Faculty of Power and Aeronautical Engineering
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Assessment of detailed chemical kinetic mechanisms performance in reproduction of ignition delay times of C1-C5 alkanes according to the Curve Matching method

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1. Introduction

The goal of this study is to assess performance of detailed chemical kinetic mechanisms for reproduction of ignition delay times (IDTs) of C1-C5 alkanes according to the Curve Matching method proposed by Bernardi et al. [1] in 2016. The Curve Matching method allows comparison of both absolute errors and shapes of functions describing experimental and simulated curves (continuous functions).

Workflow

1. Analysis based on ignition delay times from shock tube experiments. More than 3400 points from more than 40 publications accumulated for seven C1-C5 alkanes.
2. Calculations of IDTs performed in Cantera in Matlab environment utilizing Constant Volume explosion model. IDTs with dP/dt lower than 3%/ms used. 15 mechanisms assessed (4. Summary block).
3. The error function definition: $$E = \lg\frac{IDT_{simulated}}{IDT_{experimental}}$$
4. Assessment of the accumulated IDTs quality done by computation of mean absolute error (MAE) for each mechanism and experimental data set.
5. Functional estimates of experimental f and simulated g datasets created with use of cubic smoothing spline function (csaps) in Matlab. (Example in Figure 1)
6. The Curve Matching metrics according to Bernardi et al. [1]:
   - original and aligned dissimilarity indices d^0_P, d^1_P, d^0_{L2}, d^1_{L2}:

$$d^0_{L^2}(f,g) = \frac{\|f-g\|}{|D|} \in (0,+\infty) \qquad d^0_{Pearson}(f,g) = \frac{1}{2}\left\|\frac{f}{\|f\|} - \frac{g}{\|g\|}\right\| \in (0,1)$$

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   - shift δ^0_P, δ^1_P, δ^0_{L2}, δ^1_{L2}: $\delta_{opt} = \operatorname{argmin}_\delta d(f(x+\delta), g(x))$
   - normalization and average of dissimilarity measures:

$$\hat{d}(f_i,g_j) = \frac{1}{4}\left(\frac{d^0_{L^2}(f_i,g_j) - m^0_{L^2}}{IQR^0_{L^2}/2} + \frac{d^1_{L^2}(f_i,g_j) - m}{IQR^1_{L^2}/2} + \frac{d^0_P(f_i,g_j) - m^0_P}{IQR^0_P/2} + \frac{d^1_P(f_i,g_j) - m^1_P}{IQR^1_P/2}\right)$$

   (D – intersection between the domains of the two functions, m – median, IQR – interquartile range)
7. Analysis of benefit of a temperature (Δ 1000/T) shift.
8. The final parameter ε is an avearage of $\hat{d}_{align}$ and $\hat{d}_{orig}$

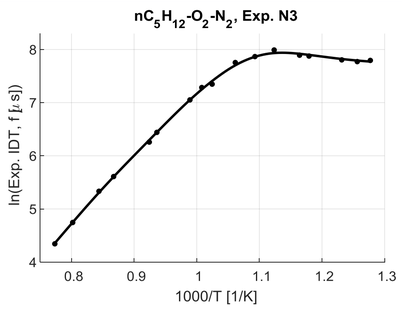

Fig. 1 Experimental IDTs (N3 set of nC_5H_{12}-O_2-N_2) measured by Bugler et al., their functional estimate (top) and the 1st derivative of the estimate (bottom).
(N3: 783-1293 K, 21.2-26.9 bar, EQR 1, N_2/O_2 3.76)

2. Experimental data collection and preparation

Summary of collected ignition delay times, Methane

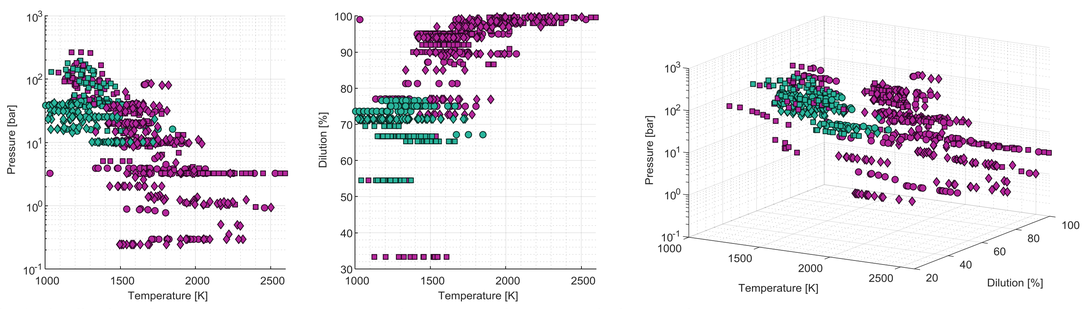

Fig. 2 Distribution of methane parameters: green- nitrogen, purple – argon; circle – EQR in <0.9;1.1>, square – EQR>1.1.

Assessment of the collected IDTs quality, CH_4-O_2-Ar

•Experimental IDTs are divided into smaller data sets (N) of uniform condition (inert gas, inert gas fraction, pressure, equivalence ratio) and source. Data sets equal to or bigger than 3 IDTs are used.

• In order to analyze a relative accuracy of prediction (within predictive ability of mechanisms) only, the MAEs are normalized to a scale from 0 to 1 within each mechanism and presented in Fig. 3 and Fig. 4.

•Normalized MAE indicates that N4 data set measured by Burcat et al. [4] in 1971 is an outlier. Consistently 13 from 15 mechanisms resulted in the highest error and much higher than compared to the other sets (2 mechanisms give normalized MAE of 0.28). Thereby, data sets 1-3 and 5-46 remained in the analysis.

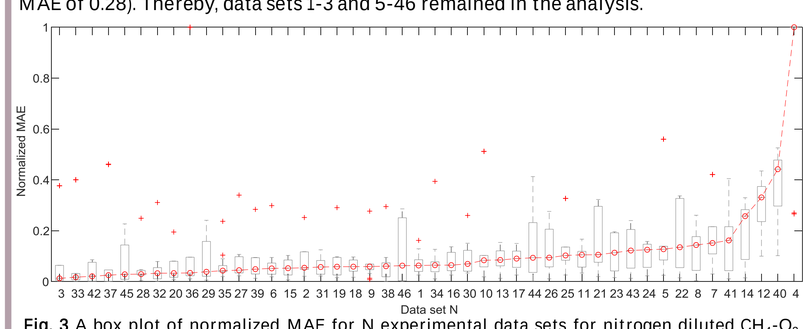

Fig. 3 A box plot of normalized MAE for N experimental data sets for nitrogen diluted CH_4-O_2 mixtures. The medians are visualized in a bubble plot in Fig. 3.
(N4: 1496-1900 K, 0.2 bar, EQR 1, dilution 76.9%, 13 points)

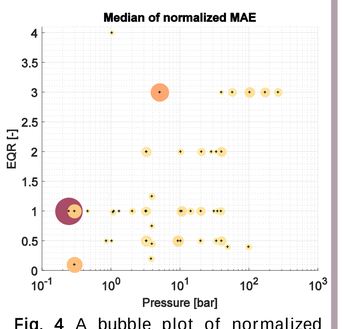

Fig. 4 A bubble plot of normalized median of MAE for CH4-O2-Ar: size and color of a bubble corresponds to values in Fig. 2.

3. Methane

Dissimilarity indices vs. DRM, CH_4-O_2-Ar

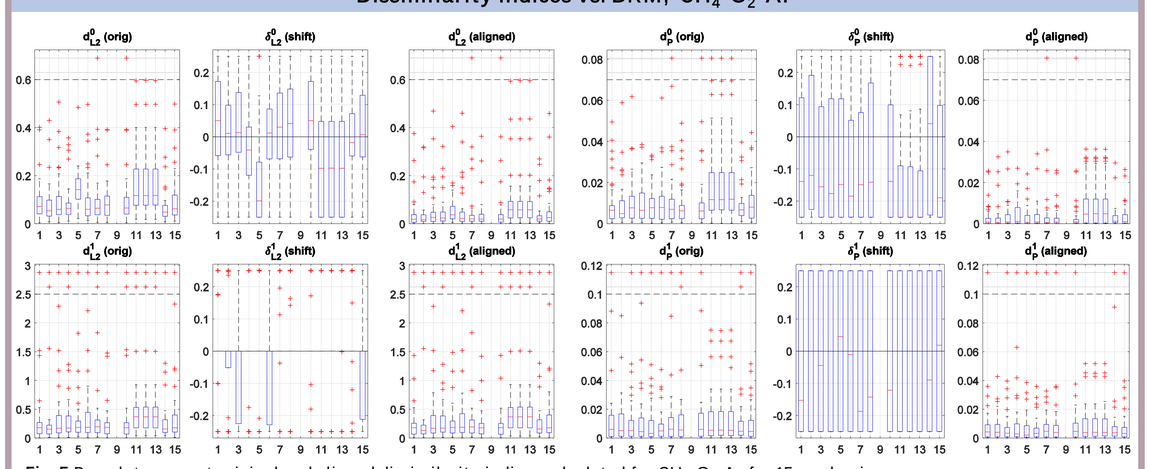

Fig. 5 Box plots present original and aligned dissimilarity indices calculated for CH_4-O_2-Ar for 15 mechanisms.

Benefit of x alignment

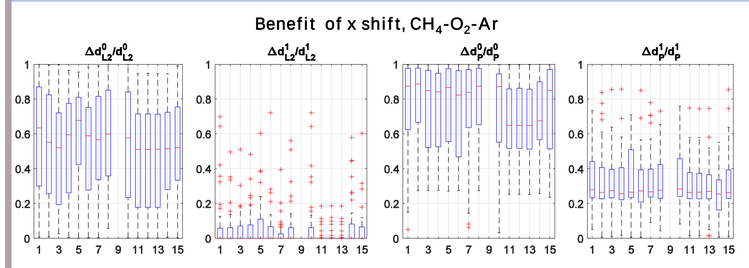

Fig. 6 Difference between original and aligned dissimilarity indices in regard to original ones indicates which mechanisms benefits most from a shift along the inverse temperature axis.

•Based on the previously introduced error function E the original and aligned dissimilarity indices d and shift δ are calculated and presented in Fig. 5.

•δ (shift) reaches maximum values in many cases for d^1_{L2} and d^1_P, but the overall improvement of the indices is small due to the x shift (Fig. 6). The reason is that majority of experimental data sets of methane IDTs have low curvature (almost constant activation energy) and because of which alignment does not improve much metrics corresponding to the 1st derivative. Hence, d_{orig} and d_{align} are used further in the analysis and δ is not.

•Within results of each mechanism medians of $\hat{d}_{orig}$ and $\hat{d}_{align}$ are computed and presented in Table 1.

•Additional parameters are defined: $\hat{d}^{IQR,m}_{align}{}_{orig}$ and $\Delta\hat{d} = \widetilde{\hat{d}_{orig}} - \hat{d}^{IQR,m}_{align}{}_{orig}$
The first one is analogical to $\widetilde{\hat{d}_{align}}$, but calculated in regard to IQR and m from the original set (before x alignment), thereby it informs on benefit of the alignment when compared to $\widetilde{\hat{d}_{orig}}$.

•The highest change due to the x alignment occurs for M11-M13 (Polimi mechanisms). Figure 7 presents performance of M11 mechanism in a case of one of the highest change of $\hat{d}_{orig}$ due to the x shift – N7 experimental set measured by Frank and Braun-Unkhoff [3].

•In order to assess comprehensively compatibility of the mechanisms and the experiments the ε parameter is used. It is defined as an average of $\hat{d}_{orig}$ and $\hat{d}_{align}$.

•Table 2 summarizes the ε parameter for alkanes from C1 up to C5.

Tab. 1 Medians of $\hat{d}_{orig}$ and $\hat{d}_{align}$ calculated for CH_4-O_2-Ar. The lowest values indicating the best mechanism within each metric are marked in bold text.

	CH_4-O_2-Ar			
	$\widetilde{\hat{d}_{orig}}$	$\widetilde{\hat{d}_{align}}$	$\hat{d}^{IQR,m_{orig}}_{align}$	$\Delta\hat{d}$
M1	-0.01	-0.09	-1.78	-1.76
M2	**-0.36**	**-0.36**	-1.80	-1.45
M3	-0.19	0.03	-1.68	-1.49
M4	0.16	0.18	**-1.82**	-1.98
M5	0.08	0.27	-1.39	-1.47
M6	-0.10	-0.03	-1.56	-1.46
M7	-0.29	-0.21	-1.67	-1.38
M8	-0.12	-0.29	**-1.82**	-1.70
M10	-0.04	-0.08	-1.69	-1.65
M11	2.80	3.41	0.33	**-2.47**
M12	2.80	3.46	0.33	**-2.47**
M13	2.80	3.49	0.22	**-2.58**
M14	-0.27	-0.33	-1.46	-1.18
M15	-0.12	-0.02	-1.71	-1.59

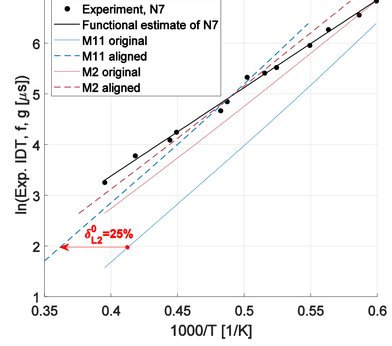

Fig. 7 Experimental IDTs (N7) measured by Frank and Braun-Unkhoff [3], functional estimate of N7 and results of M2 (Caltech) and M11 mechanisms before and after alignment.
(N7: 1669-2531 K, 3.2 bar, EQR 0.5, dilution 99%)

4. Summary

Tab. 2 The ε parameter for C1-C5 alkanes. Color: white – 0, red – (-1), green – (1).

Mechanisms	CH_4		C_2H_6	C_3H_8		n-C_4H_{10}		iso-C_4H_{10}		n-C_5H_{12}		iso-C_5H_{12}	
	Ar	N_2	Ar	Ar	N_2	Ar	N_2	Ar	N_2	Ar	N_2	Ar	N_2
(M1) AramcoMech2.0 [5]	-0.092	-0.159	-0.239	0.211	0.213	0.229	**-0.164**	-0.102	**-0.252**				
(M2) CaltechMech [6]	**-0.330**	**-0.271**	-0.438	0.509	-0.523								
(M3) USC Mech C1-C3 [7]	-0.030	0.092	-0.436	-0.004	-0.318								
(M4) GRI-mech 3.0 [8]	0.189	0.641	0.727	0.812	3.416								
(M5) Konnov 0.5 [9]	0.263	0.489	**-0.779**	-0.039	**-0.898**								
(M6) JetSurF 2.0 [10]	-0.038	0.259	0.971	-0.364	-0.083	**-0.37**	0.150	0.199	0.107	1.938	1.760		
(M7) NUIG Butane [5]	-0.238	-0.165	-0.615	0.013	1.364	-0.051	-0.107	**-0.435**	-0.050				
(M8) NUIG Pentane Iso. [5]	-0.172	-0.167	0.121	0.290	0.548	-0.081	0.140	-0.006	0.000	-0.134	**-0.188**	**-0.333**	0.188
(M9) NUIG n-Hexane [6]										**-0.389**	-0.146	0.632	**-0.373**
(M10) NUIG n-Heptane [7]	-0.116	-0.162								-0.056	-0.049	0.212	0.501
(M11) P. C1C3 LT HT [11]	3.253	0.812	0.315	0.745	-0.162								
(M12) P. C1C3 HT NOx [11]	3.253	0.813	0.315	0.771	-0.651								
(M13) P. PRF PAH LT [11]	3.253	0.816	0.306	0.910	-0.269	3.174	1.540	5.318	1.440	1.225	1.518		
(M14) UC San Diego [12]	-0.293	-0.153	-0.084	**-1.054**	-0.354								
(M15) USC Mech II [13]	-0.054	0.153	3.020	-0.307	-0.741								

The ε value equal to 0 indicates an average performance of a mechanism within one mixture (white color in Table 2). Values lower than 0 inform on a good compatibility of a DRM with experiment (green color) and values higher than 0 mean that a performance is worse than an average mechanism (red color). The best mechanisms in regard to the Curve Matching method are marked in bold font in Table 2. However, one need to keep in mind that the high values of ε might be a reason of local worse performance of a mechanism as shown in Fig. 8 on heat maps of the error function E against pressure and temperature for CH_4-O_2-Ar.

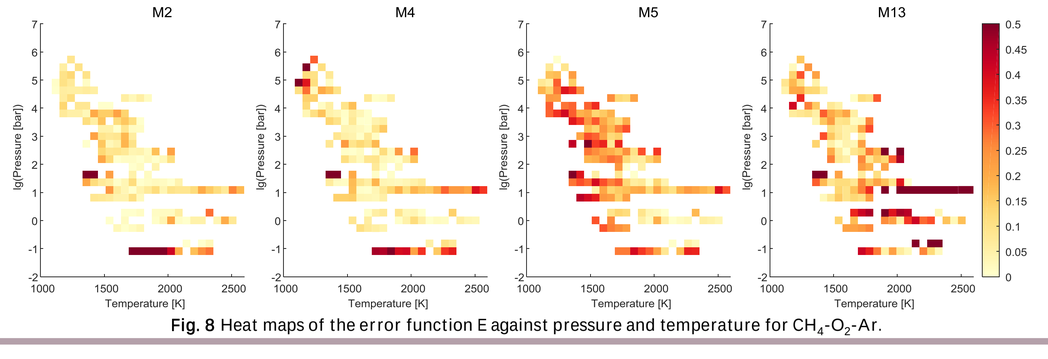

Fig. 8 Heat maps of the error function E against pressure and temperature for CH_4-O_2-Ar.

5. References

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