Comparison of Detailed Reaction Mechanisms for Nitrogen Chemistry in Syngas Combustion Systems

A. Gy. Szanthoffer, I. Gy. Zsély, T. Turányi*

Institute of Chemistry, ELTE Eötvös Loránd University, Budapest, Hungary

Abstract

In the last two years, three comprehensive reaction mechanisms were published, which can be used to simulate NO_x formation during syngas combustion. The aim of this work is to investigate the performances of these mechanisms at various experimental conditions. The mechanisms of Zhang et al. and Glarborg et al. provided somewhat better results than the POLIMI_2018 mechanism. The HOCO chemistry and the importance of reaction $N_2O + H_2 = N_2 + H_2O$ were also investigated.

Introduction

The direct combustion of low-quality coal or biomass is not easy to control and may generate much air pollution. An alternative approach is the gasification of these fuels producing syngas. Syngas (or "wet CO") is a fuel mixture consisting of carbon monoxide and hydrogen. However, the combustion of syngas may produce nitrogen oxides (NO_x). Recently Zhang et al. [1] published an article on the elaboration of a new reaction mechanism that describes the generation of NO_x during hydrogen and syngas combustion. This mechanism was tested by Zhang et al. [1] against a large set of experimental data. Almost the same collection of experimental data was used here to investigate the performance of not only the Zhang et al. [1] mechanism, but also two other recently published NO_x reaction mechanisms [2,3].

Two mechanistic details were also investigated. Zhang et al. [1] indicated that in syngas combustion systems HOCO chemistry can have a significant effect on the CO and CO_2 concentrations above 700 K and at pressures higher than 20 bar. Since all these three mechanisms contain HOCO reactions, the effect of these reactions on the simulated CO and CO_2 concentrations was also investigated for each mechanism.

The other investigated mechanistic detail was the importance of reaction $N_2O + H_2 = N_2 + H_2O$. The rate coefficient of this reaction was measured by Kosarev et al. [4] in 2007. However, in 2018 Mulvihill et al. [5] measured the rate coefficient of this reaction again and it was found to be 30 times smaller. According to Mulvihill et al. [5] the measurement of Kosarev et al. [4] was technically wrong, and therefore it should not be used in the future for mechanism validations. This disagreement is also investigated in this work with the help of the three reaction mechanisms.

The investigated reaction mechanisms

The investigated reaction mechanisms included the Zhang_2017 mechanism [1], which was recently created to describe the transformation nitrogen compounds during syngas combustion. This mechanism contains 262 reactions of 44 species.

Glarborg et al. [2] recently published a comprehensive review on the nitrogen species combustion and a new mechanism was published in the Electronic Supplementary of this article. This Glarborg_2018 mechanism describes the combustion of natural gas, the NO production during combustion (in all known ways) and it is able to reproduce the various NO removal methods. This mechanism consists of 1639 reactions of 153 species.

Song et al. [3] investigated the sensitizing effects of NO_2 and NO on methane low temperature oxidation in a jet stirred reactor. As a part of its Electronic Supplementary, this article contains the latest POLIMI mechanism (POLIMI_2018). The previous version of this mechanism (Version 1412, December 2014, high temperature kinetic mechanism with NO_x) was published on the POLIMI web site [6]. The POLIMI_2018 mechanism [3] contains 2361 reactions of 153 species and it is a detailed mechanism for the pyrolysis, partial oxidation and combustion of hydrocarbon fuels up to 24 C-atoms, coupled with the NO_x reactions. POLIMI_2018 mechanism was slightly modified for the current simulations by removing the reactions that contain C-species except CO, CO_2 and HCO and by adding a mechanism block of excited OH reactions from the optimised syngas mechanism of Varga et al. [7]. The latter allowed the reproduction of shock tube experiments where the ignition delay time was measured via the OH^* fluorescence signal.

The utilized experimental data

The experimental data assembled by Zhang et al. [1] included measurements of shock tube ignition delay times, laminar burning velocities and shock tube, flow reactor and jet stirred reactor (JSR) species profile measurements. These data were collected from 23 publications and contain about 88000 data points in 310 datasets. The experimental data cover a wide range of conditions: $p = 0.20$–98.7 atm, $\varphi = 0$–5, cold side temperatures of flames $T_c = 294$–304 K; temperatures of shock tube, flow and jet stirred reactor experiments $T = 702$–2712 K. The investigated systems could be classified to the following chemical categories: H_2/N_2O,

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* Corresponding author: turanyi@chem.elte.hu

$H_2/O_2/NO_x$ and NH_3/O_2 systems; investigation of the combustion of $H_2/CO/N_2O/Ar$, $H_2/CO/O_2/NH_3/Ar$, and $H_2/CO/O_2/NO_x$ mixtures. The details of the experimental data used here is summarized in **Table 1**.

The mechanisms were tested using the suite of methods and computer codes developed in our group. First, all experimental data were encoded in ReSpecTh Kinetics Data (RKD) 2.0 format XML files [8]. Advantage of using RKD format XML data files is that these files are both machine and human readable and contain all the information needed for the simulation of the experiment. Technically, the RKD files were created by program Optima++ [9], which is able to read the experimental data from a text file and print the RKD format XML files. The definition of the latest RKD 2.2 format (which is only slightly different from version 2.0) and program Optima++ (version 1.02) [9] are available at the ReSpecTh Information System [8].

In the next step, program Optima++ [9] was used for the automatic simulation of all data points with each selected reaction mechanism. In this role, Optima++ reads the RKD format experimental datafile, sets up the simulation environment, and calls the FlameMaster [10] simulation code, using a 0D (for shock tube, flow reactor and JSR experiments) or 1D (for laminar flame speed calculations) model. All simulations were carried out with the FlameMaster [10] code. The results were plotted, allowing the comparison of the experimental and simulation results.

Table 1
The experimental data used for the investigation of the performances of the reaction mechanisms. [a]: Datasets/Datapoints, [b]: concetration–time species profile, [c]: ignition delay time, [d]: concentration–temperature species profile, [e]: spherical combustion bomb, [f]: laminar flame velocity.

Apparatus	Measured quantity	Ds./Dp.[a]	Mixture	Temperature	Pressure	Ref.
shock tube	c–t [b]	4/39	$H_2/O_2/N_2$	2150–2800 K	2.2 atm	[11]
shock tube	c–t [b]	24/84307	N_2O/Ar	1490–2490 K	58–347 kPa	[12]
shock tube	IDT[c]	15/153	$H_2/O_2/NO_2/Ar$	1038–1744 K	1.5–30 atm	[13]
shock tube	IDT[c]	12/101	$H_2/O_2/N_2O/Ar$	940–1675 K	1.6–32 atm	[14]
shock tube	IDT[c]	3/29	$H_2/CO/O_2/NH_3/Ar$	993–1975 K	1.8–32 atm	[15]
shock tube	IDT[c]	2/20	$H_2/(O_2)/N_2O/Ar$	1007–1574 K	0.14–0.47 atm	[4]
shock tube	IDT[c]	1/6	$H_2/N_2O/Ar$	1248–1491 K	0.68–0.69 atm	[5]
shock tube	IDT[c]	3/152	$H_2/N_2O/Ar$	1300–1860 K	910 kPa	[16]
shock tube	IDT[c]	6/82	$H_2/N_2O/Ar$	1300–2000 K	300 kPa	[17]
shock tube	IDT[c]	4/46	$H_2/N_2O/Ar$	1700–2600 K	1.29–1.91 atm	[18]
shock tube	IDT[c]	3/27	$H_2/N_2O/Ar$	1400–2000 K	2.0 atm	[19]
shock tube	IDT[c]	2/20	$H_2/N_2O/Ar$	1919–2781 K	1.5 atm	[20]
shock tube	IDT[c]	2/33	$H_2/CO/N_2O/Ar$	1654–2021 K	1.4–10.4 atm	[21]
shock tube	IDT[c]	12/103	$NH_3/O_2/Ar$	1560–2455 K	1.4–30 atm	[22]
shock tube	c–T [d]	2/11	$H_2/N_2O/Ar$	1700–2600 K	1.29–1.91 atm	[18]
JSR	c–T [d]	78/945	$H_2/O_2/NO_x/N_2$	700–1150 K	1–10 atm	[23]
JSR	c–T [d]	9/87	$H_2/CO/O_2/NO/N_2$	800–1400 K	1.0 atm	[24]
flow reactor	c–T [d]	6/54	$H_2/O_2/N_2$	702–900 K	50 atm	[25]
flow reactor	c–T [d]	4/20	O_2/N_2	1700–1800 K	1.0 atm	[26]
flow reactor	c–T [d]	15/195	$CO/H_2/O_2/NO_x/N_2$	600–900 K	20–100 bar	[27]
flow reactor	c–T [d]	23/334	$(CO)/H_2O/O_2/NO_x$	800–1400 K	1.05 atm	[28]
flow reactor	c–t [b]	74/1284	$(H_2)/(CO)/O_2/(H_2O)/NO_x/N_2/Ar$	750–1100 K	0.5–14 atm	[29]
SCB[e]	v_L[f]	1/30	$H_2/N_2O/Ar$	300 K	1 atm	[30]
SCB[e]	v_L[f]	5/46	$H_2/N_2O/(N_2)$	298 K	0.2–0.8 atm	[31]

The simulation results

The results indicated that most of the experimental data could be well reproduced by the simulations. The three recent NO_x mechanisms provided quite similar simulation results at most of the experimental conditions, although these mechanisms had different development history and contained different rate parameters for several elementary reactions. Examples for this case can be seen in **Figure 1**. The figure shows that the simulations using any of the three mechanisms could well reproduce the experimental data.

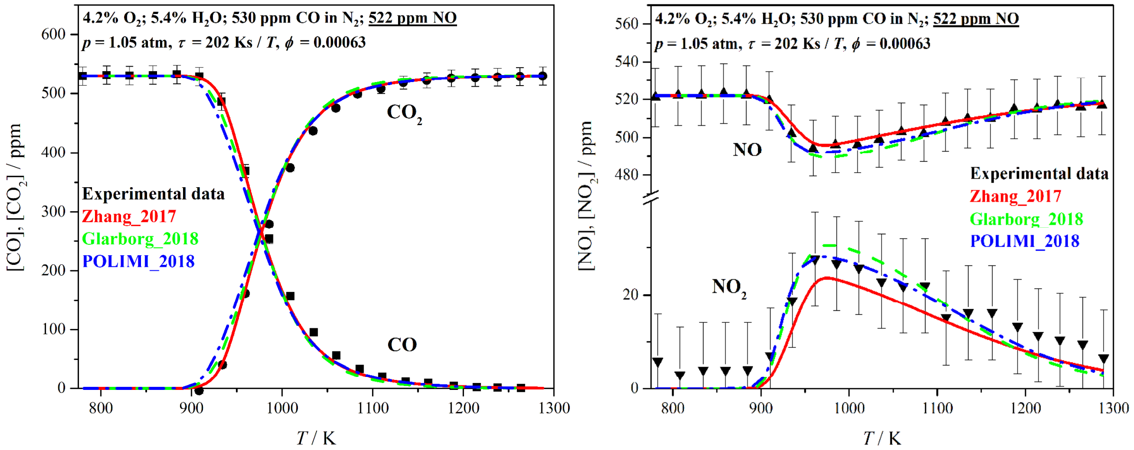

Figure 1. Species profiles in a flow reactor by Glarborg et al. [28]. Symbols represent experimental data, lines denote model results.

Some of the experimental data were not well reproduced by these three mechanisms. For example, Javoy et al. [12] investigated the decomposition of N_2O in Ar bulk gas in a shock tube in the temperature range of 1500–2500 K by measuring the O-atom concentration profile. The experimental results could be well reproduced at low initial N_2O concentrations but not at high initial N_2O concentrations (**Figure 2**).

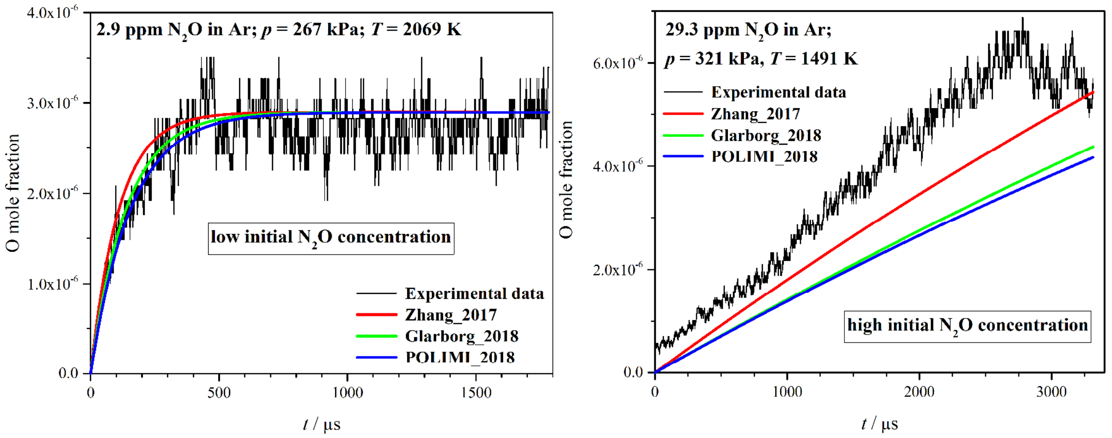

Figure 2. Species profiles in a shock tube by Javoy et al. [12]. Black lines represent experimental data, color lines denote model results.

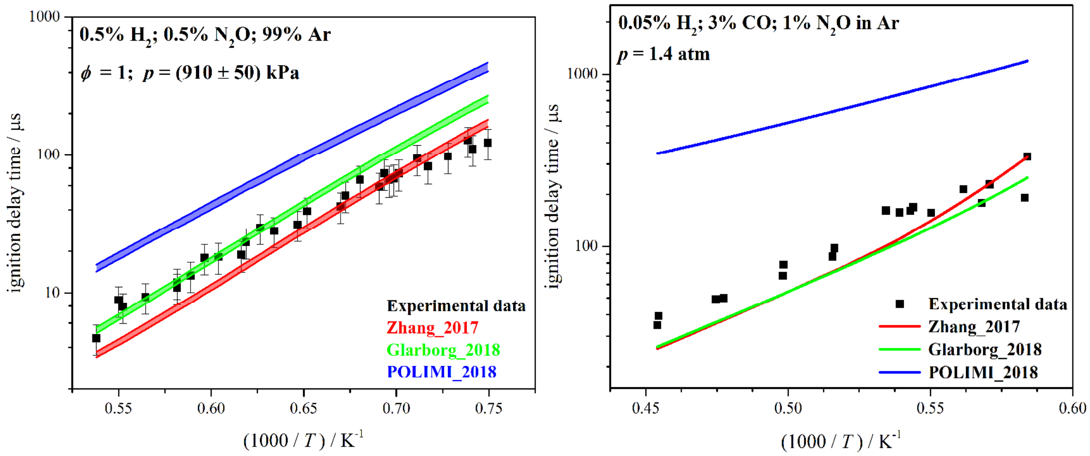

Figure 3. Ignition delay time measurements by Mével et al. [16] (left) and by Kopp et al. [21] (right). Symbols represent experimental data and lines denote model results. In the left figure there are two lines for each mechanism (model results at 860 and 960 kPa) and the areas between each pair of lines are colored.

The POLIMI_2018 mechanism, unlike the other two mechanisms, did not reproduce well the experimental data of Mével et al. [16,17] (ignition delay time in $H_2/N_2O/Ar$ mixtures, measured by shock tube, $T = 1300$–2000 K) and the data of Kopp et al. [21] (ignition delay time in $H_2/CO/N_2O/Ar$ mixtures, measured by shock tube, $T = 1654$–2221 K). This indicates conditions where this mechanism has to be improved. Examples for this can be seen in **Figure 3**.

The effect of HOCO chemistry

Until now, most published syngas combustion mechanisms (see [7] and [32]) have not contained the reactions of species HOCO. However, the three recent mechanisms investigated in this work contain such reactions (Zhang_2017: 9 HOCO reactions, Glarborg_2018: 15 HOCO reactions, POLIMI_2018: 2 HOCO reactions). Reactions of HOCO collected from each mechanism are shown in **Table 2**.

Zhang et al. [1] indicated that HOCO chemistry promote the CO to CO_2 conversion above 700 K and at pressures higher than 20 bar. To investigate this effect the HOCO reactions were eliminated from each mechanism and simulations were carried out with the original mechanisms and also with these “reduced” mechanisms. The targets of the simulations were the CO and CO_2 concentrations of the Rasmussen et al. [27] flow reactor measurements (20, 50 and 100 bar). It was found that the elimination of the HOCO reactions did not change the POLIMI_2018 results, but significantly changed the Zhang_2017 and especially the Glarborg_2018 results in high-pressure experiments ($p > 20$ bar) (see **Figure 4**). This indicates that consideration of the HOCO reactions could be really important for the reproduction of high-pressure syngas combustion experiments.

Table 2
Reactions that contain species HOCO in each mechanism.

Zhang_2017	Glarborg_2018	POLIMI_2018
HOCO = CO + OH	HOCO = CO + OH	HOCO = CO + OH
HOCO = CO_2 + H	HOCO (+ M) = CO_2 + H (+ M)	HOCO = CO_2 + H
HOCO + H = CO_2 + H_2	HOCO + H = CO_2 + H_2	
HOCO + O = CO_2 + OH	HOCO + H = CO + H_2O	
HOCO + OH = CO_2 + H_2O	HOCO + O = CO_2 + OH	
HOCO + HO_2 = CO_2 + H_2O_2	HOCO + OH = CO_2 + H_2O	
HOCO + O_2 = CO_2 + HO_2	HOCO + OH = CO + H_2O_2	
HOCO + NO = CO_2 + HNO	HOCO + HO_2 = CO_2 + H_2O_2	
HOCO + NO_2 = CO_2 + HONO	HOCO + O_2 = CO_2 + HO_2	
	HOCO + NO = CO + HONO	
	HOCO + H_2 = HOCHO + H	
	HOCO + OH = HOCHO + O	
	HOCO + H_2O = HOCHO + OH	
	HOCO + H_2O_2 = HOCHO + HO_2	
	HOCO + HO_2 = HOCHO + O_2	

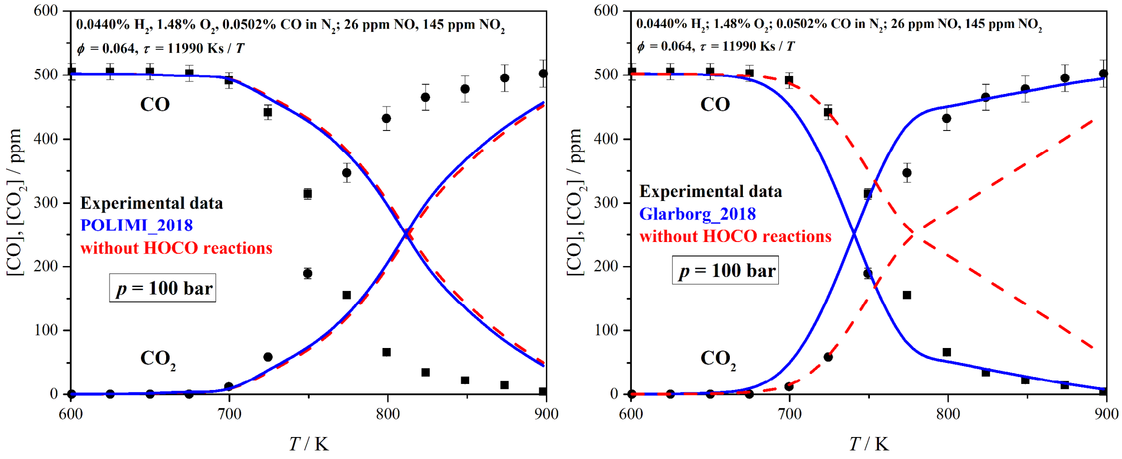

Figure 4. The investigation of the effect of HOCO chemistry at high pressures on the flow reactor measurements by Rasmussen et al. [27]. Symbols represent experimental data, lines denote model results with the original mechanisms (blue solid lines) and model results without HOCO chemistry (red dash lines).

The $N_2O + H_2 = N_2 + H_2O$ reaction

The Zhang_2017 mechanism contains reaction $N_2O + H_2 = N_2 + H_2O$, while this reaction is missing from the Glarborg_2018 and POLIMI_2018 mechanisms. The rate coefficient of this reaction was determined by Kosarev et al. [4] in 2007 (by measuring H_2O time histories in a shock tube) but in 2018 Mulvihill et al. [5] measured it again but with higher accuracy and it was found to be 30 times smaller. In the same article Kosarev et al. [4] published ignition delay time measurements as well (see **Table 1**). According to Mulvihill et al. [5] both measurements of Kosarev et al. [4] were technically wrong and therefore these data should not be used in the future. An evidence of this can be seen in **Figure 5**. The Kosarev et al. [4] ignition delay time measurements could not be reproduced with neither the Glarborg_2018 nor the POLIMI_2018 mechanism, only with the Zhang_2017 mechanism that contained the wrong rate coefficient for the title reaction.

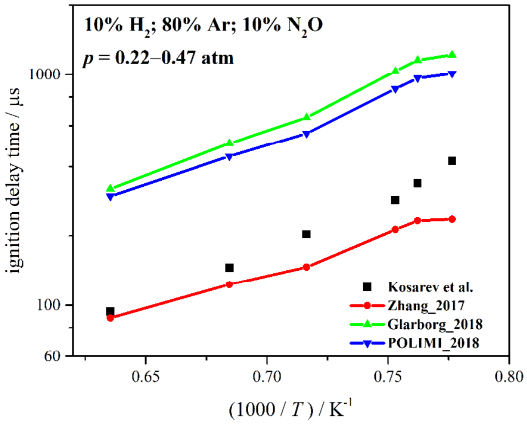

Figure 5. Ignition delay time measurements by Kosarev et al. [4] in a shock tube. Symbols represent experimental data, lines denote model predictions.

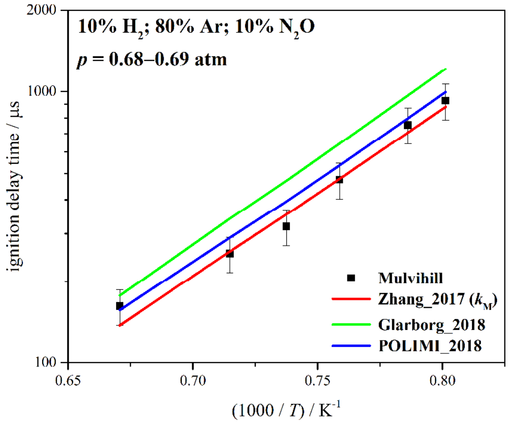

Figure 6. Ignition delay time measurements by Mulvihill et al. [5] in a shock tube. Symbols represent experimental data, lines denote model predictions.

Therefore, Mulvihill et al. [5] measured the ignition delay times of the same mixture at similar experimental conditions and this data could be reproduced well with Glarborg_2018 and POLIMI_2018 models. In addition, the rate coefficient in the Zhang_2017 model was replaced by that measured by Mulvihill et al. [5] and very good agreement was found between the model results and the experimental data (**Figure 6**). This indicates that the measurements of Mulvihill et al. [5] should be used in the future instead of the Kosarev et al. [4] data.

Conclusions

The performances of three recently published combustion mechanisms that can describe the combustion syngas/NO_x gas mixtures were investigated against a large set of experimental data. It was found that although the models could reproduce the experimental data well, at some conditions they should be improved. The mechanisms of Zhang et al. [1] and Glarborg et al. [2] provided somewhat better results than the POLIMI_2018 mechanism [3].

Two mechanistic detailed were also investigated. In future syngas combustion mechanisms the HOCO chemistry should be included since has a significant effect in high-pressure ($p > 20$ bar) experiments. In terms of the $N_2O + H_2 = N_2 + H_2O$ reaction, the disagreement between two measurements [4,5] was investigated and it was found that in the future, the rate coefficient measured by Mulvihill et al. [5] should be used for the reaction instead of that measured by Kosarev [4] et al. The same conclusion is valid for the ignition delay time measurements published in these articles [4,5].

Acknowledgements

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