

TESTING OF KINETIC MECHANISMS USING A LARGE AMOUNT OF EXPERIMENTAL DATA ON NH₃/H₂ AND NH₃/SYNGAS COMBUSTION

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Introduction

Ammonia can be synthesized using renewable energy sources (such as wind or solar power) or fossil fuels with carbon capture and storage (CCS) [1,2]; therefore, it is a promising circular carbon-free fuel. However, some characteristics of ammonia hinder its application as a pure fuel [1,3,4]. These unfavorable combustion properties include: its high ignition energy, long ignition delay time, and small burning velocity relative to traditional hydrocarbon fuels and hydrogen. To improve these combustion properties of ammonia, it is often blended with other fuels (co-fuels), most often with hydrogen [5-10], CO or synthesis gas (H₂/CO) [9-12], or methane [8,9].

There are several reaction mechanisms available in the literature that aim to describe the oxidation of NH₃/H₂ [13-21] and NH₃/syngas fuel mixtures [11,12,22-26]. However, while the predictions of these models often agree with experimental results under certain conditions, they deviate from those under other conditions. Furthermore, as Da Rocha et al. [27] showed for laminar burning velocity and ignition delay time measurements, predictions of the different models often deviate from each other significantly. Consequently, comprehensive validation and further development of these models are needed based on a large set of available experimental data.

Therefore, this study aims to assess the performance of 18 recently published detailed reaction mechanisms using a large amount of experimental data on the combustion of NH₃/H₂ and NH₃/syngas fuel mixtures. The best-performing models are further investigated by local sensitivity analysis to identify the key model parameters. The results of these investigations provide more insight into the current state of the modeling of ammonia combustion and may facilitate the development of better reaction mechanisms.

Materials and Methods

The literature of the experimental investigation of ammonia combustion has been extensively reviewed, and altogether, 4970 experimental data points (in 479 datasets) were utilized from 31 publications. In this work, only shock tube ignition delay time (ST-IDT) measurements, concentration measurements in jet stirred and flow reactors (JSR and FR), and laminar burning velocity (LBV) measurements are studied in which the fuel contains NH₃ and the co-fuels are H₂ and/or CO. Experiments with NH₃/H₂ fuel mixtures include also measurements in which the fuel is pure NH₃. The investigated experiments cover a wide range of combustion conditions (Table 1). In the case of LBV measurements, the temperature values in Table 1 refer to the cold side temperatures. The experimental data were encoded in ReSpecTh Kinetic Data (RKD) format XML files [28] and are available in the ReSpecTh site [29]. One XML file may contain more than one dataset, e. g., in concentration measurements.

Table 1. Summary of NH₃/H₂ and NH₃/syngas combustion experiments utilized in this work.

Experiment type	Datasets	Data points	<i>T</i> / K	<i>p</i> / atm	<i>φ</i>
NH₃/H₂ combustion experiments:					
ST-IDT	26	200	1022–2489	1.01–41.65	0.50–2.00
JSR	113	1651	500–1452	1.00–1.20	0.01–1.50
FR	89	1141	451–1973	1.00–98.69	0.00–2.44
LBV	129	850	298–476	0.50–10.00	0.40–1.80
<u>Overall:</u>	<u>357</u>	<u>3842</u>			
NH₃/syngas combustion experiments:					
JSR	40	229	900–1350	1.00	0.38–1.51
FR	2	18	873–1273	1.00	0.01
LBV	80	881	298–443	1.00–10.00	0.70–1.70
<u>Overall:</u>	<u>122</u>	<u>1128</u>			

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Simulations were carried out with the Optima++ simulation framework code [30], developed at the ELTE Chemical Kinetics Laboratory. Optima++ reads the RKD format data files, sets up simulation tasks based on its content, and invokes a simulation package to perform the simulation(s). In our present work, the OpenSMOKE++ program [31-34] was used for the simulations. Using it with Optima++, a mechanism can be tested against several thousands of data points in a single run.

The performances of the mechanisms were assessed based on the evaluation of an averaged error function defined as follows:

$$E = \frac{1}{N_{\text{XML}}} \sum_{i=1}^N \frac{1}{N_i} \cdot \frac{1}{N_{\text{ds},i}} \sum_{j=1}^{N_i} \left(\frac{Y_{ij}^{\text{sim}} - Y_{ij}^{\text{exp}}}{\sigma(Y_{ij}^{\text{exp}})} \right)^2 \quad (1)$$

where N_{XML} is the number of XML data files, N is the number of datasets, N_i is the number of data points in the i -th dataset, $N_{\text{ds},i}$ is the number of datasets in the XML file to which the i -th dataset belongs. Y_{ij}^{exp} and $\sigma(Y_{ij}^{\text{exp}})$ are the j -th data point in the i -th experimental dataset and its standard deviation, respectively. The corresponding Y_{ij}^{sim} value is the simulation result for that data point. We assume that the experimental data follow normal (Gaussian) distribution; therefore, the function E follows a reduced chi-square distribution. For example, if $E \leq 9$, then the model can reproduce the experimental data within their 3σ uncertainty limits, on average.

Brute force local sensitivity analysis [35] was applied to identify the most important parameters of the best-performing models. The sensitivities of the kinetic and thermodynamic ($c_p^\ominus$, $\Delta_f H_k^\ominus$, $S_k^\ominus$) parameters of the selected mechanisms were investigated.

Results and Discussions

Significant differences were found between the performances of the different models investigated. In the case of NH_3/H_2 fuel mixtures, the averaged error function values range from 8.1 to 44.1, and from 7.0 to 42.8 in the case of $\text{NH}_3/\text{syngas}$ fuel mixtures. One example for the large deviations in the predictions of the mechanisms is shown in Fig. 1. Also, the performance of one mechanism usually varies significantly with the type of experiments. For instance, the E value of KAUST-2021 [20] is 2.91 for flow reactor measurements, while it is 17.5 for ST-IDT experiments.

The best-performing mechanisms are KAUST-2021 [20], POLIMI-2020 [36], and Otomo-2018 [16] for NH_3/H_2 fuel mixtures, and Mei-2021 [26], Mei-2020 [12], and Shrestha-2021 [25] for $\text{NH}_3/\text{syngas}$ systems. The results indicate that further mechanism development is needed to reproduce the measurements more accurately.

Even though the investigated models have different parameter sets, local sensitivity analysis revealed that the most important reactions and thermodynamic properties are similar. The most important reactions are not the same for the different types of experiments but most of them include the NH_3 , NH_2 , and/or NNH species. Among the thermodynamic parameters, model outputs are most sensitive to the data of NH_3 and NH_2 .

Conclusions

A comprehensive quantitative comparison of 18 detailed reaction mechanisms was performed using a large set of experimental data in the combustion of NH_3/H_2 and $\text{NH}_3/\text{syngas}$ fuel mixtures including shock tube ignition delay time measurements, concentration measurements in jet stirred and flow reactors, and laminar burning velocity measurements. Results showed that even though some models can reproduce the experimental results very well under some circumstances, their overall performance should be improved significantly. The authors believe that the results presented in this work will help in the selection of the best-performing mechanisms for the combustion of NH_3/H_2 and $\text{NH}_3/\text{syngas}$ fuel mixtures and facilitate further mechanism development for these systems.

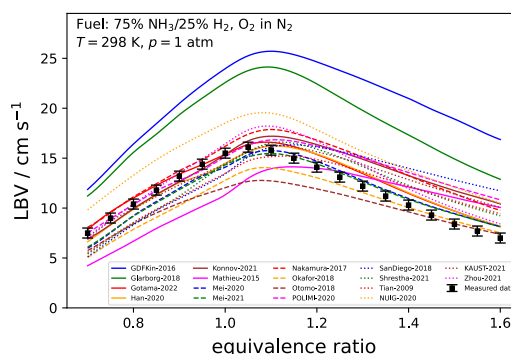


Fig. 1. Comparison of the performances of the investigated mechanisms for the LBV measurements of Han et al. [9]. Symbols denote experimental results and lines are model predictions.

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