Final report of project KH-126515
Analysis and comparison of natural gas combustion reaction mechanisms
(Földgáz-égési reakciómechanizmusok vizsgálata és összehasonlítása)

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Abstract

Methane is the major component of natural gas, which is one of the most widely used fuels. Large amount of shock tube (ST) and rapid compression machine (RCM) ignition delay measurements are available for validating detailed mechanisms. A large set of experimental data was collected for methane combustion: ignition studies in shock tubes (4939 data points in 574 datasets) and in rapid compression machines (582/69). In total, 5521 data points in 643 datasets from 73 publications were collected covering wide ranges of temperature T, pressure p, equivalence ratio φ and diluent concentration. 13 recent methane 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. Most mechanisms could reproduce well the experimental ignition delay times measured in shock tubes at initial temperatures higher than 1000K. Ignition delay times measured in RCMs and STs at low temperatures (below 1000K) could also be well predicted by several mechanisms. For a quantitative assessment of methane combustion modelling, a least-squares-function is used here to show the agreement between measurements and simulations. Caltech-2015, Aramco_II-2016, and Glarborg-2018 proved to be the most accurate mechanisms for the simulation of methane combustion at ST experimental conditions, while Aramco_II-2016 has the smallest prediction error at RCM conditions. Analysis of local sensitivity coefficients was carried out to determine the influence of selected reactions at given experimental conditions and to identify those reaction steps that require more attention in the future for the development of methane combustion models.

Introduction

Majority of energy used and electricity produced comes from combustion processes. The most important fuel is natural gas, which is utilized for electricity production, heating and transport. The main ingredient of natural gas is methane, and therefore methane combustion is one of the practically most important chemical processes. Knowing the combustion kinetics of methane better, more efficient natural gas engines and gas turbines can be designed. One of the most important characteristic features of the combustion of methane containing gas mixtures is the ignition delay time. Majority of such experiments was carried out in shock tubes, but some others also in rapid compression machines.

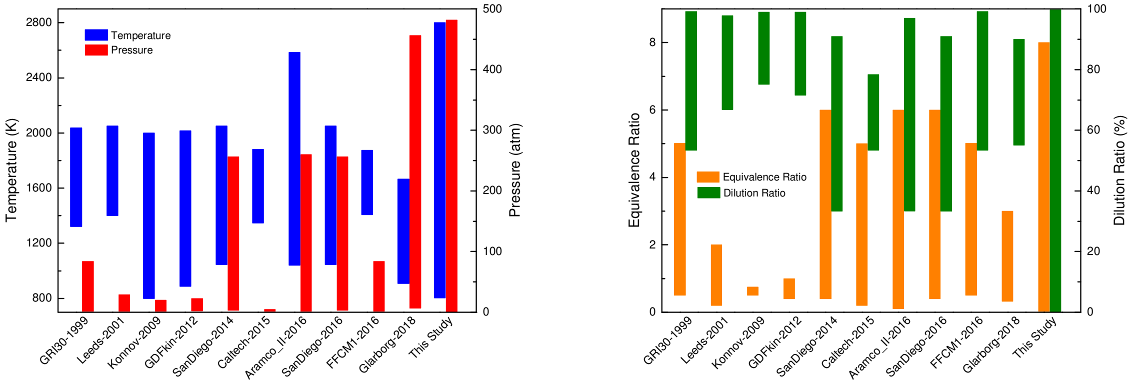
Previously, we have developed a methodology for the testing of combustion mechanisms and used it for several other fuels [1] [2] [3] [4]. During this project, this methodology was applied for methane combustion based on shock tube and rapid compression machine ignition delay measurements.

The investigated mechanisms

Our aim was to test all major methane combustion mechanisms that were published in the last decade. Furthermore, GRI-Mech 3.0 [5] was added to the comparison, which was published in 1999, primarily developed for methane combustion, and is widely used even nowadays. Three further mechanisms were investigated, which were published between 2001 and 2010. In the forthcoming discussions, an identifier of each mechanism is used, which combines the name of the author or research group and the publishing year. Table 1 contains the list of these mechanisms and provides further information about size and included diluents. The order of the mechanisms in Table 1 is according to their year of publication. Figure 1 shows the original ranges of testing by the authors of the mechanisms and the ranges applied in this work.

Table 1 General features of the compared reaction mechanisms: number of species and reactions involved and the conditions at which they were originally validated.

No.	Mechanisms ID	Ref.	Reactions/ Species Number	Diluents	Validating conditions			
					Temperature / K	Pressure / atm	φ	Dilution Ratio / %
1	GRI30-1999	[5]	325 / 53	Ar/-	1323 - 2036	1.6 - 83.9	0.5 - 5.01	53.4 - 99.16
2	Leeds-2001	[6]	175 / 37	Ar/-	1400 - 2050	1.56 - 29	0.2 – 2	66.7 - 97.8
3	USC-II-2007	[7]	784 / 112	Ar/He	No validation based on CH_4 – IDT experiment.			
4	Konnov-2009	[8]	1231 / 129	Ar/-	800 - 2000	1.5 - 20	0.5 - 0.75	75.05 – 99
5	GDF-Kin-2012	[9]	1144 / 141	Ar/He	886.85 - 2015	1.87 - 22.38	0.4 – 1	71.5 – 99
6	SanDiego-2014	[10]	247 / 50	Ar/He	1045 - 2050	2.96 - 256.6	0.4 – 6	33.3 - 90.9
7	CRECK-2014	[11]	2642 / 107	Ar/He	No validation based on CH_4 – IDT experiment.			
8	Caltech-2015	[12]	1156 / 192	Ar/-	1348 - 1881	1.56 - 4.83	0.2 – 5	53.4 - 78.4
9	Aramco_II-2016	[13]	2716 / 502	Ar/He	1040 - 2584	1.46 - 260	0.1 – 6	33.3 – 97
10	SanDiego-2016	[10]	268 / 57	Ar/He	1045 - 2050	2.96 - 256.6	0.4 – 6	33.3 - 90.9
11	FFCM-1-2016	[14]	291 / 38	Ar/He	1408.1 - 1875	1.6 - 83.9	0.503 - 5.01	53.4 - 99.16
12	Konnov-2017	[15]	1236 / 107	Ar/He	No validation based on CH_4 – IDT experiment.			
13	Glarborg-2018	[16]	1407 / 154	Ar/He	908 - 1665	6.9 - 456	0.32 – 3	55 – 90



(a) (b)

Fig. 1. Ranges of experimental data originally used for the validation of the mechanisms. The figures also show the ranges used for the testing of the mechanisms in this study.

Collection of experimental data

The combustion characteristics of methane containing mixtures have been studied extensively. In this work we consider only those experiments in which the reactant mixture contains methane, but no higher hydrocarbons or oxygenated species. This means that mixtures of methane and H_2 or CO are in the focus of this paper, but no mixture containing ethane or methanol). Having this restriction on the chemical system, the data sets to be considered are still numerous, close to two thousand. Therefore we decided to focus only on ignition delay time experiments in this study. An extensive literature review was performed and 574 datasets were collected from shock tube and 69 datasets from rapid compression machine measurements, including in total 5521 data points.

The collection of ignition time measurements in shock tubes covers a wide range of conditions. The initial temperature and pressure were varied in the range of 803–2800 K and 0.069–481.4 atm, respectively; the equivalence ratio was changed between 0.03 and 8.0; the mole fraction of diluent concentration was within the interval 0–99.7%. In the earlier shock tube (ST) measurements constant pressure was assumed. In the recent ST measurements the pressure rise rate (PRR) during the ignition was also measured and published.

In some cases, several experimental ignition delay times were deduced from the same experiment in such a way that different profiles, such as pressure, excited OH radical, or other species profiles were measured. In the present study, we added all kinds of these ignition delay times to the database, but used only one of them for mechanism comparison.

As for the conditions of rapid compression machine experiments, the ranges of temperature and pressure were 869.9 – 1200 K, and 9.87 – 156.62 atm, respectively; equivalence ratio changed within 0.3 – 2.0; the diluent ration was between 62.58 – 90%.

Simulation of experiments

All experimental data collected were encoded in ReSpecTh Kinetics Data Format v2.2 (RKDF2.2) [17] XML files. The RKD format is an XML data format for the storage of indirect combustion measurements and rate coefficient determinations by direct gas kinetics experiments and theoretical calculations. The RKD format is a modified and extended version of the PrIMe Kinetics Data Format [18]. All the prepared XML files will be available in the ReSpecTh Information System [19].

The RKD files contain all information required for the simulation of the experiments. For example, they contain the definition of the ignition delay time as used in the corresponding experiments. Usage of these files allowed the fully automatized run of thousands of simulations. In principle, the complete investigation of a mechanism against several thousand experimental data can be carried out in a single run using these files and the Optima++ environment [20]. Optima++ is able to handle several simulation packages and both simulation packages FlameMaster [21] and OpenSmoke++ [22] were used in this work. For the ST data (shock tubes with constant pressure) all calculations were carried out with both simulation codes and the agreement of the calculated IDTs were always better than 1%. For the simulation of experiments with pressure/volume profiles, *i.e.* for the ST-PRR and RCM experiments FlameMaster (FM) was much slower and therefore OpenSmoke++ (OS) was used routinely. In several points the OS results were checked with FM and again good agreement (within 1%) was obtained.

Results and Discussion

In this work the agreement of experimental and simulation results is investigated using the following objective function:

$$E = \frac{1}{N}\sum_{i=1}^{N} E_i$$

and

$$E_i = \frac{1}{N_i}\sum_{j=1}^{N_i}\left(\frac{Y_{ij}^{sim} - Y_{ij}^{exp}}{\sigma\left(Y_{ij}^{exp}\right)}\right)^2$$

where

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

Here N is the number of datasets and N_i is the number of data points in the i-th dataset. A dataset contains those data points that were measured on the same apparatus at the same time at similar conditions except for one that was systematically changed. Values y_{ij}^{exp} and $\sigma\left(y_{ij}^{exp}\right)$ are the j-th data point and its standard deviation, respectively, in the i-th dataset. The corresponding simulated (modeled) value is Y_{ij}^{sim} obtained from a simulation using an appropriate detailed mechanism and simulation method. Ignition time measurement errors are typically relative ones (the scatter is proportional to the value of y_{ij}), therefore we used the option $Y_{ij} = \ln(y_{ij})$.

Error function values E_i belonging to dataset i and E belonging all considered N datasets are expected to be near unity if the chemical kinetic model is accurate, and deviations of the measured and simulated results are caused by the scatter of the experimental data only. Note that due to the squaring in the definition of E, a twice as high deviation of the simulated and experimental values of one mechanism in comparison to another leads to a four times higher value of E.

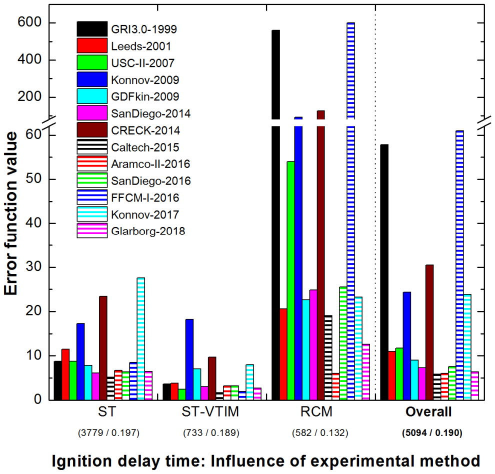


Fig. 2. Errors of the reproductions of ignition delay times according to the different types of experiments. The number given in the parentheses are the number of data points used and the average estimated error of the datasets.

Fig. 2 shows the average error function values of all mechanisms for simulating the shock tube measurements with constant pressure assumption (ST group), shock tube experiments with PRR (ST-PRR group, denoted as ST-VTIM), rapid compression machine measurements (RCM group) and the overall results (Overall group). There are five mechanisms with error lower than three times of the estimated experimental error; these are Caltech-2015, Aramco-II-2016, Glarborg-2018, SanDiego-2014, and SanDiego-2016, in the order of increasing error. For both the ST and ST-PRR groups, the simulation error values of Caltech-2015 and Glarborg-2018 are the lowest, while for the RCM measurements, Aramco-II-2016 has significantly the best performance among all mechanisms. All mechanisms reproduce the ST-PRR experiments better than the ST experiments. The GRI3.0-1999 and FFCM-I-2016 mechanisms do not reproduce well the RCM experimental results.

In Figure 3, the performance of the mechanisms in reproducing ignition delays is shown in the various intervals of experimental conditions, like temperature, pressure, equivalence ratio, and diluent ratio. In these figures, the intervals were selected by ensuring statistically enough data points within each interval. The numbers of used data points for all ranges are shown in the top area of the corresponding intervals.

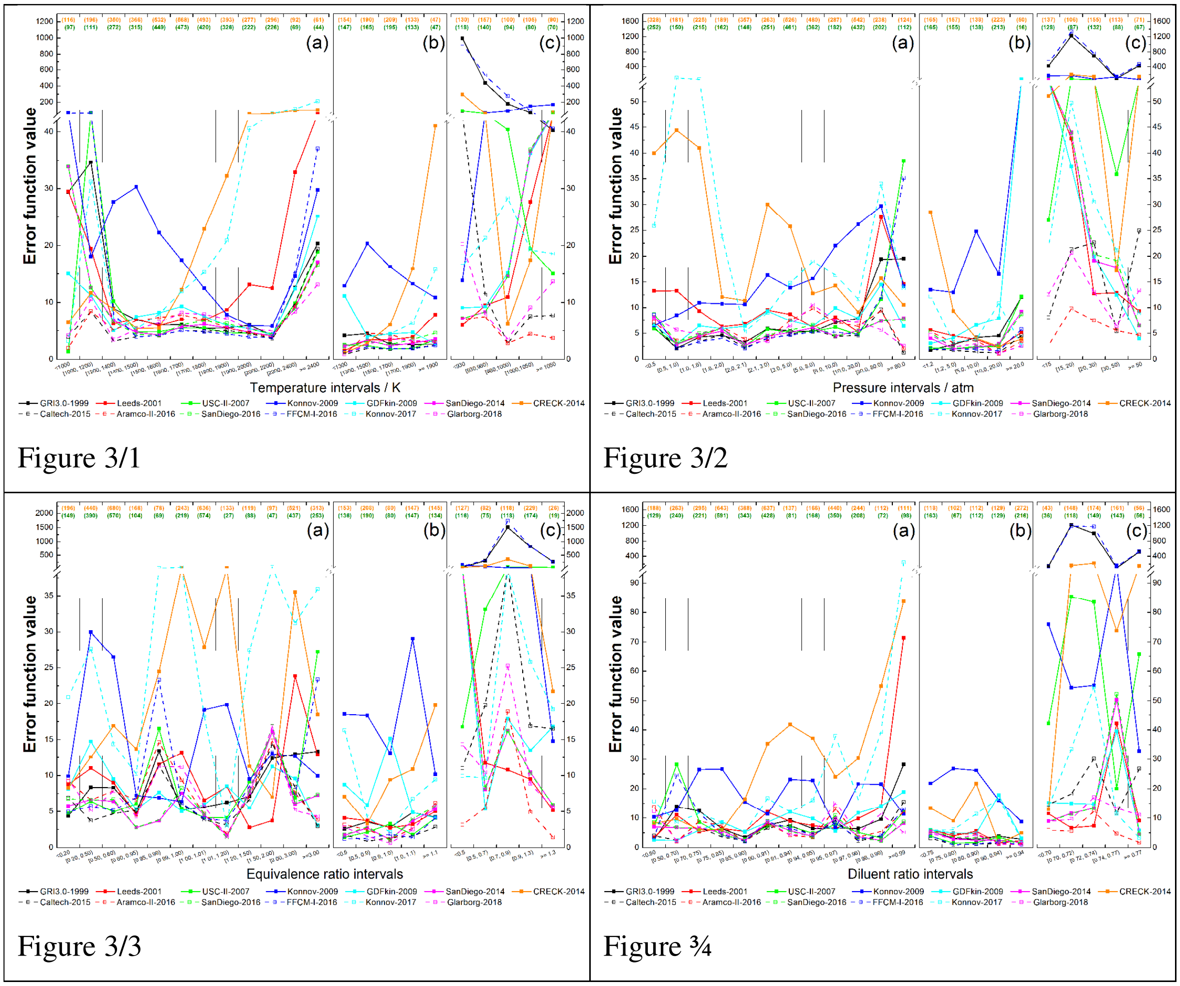


Figure 3/1

Figure 3/2

Figure 3/3

Figure ¾

Fig. 3. Performance of the mechanisms in various intervals of (1) temperature, (2) pressure, (3) equivalence ratio, and (4) diluent ratio with respect to ignition delay time. Each plot shows the results for shock tubes without PRR (a), shock tubes with PRR (b) and RCM (c).

Fig. 3/1 shows the dependence of *E* values of the mechanisms on the initial temperature. In Fig. 3/1(a), the overall trend is that most mechanisms can reproduce the experiments with better accuracy in middle temperature range, (1200K – 2200K) except for Leeds-2001, Konnov-2009, CRECK-2014, and Konnov-2017. The *E* values of these four mechanisms follow a similar trend, but with higher values. In this middle temperature range, Caltech-2015 and FFCM1-2017 have the lowest error values. However, the *E* values of FFCM1-2017 increase dramatically towards lower and higher temperatures, while Caltech-2015 has stable performance in the whole temperature range. Similarly, Aramco-II-2016 and Glarborg-2018 are accurate at all initial temperatures. As Fig. 3/1(b) shows, for the reproduction of the shock tube with PRR experimental data, five mechanisms (Leeds-2001, Konnov-2009, GDF-Kin-2012, CRECK-2014, and Konnov-2017) have large errors in the whole temperature range, while the other mechanisms have very low error.

According to Fig. 3/1(c), the majority of mechanisms reproduce the RCM experimental data poorly, while Aramco-II-2016 is the only one, which has *E* values lower than 9 (*i.e.* below 3σ deviation) at all initial temperatures. Konnov-2017 and Glarborg-2018 have error values larger than those of Aramco-II-2016, but these are better than the other mechanisms.

Fig. 3/2 (a) shows that all mechanisms can reproduce the shock tube experiments without PRR data well in the low and middle pressure range, but their performance is not as good at pressures higher than 30 atm. However, the trend of the performance of CRECK-2014 and Konnov-2017 is just the opposite. As shown in Fig. 3/2(b) for the ST-PRR data, Konnov-2009, CRECK-2014, and Konnov-2017 have significant change of *E* values for all ranges of pressure, while the other mechanisms are satisfactory for reproducing all datasets. In Fig. 6(c), Aramco-II-2016 is the most accurate mechanism for the reproduction of the RCM data in all pressure ranges and the deviations of Caltech-2015 and Glarborg-2018 are also within the reasonable range. However, the predicting capability of all other mechanisms are much poorer.

Fig. 3/3(a) shows that at the reproduction of shock tube data without PRR there is no clear trend for changing the error function values with equivalence ratios. However, in the low equivalence ratio range SanDiego-2104, SanDiego-2016, and Caltech-2015 have the lowest error. Near the stoichiometric equivalence ratio, the errors of most mechanisms are low, except for Konnov-2009 and Konnov-2017. In the range of moderately rich equivalence ratio ($1.2<\varphi<2.0$), the Leeds-2001 mechanism has significantly lower error compared to other mechanisms. For fuel-rich mixtures, Glarborg-2018 and Caltech-2015 could reproduce the experimental data well. For the reproduction of shock tube data with PRR (Fig. 3/3(b)), Caltech-2015 and Glarborg-2018 are the most accurate mechanisms. For reproducing the RCM data (Fig. 3/3(c)), most mechanisms are less accurate at stoichiometric conditions compared to both the lean and rich mixtures. Aramco-II-2016 has the same trend, but its error is the lowest one at most equivalence ratios.

Figure 3/4 shows the performance of the mechanisms for various intervals of diluent ratio. For the shock tube data without PRR (Fig. 3/4(a)), Glarborg-2018 and Caltech-2015 have advantage in predicting experiments in the full condition range. Glarborg-2018 and Caltech-2015 are still the most accurate for reproducing the shock tube experimental data with PRR, as shown in Fig. 3/4 (b). For the prediction of RCM data (Fig. 3/4(c)), Aramco-II-2016 is the best mechanism again, although its error is slightly higher in the diluent ratio range 72% to 74%. As shown in Fig. S7 (f) of the Supplementary Material, Aramco-II-2016 over predicts the ignition delays measured with RCM in the whole range of diluent ratio.

Summary

The main results of the project:

1. We intended to find all published ignition delay time measurements on methane containing reactive mixtures that do not contain higher hydrocarbons. The published data were encoded in 643 XML data files and will be available in the ReSpecTh information site for the combustion community for further utilization.
2. All widely used, recently published methane combustion mechanisms were investigated. We could clearly distinguish very accurate and very inaccurate mechanisms in the various ranges of temperature, pressure and fuel-to-air equivalence ratio. This will allow the selection of an appropriate detailed reaction mechanism for a given engineering calculation.
3. The sensitivity analysis results (not discussed in the present report due to the large amount of processed data) indicate the influence of the elementary reaction steps at given experimental conditions. The performance data of the mechanisms and the sensitivity analysis results together allow the identification of those reaction steps that require more attention for the development of methane combustion models.

Publications related to the project

A four pages long conference proceedings paper has been published:

P. Zhang, I. Gy. Zsély, V. Samu, T. Turányi:
Comparison of methane combustion mechanisms based on shock tube and
RCM ignition delay time measurements,
Proceedings of the European Combustion Meeting – 2019, Paper S3_AII_10, 2019

A more detailed publication has been prepared. It is in the phase of final checking and will be submitted soon:

P. Zhang, I. Gy. Zsély, V. Samu, T. Nagy, T. Turányi
Comparison of methane combustion mechanisms based on shock tube and rapid compression machine ignition delay time measurements
Combustion and Flame, to be submitted

Two more publications are in a preparatory phase:

1. During the processing of rapid compression machine (RCM) experiments it became obvious that the experimental data can be interpreted only knowing the measured pressure–time profiles belonging to both the reactive and the corresponding nonreactive mixtures, i.e. the oxygen containing mixture and when O_2 was replaced with a nonreactive gas, respectively. However, the experimental papers usually publish the derived volume–time profiles only, which already contain the influence of an assumed model. A methodical paper is planned about the correct interpretation of published RCM data.
2. An almost complete XML file collection is ready about measured laminar burning velocities of methane containing fuel/oxygen mixtures and burning stabilized flame measurements. Most of the related simulations are also ready and a related paper is in preparation.

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