Chemical reaction mechanisms validation based on ignition delay time of C1-C5 hydrocarbons

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1 Introduction

Ignition delay time (IDT) is one of the most important combustion properties of flammable mixture. It is used as an input for modeling diesel engine combustion, knock modeling, gas turbines and any device where high initial temperature and pressure occur. IDT value is also used to calculate induction zone length in ZND detonation model and therefore lets it correlate with detonation cell size or detonability parameters like KSI and RSB [1]. Example induction zone length calculations in stoichiometric ethane-air mixture with use of different reaction mechanisms: GRI 3.0 [2], Konnov 0.5 [3] and Aramco 2.0 [4] give the values of 1.9 mm, 1.0 mm and 0.85 mm, respectively. Taking into account the importance of the IDT value in many areas of modeling the proper selection of the chemical reaction mechanism becomes crucial. Up to date there are many chemical reaction mechanisms available of which the majority were validated against limited experimental data. The main aim of the analysis presented in this paper is to quantify the quality of the available chemical reaction mechanisms by comparing numerical IDTs with the experimental ones. The results may be used as a guide for selecting reaction mechanism for modeling combustion of particular fuel and for further analyses.

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2 Cantera code, input parameters

The IDT simulations were performed with use of Cantera code version 2.2.1 [5] with Python 2.7 interface. The model utilized was constant volume reactor model with adaptive time step with relative and absolute tolerances values of 1.0E-09 and 1.0E-20, respectively. The input data necessary for single calculation were: initial temperature, initial pressure, mixture composition, chemical reaction mechanism file, experimental IDT value and its definition. The single calculation was terminated at the time when all conditions were fulfilled: the temperature was at least half the way from initial to the adiabatic flame temperature, the temperature rate was less than 0.45 of its maximal value and all predefined IDTs have been determined. Such approach let one to use the code efficiently and to consider high temperature ignition event only. Approximate number of time steps for each case was less than around 3000. Due to the various IDT definitions reported in the literature (tangential method for pressure, maximum chemiluminescence of OH*, CH* etc.) the Cantera script has been updated to calculate IDTs in similar way as in experiments to keep consistency in comparison. In case of no IDT definition reported in some papers the time of the maximum rate of temperature rise $(dT/dt)_{max}$ has been used from the simulation for comparison. The experimental data of IDT were taken from experiments performed with use of shock tubes only. The majority of the data come from the reports of Davidson and Hanson [6,7] so the reader is referred to these reports for more detailed references. The analysis performed included 17 chemical reaction mechanisms in total including older ones like LUTZ [8], Konnov 0.5 [3] or GRI 3.0 [2] and recent ones mainly from NUI Galway C3 group [4]. Table 1. summarizes all of the mechanisms considered and the experimental data range with detailed references not provided in the reports [6,7].

Table 1: Summary of the mechanisms used in numerical analysis and experimental data ranges.

Mech name	Ref.	Rel.	CH_4		C_2H_6	C_3H_8		C_4H_{10}		C_5H_{12}		
								n-C_4H_{10}	iso-C_4H_{10}	n-C_5H_{12}	iso-C_5H_{12}	neo-C_5H_{12}
			air	O_2/Ar	O_2/Ar	air	O_2/Ar	air	air	air	air	air
GRI 3.0	[2]	2000	X	X	X	X	X					
Konnov 0.5	[3]	1998	X	X	X	X	X					
NUIG_NG1	[4]	2006	X	X	X	X	X					
NUIG_NG2	[4]	2007	X	X	X	X	X	X	X	X		
NUIG_NG3	[4]	2010	X	X	X	X	X	X	X	X		
NUIG_CH4DME	[4]	2015	X	X	X	X	X					
NUIG_c3h6	[4]	2015	X	X	X	X	X	X	X			
ARAMCO 2.0	[4]	2016	X	X	X	X	X	X	X			
JETSURF 2.0	[9]	2010	X	X	X	X	X	X	X	X		
POLIMI	[10]	2014	X	X	X	X	X					
San Diego 2016	[11]	2016	X	X	X	X	X					
LUTZ	[8]	1988	X	X	X							
CaltechForce	[12]	2014	X	X	X	X	X					
NUIG_c4h10	[4]	2010				X	X	X	X			
NUIG_c5h12	[4]	2015				X	X	X	X	X	X	X
NUIG_c6h14	[4]	2015						X	X	X	X	X
NUIG_c7h16	[4]	2016						X	X	X	X	X
Experimental data details:												
T range [K]			1004-1729	1032-2097	1049-1862	1154-1510	909-1720	1007-1498	1000-1484	778-1538	1006-1551	786-1619
P range [atm]			2.5-477	0.2-264	0.6-20	3.4-24	1.0-68	0.9-47	0.8-39	0.8-68	0.96-26.5	0.78-26
Φ range [-]			0.3-3.0	0.5-4.0	0.5-2.0	1.0	0.12-2.0	0.3-2.0	0.3-2.0	0.3-2.0	0.3-2.0	0.5-1.0
Dilution (N_2/Ar) [vol.%]			54.5-75.1	54.5-99.6	75-98	75-75.8	75-99	74.1-81.2	74.1-78.2	76.5-78.6	76.5-78.6	76.5-78.4
Number of points			238	392	164	34	487	85	78	183	116	89
Ref.			[13–16]	[17–25]	[25–30]	[31,32]	[31,33–35]	[25,36]	[37]	[38,39]	[38]	[38]

To confirm the quality of the IDT values obtained by Cantera the simulations of Chemkin Pro (CKPro) and published by Burke et al. [13] have been repeated with Cantera with the same input files, mechanism

and settings. The comparison is shown in Fig. 1 with additional experimentally obtained IDT points. Figure 1 shows the results from shock tube and rapid compression machine (RCM) as well. The latter data have been calculated with Cantera and RCM volume history input files as in [13] and available from [4]. As one can see in the figure, the results obtained with Cantera and CKPro almost overlap, especially for high and low temperature ranges.

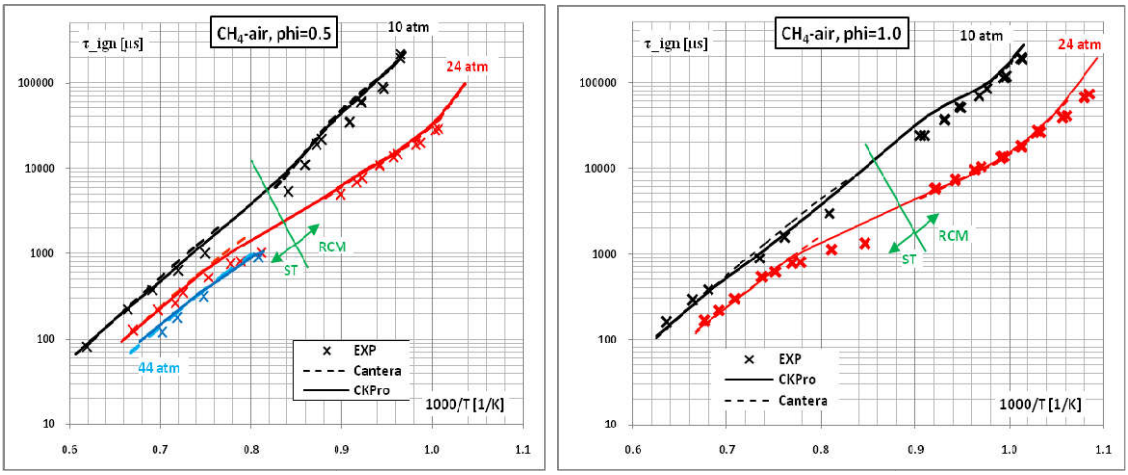

Figure 1. Comparison between Cantera and CKPro results. Experimental and numerical data from shock tube (ST) and rapid compression machine (RCM) taken from [13].

3 Mechanisms quality parameters

Numerical result quality for particular point is assessed by introducing parameter Q defined as:

$$Q = log\left(\frac{\tau_s}{\tau_e}\right) \quad (1)$$

Where τ_s, τ_e are IDT simulated and experimental, respectively. If Q < 0 then simulated IDT is underestimated, and on the contrary, Q > 0 means that simulated IDT is overestimated with respect to experimental value. Due to the large number of data points, 1st, 2nd and 3rd quartiles were calculated for the set of points within particular temperature range (normally 100 K, 200 K in case of lower number of points). The 1st quartile value Q_{1st} is the value of particular Q point which splits off the lowest 25% of data points from the remaining 75% with higher values. The 2nd quartile value Q_{2nd} splits data set in half, it is also called median, in this paper named $\bar{Q}$. The 3rd quartile Q_{3rd} splits off the highest 25% of data from the lowest 75%.

The results of the simulations are presented by two means:

1) Graphical, the median values $\bar{Q}$ of data points in particular temperature range obtained with particular mechanism. Each median point is also equipped with whiskers with lower and upper values as a 1st and 3rd quartiles, respectively, so the whiskers confines 50% of Q values.
2) Calculated, quality parameter M, defined as:

$$M = \frac{\sum_{i=1}^{n}(|\bar{Q}_i| \cdot w_i)}{w} \quad (2)$$

Where:

n – total number of temperature ranges, i – index of temperature range, $\bar{Q}_i$ - 2nd quartile value (median) for particular mechanism in i-th temperature range, w_i – number of data points in i-th temperature range, w– total number of data points.

Parameter M represents therefore weighted mean of absolute values of medians. By these means, the quality of the mechanism is considered as 'the best one' should have M value as low as possible as it represents the weighted distance from the ideal value of $\bar{Q} = 0$.

4 Results and summary

The example results for CH_4/air, CH_4/O_2/Ar, C_2H_6/O_2/Ar and C_3H_8/air mixtures are presented in Fig. 2. It is characteristic that almost every mechanism overestimates the results in the temperatures below approximately 1200 K. Characteristic for almost all mixtures considered is the fact that the chemical reaction mechanisms from NUIG [4] are grouping at the similar levels and with similar range of quartiles which should be expected because these mechanisms have been generated in a hierarchical manner.

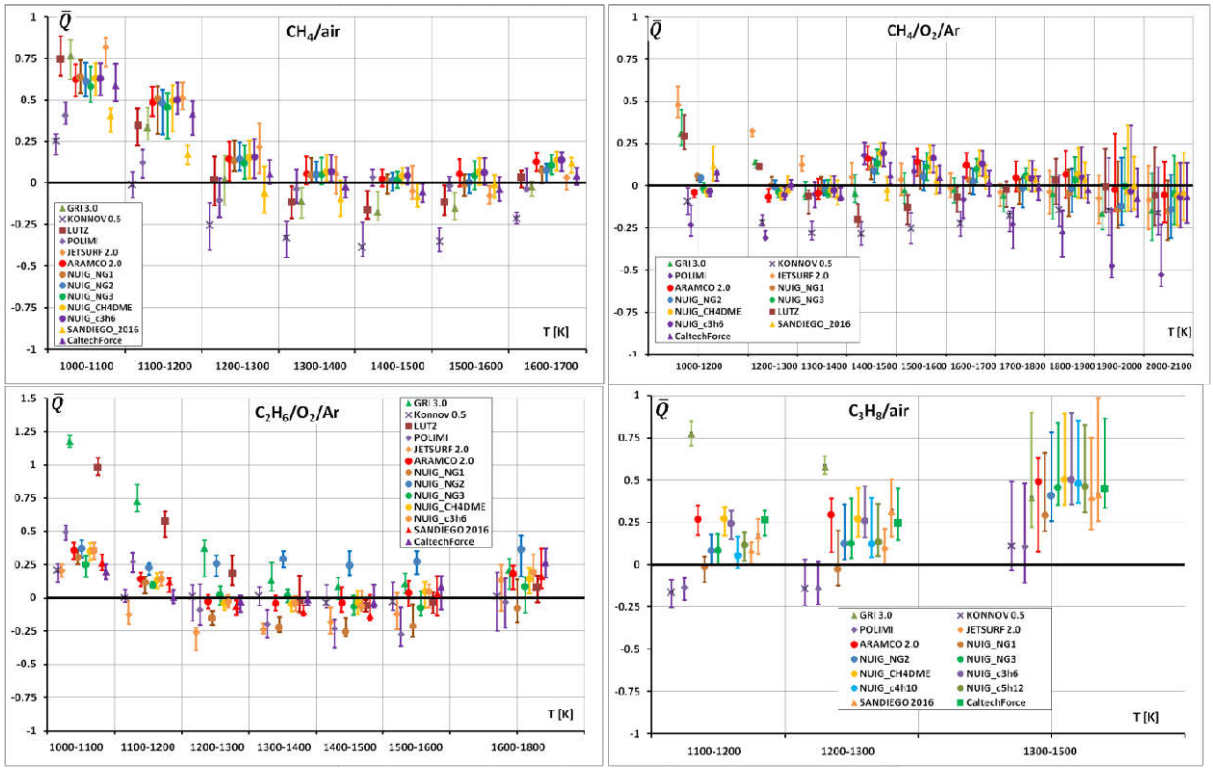

Figure 2. Example results of the median $\bar{Q}$ values in CH_4/air, CH_4/O_2/Ar, C_2H_6/O_2/Ar, and C_3H_8/air mixtures in particular temperature ranges.

The summary of the numerical analysis is presented in Table 2. The table contains the M values obtained by each mechanism in particular mixtures. Each column is colored in scale from green to red showing the lowest to the highest M values, respectively. As the results show, there is no universal mechanism suitable for more than one fuel. Remarkable are the differences between the results obtained in fuel-air mixtures and argon diluted mixtures. For instance POLIMI mechanism seems to be the best for CH_4/air mixture but is almost the worst one in case of CH_4/O_2/Ar mixtures. In case of ethane, surprisingly, mechanism of Konnov shows very low M value of 0.0188 which gives less than 5% mean difference between simulated and experimental IDTs. GRI 3.0 seems to be unsuitable for C_2H_6 or C_3H_8 mixtures and barely suitable for CH_4/O_2/Ar mixtures. Mechanisms which simulates the best C3-C5 fuels come from the NUI Galway

group. The best in this group seems to be NUIG_c5h12 mechanism which gives low M values for all of butane and pentane isomers.

Table 2: M values for each fuel and mechanism. Color scale in each column shows the lowest (green) and the highest (red) M values.

Mech name	CH_4		C_2H_6	C_3H_8		C4H10		C5H12		
						nC4H10	isoC4H10	nC5H12	isoC5H12	neoC5H12
	air	O_2-Ar	O_2-Ar	air	O_2-Ar	air	air	air	air	air
GRI 3.0	0.1976	0.0638	0.3005	0.6149	0.3566					
Konnov 0.5	0.2607	0.2140	**0.0188**	0.1441	0.3400					
NUIG NG1	0.1847	0.0630	0.1835	**0.0752**	0.1748					
NUIG NG2	0.1816	0.0512	0.2726	0.1660	**0.1536**	**0.0324**	0.0794	0.1532		
NUIG NG3	0.1747	0.0807	0.0511	0.1774	0.2198	0.1429	0.0758	0.1837		
NUIG_CH4DME	0.2058	0.1130	0.0746	0.3210	0.3152					
NUIG_c3h6	0.2081	0.1106	0.0787	0.3017	0.2898	0.2141	0.1394			
ARAMCO 2..0	0.1939	0.0994	0.0729	0.3242	0.2612	0.1203	0.1388			
JetSurf 2.0	0.2330	0.0645	0.2001	0.1476	0.2230	0.0906	0.0630	0.2857		
POLIMI	**0.0965**	0.1889	0.1832	0.1311	0.2780					
San Diego 2016	0.1186	**0.0409**	0.1001	0.2809	0.1961					
CaltechForce	0.1513	0.0422	0.0550	0.1580	0.2717					
LUTZ	0.1927	0.0964	0.1719							
NUIG_c4h10				0.1706	0.2226	0.1093	0.0833			
NUIG_c5h12				0.1960	0.3146	0.0524	0.0509	0.0677	**0.0664**	**0.0447**
NUIG_c6h14						0.1119	0.0512	**0.0674**	0.0690	0.1350
NUIG_c7h16						0.0846	**0.0427**	0.0732	0.1054	0.0505

This paper presents the results of comparison between various reaction mechanisms used to simulate IDT of C1-C5 hydrocarbon fuels. The analysis pointed out the mechanisms which give IDT the least deviation from the experimentally obtained values. The results may be used as an initial guide for selecting reaction mechanism for modeling combustion of particular fuel and for further analyses.

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References

[1] Radulescu MI, Sharpe GJ, Bradley D, in:, Proc. 7th Int. Sem. Fire Explos. Hazards, 2012.
[2] GRI v.3.0, http://combustion.berkeley.edu/gri-mech/version30/text30.html (accessed: 15/05/2015).
[3] Konnov AA, in:, 28th Smposium(int.) Combust., Edinburgh, 2000, pp. 317.
[4] http://c3.nuigalway.ie/mechanisms.html (accessed: 01/09/2016).
[5] Goodwin DG, Moffat HK, Speth RL, www.cantera.org (accessed: 01/02/2016).
[6] Davidson DF, Hanson RK, Fundamental Kinetics Database Utilizing Shock Tube Measurements Vol. 1, 2005.
[7] Davidson DF, Hanson RK, Fundamental Kinetics Database Utilizing Shock Tube Measurements Vol. 4, 2014.
[8] Lutz AE, Kee RJ, Miller JA, Dwyer HA, Oppenheim AK, (1988). 22nd Symp. Combust. 1683.

[9] Wang H, Dames E, Sirjean B, Sheen DA, Tango R, Violi A, Lai JYW, Egolfopoulos FN, Davidson DF, Hanson RK, Bowman CT, Law CK, Tsang W, Cernansky NP, Miller D, Lindstedt RP, (2010).
[10] Polimi C1-C3 NOx Ver.1412, http://creckmodeling.chem.polimi.it/ (accessed: 01/09/2016).
[11] The San Diego mechanism, rel. 15.08.2016, http://web.eng.ucsd.edu/mae/groups/combustion/mechanism.html (accessed: 15/09/2016).
[12] CaltechMech v.2.3, http://theforce.caltech.edu/CaltechMech/index.html (accessed: 15/04/2016).
[13] Burke U, Somers KP, O'Toole P, Zinner CM, Marquet N, Bourque G, Petersen EL, Metcalfe WK, Serinyel Z, Curran HJ, (2015). Combust. Flame 162: 315.
[14] Huang J, Hill PG, Bushe WK, Munshi SR, (2004). Combust. Flame 136: 25.
[15] Heufer KA, Olivier H, (2010). Shock Waves 20: 307.
[16] Zhukov VP, Sechenov VA, Starikovskii AY, (2003). Combust. Explos. Schock Waves 39: 487.
[17] Tsuboi T, Wagner HG, (1974). Proc. Combust. Inst. 15: 883.
[18] Seery DJ, Bowman CT, (1970). Combust. Flame 14: 37.
[19] Spadaccini L.J., Colket MB, (1994). Prog. Energy Combust. Sci. 22: 431.
[20] Frank P, Braun-Unkhoff M, in:, Proc. Sixt. Symp. (Int.)on Shock Tube Waves, 1987, pp. 379–385.
[21] Lifshitz A, Scheller K, Burcat A, Skinner GB, (1971). Combust. Flame 16: 331.
[22] Skinner GB, Lifshitz A, Scheller K, Burcat A, (1972). J. Chem. Phys. 56.:
[23] Hidaka Y, Gardiner WC, Eubank CS, (1982). Commun. J. Mol. Sci. 2: 141.
[24] Merhubi HE, Keromnes A, Catalano G, Lefort B, Moyne L, (2016). Fuel 177: 164.
[25] Burcat A, Scheller K, Lifshitz A, (1971). Combust. Flame 16: 29.
[26] Aul Christopher J, Metcalfe Wayne K, Burke Sinéad M, Curran Henry J, Petersen Eric L, (2013). Combust. Flame 160: 1153.
[27] Hu E, Chen Y, Zhang Z, Li X, Cheng Y, Huang Z, (2015). Energy Fuels 29: 4557.
[28] Lamoureux N, Paillard CE, Vaslier V, (2002). Shock Waves 13: 57.
[29] Pan L, Zhang Y, Zhang J, Tian Z, Huang Z, (2014). Int. J. Hydrogen Energy 39: 6028.
[30] De Vries Jaap, Hall Joel M, Simmons Stefanie L, Rickard Matthew Ja, Kalitan Danielle M, Petersen Eric L, (2007). Combust. Flame 150: 137.
[31] Brown CJ, Thomas GO, (1999). Combust. Flame 117: 861.
[32] Steinberg M, Kaskan WE, in:, 6th Symp. Combust., 1955, pp. 664–672.
[33] Cadman P, Thomas GO, Butler P, (2000). Phys. Chem. Chem. Phys. 2: 5411.
[34] Tang C, Man X, Wei L, Pan L, Huang Z, (2013). Combust. Flame 160: 2283.
[35] Man X, Tang C, Wei L, Huang Z, (2013). Int. J. Hydrogen Energy 38: 2523.
[36] Healy D, Donato NS, Aul CJ, Petersen EL, Zinner CM, Bourque G, Curran HJ, (2010). Combust. Flame 157: 1526.
[37] Healy D, Donato NS, Aul CJ, Petersen EL, Zinner CM, Bourque G, Curran HJ, (2010). Combust. Flame 157: 1540.
[38] Bugler John, Marks Brandon, Mathieu Olivier, Archuleta Rachel, Camou Alejandro, Grégoire Claire, Heufer Karl a, Petersen Eric L, Curran Henry J, (2015). Combust. Flame 163: 138.
[39] Zhukov VP, Sechenov VA, Starikovskii AY, (2005). Combust. Flame 140: 196.