

# Validation of detailed chemical kinetics mechanisms for reproduction of ignition delay times of C2–C5 alkenes

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## 1 Introduction

The goal of the paper is to assess a performance of 15 detailed chemical kinetics mechanisms for combustion of C2–C5 alkenes based on ignition delay times. The paper provides an indication which mechanism ought to be used and under what conditions. Mechanisms being assessed are: Aramco 2.0 [1], Blanquart 2009 [2], Davis Law Wang C3 [3], GRI-mech 3.0 [4], Konnov 0.5 [5], JetSurF 2.0 [6], NUIG Butane [1], NUIG Pentane Isomers [1], NUIG n-Hexane [1], NUIG n-Heptane [1], Polimi C1C3 LT HT - Version 1412 [7], Polimi C1C3 HT NO<sub>x</sub> - Version 1412 [7], Polimi PRF PAH LT - Version 1412 [7], San Diego 2014 [8], Wang High T [9].

## 2 Experimental data collection and calculations

A large data set of ignition delay times (IDTs) from shock tube experiments was collected for C2–C5 alkenes (1020 points in total). Summary of accumulated dataset is presented in Table 1. The highest  $dP/dt$  reported in the literature was 3%/ms. Such increase of pressure has negligible influence on ignition delay time. Constant volume calculations with adaptive time step were performed in Cantera 2.2.1. in Matlab R2016a environment. Initial conditions for calculations were: experimental temperature ( $T_5$ ), experimental pressure ( $P_5$ ) and composition of investigated mixture ( $T_5$  and  $P_5$  are conditions behind a reflected shock wave). Ignition delay times in the literature were determined with use of 6 definitions of IDTs (maximal gradient of pressure, pressure tangential, tangential OH\*, maximum of OH\*, maximum of CH\*, 50% of maximum of OH\*). All 6 methods were implemented into the Cantera script to keep consistency in comparison. When experimental IDT was assessed using more than one definition, a minimal error was used later on.

In order to assess performance of a mechanism a following error function is used:

$$E = \log_{10} \frac{\tau_{sim}}{\tau_{exp}} \quad (1)$$

where  $\tau_{sim}$  and  $\tau_{exp}$  are calculated and experimental IDT respectively. The mechanism which computes the IDT best, gives error function value closer to zero. Error function of 1 (or -1) informs that simulated IDT is an order of magnitude higher (or lower) than experimental IDT.

Table 1: Summary of collected ignition delay times from literature.

C2–C5 Alkanes	Ethene C <sub>2</sub> H <sub>4</sub>	Propene C <sub>3</sub> H <sub>6</sub>	iso-Butene iso-C <sub>4</sub> H <sub>8</sub>	1-Butene 1-C <sub>4</sub> H <sub>8</sub>	2-Butene 2-C <sub>4</sub> H <sub>8</sub>	1-Pentene 1-C <sub>5</sub> H <sub>10</sub>
Temperature [K]	1058–2211	999–1756	643–1715	921–1835	919–1397	1040–1880
Pressure [atm]	1.1–40.8	1.5–51.2	1.7–55.5	1.2–50	8.9–53	1.0–11.1
Equivalence ratio [-]	0.13–2.0	0.5–2.0	0.3–2.0	0.5–2.0	0.5–2.0	0.5–2.0
Dilution [%]	75–99	72.3–95.6	73.8–90	75.4–96.5	73.8–77.6	91.5–97.6
No of points	224	261	278	124	69	64
Reference	[10] [11] [12] [13]	[14]	[15] [16]	[15] [17]	[15]	[18]

Results of analysis are presented in two ways:

1. graphical representation of averaged error function vs. temperature (Figure 1), equivalence ratio EQR (Figure 2), pressure (Figure 3) and dilution level (Figure 4) for each alkene.

Error function values are averaged within ranges of: **pressure:** every 5 bars, **temperature:** every 100 K, **dilution level:** every 10% of diluent, **EQR:** EQR < 1 - lean mixture, EQR = 1 - stoichiometric mixture, EQR > 1 - rich mixture.

Averaging of error function values in regard to one property means that all points are taken into account irrespective of other properties (for instance: when the average of error function is calculated for a range of 1400 – 1500 K for *iso*-C<sub>4</sub>H<sub>8</sub> there are 37 points taken into account, whose pressure range is 1.7 – 11.4 bar, EQR: 0.3 – 2.0, dilution concentration: 73.83 – 99.0% of Ar or N<sub>2</sub>).

2. average error value for particular species and mechanism (Table 2).

It was defined as an average of absolute error values:

$$\bar{E}_{mech,species} = \sum_{i=1}^{N_{sim}} \frac{\left| \log_{10} \frac{\tau_{sim}}{\tau_{exp}} \right|}{N_{sim}} \quad (2)$$

where  $N_{sim}$  is number of points calculated by a mechanism ( $N_{sim}$  usually equals to number of experimental points, with exceptions when convergence could not be reached with a given mechanism).

Similarly to defined error value  $E$ , when the average error function  $\bar{E}_{mech,species}$  tends toward zero a mechanism simulates well ignition delay times. Table 2 presents calculated average error values.

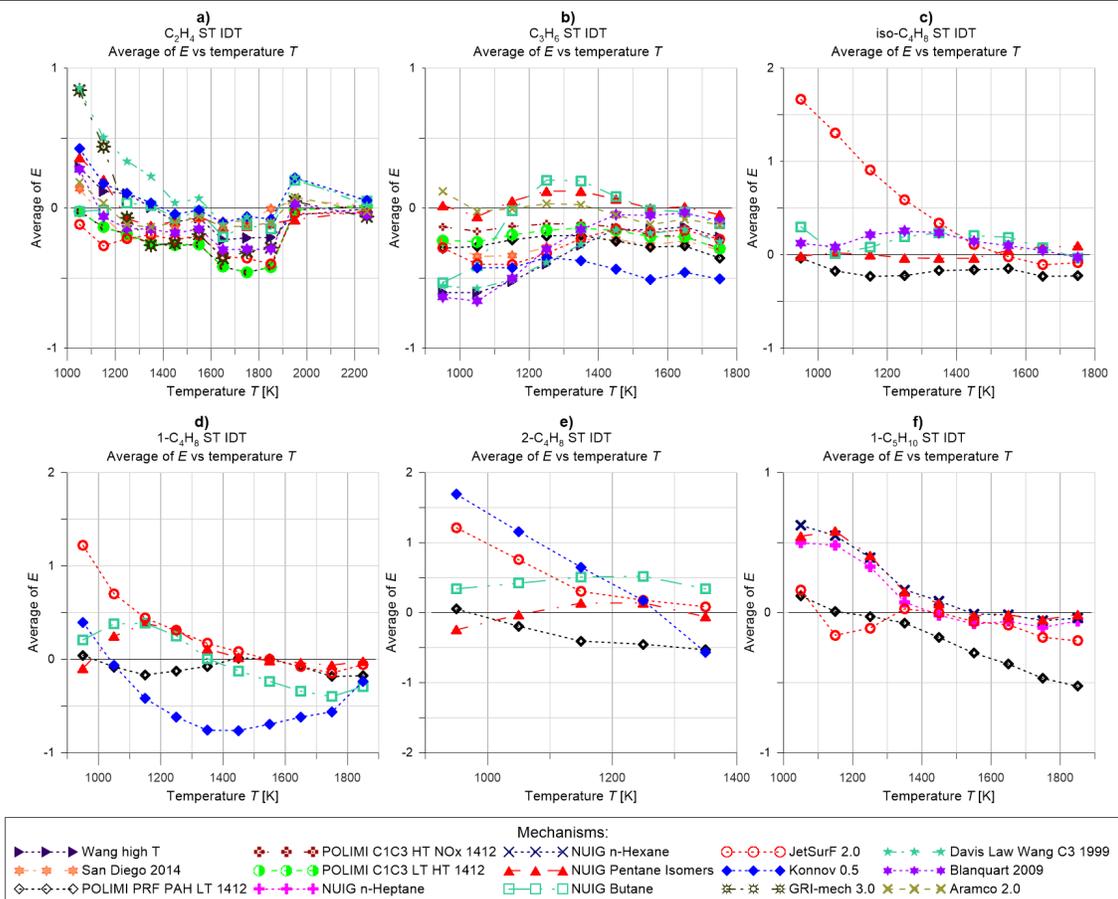


Figure 1: Error function against temperature for the C2-C5 alkenes.

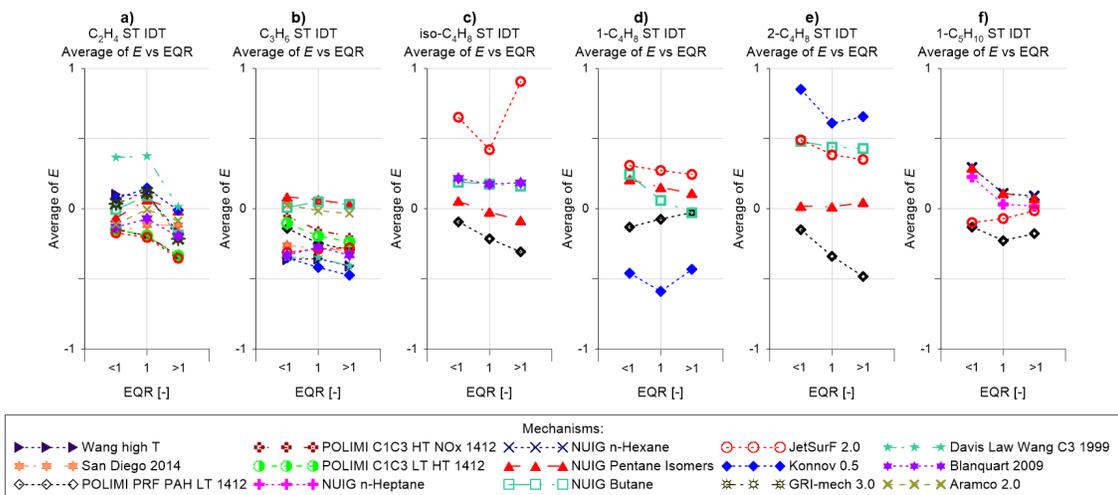


Figure 2: Error function against EQR for the C2-C5 alkenes.

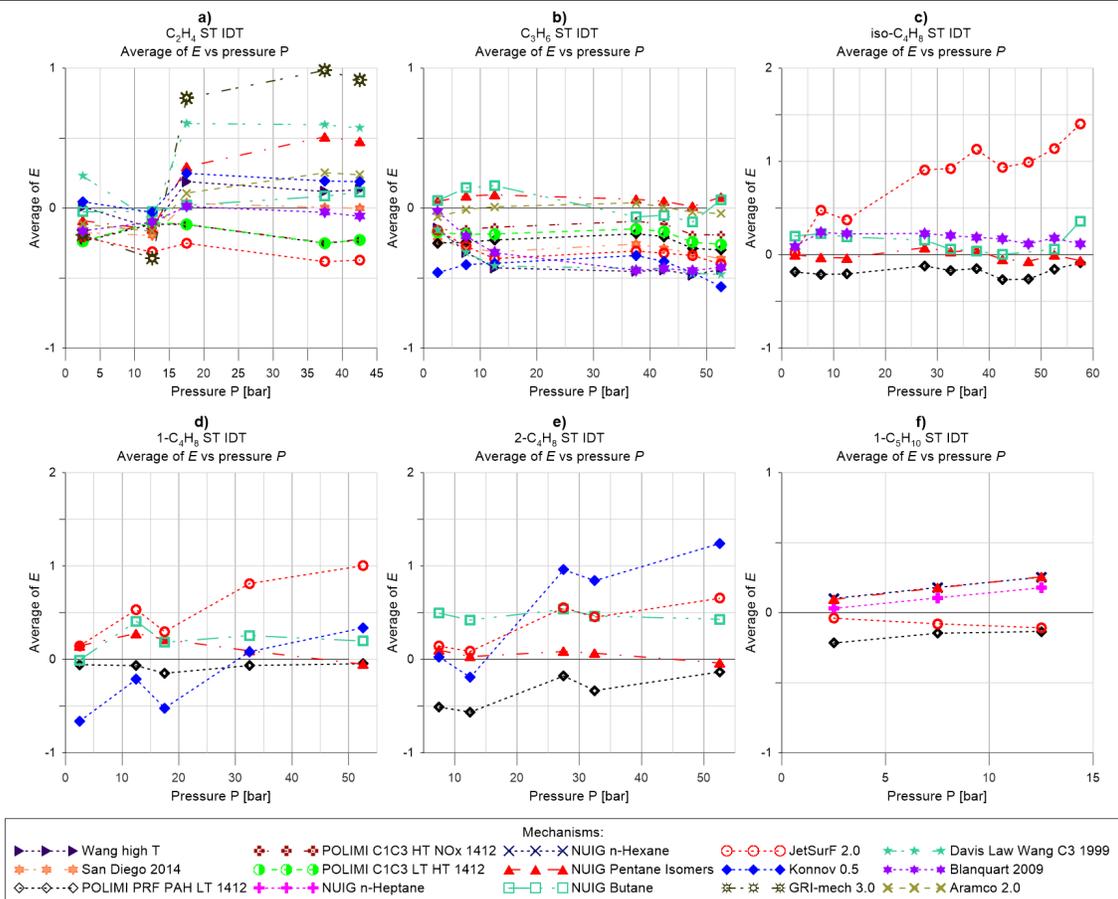


Figure 3: Error function against pressure for the C2-C5 alkenes.

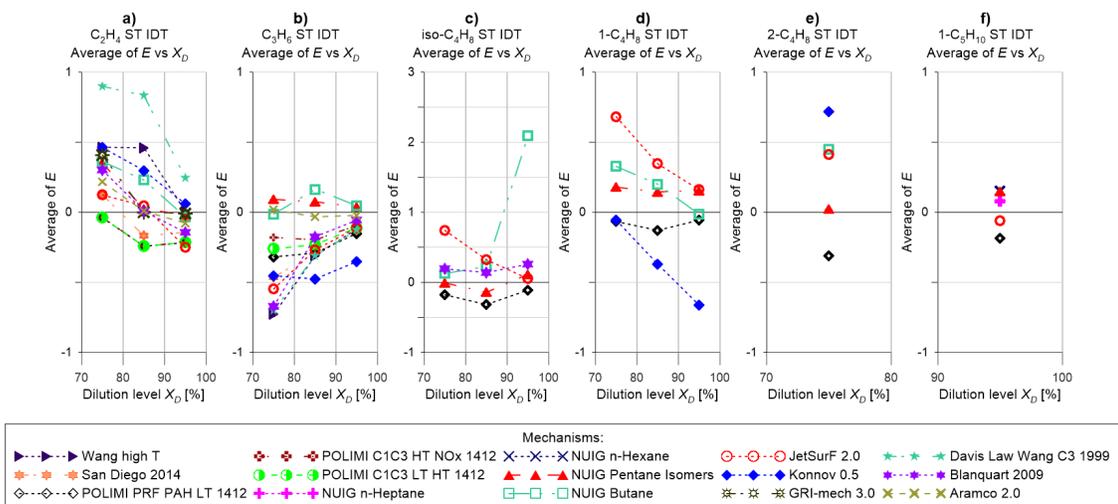


Figure 4: Error function against dilution level for the C2-C5 alkenes.

**Jach, A. Validation of detailed chemical kinetics mechanisms for reproduction of IDTs of C2–C5 alkenes**

Table 2: Summary of performance of detailed chemical kinetics mechanisms for reproduction of C2–C5 alkenes' ignition delay times (the lowest average error for each alkene is marked by a bold font).

Mechansims	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	iso-C <sub>4</sub> H <sub>8</sub>	1-C <sub>4</sub> H <sub>8</sub>	2-C <sub>4</sub> H <sub>8</sub>	1-C <sub>5</sub> H <sub>10</sub>
Aramco 2.0	0.147	<b>0.063</b>				
Blanquart 2009	0.167	0.312	0.198			
Davis Law Wang C3 1999	0.355	0.363				
GRI-mech 3.0	0.396	0.396				
Konnov 0.5	0.143	0.406		0.562	<b>0.861</b>	
JetSurF 2.0	0.247	0.313	0.612	0.300	0.414	<b>0.114</b>
NUIG Butane	<b>0.126</b>	0.186	0.186	0.252	0.451	
NUIG Pentane Isomers	0.187	<b>0.092</b>	<b>0.090</b>	0.188	<b>0.138</b>	0.174
NUIG n-Hexane						0.175
NUIG n-Heptane						0.160
POLIMI C1C3 LT HT 1412	0.221	0.186				
POLIMI C1C3 HT NO <sub>x</sub> 1412	0.221	0.146				
POLIMI PRF PAH LT 1412	0.223	0.232	0.201	<b>0.126</b>	0.344	0.227
San Diego 2014	0.168	0.281				
Wang high T	0.174	0.370				

### 3 Conclusion

Taking into account the whole range of experimental conditions and defined averaged error function, the best mechanism for combustion of C<sub>2</sub>H<sub>4</sub> is NUIG Butane, for C<sub>3</sub>H<sub>6</sub> - Aramco 2.0, iso-C<sub>4</sub>H<sub>8</sub> - NUIG Pentane Isomers, 1-C<sub>4</sub>H<sub>8</sub> - POLIMI PRF PAH LT 1412, 2-C<sub>4</sub>H<sub>8</sub> - NUIG Pentane Isomers, 1-C<sub>5</sub>H<sub>10</sub> - JetSurF 2.0. However, based on Figures 1–4 one can make the best choice knowing conditions for which a mechanism is going to be used.

### 4 Acknowledgements

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