Comparison of the performance of recent reaction mechanisms for describing the combustion of hydrogen doped with nitrogen oxides

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Introduction

Nitrogen oxides have several harmful environmental effects when emitted to the atmosphere. Environmental regulations of industrial processes require the exploration of the behaviour of nitrogen oxides (NO_x) in combustion systems. On the other hand, the NO_x compounds have sensitizing effect on combustion, which may also be crucial for some industrial processes.

It is important to possess good description of the chemical kinetics of the transformations of nitrogen species in combustion systems, which can be utilized for building good detailed reaction mechanisms. Several NO_x mechanisms have been published in the last twenty years, but these are not perfect and further improvements are required. Therefore, a comprehensive comparison of the performance of recent reaction mechanisms describing NO_x reactions in combustion systems is needed. In this work, influence of NO_x reactions on hydrogen combustion is investigated based on ignition delay time and concentration profile measurements.

Methodology

The method of comparison has been discussed elsewhere in details [1], only a brief summary is presented here. The main steps are the following: (1) Collection and processing of all relevant publications dealing with hydrogen combustion doped with nitrogen oxides. (2) Encoding the experimental data in ReSpecTh Kinetics Dataformat (RKD) XML files [2]. (3) Estimation of the error of the experimental datasets based on the scatter of the measured points and the reported experimental errors. (4) Program *Optima++* [3] reads the RKD files and performs the simulations automatically for a selected reaction mechanism using the *FlameMaster* [4] code. It is repeated for each reaction mechanism investigated. (5) Program *outgen* [5] processes the results and calculates various performance indicators for all experiments or for a selected subset of them.

The agreement of experimental and simulation results is characterized using the average error function *E*:

$$E = \frac{1}{N}\sum_{i=1}^{N}\frac{1}{N_i}\sum_{j=1}^{N_i}\left(\frac{Y_{ij}^{\mathrm{mod}} - Y_{ij}^{\mathrm{exp}}}{\sigma\left(Y_{ij}^{\mathrm{exp}}\right)}\right)^2$$

where

$$Y_{ij}^{\mathrm{mod/exp}} = \begin{cases} y_{ij}^{\mathrm{mod/exp}} & \text{if } \sigma\left(y_{ij}^{\mathrm{exp}}\right) \approx \text{constant} \\ \ln y_{ij}^{\mathrm{mod/exp}} & \text{if } \sigma\left(\ln y_{ij}^{\mathrm{exp}}\right) \approx \text{constant} \end{cases}$$

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Here N is the number of datasets and N_i is the number of data points in the i-th dataset. Values $y_{ij}^{\exp}$ and $\sigma(y_{ij}^{\exp})$ are the j-th data point and its standard deviation, respectively, in the i-th dataset. The corresponding simulated (modelled) value is Y_{ij}^{mod} obtained from a simulation using a detailed mechanism and an appropriate simulation method. If a measured value is characterized by absolute errors (the scatter is independent of the magnitude of y_{ij}), then $Y_{ij} = y_{ij}$. This option is used for measured concentration profiles. If the experimental results are described by relative errors (the scatter is proportional to the value of y_{ij}), then option $Y_{ij} = \ln(y_{ij})$ is used, which is characteristic for ignition delay time measurements. Error function value E is expected to be near unity if the chemical kinetic model is accurate, and deviations of the measured and simulated results are caused by the scatter of the experimental data only.

The experimental data collected

A large number of experimental results describing hydrogen combustion doped with nitrogen oxides were collected. Shock tube and flow reactor measurements published in 13 experimental articles were considered, and 2116 data points related to 93 data series were encoded into RKD format files. 636 data points are related to ignition delay times measured in shock tubes. In these measurements the initial temperature and pressure were varied in the range of 737–2354 K and 0.14–35.4 atm, respectively, while the equivalence ratio and the diluent concentration were changed between φ = 0.3–2.0 and mole fraction 0.45–0.99, respectively, using various diluents. 1480 data points are related to concentration profile measurements in flow reactors. In these experiments the initial temperature and pressure were varied in the range of 780–1382 K and 0.5–12.5 atm, respectively, the equivalence ratio and the diluent concentration were changed between φ = 0.25–3.77 and mole fraction 0.96–0.99, respectively, using also various diluents.

Results and discussion

Ten detailed reaction mechanisms [6-15], recently developed for NO_x chemistry in combustion systems were investigated. Table 1 contains the list of the mechanisms, the numbers of species and reactions in the mechanisms, and characterization of their performance based on five different error function definitions. E_{all}, E_{IDT} and E_{conc} are the computed error function values based on the all data (2116 data points), all ignition delay time data (636) and all concentration profile data (1480), respectively. Some of the experimental results could not be reproduced using any of the mechanisms. In this case either the data are wrong, or all mechanisms miss the description of the related chemistry. To decrease the influence of wrong data on the characterization of the mechanisms, two further types of E values were defined. At the calculation of $E_{\mathrm{exclude,1}}$ 1613 data points were used and those datasets were excluded where any of the mechanisms had $E > 400$ values related to this dataset. This approach assumes that if any of the mechanisms cannot reproduce a measurement, then it is probably wrong. At the calculation of $E_{\mathrm{exclude,2}}$ 1972 data points were used and those datasets were kept where any of the three selected mechanisms (Glarborg-2017, POLIMI-2017 and Curran-2017) had E values less than 100. This selection assumes that if one of these mechanisms is able to reproduce a measurement, then it is probably good.

Mechanisms		Number of		Error function values				
		spec.	react.	E_{all}	E_{IDT}	E_{conc}	$E_{exclue,1}$	$E_{exclude,2}$
Glarborg-2017	[6]	35	207	133.52	170.00	89.23	**58.39**	**64.03**
POLIMI-2017	[7]	32	179	174.19	190.96	153.84	**76.19**	**89.23**
Curran-2017	[8]	44	198	144.41	71.55	229.41	**58.33**	**123.12**
Abian-2015	[9]	37	219	228.45	333.02	101.49	**94.15**	**167.50**
Klippenstein-2011	[10]	37	219	228.58	333.24	101.50	**94.30**	**167.63**
Mevel-2009	[11]	32	215	215.10	188.16	245.89	**119.81**	**202.60**
GRI3.0-1999	[12]	53	354	306.22	181.41	461.48	**240.78**	**318.07**
SanDiego-2014	[13]	64	323	574.72	329.16	880.16	**342.08**	**536.58**
GDFKin3.0-2016	[14]	123	934	664.15	964.26	299.74	**172.38**	**591.52**
Rasmussen-2008	[15]	62	460	1509.76	157.66	2475.54	**734.95**	**1598.73**

Table 1 Comparison of the mechanisms describing the combustion of hydrogen doped with nitrogen oxides. The ordering is based on the $E_{exclude,2}$ values.

The three best mechanisms are Glarborg-2017, POLIMI-2017 and Curran-2017, which are also the newest ones. The best performance related to concentration profiles and ignition delays is from the Glarborg-2017 and Curran-2017 mechanisms, respectively. The POLIMI-2017 mechanism has a balanced performance at both experiment types. The Abian-2015 and Klippenstein-2011 mechanisms have a good performance on concentration profiles but a weaker performance on ignition delays.

Error function value E is expected to be near unity if the chemical kinetic model is accurate, and the best result seen here is about 58. This indicates that these mechanisms have to be further developed. Fig. 1 shows the simulation results obtained with the different mechanisms at the conditions of two chosen datasets.

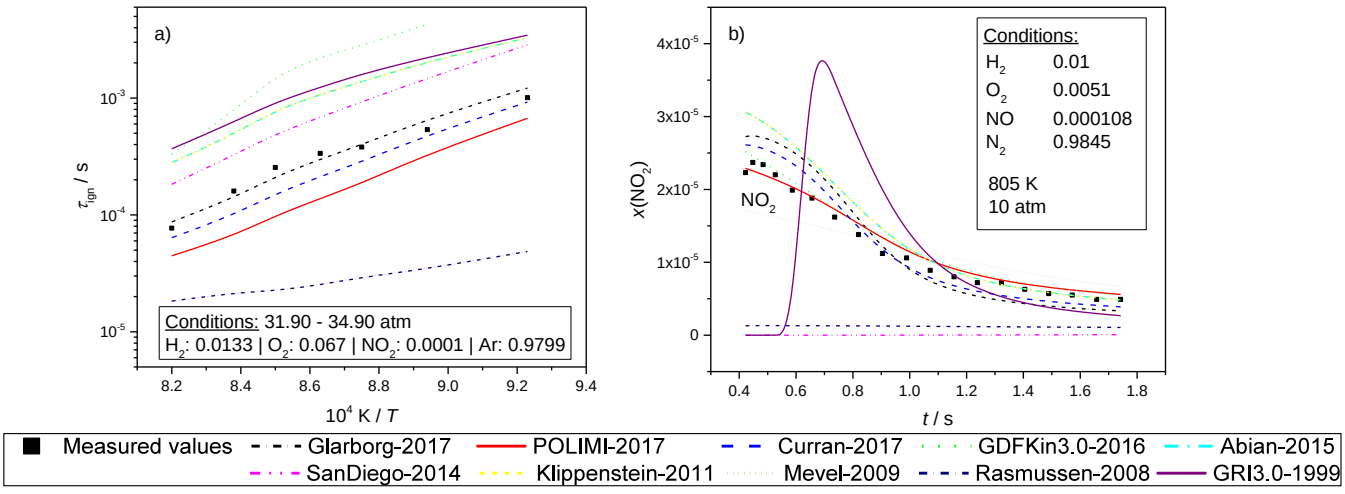

Fig. 1 Comparison of the mechanisms based on two datasets. a) *Ignition delay time measurement by Mathieu et al.* [16] b) *Concentration profile measurement by Mueller et al.* [17]

Fig. 2 shows the comparison of the average normalized local sensitivity coefficients computed for the ignition delay time measurements of Mathieu *et al.* [18] for the three leading mechanisms.

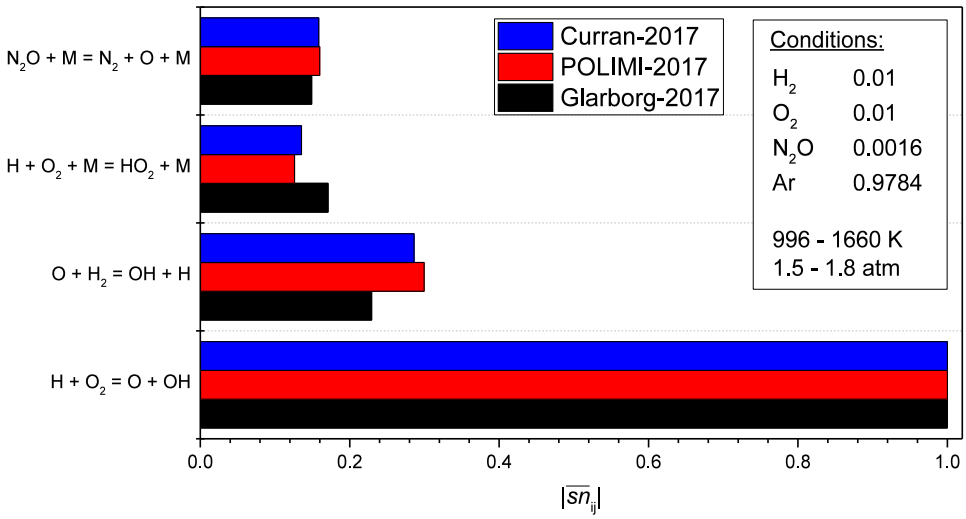

Fig. 2 *Comparison of the average normalized sensitivity coefficients related to three mechanisms for an ignition delay measurement dataset of Mathieu et al.* [18]

There is a good agreement among the sensitivity coefficients, and similar results were obtained for all other ignition delay time and concentration profile datasets. This means that the most important reactions can be selected independently of the actual mechanism considered. These important elementary reactions include both H/O and N/H/O reactions. The rate parameters of the first group of reactions are better known due to the large number of studies related to hydrogen combustion, and therefore the improvement of the $NO_x/H_2/O_2$ models has to concentrate on the important N/H/O elementary reactions.

Using local sensitivity analysis based on the POLIMI-2017 mechanism, the following 15 most important N-reactions could be identified at the conditions of 1972 data points:

$NO_2 + H = NO + OH$, $NO + HO_2 = NO_2 + OH$, $NO_2 + HO_2 = HONO + O_2$,
$NO + OH + M = HONO + M$, $H + NO + M = HNO + M$, $NO + O + M = NO_2 + M$,
$2\ NO_2 = 2\ NO + O_2$, $NO + OH + M = HONO + M$, $N_2O + M = N_2 + O + M$,
$HNO_2 + H = NO_2 + H_2$, $N_2O + H = N_2 + OH$, $NO_2 + O = NO + O_2$,
$HONO + H = NO_2 + H_2$, $NO + O + M = NO_2 + M$, $2\ HONO = NO + NO_2 + H_2O$

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