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

P. Zhang, I. Gy. Zsély, V. Samu, T. Turányi

Institute of Chemistry, ELTE Eötvös Loránd University, Budapest, Hungary

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. Natural gas contains mainly 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 were carried out in shock tubes, but there are some also in rapid compression machines (RCMs).

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 several related experimental data. Also, even the best mechanisms may perform surprisingly badly at some particular 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] 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 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 mechanisms.

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

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

where

corresponding author: István Gy. Zsély (zsigy@chem.elte.hu)

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

Here N is the number of datasets and N_i is the number of data points in the i-th dataset. 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 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 trends like systematic under- or over-prediction. 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 collected

Methane ignition delay times measured at a wide range of experimental conditions in shock tubes and rapid compression machines were collected. The initial temperature and pressure were varied in the range of 870–2800 K and 0.1–260 atm, respectively; the equivalence ratio and the diluent concentration were changed between $\varphi = 0.04$–8.00 and mole fraction between 0.00–0.997, respectively, using various diluents. In several experiments, methane was mixed with H_2 and/or CO. Altogether 5000 data points in more than 500 datasets were encoded in RKD-format XML files based on 70 publications [11].

Mechanisms investigated

Thirteen detailed reaction mechanisms recently developed for the combustion of methane were investigated. Namely, GRI-Mech 3.0 [12] from 1999 (abbreviated in this paper as: GRI3.0-99); the Leeds Methane Combustion Mechanism [13] (Leeds-01) from 2001; USC-II mechanism [14] from 2007 (USC-II-07); enhanced version of GDF-Kin® 3.0 mechanism (GDF-Kin-12) from 2012 [15]; Konnov mechanism from 2009 [16] (Konnov-09) and from 2017 [17] (Konnov-17); San Diego mechanisms version 2014-10-04 [18] (SanDiego-14) and 2016-12-14 [19] (SanDiego-16); CRECK mechanism version C1C3LT_1412 [20] (CRECK-14) from 2014; the reaction mechanism of the California Institute of Technology from 2015 [21] (CaltechMech-15); the AramcoMech 2.0 [22] (AramcoII-16) from 2016; FFCM-1 mechanism from 2016 [23] (FFCM1-16) and Glarborg mechanism [24] (Glarborg-18) from 2018. The ignition delay of 1045 experimental points in 144 datasets were determined from the measured excited OH concentration. Ground state OH concentration cannot be used instead of it due to their different concentration profiles during these experiments. However, only four of fourteen mechanisms (AramcoII-16, FFCM1-16, Konnov-17, Glarborg-18) contain excited OH chemistry, but the others do not. 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.

Performance of the mechanisms

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 showed that about one-sixth part of the experimental points cannot be described within 3σ deviation using any of the mechanisms. This means that either these measure-

ments are wrong, the assumed idealistic experimental conditions are not applicable, or none of the mechanisms contain the necessary elementary reactions with good rate parameters. These data points were filtered out and 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 (CaltechMech-2015, AramcoII-2016 and Glarborg-2018) reproduce the shock tube ignition delay measurements within 3σ deviation on average for argon/nitrogen containing mixtures. Only 9 mechanisms contain helium, but 7 of them perform quite well. Glarborg-2018 mechanism is the only one which can reproduce the experimental results for all kinds of diluents.

Besides the shock tube results presented above, RCM ignition delay experiments were also investigated and the variations of the error values depending on the initial temperature, pressure and stoichiometric ratio, type and amount of the diluents were also analyzed.

Mechanisms	Species number (orig.)	Reactions number (orig.)	For all data points		For the filtered subset	
			$Ar+N_2$	He	$Ar+N_2$	He
GRI30-99	53	325	401.2	-	10.0	-
Leeds-01	37	175	315.0	-	14.5	-
USC-II-07	112	784	300.4	30.4	10.6	21.2
Konnov-09	129	1231	403.7	-	23.0	-
GDFkin-12	141	1144	308.6	6.0	11.5	5.7
SanDiego-14	50	247	316.3	5945.1	10.0	3.1
CRECK-14	107	2642	360.4	8118.1	21.0	6.3
Caltech-15	192	1156	385.6	-	6.4	-
AramcoII-16	502	2716	245.2	7321.4	7.0	9.6
SanDiego-16	57	268	346.5	8.8	10.6	3.2
FFCM1-16	38	291	362.2	6537.8	10.0	8.0
Konnov-17	107	1236	218.4	9.9	21.0	5.5
Glarborg-18	154	1407	256.1	6.2	7.4	2.5

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

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