



Comparison of detailed NO_x reaction mechanisms on syngas combustion systems

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Introduction

- The combustion of syngas may produce nitrogen oxides (NO_x). The **environmental effects** of NO_x require the detailed description of the chemical reactions of NO_x species in such systems.
- Recently, **Zhang et al. [1] published a new reaction mechanism** that describes the combustion of hydrogen and syngas doped with NO_x species. The mechanism was tested by Zhang et al. [1] against a large set of experimental data.
- In this work we investigate the performance of the Zhang et al. [1] mechanism and also **two other recently published mechanisms** [2], [3] that can also describe NO_x/syngas combustion. The experimental data used here are almost the same as those used by Zhang et al. [1].

Experimental data

- 23 experimental articles** were used in the simulations:

Apparatus	Meas. quant.	Ds./Dp. ⁱ	Mixture	Ref.
ST ^a	c–t ^e	4/39	H ₂ /O ₂ /N ₂	[5]
ST ^a	c–t ^e	24/84307	N ₂ O/Ar	[6]
ST ^a	IDT ^f	15/153	H ₂ /O ₂ /NO ₂ /Ar	[7]
ST ^a	IDT ^f	12/101	H ₂ /O ₂ /N ₂ O/Ar	[8]
ST ^a	IDT ^f	3/29	H ₂ /CO/O ₂ /NH ₃ /Ar	[9]
ST ^a	IDT ^f	2/20	H ₂ /(O ₂)/N ₂ O/Ar	[10]
ST ^a	IDT ^f	1/6	H ₂ /N ₂ O/Ar	[11]
ST ^a	IDT ^f	3/152	H ₂ /N ₂ O/Ar	[12]
ST ^a	IDT ^f	6/82	H ₂ /N ₂ O/Ar	[13]
ST ^a	IDT ^f	4/46	H ₂ /N ₂ O/Ar	[14]
ST ^a	IDT ^f	3/27	H ₂ /N ₂ O/Ar	[15]
ST ^a	IDT ^f	2/20	H ₂ /N ₂ O/Ar	[16]
ST ^a	IDT ^f	2/33	H ₂ /CO/N ₂ O/Ar	[17]
ST ^a	IDT ^f	12/103	NH ₃ /O ₂ /Ar	[18]
ST ^a	c–T ^g	2/11	H ₂ /N ₂ O/Ar	[14]
JSR ^b	c–T ^g	78/945	H ₂ /O ₂ /NO _x /N ₂	[19]
JSR ^b	c–T ^g	9/87	H ₂ /CO/O ₂ /NO/N ₂	[20]
FR ^c	c–T ^g	6/54	H ₂ /O ₂ /N ₂	[21]
FR ^c	c–T ^g	4/20	O ₂ /N ₂	[22]
FR ^c	c–T ^g	15/195	CO/H ₂ /O ₂ /NO _x /N ₂	[23]
FR ^c	c–T ^g	23/334	CO/O ₂ /H ₂ O/NO _x /N ₂	[24]
FR ^c	c–t ^e	74/1284	(CO)/H ₂ O/O ₂ /NO _x	[25]
SCB ^d	v _f ^h	1/30	H ₂ /N ₂ O/Ar	[26]
SCB ^d	v _f ^h	5/46	H ₂ /N ₂ O/(N ₂)	[27]

^a: shock tube, ^b: jet stirred reactor, ^c: flow reactor, ^d: spherical combustion bomb, ^e: concentration–time profile, ^f: ignition delay time, ^g: outlet concentration–temperature profile, ^h: laminar flame speed, ⁱ: Dataset(s)/Data points

- Experimental data were encoded in **ReSpecTh Kinetics Data (RKD) 2.0 format** XML files [28].
- Program **Optima++** [29] reads the XML datafile, sets up the simulation environment and calls the **FlameMaster** [30] simulation code to carry out the simulation.
- All simulations were made with FalmeMaster [30] using a **0D** (ST, JSR, FR) or a **1D model** (laminar flames).

The investigated reaction mechanisms

- The details of the investigated reaction mechanisms:

Authors	Name used here	Year	Reactions	Species
Zhang et al. [1]	Zhang_2017	2017	262	44
Glarborg et al. [2]	Glarborg_2018	2018	1639	153
Song et al. [3]	POLIMI_2018	2018	2361	153

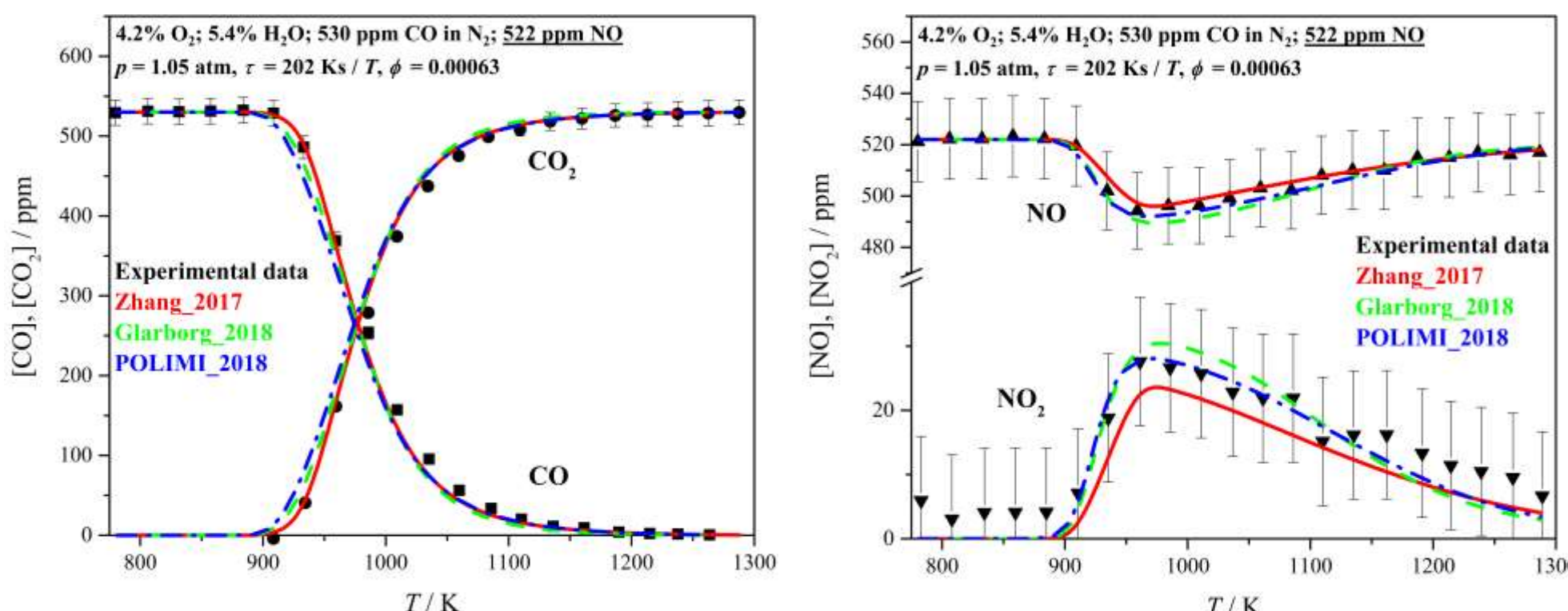
- The **Zhang_2017** mechanism was created to describe the syngas/NO_x combustion.
- The **Glarborg_2018** mechanism describes the combustion of light hydrocarbons (mostly CH₄), the NO_x formation and consumption during combustion (in all known ways) and it can also model the different NO_x removal methods.
- The **POLIMI_2018** is a mechanism for the combustion of hydrocarbon fuels up to 24 C-atoms, coupled with NO_x reactions. For this work **we removed the reactions that contained C-species except CO, CO₂ and HCO and we added an excited OH submechanism** from the optimized syngas mechanism of Varga et al. [4]. With the latter modification we were able to simulate the shock tube experiments in which the ignition delay time was defined via the OH* fluorescence signal.

Performance of the mechanisms

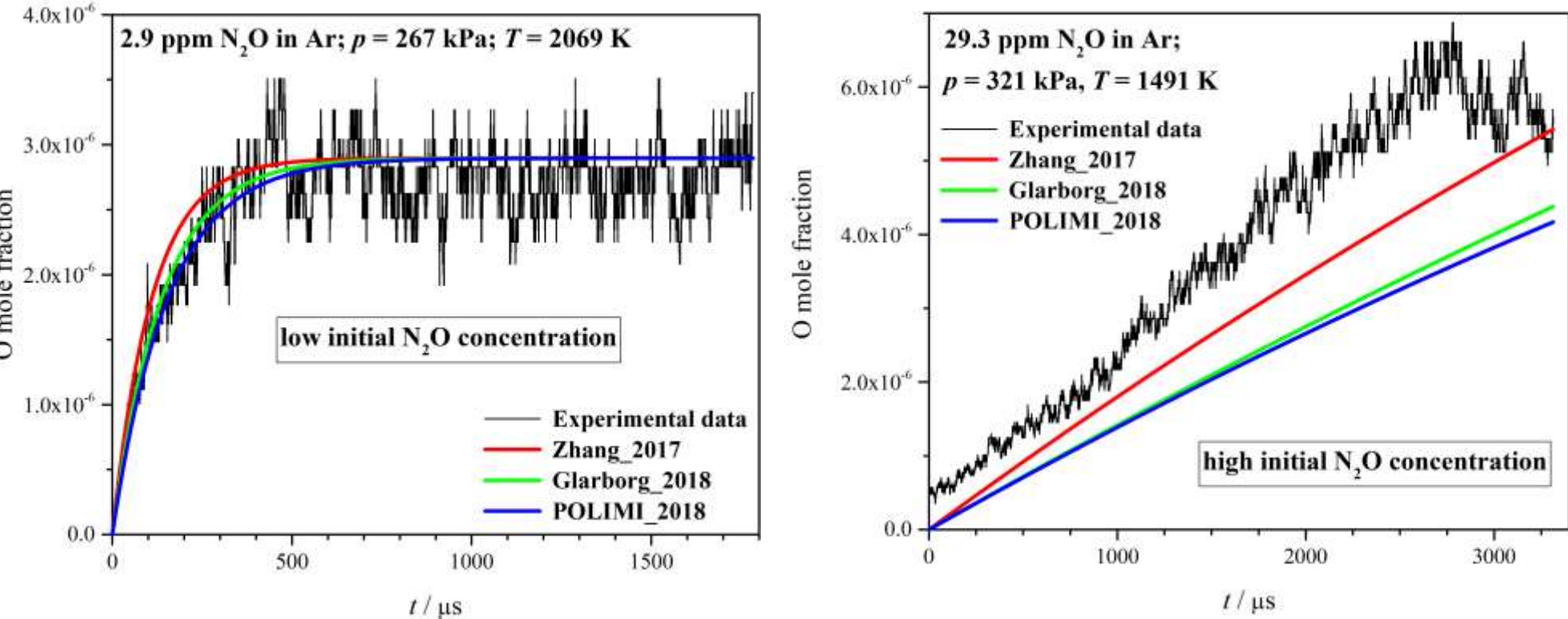
- Simulation results were plotted together with the experimental data to make the comparison easier.

✓ **In most cases the simulations reproduced the experimental data well** and the various mechanisms provided similar results despite their different development history and the different rate parameters.

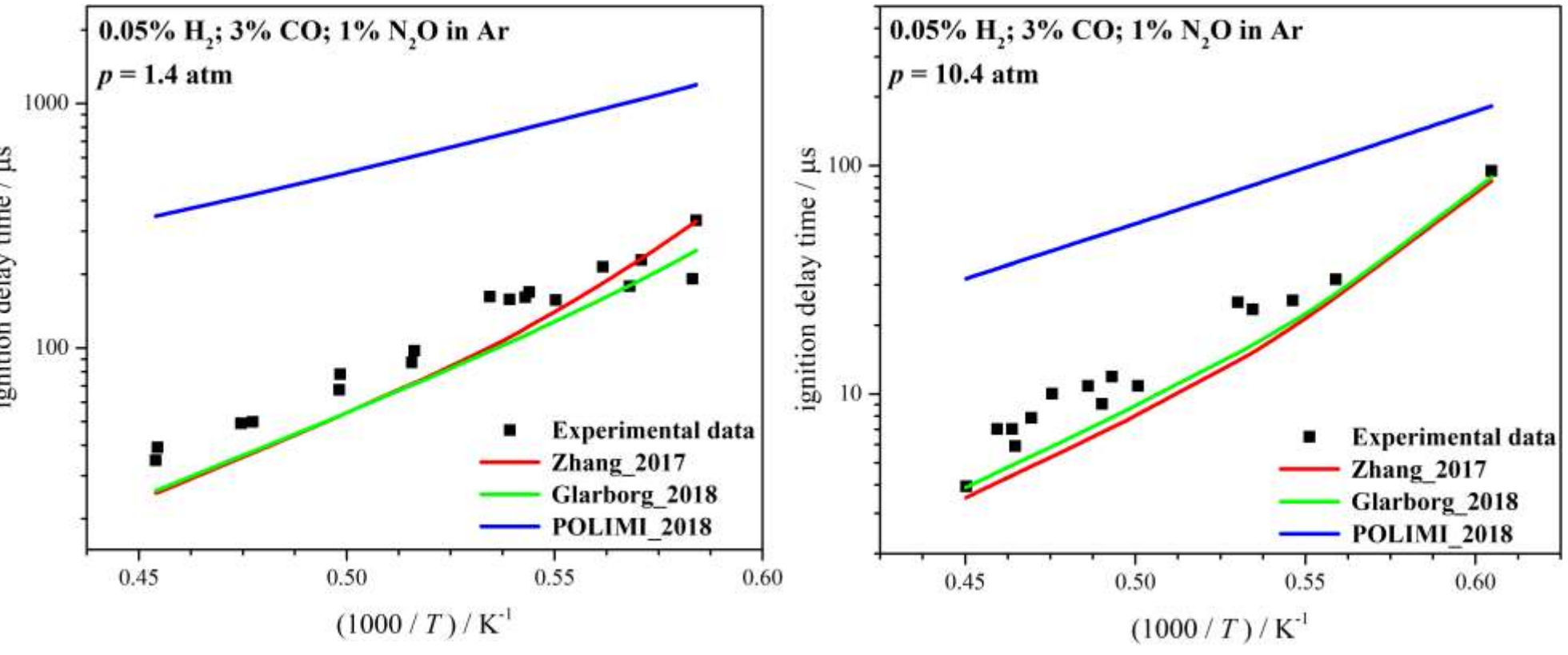
Two examples can be seen here (FR measurements by Glarborg et al. [24]):



✗ **Some of the experimental data could not be well reproduced by the mechanisms.** For example, the Javoy et al. [6] ST measurements were not reproduced well at high initial N₂O concentrations by any of the mechanisms:



✗ **In some cases, the performance of the POLIMI_2018 model was worse** than that of the other two mechanisms. Examples for that are the Kopp et al. [17] ST measurements:

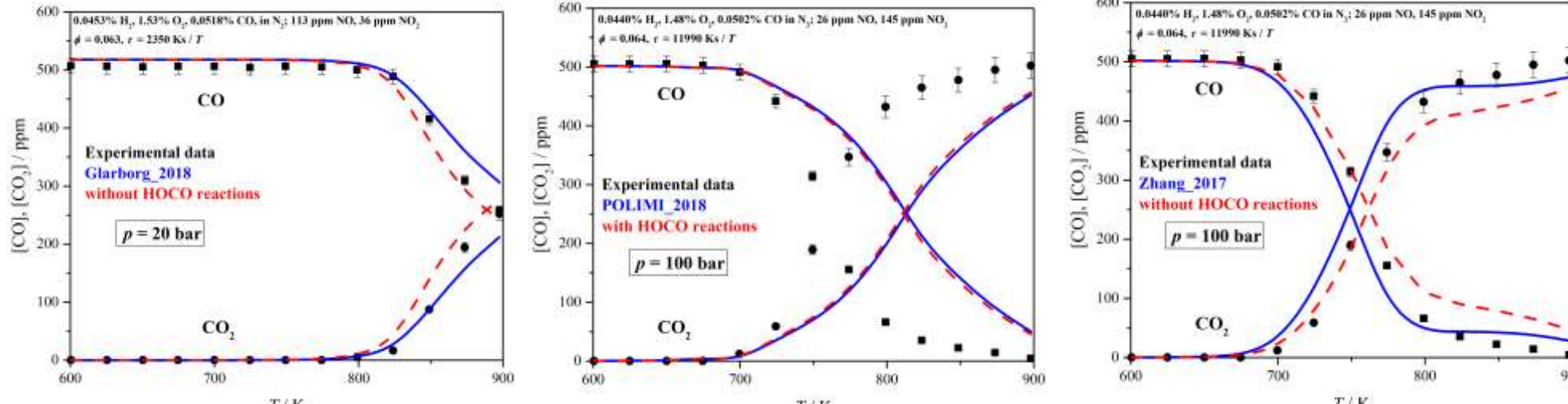


The effect of HOCO chemistry

- Until now, most syngas combustion mechanisms have not contained HOCO chemistry (see [4], [31]). However, the investigated mechanisms contain such reactions:

Zhang_2017	Glarborg_2018	POLIMI_2018 (original)
9 reactions	15 reactions	2 reactions

Examples are the FR measurements by Rasmussen et al. [23]:



➡ **Elimination of HOCO reactions significantly changed the Zhang_2017 and the Glarborg_2018 results in high pressure experiments (p > 20 bar), but did not change the POLIMI_2018 results.**

➡ **HOCO reactions should be considered to reproduce the high pressure syngas combustion experiments**

The N₂O + H₂ = N₂ + H₂O reaction

- The rate coefficient for this reaction was determined by Kosarev et al. [10] in 2007, but in 2018 Mulvihill et al. [11] determined it with higher accuracy:

$$k_{\text{Mulvihill}} = \frac{k_{\text{Kosarev}}}{30}$$

- Only the Zhang_2017 mechanism contains this reaction, but with the rate coefficient measured by Kosarev et al. [10].
- We carried out the simulations with the Zhang_2017 model again but with the rate coefficient of Mulvihill et al. [11] for this reaction.

➡ **This reaction is utterly unimportant at any of the investigated experimental conditions when the rate coefficient of Mulvihill et al. [11] is used.**

Acknowledgements

The authors thank the support of the Hungarian National Research, Development and Innovation Office – NKFIH grant K116117. This work was facilitated by COST Action CM1404 (SmartCats).

References

[1] Y. Zhang et al., *Combust. Flame* 182 (2017) 122–141
[2] P. Glarborg et al., *Prog. Energy Combust. Sci.* 67 (2018) 31–68
[3] Y. Song et al., *Proc. Combust. Inst.* in press (2018)
[4] T. Varga et al., *Int. J. Chem. Kinet.* 48 (2016) 407–422
[5] C. T. Bowman, *Combust. Sci. Technol.* 3 (1971) 37–45
[6] S. Javoy et al., *Int. J. Chem. Kinet.* 41 (2009) 357–375
[7] O. Mathieu et al., *Proc. Combust. Inst.* 34 (2013) 633–640
[8] O. Mathieu et al., *Int. J. Hydrogen Energy* 37 (2012) 15393–15405
[9] O. Mathieu et al., *Proc. Combust. Inst.* 34 (2013) 3211–3218
[10] I. N. Kosarev et al., *Combust. Flame* 151 (2007) 61–73
[11] C. R. Mulvihill et al., *Combust. Flame* 196 (2018) 478–486
[12] R. Mével et al., *Combust. Sci. Technol.* 180 (2008) 1858–1875
[13] R. Mevel et al., *Proc. Combust. Inst.* 32 (2009) 359–366
[14] S. H. Henrici et al., *J. Chem. Phys.* 50 (1969) 1333–1342
[15] Y. Hidaka et al., *J. Phys. Chem.* 89 (1985) 4903–4905
[16] K. M. Pamidukkala et al., *J. Chem. Phys.* 76 (1982) 311–315
[17] M. Kopp et al., *Appl. Phys. B Lasers Opt.* 107 (2012) 529–538
[18] O. Mathieu et al., *Combust. Flame* 162 (2015) 554–570
[19] G. Dayma et al., *Combust. Sci. Technol.* 178 (2006) 1999–2024
[20] P. Dagaut et al., *Int. J. Chem. Kinet.* 35 (2003) 564–575
[21] H. Hashemi et al., *Proc. Combust. Inst.* 35 (2015) 553–560
[22] M. Abian et al., *Int. J. Chem. Kinet.* 47 (2015) 518–532
[23] C. L. Rasmussen et al., *Int. J. Chem. Kinet.* 40 (2008) 454–480
[24] P. Glarborg et al., *Combust. Sci. Technol.* 110–111 (1995) 461–485
[25] M. A. Mueller et al., *Int. J. Chem. Kinet.* 31 (1999) 705–724
[26] R. Mével et al., *Int. J. Hydrogen Energy* 34 (2009) 9007–9018
[27] S. P. M. Bane et al., *Int. J. Hydrogen Energy* 36 (2011) 10107–10116
[28] ReSpecTh Kinetics Data Format, www.respecth.hu
[29] T. Varga et al., Optima++ v1.0, www.respecth.hu
[30] H. Pitsch, FlameMaster v4.0., www.itv.rwth-aachen.de
[31] C. Olm et al., *Combust. Flame* 162 (2015) 1793–1812