm, mol, K and s. Values of the prior and posterior uncertainty parameters are given for the temperature range of 500–2500 K.

No.	**Reaction string**	f_{prior}	$f_{\text{posterior}}$	A_{opt}	n_{opt}	E_{opt}
R60	$CH_3+OH = CH_2(S)+H_2O$	1.0	0.76–0.86	6.812E+12	–	1426.51
R63	$CH_3+HO_2 = CH_3O+OH$	1.0	1.22–2.42	6.106E+02	2.510	-3294.85
R68 LPL	$H+CH_3+M = CH_4+M$	0.70–1.06	0.16–0.72	4.163E+34	-5.264	-23.09
R104	$C_2H_4+OH = C_2H_3+H_2O$	0.32–0.73	0.28–0.49	1.088E+04	2.684	874.59
R116	$C_2H_3+O_2 = CH_2CHO+O$	0.4	0.19–1.05	6.138E+04	2.327	547.76
R176 HPL	$C_2H_5OH = CH_3+CH_2OH$	1.0	0.68–0.83	9.415E+28	-4.050	43292.13
R176 LPL	$C_2H_5OH +M = CH_3+CH_2OH+M$	1.0	1.02–1.10	2.969E+17	–	29211.08
R177 HPL	$C_2H_5OH = C_2H_4+H_2O$	1.0	0.22–0.34	3.937E+13	–	33198.31
R177 LPL	$C_2H_5OH+M = C_2H_4+H_2O+M$	1.0	0.75–0.94	9.876E+17	–	27173.94
R178	$C_2H_5OH+OH = CH_2CH_2OH+H_2O$	1.0	0.30–0.62	9.419E+23	-3.462	2855.69
R179	$C_2H_5OH+OH = CH_3CHOH+H_2O$	1.0	0.48–1.23	1.143E+10	0.544	-601.84
R180	$C_2H_5OH+OH = CH_3CH_2O+H_2O$	1.0	0.38–0.54	2.991E+06	2.113	878.67
R182	$C_2H_5OH+H = CH_3CHOH+H_2$	1.0	0.36–0.65	2.278E+27	-4.294	5429.12
R188	$C_2H_5OH+CH_3 = CH_3CHOH+CH_4$	0.4	0.39–0.62	1.475E+05	2.487	5055.49
R190	$C_2H_5OH+HO_2 = CH_3CHOH+H_2O_2$	1.0	0.22–0.58	2.611E+25	-3.694	10358.18
R196 LPL	$CH_3CH_2O+M = CH_3+CH_2O+M$	0.7	1.17–1.34	9.154E+31	-5.484	10738.93

4) Ethane combustion

Tranter *et al.* [54-56] conducted a series of experiments of ethane oxidation and pyrolysis covering a wide range of temperature (800 K – 1500 K) and pressure (5 bar – 1000 bar) in a high pressure shock tube. The oxidation and pyrolysis of ethane were carried out behind reflected shock waves, and the concentrations of the reaction products were measured by gas chromatography. The results of these experiments were re-evaluated by optimizing selected rate parameters of the NUIG C5 combustion mechanism. The rate coefficients of 14 reactions were selected based on sensitivity analysis and preliminary uncertainty estimations for optimization. Arrhenius parameters (*A*, *n*, *E*) of the selected reaction steps were optimized using not only the experimental data of Tranter *et al.*, but also the results of direct measurements related to these reactions. The obtained mechanism with the optimized rate parameters described the experiments of Tranter *et al.* much better than the original mechanism. New rate coefficient recommendations were obtained for all reactions with temperature dependent uncertainties including well studied reactions such as $C_2H_6+OH = C_2H_5+H_2O$ and less-known reactions like $C_2H_3+O_2 = CH_2CHO+O$.

The results have been published in the 6-page conference paper of the European Combustion Meeting 2015, and a more detailed publication is in preparation.

Related publication:

V. Samu, T. Varga, T. Turányi: Investigation of ethane pyrolysis and oxidation at high pressures using global optimization based on shock tube data, *Proceedings of the European Combustion Meeting 2015*, Paper P1-38, ISBN 978-963-12-1257-0, 2015

5) Ultra-rich methane combustion

Large amount of experimental data, related to measurements of oxidative coupling and partial oxidation of methane in stirred and flow reactors were collected in which distributions of C_2 and partially oxygenated products were determined. Several detailed reaction mechanisms published for the description of these processes were also gathered. Some of these mechanisms were developed primarily for the modeling of ultra-rich combustion of methane, while others were developed for a wider range of conditions. Simulations using all these reaction mechanisms were carried out at the conditions of all collected experimental data. A large part of the experimental data could be described well using one or another reaction mechanism. In general, the modern comprehensive mechanisms performed better compared to the specialized mechanisms. However, there is not a single published mechanism that is able to reproduce all these experimental data. Some other experiments reported a slow conversion from methane to oxygenates and higher hydrocarbons, which could not be described by any of the investigated mechanisms. This behavior of the models might indicate a fundamental lack of understanding of the main reaction pathways, or an incomplete description of the physical-chemical phenomena that occur during the experiments (*e.g.* heat loss, radical recombination at walls). Simple models for taking into account the effect of the reactor wall were investigated, but a good reproduction of these “problematic” experiments could not be achieved.

The results have been published in the 6-page conference paper of the European Combustion Meeting 2015, and a more detailed manuscript is in preparation.

Related publication:

R. Pálvölgyi, T. Varga, T. Turányi: Investigations of available experimental and modeling data on the oxidative coupling and partial oxidation of methane, *Proceedings of the European Combustion Meeting 2015*, Paper P1-70, ISBN 978-963-12-1257-0, 2015

6) Comprehensive investigation of methane combustion

The development of a new methane combustion mechanism started with a detailed search of the literature to collect experimental data. Only those experiments were considered in which methane was not blended with higher hydrocarbons or oxygenates, but blends with H_2 or CO were included. The collection included experiments where fundamental combustion properties were measured, such as homogenous ignition delays and concentration profiles measured in various types of facilities. Altogether 3559 ignition delay measurements (429 datasets from 52 publications) and 236 concentration measurements from flow reactors (5 datasets from 3 publications) were collected. All data was digitized, and stored according to the ReSpecTh Kinetics Data format [25, 26].

Mechanisms developed for the modelling of the combustion of methane were also collected. Interestingly, a relatively small number of mechanisms were recently developed for methane combustion. In the present work the GRI Mech 3.0 [57], USC II [58], San Diego 2014 [36], Leeds v1.5 [59], NUIG C5 v49 [60] mechanisms, and those of Konnov *et al.* [33] were investigated.

The optimization method requires a starting mechanism that is capable of at least qualitatively describing the basic combustion properties of the fuel for which a mechanism is being developed. The NUIG C5 v49 mechanism [60] was selected as a starting point, which contains 293 species and 1593 reactions. This mechanism was developed primarily for modelling the combustion of saturated hydrocarbons containing up to 5 carbon atoms, and it was extensively tested and validated specifically for methane combustion. As the mechanism was also developed for the combustion of higher hydrocarbons, it contains a large number of species which are not necessary for the modelling of methane combustion. To make simulations faster all species containing 3 or more carbon atoms, and several oxygenated species and their reactions were removed from the model. Simulations were performed using both the full and reduced versions of the mechanism, and the removal of the species was found to have a negligible effect on the simulation results of the collected indirect experiments. The H_2/CO submechanism of the reduced model was updated with the results of the recently developed hydrogen and syngas mechanism of Varga *et al.* [38]. The initial mechanism contained 50 species and 285 reactions.

Simulations were carried out at the conditions of the collected indirect experiments, and the initial model was able to reproduce the experimental results well enough to serve as a starting point of the optimization (see Table 5). Sensitivity analysis was carried out at the conditions of the collected indirect experiments, with respect to the *A* Arrhenius parameters of each reaction in the initial model, including the *A* Arrhenius parameters describing the low pressure limits for pressure dependent reactions. Based on the results, 50 rate parameters of 16 reactions were selected for optimization. Apart from these 16 reactions, some reactions that had been optimized in the study of Varga *et al.* [38] on hydrogen and syngas combustion, also appeared as highly sensitive reactions for methane combustion. However, these reactions were not selected for optimization as these had been determined with higher accuracy based on the hydrogen and syngas measurements.

All three Arrhenius parameters (A, n, E) were optimized for all reactions, except for reaction $CH_3+O_2=CH_3O+O$, where Arrhenius parameters A and E were found to be sufficient. In one case ($CH_3+CH_3+M=C_2H_6+M$) both the high- and low-pressure limit rate parameters were selected for optimization, and in two cases ($CH_3O+M=CH_2O+H+M$; $CH_3+H+M=CH_4+M$) only the low-pressure limit rate parameters were selected. The other 12 selected reactions are pressure independent. The selected reactions are summarized in Table 6.

For the selected elementary reactions direct rate coefficient measurements were collected from the literature. Altogether 506 direct rate coefficient measurements (32 datasets) for 7 reactions were used. These data were also encoded according to the ReSpecTh Kinetics Data format. Following the method described by Nagy *et al.* [41], temperature dependent prior uncertainty limits were calculated for the rate coefficients of the selected reactions, based on direct rate coefficient measurements and theoretical studies. This method provides uncertainty limits which represent the range in which a rate coefficient can still be considered physically meaningful. Therefore, these uncertainty limits can be used as boundaries for the optimization method, and still ensure that no physically feasible parameter sets are excluded.

A preselection of the experimental data was carried out before optimization. Experimental data that could not be reproduced within 3σ of their experimental scatter were excluded from the collection and were not considered when evaluating error function (1), either for comparison of the performance of different mechanisms or during the optimization procedure.

Altogether 3007 ignition delay times (in 305 datasets), 236 concentration values (in 5 datasets), and 506 direct rate coefficient measurements (in 32 datasets) were used as optimization targets. Due to the optimization, the value of the error function could be significantly decreased, therefore an overall better description of the optimization targets was achieved. A comparison was performed between the performance of the optimized mechanism and those available in the literature. Table 5 shows the results averaged over the set of experiments, and also for the individual experimental categories. The optimized mechanism provides the best overall results for ignition delay time and concentration profile measurements. Only a relatively small improvement could be achieved for ignition delay simulations, as the NUIG C5 v49 mechanism already provided an overall good description of the data, but it is important that the obtained mechanism could also well describe concentration profile data simultaneously.

The covariance matrix of the optimized parameters was also calculated, from which the temperature dependent uncertainty of the optimal rate coefficients can be expressed. For 13 out of the 17 optimized rate coefficients the obtained posterior uncertainty was significantly smaller than the prior uncertainty. There were reactions, $CH_3O + M = CH_2O + H$; $CH_3 + H + M = CH_4 + M$; $CH_3 + CH_3 + M = C_2H_6 + M$ (both high- and low-pressure limit); $CH_2O + H = HCO + H_2$; $CH_4 + H = CH_3 + H_2$; $CH_4 + OH = CH_3 + H_2O$; $CH_4 + HO_2 = CH_3 + H_2O_2$; $CH_3 + OH = CH_2(S) + H_2O$; $CH_3 + HO_2 = CH_3O + OH$; $CH_3 + HO_2 = CH_4 + O_2$; $CH_3 + O_2 = CH_3O + O$; $CH_3 + O_2 = CH_2O + OH$. For the other 4 reactions the obtained uncertainty limits were similar or larger than the prior uncertainty limits, which means that despite these are relatively important reactions in a methane combustion system, their values could not be determined accurately from the experimental data used.

Table 5. Comparison of error function values calculated for the optimized mechanism and mechanisms collected from the literature. The values are averaged over each experimental category.

Mechanism	Ref.	Average error function value Ignition delay times	Concentration profiles	**Overall**
Optimized mechanism	**This work**	10.27	20.02	**10.43**
NUIG C5 v49-2010	[60]	11.56	38.91	**12.00**
SanDiego-2014	[36]	13.54	68.74	**14.43**
USC II-2007	[58]	17.01	76.51	**17.97**
GRI3.0-1999	[57]	18.49	43.34	**18.89**
Leeds c1.5-2001	[59]	20.03	25.36	**20.12**
Glarborg-2008	[61]	20.33	27.24	**20.44**
Konnov-2009	[33]	38.22	63.28	**38.63**
No. of datasets		**305**	**5**	**310**
No. of data points		**3007**	**236**	**3243**

Table 6. The reactions selected for optimization, and the optimized values of the respective rate parameters. The numbering of the reactions correspond to the ordering of reactions in the optimized mechanism. For pressure dependent reactions HPL and LPL after the reaction number mark whether the rate parameters correspond to the high- or low-pressure limit, respectively. Units are in cm^3 mol s K.

Optimized subset of reactions		Optimized parameters		
		ln *A*	*n*	*E*/*R*
R55	$CH_2O + H = HCO + H_2$	11.23	2.778	915.8
R57	$CH_2O + CH_3 = HCO + CH_4$	2.858	3.400	2171
R72 LPL	$CH_3O + M = CH_2O + H + M$	43.82	−1.436	8738
R73	$CH_3O + O_2 = CH_2O + HO_2$	−57.02	11.02	−4701
R102 LPL	$CH_3 + H + M = CH_4 + M$	76.15	−4.691	1128
R103	$CH_4 + H = CH_3 + H_2$	14.15	2.438	4660
R104	$CH_4 + OH = CH_3 + H_2O$	3.665	3.406	197.0
R105	$CH_4 + O = CH_3 + OH$	25.49	0.966	5195
R106	$CH_4 + HO_2 = CH_3 + H_2O_2$	7.759	2.435	8345
R109	$CH_3 + OH = CH_2(S) + H_2O$	−13.97	5.626	−4628
R113	$CH_3 + HO_2 = CH_3O + OH$	24.95	0.630	−1066
R114	$CH_3 + HO_2 = CH_4 + O_2$	0.3355	3.591	−3927
R115	$CH_3 + O = CH_2O + H$	68.57	−5.057	4444
R116	$CH_3 + O_2 = CH_3O + O$	30.12	–	14570
R117	$CH_3 + O_2 = CH_2O + OH$	36.15	−1.432	5365
R153 HPL	$CH_3 + CH_3 = C_2H_6 + M$	38.42	−1.194	321.1
R153 LPL	$CH_3 + CH_3 + M = C_2H_6 + M$	83.60	−5.194	1020

Concluding remarks

Several mechanism optimization studies have been published in the literature of combustion related chemical kinetics [5-14]. In these works, usually a few dozen experimental data points (ignition delay times and flame velocity measurements) were used as target values and the *A*-factors of the selected elementary reactions were fitted. Consequently, the optimized mechanism described better the selected experimental data, but the optimized set of rate parameters could not be considered as a better approximation of their physical values.

During this OTKA project, our aim was to find and encode all experimental data that were ever published on the combustion of methanol, ethanol and methane. Based on this very comprehensives set of data (several ten thousand data points), we could carry out a comprehensive comparison of all recently (within about ten years) published combustion mechanisms.

The experimental data were encoded in an own XML data format (“ReSpecTh data format”). A computer code called Optima was written, that reads the data files and carries out the corresponding simulations with the assigned reaction mechanism. This code was the basis of mechanism comparison and mechanism optimization studies.

Mechanism optimization for each investigated fuel included the following steps:

(i) All recently published related mechanisms were tested and the best one was selected for further optimization.

(ii) The selected mechanism was improved based on recent publications by adding newly suggested elementary reactions, newly measured rate parameters and thermodynamic data. This updated mechanism was called the initial mechanism.

(iii) Using the initial mechanism, each experimental data was reproduced by computer simulations. Also, local sensitivity analysis was carried out at the conditions of each experimental data point. The list of important elementary reactions was determined on the basis of the results of sensitivity analysis.

(iv) The prior domains of uncertainty of the rate parameters of the important elementary reactions were determined on the basis of direct measurements and theoretical calculations found in the literature.

(v) The optimal values of the rate parameters were determined within the prior uncertainty domains based on all available indirect and direct measurements.

The algorithm above has been used for producing new mechanisms for the combustion of hydrogen, carbon-monoxide, methanol, ethanol, and methane. Mechanism optimization for the latter three fuels is the topic of this project. We met several technical problems during the studies; for example, the widely used PREMIX code was found to be unstable in these chemical systems at the conditions of several experimental data. By the end of the project, we managed to create the planned optimized mechanisms, and these proved to be better than the previously published ones. The article discussing the new ethanol combustion mechanism has been submitted for publication. The manuscripts about the new methanol and methane mechanisms are in preparation and will be submitted in the near future.

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