Final report about the results of the consortium of OTKA projects K84054 and K84060

Main project: K84054 entitled „Development of combustion mechanisms based on both direct and bulk measurements" (Égési mechanizmusok fejlesztése közvetlen és közvetett mérések alapján); PI: Tamás Turányi (ELTE)
Co-project: K84080; PI: János Tóth (BME)

The aim of coupled OTKA projects K84054 and K84080 was to develop a new hydrogen and syngas combustion mechanism using all available (both direct and bulk types) experimental data. This aim has been achieved, and also new methodologies were developed and tested for the creation, analysis and optimization of detailed reaction mechanisms.

The projects started on 1 July, 2011 and were originally planned to run till 30 June, 2015. However, due to the several ongoing works in both research groups in early 2015, the PIs requested and received permission for the extension of the projects till 30 June, 2016.

The project went according to the original plans and resulted in many results. During the five years, the two research groups published 51 works with indicating the support of OTKA (ELTE: 23; BME: 28), including 25 journal articles (ELTE: 13; BME: 12), 7 books or book chapters (ELTE: 5; BME: 2) and 19 other works (ELTE: 5; BME: 14). The results are detailed below.

Results obtained at the ELTE research group (main project K84054, PI: Tamás Turányi):

In the context of the development of reaction mechanisms, the term "optimization" refers to a systematic search of parameter values (primarily rate parameters, but in principle also thermodynamic properties or transport data) of a chemical kinetic model within their physically realistic domain of uncertainty in order to achieve the best possible reproduction of selected direct and indirect experimental results. An experimental data is called direct, if a single elementary reaction was investigated in the experiment. Indirect data (also called bulk data) cannot be related to a single elementary reaction, but characterize the behaviour of a whole reaction system at certain conditions. Typical bulk type experimental data are the measured ignition delay times or laminar flame velocities.

Prior to this project, several authors have published articles reporting the optimization of reaction mechanisms. The obtained reaction mechanisms were well performing, widely used and highly cited. However, these authors did not use all possibilities of mechanism optimization. Usually only a few dozen data points were used, the uncertainties of the kinetic parameters and experimental data were only roughly estimated, and only Arrhenius parameter A was fitted from the three Arrhenius parameters A, n, and E.

Logically our project can be divided to three stages: (i) development of a new mechanism optimization methodology; (ii) derivation of new hydrogen and syngas combustion mechanisms; (iii) utilizations of the obtained results.

I. Development of a new mechanism optimization methodology

A comprehensive literature search was carried out to determine the state-of-art in the field of the creation, analysis, and optimization of detailed reaction mechanisms. The results of this survey were published in three chapters of a multi-authored book (*Development of detailed chemical kinetic models for cleaner combustion*, Springer, 2013) and a monograph (Turányi and Tomlin, *Analysis of kinetic reaction mechanisms*, Springer, 2014; 363 pages with 1025 references). These works describe methods that are applicable in many fields of science and technology, including combustion, atmospheric chemistry, environmental modelling, process engineering, and systems biology. The topics addressed include: how sensitivity and uncertainty analyses allow the calculation of the overall uncertainty of simulation results and the identification of the most important input parameters, and the ways in which mechanisms can be reduced without losing important kinetic and dynamic detail.

A comprehensive optimization methodology was developed, which differs from the previous methods as follows: (i) a much larger number of indirect and direct experimental data is used as optimization targets, (ii) all Arrhenius parameters (A, n, E) of the important reactions are optimized instead of A-factors only, (iii) polynomial surrogate models ("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 determined. Most of these new methods were published in the article of T. Turányi *et al.* (*Int.J.Chem.Kinet.*, **44**, 284–302 (2012)). The methods were demonstrated on the determination of the rate parameters of two important elementary reactions of hydrogen combustion.

The method was tested and improved by carrying out the optimization of a kinetic mechanism of the pyrolysis of ethyl iodide. The optimization was based on data obtained from reflected shock wave experiments with H-ARAS and I-ARAS detection measured by the cooperation partner, and also on several direct rate coefficient measurements. Each fitted rate coefficient was determined with much lower uncertainty compared to the corresponding estimated uncertainty based on literature data. Since ethyl iodide is a frequently used H-atom precursor in shock tube experiments, the results allow a better evaluation of all shock tube experiments that use this precursor. Related publication: T. Varga *et al.*, *Int.J.Chem.Kinet.*, **46**, 295–304 (2014).

II. Derivation of new hydrogen and syngas combustion mechanisms

II.1. Hydrogen combustion: collection of experimental data and investigation of the existing mechanisms

A large set of experimental data was accumulated for hydrogen combustion: ignition measurements in shock tubes (770 data points in 53 datasets) and rapid compression machines (229/20), concentration–time profiles in flow reactors (389/17), outlet concentrations in jet-stirred reactors (152/9) and flame velocity measurements (631/73) covering wide ranges of

temperature, pressure and equivalence ratio. The performance of 19 recently published hydrogen combustion mechanisms was tested against these experimental data, and the dependence of accuracy on the types of experiment and the experimental conditions was investigated. The best mechanism for the reproduction of ignition delay times and flame velocities is Kéromnes-2013, while jet-stirred reactor (JSR) experiments and flow reactor profiles are reproduced best by GRI3.0-1999 and Starik-2009, respectively. According to the reproduction of all experimental data, the Kéromnes-2013 mechanism is the best, but the mechanisms NUIG-NGM-2010, ÓConaire-2004, Konnov-2008 and Li-2007 have similarly good overall performances. Several clear trends were found when the performance of the best mechanisms was investigated in various categories of experimental data. Low-temperature ignition delay times measured in shock tubes (below 1000 K) and in RCMs (below 960 K) could not be well-predicted. The accuracy of the reproduction of an ignition delay time did not change significantly with pressure and equivalence ratio. Measured H_2 and O_2 concentrations in JSRs could be better reproduced than the corresponding H_2O profiles. Large differences were found between the mechanisms in their capability to predict flow reactor data. The reproduction of the measured laminar flame velocities improved with increasing pressure and total diluent concentration, and with decreasing equivalence ratio. Reproduction of the flame velocities measured using the flame cone method, the outwardly propagating spherical flame method, the counterflow twin-flame technique, and the heat flux burner method improved in this order. Flame cone method data were especially poorly reproduced. The investigation of the correlation of the simulation results revealed similarities of mechanisms that were published by the same research groups. Also, simulation results calculated by the best-performing mechanisms are more strongly correlated with each other than those of the weakly performing ones, indicating a convergence of mechanism development. An analysis of sensitivity coefficients was carried out to identify reactions and ranges of conditions that require more attention in future development of hydrogen combustion models. The influence of poorly reproduced experiments on the overall performance was also investigated. The results were published in: C. Olm *et al.* (*Combustion and Flame*, **161**, 2219-2234 (2014).

II.2. Syngas combustion: collection of experimental data and investigation of the existing mechanisms

The mixture of CO with H_2 or H_2O is called the wet CO gas mixture or syngas. A large set of experimental data was accumulated for syngas combustion: ignition studies in shock tubes (732 data points in 62 datasets) and in rapid compression machines (492/47), flame velocity determinations (2116/217) and species concentration measurements from flow reactors (1104/58), shock tubes (436/21) and jet-stirred reactors (90/3). In total, 4970 data points in 408 datasets from 52 publications were collected covering wide ranges of temperature T, pressure p, equivalence ratio φ, CO/H_2 ratio and diluent concentration. 15 recent syngas combustion mechanisms were tested against these experimental data, and the dependence of their predictions on the types of experiment and the experimental conditions was investigated. Several clear trends were found. Ignition delay times measured in rapid compression machines (RCM) and shock tubes (ST) at temperatures below 1000 K could not

be well-predicted. Especially for shock tubes, facility effects below 1000 K could not be excluded. The accuracy of reproduction of ignition delay times did not change significantly with pressure. The agreement of measured and simulated laminar flame velocities is better at low initial (*i.e.* cold side) temperatures, fuel-lean conditions, CO-rich and highly diluted mixtures. The reproduction of the experimental flame velocities is better when these were measured using the heat flux method or the counterflow twin-flame technique, compared to the flame cone method and the outwardly propagating spherical flame approach. With respect to all data used in this comparison, five mechanisms were identified that reproduce the experimental data similarly well. These are the NUIG-NGM-2010, Kéromnes-2013, Davis-2005, Li-2007 and USC-II-2007 mechanisms, in decreasing order of their overall performance. The results were published in: C. Olm *et al.*, *Combustion and Flame*, **162**, 1793-1812 (2015).

II.3. Determinations of the uncertainty of the rate parameters of the elementary reactions of hydrogen and syngas combustion systems

As described above, several thousand indirect experimental datapoints were collected from the literature (ignition delay times, flame velocity measurements, concentrations measured in reactors) for hydrogen and syngas ("wet CO") combustion systems. Using sensitivity analysis, all important elementary reaction steps (22 reactions in total) at the conditions of the experiments were identified. Following a literature search, the Arrhenius parameters and 3rd body collision efficiencies of these reactions were collected from experimental, theoretical and review publications. For each elementary reaction, k_{min} and k_{max} limits were determined at several temperatures within a defined range of temperature. These rate coefficient limits were used to obtain a consistent uncertainty function $f(T)$ and to calculate the covariance matrix of the transformed Arrhenius parameters. The results were published in a journal article (T. Nagy *et al.*, *Combust. Flame*, **162**, 2059-2076 (2015)) and in its 118-page-long supplementary material that contains 485 references.

II.4. Optimization of hydrogen and syngas combustion mechanisms

The Kéromnes *et al.* (2013) mechanism for hydrogen combustion was selected for optimization, based on the previously collected experimental data. These data cover wide ranges of temperature (800 K - 2300 K), pressure (0.1 bar - 65 bar) and equivalence ratio (φ = 0.2 - 5.0). According to the sensitivity analysis carried out at each experimental datapoint, 30 Arrhenius parameters and 3 third body collision efficiency parameters of 11 elementary reactions could be optimized using these experimental data. 1749 directly measured rate coefficient values in 56 datasets belonging to the 11 reaction steps were also utilized. Mechanism optimization has led to a new hydrogen combustion mechanism, a set of newly recommended rate parameters with their covariance matrix, and temperature-dependent posterior uncertainty ranges of the rate coefficients. The optimized mechanism was tested together with 13 recent hydrogen combustion mechanisms and proved to be the best one. These results were published in: T. Varga *et al.*, *Proc. Combust. Inst.*, **35**, 589-596 (2015).

The next step was a comprehensive and hierarchical optimization of a joint syngas and hydrogen combustion mechanism. The Kéromnès *et al.* (2013) mechanism for syngas combustion was updated with our optimized hydrogen combustion mechanism, and it was optimized using a large set of indirect and direct experimental data relevant to syngas and hydrogen combustion. In total 48 Arrhenius parameters and 5 third-body collision efficiency parameters of 18 elementary reactions were optimized using these experimental data. 2275 directly measured rate coefficient values in 85 datasets belonging to 15 of the reaction steps were also utilized. The result of mechanism optimization is a H_2/CO combustion mechanism, which is well applicable to wide ranges of conditions; new recommended rate parameters with their covariance matrix; and temperature-dependent uncertainty ranges of the optimized rate coefficients. The obtained mechanism was compared to 19 recent hydrogen and syngas combustion mechanisms and was shown to provide the best reproduction of the experimental data. This work was published in: T. Varga *et al.*, *Int.J.Chem.Kinet.*, **48**, 407–422 (2016).

III. Derivation of futher results from the collected data and the optimized mchanisms

The results obtained in the main phase of the project allowed us to achieve several derived results, like the creation of the ReSpecTh information service and global uncertainty analysis based on the covariance matrix of the fitted rate parameters.

III.1. ReSpecTh information service

In collaboration with the research group of Prof. Attila G. Császár, a new website called ReSpecTh was created (*http://respecth.hu/*). The acronym refers to a joint **re**action kinetics, **spec**troscopy, and **th**ermochemistry information system. The first publication about the ReSpecTh site is a 6-page conference proceedings paper of Varga *et al.* (*Proceedings of the European Combustion Meeting* – 2015, Paper P1-04). A more detailed publication is in preparation. The web site is open to any user after registration. It contains all experimental data that we collected for hydrogen and syngas combustion. The site also contains a formal definition of the applied experimental data format, which we call RKD format ("ReSpecTh Kinetics Data Format"). Utility codes were published for writing, reading and interpreting the RKD data files. The site also contains code "**ReactionKinetics**" developed by János Tóth *et al.* in co-project K84060.

III.2. Extended HDMR global uncertainty analysis of reaction kinetics models with correlated parameters.

The High Dimensional Model Representation (HDMR) method has been applied in several previous studies to obtain global sensitivity indices of uncorrelated model parameters in combustion systems. The HDMR method was extended for the investigation of reaction mechanisms with correlated parameters. The new approach uses the Rosenblatt transformation on a correlated model parameter sample to obtain a sample of independent parameters. The extended HDMR method was applied for the determination of sensitivity

indices of our optimized hydrogen combustion model (Varga et al., 2015). The effect of the correlation of rate parameters on the calculated sensitivity indices of ignition delay times was investigated. The results were published in: É. Valkó et al., *Proc. Combust. Inst.*, *in press, available online*, DOI: 10.1016/j.proci.2016.07.061. A more detailed analysis of the global sensitivity measures of models with correlated parameters based on our optimized syngas mechanism (Varga et al., 2016) has been published in Hungarian in the *Alkalmazott Matematikai Lapok*. A manuscript about further results in this topic has been prepared and will be submitted soon to *J. Math. Chemistry*.

III.3. Identification of optimal chemical markers for heat release in syngas flames

In a cooperation work, a quantitative marker of the heat release rate (HRR) distribution using experimentally measurable species was looked for. Turbulent syngas (CO/H_2/air) flames were computed by Direct Numerical Simulations (DNS). Based on a direct image analysis of the DNS results, normalized species concentrations combined with exponents were systematically tested to reconstruct the field of heat release rate. A systematic comparison was used to identify the best possible exponents associated with each species combination. The heat release rate of atmospheric syngas flames can be best approximated using the measured concentrations of HCO and OH. The related manuscript of C. Chi *et al.* has been submitted to *Flow, Turbulence and Combustion.*

Results obtained at the BME research group (co-project K84060, PI: János Tóth):

A series of mathematical problems were investigated that are related to the analysis and development of kinetic reaction mechanisms. These topics are listed below.

Development and applications of program package **ReactionKinetics**

Requirements were formulated for a reaction kinetics analysis program package to be useful for an as-wide-as-possible circle of users. This resulted in **ReactionKinetics**, a *Mathematica* based package, which has been developed in this project. Applications showed that it is capable of qualitatively analyzing detailed combustion mechanisms, like those of hydrogen, carbon monoxid or methanol.

Thirty-nine detailed mechanisms for the combustion of hydrogen, carbon monoxide and methanol were investigated using **ReactionKinetics**. The involved methods are mainly structural and graph theoretical approaches as well as techniques which are related to the time evolution of the considered mechanisms. Our investigations support the view that the list of elementary reactions considered in the hydrogen mechanisms tend to take on a final form in these days. CO combustion mechanisms, however, showed a larger variety both in species and in reaction steps. There exist only few mechanisms directly developed to describe methanol combustion, but mechanisms developed for larger fuels may contain a submechanism for methanol combustion. The big differences among the methanol combustion mechanisms show that these mechanisms are structurally different. Most of our results do not depend on the selection of the reaction rate coefficients; the methods use only

the sets of reaction steps, hence are robust and general. These investigations can be used before or in parallel with the usual numerical investigations, such as simulation, pathway analysis, sensitivity analysis, and parameter estimation. The package and the methods may be useful for automatic mechanism generations, testing, comparison and reduction of mechanisms, especially in the case of large systems. (Participants in this subproject were A. L. Nagy, Papp, Takács, Tóth, and Zsély.)

Otto engine

The theory of thermodynamics developed by T. Matolcsi and his coworkers has been applied to describe the periodic functioning of the Otto engine. First, parameters were defined to get a physically realistic picture. Conditions to ensure the stability of the stationary point were also determined. (Szekeres)

On the inverse problem

The characterization of kinetic differential equations was generalized for the case when the reaction rates are not of mass action type. We have also shown that in the mass action case Arrhenius type reaction rate coefficients can be eliminated in such a way that a polynomal equation is obtained. One family of these problems is the determination of the inducing reactions to given kinetic differential equations. The main result is the description of the general form of the induced kinetic differential equations of a reversible reaction. (Takács, B. M., Tóth, Zsámboki)

First integrals

First integrals of kinetic differential equations are not only useful tools to reduce the number of equations, but they also have physical meaning, like the conservation of mass or energy. We defined classes of kinetic differential equations having first integrals. A more general approach is looking for invariant surfaces of reactions, which may also lead to first integrals. Calculating invariant surfaces we were able to find oscillatory solutions to some kinetic models. (I. Nagy, Tóth)

Detailed balance

Detailed balance and microscopic reversibility are usually used as synonyms describing a general principle. However, if one tries to give rigorous definitions at least within the class of models of reaction kinetics, it turns out that the natural formulations differ for deterministic and stochastic models. We have investigated a series of deterministic and stochastic reaction kinetics models that show these relations. Some of these examples indicated that if the stochastic model of a reaction obeys this principle its deterministic model may not. Our conjecture is just the opposite what might be expected: fulfilment of the principle in the deterministic model implies that it holds also in the stochastic case. (Nagy, I., Tóth)

Numerical methods

The usual mathematical model of reaction–diffusion systems is a system of partial differential equations which do not allow symbolic treatment: numerical methods are needed.

Even the application of these methods is not trivial. Therefore, we have developed a series of splitting methods to solve such equtions and applied it to smaller kinetic problems.

In practice the subproblems of a splitted problem are solved numerically, thus it is crucial to investigate the properties of combined methods obtained by applying splitting and some numerical methods. We proved that in the case when the operator is a sum of arbitrary number of suboperators, the local order of iterative splitting is equal to the number of subproblems solved in the process for the two-level method. This is the extension of the results for two suboperators. We also defined a large class of multi-level methods and presented a characterization of these methods concerning the local order.

The waveform relaxation method has been intensively investigated in the last 30 years since its first application in the modeling of large scale circuits. We have been studying the possible extensions of the direct application of the method on partial differential equations. Furthermore, we performed an error analysis of the combination of this method with convergent numerical methods. (Ladics)

Hysteresis, chaos and blow up

We made a large step into the direction of a complete symbolic proof of the fact that the temperature dependent Scott–Tomlin model blows up (or: a thermal runaway occurs) in a finite time. It turned out that even picewise linear systems are able to show quite complicated behaviour. As a continuation of our previous work, we studied the appearance of chaotic behaviour in such systems by rigorous symbolic investigations. We investigated the topological properties of dynamical systems with hysteresis. A description of symbolic dynamics for 1D interval maps with hysteresis has been given and the (one parameter) bifurcation of such systems was studied.

We have studied the dynamics of a two-degree-of-freedom (pitch and plunge) aeroelastic system where the aerodynamic forces are modeled as a piecewise linear function of the effective angle of attack. Stability and bifurcations of equilibria were analyzed. We found border collision and rapid bifurcations. Bifurcation diagrams of the system were calculated utilizing MATCONT and *Mathematica*. Chaotic behavior with intermittent switches between the two nontrivial equilibria was also observed. (Csikja, Elgohary, Kalmár-Nagy, Szili, Tóth)

Controllability of reactions

Fine control of chemical reactions leads to optimized production and gives rise to advanced chemical applications, *e.g.* decreasing the production of pollutants and waste materials or developing intelligent drugs. Therefore, we started to investigate global controllability of reactions using Lie algebraic methods. Reaction rate coefficients were used as inputs; the number of necessary inputs was reduced as far as possible. If one can control all reaction rate coefficients then the reaction is globally controllable at almost all points of the state space. A reaction completely controllable at a point is completely controllable at almost all the other points. The concept of initializator step was introduced. Some of the results are generalizations of earlier published results of Gy. Farkas. Later, we systematically studied the controllability of reactions using both the reaction rate coefficients and temparature as control variables, assuming Arrhenius form parameterization of the reaction rate coefficients. The general results were also applied to real chemical reactions. (Drexler, Tóth, Virág)

Delay systems

In many cases delay systems are also important to describe reactions. We devoted a paper to the stability analysis of discrete-time delay systems based on a set of Lyapunov–Krasovskii functionals. New multiple summation inequalities were derived that involved the famous discrete Jensen′s and Wirtinger′s inequalities, as well as the recently presented inequalities for single and double summation. The paper showed that the proposed set of sufficient stability conditions can be arranged into a bidirectional hierarchy of LMIs establishing a rigorous theoretical basis for the comparison of conservatism of the investigated methods. Numerical examples illustrated the efficiency of the method. (Gyurkovics, Kiss, K., Nagy, I.,Takács, T.)

Biological kinetics

A reaction kinetic model to describe flow cytometric measurements of the calcium transport in lymphocytes was created and the model parameters were estimated. Principal component analysis of the sensitivity matrix indicated that the parameters are interdependent and their individual estimation is not possible. As the measurements do not provide absolute concentrations, calibration is needed from by the experimentalists' to finish our calculations. The derived model would show the role of passive and pumped transport of calcium. (Busai)

We have proposed an approach for the qualitative investigation of polynomial systems of ODEs, based on algorithms of computational commutative algebra. It can be applied to study various models of chemical reactions derived using the mass action law. We have found all families of systems with invariant planes different from the trivial one in the May-Leonard asymmetric model, which is a three-dimensional Lotka-Volterra system depending on six parameters. We also proved the existence of periodic solutions for some of these families. (Antonov, Dolicanin, Romanovski, Tóth)