Comparison of methane combustion mechanisms based on shock tube and RCM ignition delay time measurements

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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. 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 were proved to be the most accurate mechanisms for the simulation of methane combustion at ST experimental conditions, while AramcoII-2016 has the lowest prediction error at RCM conditions.

Introduction

Majority of energy used and electricity produced comes from combustion processes. The most important fuel is natural gas, which is used 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 effective 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.

We have investigated a series of detailed reaction mechanisms for the combustion of hydrogen [1], synthesis gas [2], methanol [3] and ethanol [4]. These works demonstrated that some of the widely used mechanisms reproduce poorly many of the experimental data points. Also, even the best mechanisms may perform surprisingly poorly at some conditions. Currently, several detailed reaction mechanisms are widely used for the description of methane combustion. A comprehensive investigation of methane combustion mechanisms has not been published so far. Jach et al. [5] published a paper on the comparison of the performance of several hydrocarbon combustion mechanisms in reproduction of ignition delay times of C1-C4 hydrocarbons, but this study was not comprehensive for methane and used a different approach. In this paper the methodology we have developed for the comparison of combustion mechanisms [1]–[4] of other fuels is applied for methane combustion based on shock tube and rapid compression machine ignition delay measurements.

Methodology

The method of comparison has been discussed elsewhere in details [1], [2], only a brief summary is presented here. The main steps are the following: (1) Collection and processing of all relevant publications dealing with methane shock tube ignition delay time measurements; (2) Encoding and storing the experimental data in ReSpecTh Kinetics Dataformat (RKD) datafiles [6], [7]; (3) Estimation of the error of the experimental datasets based on the scatter of measured points and the reported experimental errors; (4) Program Optima++ [8] reads the RKD files and performs the simulations automatically for a selected reaction mechanism using the FlameMaster code [9] and it is repeated for each reaction mechanism investigated; (5) Program outgen [10] processes the results and calculates various performance indicators based on all experiments or a selected subset of them for each mechanism.

In this work the agreement of the experimental and simulation results is characterized using the average error function E and average absolute deviation D:

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

$$D = \frac{1}{N}\sum_{i=1}^{N}\frac{1}{N_i}\sum_{j=1}^{N_i}\frac{D_{ij}}{\sigma(Y_{ij}^{exp})} = \frac{1}{N}\sum_{i=1}^{N}\frac{1}{N_i}\sum_{j=1}^{N_i}\frac{(Y_{ij}^{sim}-Y_{ij}^{exp})}{\sigma(Y_{ij}^{exp})}$$

where

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

Here N is the number of datasets and Ni is the number of data points in the i-th dataset. Values y_{ij}^{exp} and $\sigma(y_{ij}^{exp})$ are the j-th data point and its standard deviation, respectively, in the i-th dataset. The corresponding simulated (modeled) value is Y_{ij}^{mod}, obtained from a simulation using a detailed mechanism and an appropriate simulation method. For ignition delay time measurements the experimental results have relative errors, so we used option $Y_{ij} = \ln(y_{ij})$. Error function value E is 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. The deviation of simulated results is within 3σ experimental scatter limits on average if $E \leq 9$. The D values may show

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trends like systematic under- or overprediction. The drawback of the *D* values is that positive and negative deviations in different data sets can cancel each other and may result in good average values.

Experimental data collection

Methane ignition delay times measured in a wide range of experimental conditions in shock tubes and rapid compression machines were collected [11]. For the data from shock tubes, the initial temperature and pressure were varied in the range of 803–2800 K and 0.1–481.4 atm, respectively; the equivalence ratio was changed between 0.03–8.0; the mole fraction of diluent concentration was within the interval 0.0–99.7%. In several experiments, methane was mixed with H_2 and/or CO. Altogether 5092 data points in 566 datasets were encoded in RKD-format XML files based on 70 publications.

As for the conditions of rapid compression machine experiments, the ranges of temperature and pressure were 870–1200 K, and 10–80 atm, respectively; equivalence ratio changed within 0.3–2.0; the diluent ration was between 66.3–94.2%. Currently, 297 data points included in 101 datasets have been abstracted from 3 articles.

Mechanism investigation

Thirteen detailed reaction mechanisms recently published for methane combustion were investigated. Namely, GRI-Mech 3.0 [12] from 1999 (abbreviated in this paper as: GRI3.0-1999); the Leeds Methane Combustion Mechanism [13] (Leeds-2001); USC-II mechanism [14] (USC-II-2007); enhanced version of GDF-Kin® 3.0 mechanism (GDF-Kin-2012) [15]; the mechanisms of Konnov from 2009 [16] (Konnov-2009) and from 2017 [17] (Konnov-2017); San Diego mechanisms version 2014-10-04 [18] (SanDiego-2014) and 2016-12-14 [19] (SanDiego-2016); CRECK mechanism version C1C3LT_1412 [20] (CRECK-2014) from 2014; the reaction mechanism of the California Institute of Technology [21] (CaltechMech-2015); the AramcoMech 2.0 [22] (Aramco_II-2016); the FFCM-1 mechanism [23] (FFCM1-2016) and the Glarborg mechanism [24] (Glarborg-2018). The information on the number of species and reactions of these mechanisms is shown in Table 1.

The ignition delays at 1045 experimental points in 144 datasets were determined from measured excited OH concentration. Ground state OH concentration simulations cannot be used due to their different concentration profiles during these experiments. However, only four of the fourteen mechanisms (Aramco_II-2016, FFCM1-2016, Konnov-2017, Glarborg-2018) contain excited OH chemistry. Therefore, we added the excited OH submechanism used in the ELTE syngas mechanism [7] to those which do not have that in their original form and performed the simulations with the extend mechanisms where needed.

Discussion

The simulations were performed with each reaction mechanism for all data points. The calculated average error function *E* values are given in Table 1 for shock tube ignition delay measurements. The results show that about one-sixth of the experimental points cannot be described within 3σ deviation using any of the mechanisms. This means that these measurements are wrong, the assumed idealistic experimental conditions are not applicable, or none of the mechanisms contain the necessary elementary reactions with accurate rate

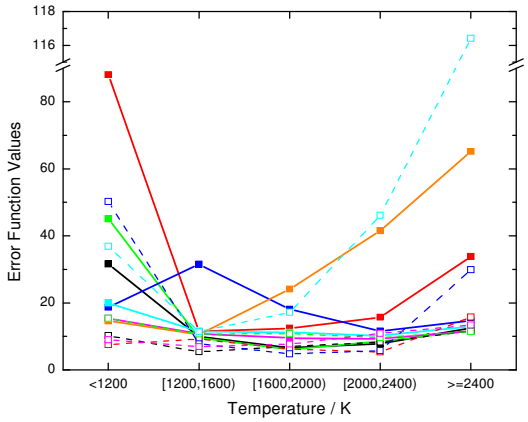
Mechanisms	Species number (orig.)	Reactions number (orig.)	For all data points		For the filtered subset	
			Ar+N_2	He	Ar+N_2	He
GRI30-1999	53	325	401.2	-	10.0	-
Leeds-2001	37	175	315.0	-	14.5	-
USC-II-2007	112	784	300.4	30.4	10.6	21.2
Konnov-2009	129	1231	403.7	-	23.0	-
GDFkin-2012	141	1144	308.6	6.0	11.5	5.7
SanDiego-2014	50	247	316.3	5945.1	10.0	3.1
CRECK-2014	107	2642	360.4	8118.1	21.0	6.3
Caltech-2015	192	1156	385.6	-	6.4	-
Aramco_II-2016	502	2716	245.2	7321.4	7.0	9.6
SanDiego-2016	57	268	346.5	8.8	10.6	3.2
FFCM1-2016	38	291	362.2	6537.8	10.0	8.0
Konnov-2017	107	1236	218.4	9.9	21.0	5.5
Glarborg-2018	154	1407	256.1	6.2	7.4	2.5

Table 1 The average error function values *E* for all data points and for a filtered subset of shock tube ignition delays. Values within 3σ deviation are denoted by green background.

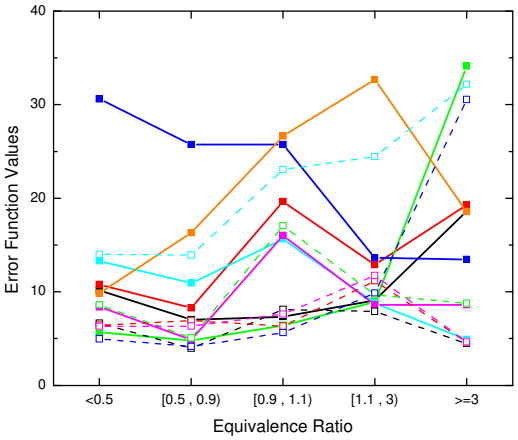
parameters. Having filtered out these data points, the remaining subset contains 3821 data points in 432 datasets. The last two columns of Table 1 contain the calculated *E* values based on the filtered subset. These results are used for the discussion of the performance of the mechanisms. Three mechanisms (Caltech-2015, AramcoII-2016 and Glarborg-2018) reproduce the shock tube ignition delay measurements within 3σ deviation on average for mixtures of argon and nitrogen bath gases. Only 9 mechanisms contain helium, but 7 of them perform quite well. Glarborg-2018 mechanism is the only one which is able to reproduce the experimental results for all three kinds of diluents.

Mechanisms	For all data	For the filtered data
GRI30-1999	-	-
Leeds-2001	-	-
USC-II-2007	460.6	132.3
Konnov-2009	605.9	52.9
GDFkin-2012	179.6	25.9
SanDiego-2014	191.2	22.7
CRECK-2014	994.1	224.6
Caltech-2015	449.9	46.3
AramcoII-2016	438.7	36.3
SanDiego-2016	191.1	22.7
FFCM1-2016	-	-
Konnov-2017	684.3	90.4
Glarborg-2018	-	-

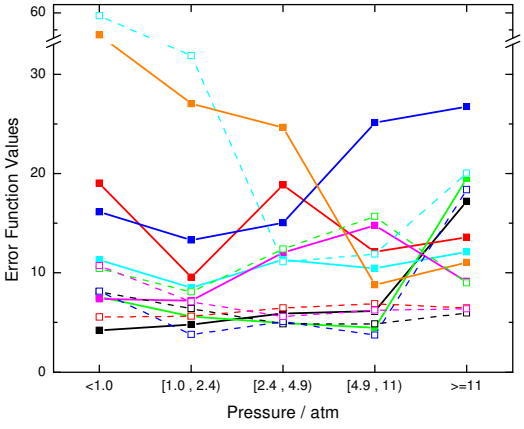
Table 2 The average error function values *E* for all data points and a filtered subset for rapid compression machine ignition delays. The lowest error value is denoted by green background.



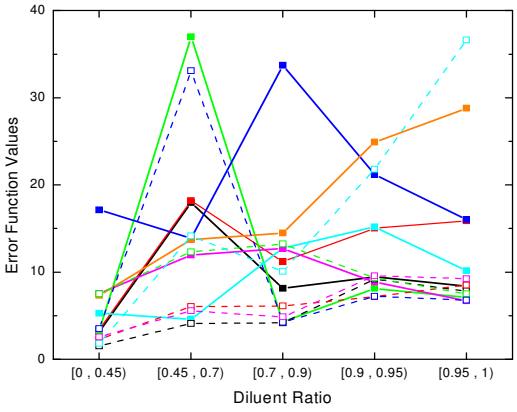
(a)



(b)



(c)



(d)

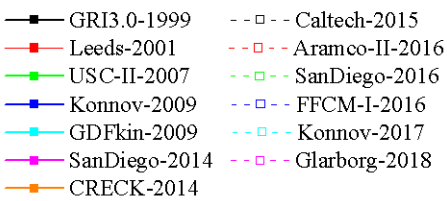


Fig. 1 The average error function values *E* for all mechanisms as a function of experimental conditions.

Besides the shock tube results presented in Table 1, RCM ignition delay experiments and corresponding simulations were also investigated. The final calculated results are displayed in Table 2. GDFkin-2012 was the best mechanism among all models before filtering. After filtering the data, SanDiego-2016 and SanDiego-2104 became the most accurate mechanisms. However, all models have error values E higher than one in high temperature (shock tube) experiments.

As shown in Fig. 1 (a), the Glarborg-2018 and Caltech-2015 mechanisms show good agreement between measurements and simulations for low and middle temperature intervals, Aramco-II-2016 is fairly accurate at all temperatures.

As described by Fig. 1 (b), FFCM-I-14 and USC-II-17 mechanisms are good at lean and stoichiometric conditions. Aramco-II-16, Caltech-15, GDFkin-09 and Glarborg-18 are the best at very rich conditions. Caltech-15 is fairly good at all equivalence ratios.
Caltech-2015 is good at medium pressures, GRI30-1999 is fairly good everywhere except for at high pressures, as seen in Fig 1. (c). According to Fig. 1 (d), the Aramco_II-2016, Caltech-2015, and Glarborg-2018 mechanisms are good for all dilutions up to 0.9. In general, decreasing dilution leads to better agreement.

Acknowledgements.

The authors thank the support of the Hungarian National Research, Development and Innovation Office – NKFIH grant KH126515. This work was facilitated by COST Action CM1404 (SmartCats). The authors thank the helpful discussions with Mr. Carsten Olm and Ms. Ágota Busai.

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