Performance of methane combustion mechanisms based on shock tube ignition delay measurements

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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 gas engines and gas turbines can be designed.

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 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]. (3) Estimation of the error of the experimental datasets based on the scatter of measured points and the reported experimental errors. (4) Program *Optima++* [7] reads the RKD files and performs the simulations automatically for a selected reaction mechanism using the FlameMaster code [8]. It is repeated for each reaction mechanism investigated. (5) Program *outgen* [9] 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

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

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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.

The experimental data collected

Methane ignition delay times measured at a wide range of experimental conditions were collected. The initial temperature and pressure were varied in the range of 1000–2800 K and 0.1–260 atm, respectively; the equivalence ratio and the diluent concentration were changed between φ = 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 3962 data points in 447 datasets were encoded in RKD-format XML files based on 94 publications [10].

Mechanisms investigated

Ten detailed reaction mechanisms recently developed for the combustion of methane were investigated. The GRI-Mech 3.0 [11] was published in 1999 and it is one the most popular combustion mechanisms designed for the combustion of natural gas (abbreviated in this paper as: GRI3.0-1999). The Leeds Methane Combustion Mechanism [12] was developed mainly for the simulation of methane combustion experiments (Leeds-2001). Version 3.0 of the GDF-Kin® mechanism (GDF-Kin-2006) was published in 2006 [13] including the kinetics of larger hydrocarbons. Researchers at the University of Southern California published the USC-II mechanism [14] in 2007 for the combustion of hydrocarbons having not more than four carbon atoms (USC-II-2007). Konnov updated his reaction mechanism for the combustion of hydrocarbons up to three carbon atoms in 2009 from version 0.5 to 0.6 [15] (Konnov-2009). The combustion research group of University of California San Diego provides several different versions of hierarchical reaction mechanisms. There are two relevant versions for the methane combustion: version 2014-10-04 [16] (SanDiego-2014) and 2016-12-14 [17] (SanDiego-2016). We included both versions in the analysis. CRECK Modeling Group of Politecnico di Milano also provides a series of reaction mechanisms. We used version C1C3LT_1412 [18] (CRECK-2014) in the comparison. Researchers of the California Institute of Technology paid special attention to the polyaromatic hydrocarbons, but their reaction mechanism [19] (CaltechMech-2015) was tested against several C1 experiments, therefore it is proper to include it here. The AramcoMech 2.0 [20] (AramcoMech-2016) from NUI Galway Combustion Chemistry Centre is the latest release of the hierarchically built mechanisms from H_2 chemistry to higher hydrocarbons published in the last decades.

Performance of the mechanisms

The simulations were performed with each reaction mechanism for 3962 data points belonging to 447 datasets. The calculated E and D values are given in Table 1. The results

showed that about 10% of the experimental points cannot be described within 3σ deviation using any of the mechanisms. This means that either these measurements 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 3658 data points in 403 datasets. The last two columns of Table 1 contain the calculated *E* and *D* values based on the filtered subset. These results are used for the discussion of the performance of the mechanisms. Four mechanisms (CaltechMech-2015, SanDiego-2016, SanDiego-2014 and AramcoMech-2016) reproduce the shock tube ignition delay measurements within 3σ deviation on average. Other three mechanisms (GRI3.0-1999, Leeds-2001, USC-II-2007) are only slightly worse. The remaining three of the investigated ten mechanisms produced much higher average deviations.

Besides the overall study, the performance of the mechanisms was investigated in ranges of initial temperature, pressure and stoichiometric ratio, and also according to the type and amount of the diluents.

Mechanisms	For all data points		For the filtered subset	
	E	*D*	*E*	*D*
CaltechMech-2015	34,58	1,18	5,82	0,32
SanDiego-2016	31,35	1,13	7,07	0,38
SanDiego-2014	30,03	0,91	7,21	0,17
AramcoMech-2016	37,85	2,06	7,48	1,18
GRI3.0-1999	36,64	0,21	10,42	–0,58
Leeds-2001	34,80	–0,09	11,15	–0,91
USC-II-2007	36,34	1,31	11,22	0,54
Konnov-2009	47,18	–2,41	23,40	–3,27
CRECK-2014	47,26	–1,65	24,92	–2,62
GDF-Kin-2006	75,80	0,97	48,40	0,15

Table 1 The average error function E and the average absolute deviation D values for all data points and a filtered subset.

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References

[1] Olm C, Zsély IG, Pálvölgyi R, Varga T, Nagy T, Curran HJ, Turányi T, Comparison of the performance of several recent hydrogen combustion mechanisms, Combust Flame 2014;161:2219–2234.

[2] Olm C, Zsély IG, Varga T, Curran HJ, Turányi T, Comparison of the performance of several recent syngas combustion mechanisms, Combust Flame 2015;162:1793–1812.

[3] Olm C, Varga T, Valkó É, Curran HJ, Turányi T, Uncertainty quantification of a newly optimized methanol and formaldehyde combustion mechanism, Combust Flame in press.
[4] Olm C, Varga T, Valkó É, Hartl S, Hasse C, Turányi T, Development of an ethanol combustion mechanism based on a hierarchical optimization approach, Int J Chem Kinet 2016;48:423–441.
[5] Jach A, Cislak I, Rudy W, Pekalski AA, Teodorczyk A, Comparison of the performance of several hydrocarbon combustion mechanisms in reproduction of ignition delay times of C1-C4 hydrocarbons, Proc 8th Europ Combust Meeting pp. 1513–1518.
[6] Varga T, Turányi T, Czinki E, Furtenbacher T, Császár AG, ReSpecTh: a joint reaction kinetics, spectroscopy, and thermodynamics information system, Proc 7th Europ Combust Meeting pp. P1–04.
[7] Varga T, Busai Á, Optima++ v0.94: A general C++ framework for performing combustion simulations and mechanism optimization (2017).
[8] Pitsch H, FlameMaster v4.0 BETA: A C++ Computer Program for 0D Combustion and 1D Laminar Flame Calculations (2016).
[9] Olm C, outgen v3.5: A Fortran computer program for flexible output generation during the investigation of combustion mechanism (2017). http://respecth.hu
[10] Samu V, Comparison of methane combustion mechanisms (in Hungarian), M.Sc. Thesis, Institute of Chemistry, Eötvös Loránd University (ELTE) (2017).
[11] Smith GP, Golden DM, Frenklach M, Moriary NW, Eiteneer B, Goldenberg M, Bowman CT, Hanson RK, Song S, Gardiner WC, Lissianski VV, Qin Z. GRI-Mech 3.0 (1999). http://www.me.berkeley.edu/gri_mech/
[12] Hughes KJ, Turányi T, Clague AR, Pilling MJ, Development and Testing of a Comprehensive Chemical Mechanism for the Oxidation of Methane, Int J Chem Kinet 2001;33:513–538.
[13] El Bakali A, Pillier L, Desgroux P, Lefort B, Gasnot L, Pauwels JF, da Costa I, NO prediction in natural gas flames using GDF-Kin 3.0 mechanism NCN and HCN contribution to prompt-NO formation, Fuel 2006;85:896–909.
[14] Wang H, You X, Joshi AV, Davis SG, Laskin A, Egolfopoulos F, Law CK, http://ignis.usc.edu/USC_Mech_II.htm/USC Mech Version II. High-Temperature Combustion Reaction Model of H_2/CO/C_1-C_4 Compounds, last Access data: May 2007 (2007). http://ignis.usc.edu/USC_Mech_II.htm/
[15] Konnov AA, Implementation of the NCN pathway of prompt-NO formation in the detailed reaction mechanism, Combust Flame 2009;156:2093–2105.
[16] Mechanical and Aerospace Engineering (Combustion Research) University of California at San Diego . Chemical-Kinetic Mechanisms for Combustion Applications, San Diego Mechanism, version 2014-10-04 (2014). http://combustion.ucsd.edu .
[17] Mechanical and Aerospace Engineering (Combustion Research) University of California at San Diego . Chemical-Kinetic Mechanisms for Combustion Applications, San Diego Mechanism, version 2016-12-14 (2016). http://combustion.ucsd.edu .
[18] CRECK modeling Group C_1-C_3 kinetic mechanism Version 1412, December 2014 (2014). http://creckmodeling.chem.polimi.it/index.php/menu-kinetics/menu-kinetics-detailed-mechanisms/menu-kinetics-c1-c3-mechanism
[19] The FORCE - California Institute of Technology. CaltechMech detailed kinetic model, version 2.3 (2015). http://www.theforce.caltech.edu/CaltechMech/
[20] NUI Galway Combustion Chemistry Centre. AramcoMech 2.0 (2016). http://www.nuigalway.ie/c3/aramco2/frontmatter.html .