

Testing of NH₃/H₂ and NH₃/syngas combustion mechanisms using a large amount of experimental data

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ABSTRACT

A possible solution to improve the combustion properties of ammonia is to blend it with other fuels. Two of the most usually used co-fuels are hydrogen and syngas (H₂/CO). To investigate the chemistry of the co-combustion with these fuels, a large amount of indirect experimental data for the combustion of neat NH₃, and NH₃/H₂ and NH₃/syngas fuel mixtures were collected from the literature including ignition delay times measured in shock tubes, concentration measurements in jet stirred and flow reactors, and laminar burning velocity measurements. Altogether, 4898 data points (in 472 data series) were recorded which cover wide ranges of equivalence ratio, temperature, and pressure. These experimental data are available in data files in the ReSpecTh site (<http://respec.th.hu>). The performances of 18 recently published detailed reaction mechanisms were quantitatively assessed using the collected experiments. There are significant differences between the performances of the models, and the performance of a mechanism may also vary significantly with the different types of experiments. The best-performing mechanisms are POLIMI-2020, Han-2020, and KAUST-2021 for NH₃/H₂ fuel mixtures, and Shrestha-2021, Mei-2021, and Mei-2020 for NH₃/syngas systems. The results indicate that further mechanism development is needed to reproduce the measurements more accurately. Local sensitivity analysis was carried out on the kinetic and thermodynamic parameters of the best-performing mechanisms. Even though the investigated models have different parameter sets, 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 NH₃, NH₂, and/or NNH species. Among the thermodynamic parameters, model outputs are most sensitive to the data of NH₃ and NH₂.

1. Introduction

Nowadays, due to the intensive global climate change, it is extremely important to find ways to reduce the carbon dioxide (CO₂) emission stemming from human activities. This can be achieved by applying renewable energy sources and/or carbon-free fuels for energy generation. A straightforward chemical reaction that produces energy without CO₂ production is the oxidation of hydrogen. However, utilization of elementary hydrogen (H₂) as a carbon-free fuel is not optimal because of its relatively low volumetric energy density, and the difficult and relatively expensive storage, handling, and transportation [1–4].

A potential alternative hydrogen source is ammonia (NH₃) [2,3,5–9] because it has some advantageous fuel properties such as high hydrogen density; higher volumetric energy density and boiling point than H₂; it can be liquified easily; and its mass-based energy density is comparable to that of traditional fossil fuels (e.g., CH₄). However, some

characteristics of ammonia hinder its application as a pure fuel [2,10,11]. These unfavorable combustion properties include: i) high ignition energy, long ignition delay time, and small burning velocity relative to traditional hydrocarbon fuels and hydrogen; ii) lower heat of combustion and radiation heat transfer from the flame than in the case of traditional hydrocarbon fuels due to the lack of CO₂ among combustion products; iii) large amounts of NO_x (NO + NO₂ + N₂O) compounds may be produced during its combustion.

To improve these combustion properties of ammonia, one widely used approach is to blend it with other fuels (co-fuels). Hydrogen [12–17], CO or synthesis gas (H₂/CO) [16–19], and methane [15,16] are the most frequently used co-fuels for ammonia, but other fuels may also be used for this purpose such as gasoline [20], diesel [21,22], dimethyl ether (DME) [23], or diethyl ether (DEE) [24]. In addition to its promising application as a fuel, ammonia is also used in the power industry as a chemical additive in the thermal deNO_x process [25–27].

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Hydrogen used for ammonia production is typically obtained from hydrocarbons in processes with large CO₂ emissions: steam reforming of methane or partial oxidation of coal. These processes account for approximately 1% of global CO₂ emission [2]. However, ammonia could also be synthesized by combining nitrogen with hydrogen generated through the electrolysis of water using only renewable energy sources such as wind or solar power [2,9]. Therefore, it is a promising green fuel with net zero CO₂ emission, which may enable a circular economy.

To facilitate the development and design of new ammonia-based reciprocating engines and gas turbines, accurate chemical kinetic models are needed that can describe the combustion of fuel mixtures containing NH₃ under typical conditions of industrial applications [21, 22,28]. There are several reaction mechanisms available in the literature that aim to describe the oxidation of NH₃/H₂ [29–37] and NH₃/syngas fuel mixtures [18,19,38–42]. However, while the predictions of these models often agree with experimental results under certain conditions, they deviate from those under other conditions. Furthermore, as Rocha et al. [43] also showed for laminar burning velocity and ignition delay time measurements, predictions of the different models often deviate from each other significantly. Therefore, comprehensive validation and further development of these models are needed based on a large collection of available experimental data.

This study aims to investigate the kinetic modeling of the oxidation chemistry of NH₃/H₂ and NH₃/syngas fuel mixtures under a wide range of combustion conditions. The main steps of the investigations are as follows: i) collection of experimental data: shock tube ignition delay time (ST-IDT) measurements, concentration measurements in jet stirred reactors (JSR) and flow reactors (FR), and laminar burning velocity (LBV) measurements; ii) utilization of recent, detailed reaction mechanisms from the literature that can describe the combustion of the investigated combustion systems; iii) testing the mechanisms using the collected experimental data and comparison of the performance of the mechanisms in a quantitative way; iv) investigation of the best-performing models by local sensitivity analysis to identify model parameters that are most influential on simulation outputs.

In 2020, our research group published a paper [44] in which eight detailed reaction mechanisms were tested against experimental data on the homogeneous combustion of ammonia. In the data collection utilized in that work [44], the fuel was pure ammonia in almost all cases, the initial gas mixtures contained H₂ in only very few of the investigated experiments. In that paper, only ST-IDT measurements and concentration measurements in FRs were investigated and the experimental data collection was much smaller (447 data points) than in the present work (4970 data points). Also, more reaction mechanisms were investigated in this study and local sensitivity analysis was applied to some selected models. Therefore, the present work may be viewed as a significant extension of the work of Kawka et al. [44].

The results of these investigations provide more insight into the

current state of the modeling of NH₃, NH₃/H₂, and NH₃/syngas combustion and may facilitate the development of better reaction mechanisms.

2. Experimental data collection

The literature of the experimental investigation of ammonia combustion has been extensively reviewed, and to our best knowledge, the data collection is comprehensive till January 2022. In this work, only shock tube ignition delay time measurements, concentration measurements in jet stirred and flow reactors, and laminar burning velocity measurements are studied in which the fuel contains NH₃ and the co-fuels are H₂ and/or CO. Experiments with NH₃/H₂ fuel mixtures also include measurements in which the fuel is pure NH₃. Covered ranges of initial conditions (temperature (*T*), pressure (*p*), equivalence ratio (*φ*), and mixture composition) are provided in Table 1, separately for each type of experiment (Exp. type). In the case of LBV measurements, the temperature values refer to the cold side temperatures. Altogether, 4898 experimental data points (in 472 data series) were utilized from 36 publications. These experimental data include those investigated in the work of Kawka et al. [44], except for the ST-IDT measurements of Drummond (1972) [45] and Fujii et al. (1981) [46]. These experiments were excluded from the investigations of this paper because the experimental conditions (pressures) had not been reported unambiguously in the publications, and also, according to the work of Chen et al. (2021)⁴⁷: “The ignition delay times of ammonia have been reported since the 1960s–80s, however, those early shock tube studies present the undesirable repeatability and low experimental accuracy. Especially, the adsorption of ammonia on the contact surface of the stainless steel equipment was not considered which lead to large experimental uncertainty.”. Chen et al. [47] refer to the works of Drummond [45] and Fujii et al. [46] as examples of these problematic experiments. Note that ST-IDT experiments were not found in the literature for NH₃/syngas fuel mixtures.

In addition to the works of Drummond [45] and Fujii et al. [46], some other collected experiments also had to be excluded from our investigations for different reasons. Details of the utilized experimental data along with justifications for the exclusions of certain experiments from our investigations are provided in the Supplementary Material (Parts 1 and 2, respectively).

Due to the accumulation of the large number of experimental data in combustion chemistry literature, there has been a demand for a database that facilitates and standardizes data storage, handling, and manipulation. Several approaches have been developed for this purpose including the PrIme [48] (Process Informatics Model) database, the CloudFlame [49] cyberinfrastructure, and the ChemKED [50] database. So far, none of these data collections contain experimental data related to NH₃ combustion.

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

Exp. type	XML/Ds./Dp.	Fuels	Oxidizer	Dopants	Diluents	<i>T</i> / K	<i>p</i> / atm	<i>φ</i>
NH₃/H₂ combustion								
ST-IDT	26/26/200	NH ₃ , NH ₃ /H ₂	O ₂	–	Ar, N ₂	1022–2489	1.01–41.65	0.50–2.00
JSR	29/108/1595	NH ₃ , NH ₃ /H ₂	O ₂	–, H ₂ O	Ar, He, N ₂	500–1452	1.00–1.20	0.01–1.50
FR	23/87/1125	NH ₃ , NH ₃ /H ₂	O ₂	–, H ₂ O	He, N ₂	451–1973	1.00–98.69	0.00–2.44
LBV	129/129/850	NH ₃ , NH ₃ /H ₂	O ₂	–	He, N ₂	298–476	0.50–10.00	0.40–1.80
Overall:	207/350/3770							
NH₃/syngas combustion								
JSR	8/40/229	NH ₃ /H ₂ /CO	O ₂	–	N ₂ , N ₂ /CO ₂	900–1350	1.00	0.38–1.51
FR	1/2/18	NH ₃ /CO	O ₂	–	N ₂	873–1273	1.00	0.01
LBV	80/80/881	NH ₃ /CO, NH ₃ /H ₂ /CO	O ₂	–	N ₂ , N ₂ /CO ₂	298–443	1.00–10.00	0.70–1.70
Overall:	89/122/1128							
Total:	296/472/4898							

The Chemical Kinetics Laboratory at ELTE created an online database, which is part of the ReSpecTh Information System [51]. The reaction kinetics section of ReSpecTh includes direct and indirect experimental data on several combustion systems, reaction mechanisms in CHEMKIN format, and computer programs that can be utilized for mechanism testing and development. The database now contains more than 150,000 data points in more than 3000 data files and a practically complete coverage of indirect experimental data for the combustion of the following fuels: hydrogen, syngas, methanol, formaldehyde, ethanol, butanol, ammonia, methane, as well as H_2/NO_x and methanol/ NO_x mixtures. Also, it contains a wide collection of direct measurements and theoretical determinations of related rate coefficients (7,000 data points in 350 data files). All data are available in RKD (ReSpecTh Kinetics Data) format [52], which is an extended and modified version of the file format used for storing measurement data in the PRiMe database [48]. Each measurement is stored in a separate data file of XML (Extensible Markup Language) format and each file has a unique identifier. One XML data file may contain more than one data series, e.g., if the concentrations of several species are measured in the same experiment. The experimental data utilized in this work were stored in 296 RKD format XML files. Table 1 shows the number of XML data files (which are also called datasets in this work), data series, and data points (XML/Ds./Dp.) for each type of investigated experiment.

3. Methodology

3.1. Simulation details

Simulations were carried out with the Optima++ simulation framework code [53], developed at the ELTE Chemical Kinetics Laboratory. Optima++ reads the RKD format data files, sets up simulation tasks based on its content, and invokes one of the following simulation packages: FlameMaster [54], OpenSMOKE++ [55], Zero-RK [56], or Cantera [57]. Then, Optima++ generates figures that compare the experimental data with the simulation results and computes various metrics about the quality of the reproduction of the experimental data. In our present investigations, OpenSMOKE++ was used for the simulations. Using it with Optima++, a mechanism can be tested against several thousands of data points in a single run.

Table 2 lists the reactor models of OpenSMOKE++ used in this study for the different types of experiments. The application of different simulation settings for the same type of experiment was determined according to the exact conditions of the experiments. Since this kind of information was sometimes missing from the publications or it was not complete, personal communication was sometimes necessary with the authors to clarify the details [30,58–61]. In Table 2, (c -t) and (c -out) indicate concentration–time profile and outlet concentration measurements, respectively.

All ST-IDT experiments were simulated using the BatchReactor model of OpenSMOKE++. More detailed description of the simulations of the investigated ST-IDT experiments can be found in Part 3 of the Supplementary Material.

Most JSR experiments were simulated using the isothermal–isobaric PerfectlyStirredReactor model of OpenSMOKE++, which is the most common approach for this kind of measurement. However, Sabia et al.

[58,59] specified that their JSR experiments should be simulated assuming constant heat exchange with the external environment (non-adiabatic approach). They derived a global heat exchange coefficient, $U = 3.5 \cdot 10^{-3} \text{ cal cm}^{-2} \text{ K}^{-1} \text{ s}^{-1}$, to be applied in the simulations of their experiments, and therefore this value was also used in our simulations.

Like in most JSR experiments, the isothermal–isobaric reactor model was used for the simulations of FR experiments. Song et al. [30] and Stagni et al. [34] published experimentally measured temperature profiles along the axis of the flow tube. In these cases, the given temperature profiles were used as inputs for the simulations. In all other FR (c -out) experiments, the temperature of the preheated inlet gas mixture was used as the constant temperature for the simulations.

Flame simulations were carried out by applying approximately 600 grid points, which ensured the required accuracy, and at the same time, simulations did not consume too much time. The gradient and curvature parameters were both set to 0.01. The Soret effect (thermal diffusion) was included, and radiative heat transfer between the flame and the environment was considered via the optically thin model (currently it is the only available approach in OpenSMOKE++).

3.2. Quantitative mechanism comparison

The performance of a mechanism is usually characterized by how accurately it can reproduce the results of indirect experimental measurements. It is advantageous to use a quantitative method for the assessment of mechanism performance, especially if we work with a large collection of experimental data points and we want to compare the performances of several models. The method applied in this study for quantitative mechanism comparison was suggested by Turányi et al. [80] and it has been used successfully for several combustion systems by our research group [44,81–92].

Let us have N experimental data series in the data collection utilized in the mechanism comparison. The data series are stored in N_f experimental data files, that is, there are N_f datasets. $N \geq N_f$ always, because one dataset may contain more than one data series (see Section 2). Let N_{fs} denote the number of data series in the f -th dataset and N_{fsd} the number of data points in the s -th data series in the f -th dataset. The averaged error of the mechanism predictions relative to the experimental results is described by the averaged error function as follows [93]:

$$E = \frac{1}{N} \sum_{f=1}^{N_f} \sum_{s=1}^{N_{fs}} \frac{1}{N_{fsd}} \sum_{d=1}^{N_{fsd}} \left(\frac{Y_{fsd}^{\text{sim}} - Y_{fsd}^{\text{exp}}}{\sigma(Y_{fsd}^{\text{exp}})} \right)^2 \quad (1)$$

where index f goes through all datasets in the data collection, index s goes through all data series in the f -th dataset, index d goes through all data points in the s -th data series in the f -th dataset, and

$$Y_{fsd} = \begin{cases} y_{fsd} & \text{if } \sigma(y_{fsd}^{\text{exp}}) \approx \text{constant} \\ \ln y_{fsd} & \text{if } \sigma(\ln(y_{fsd}^{\text{exp}})) \approx \text{constant} \end{cases} \quad (2)$$

where y_{fsd}^{exp} and $\sigma(y_{fsd}^{\text{exp}})$ are the fsd -th experimentally measured result

Table 2
Reactor models of OpenSMOKE++ applied for the simulations in this study.

Type of experiment	Solver	Reactor settings	Experiments
ST-IDT	BatchReactor	adiabatic–isochoric	[38,47,61]
JSR	PerfectlyStirredReactor	isothermal–isobaric	[34,36,62–64]
		adiabatic–isobaric	[58,59]
FR (c -t)	BatchReactor	isothermal–isobaric	[65]
FR (c -out)	PlugFlowReactor	isothermal–isobaric	[30,34,60,66–68]
LBV	PremixedLaminarFlame1D	See text.	[14,16,17,33,37,41,42,69–79]

(data point) and its standard deviation, respectively. The corresponding y_{fsd}^{sim} value is the simulation result for that data point. If an absolute error belongs to the measured (experimental) data point, $Y_{fsd} = y_{fsd}$ was taken in Eq. (1) for both the experimental and simulation results. This applies to laminar burning velocity [88] and concentration measurements [83]. If, however, a relative error describes the data point, $Y_{fsd} = \ln y_{fsd}$ was taken. This assumption was applied for shock tube ignition delay time measurements [83,89]. An error value can also be defined for each data point (E_{fsd}), and an averaged error for each data series (E_{fs}) and dataset (E_f) as follows:

$$E_{fsd} = \left(\frac{Y_{fsd}^{sim} - Y_{fsd}^{exp}}{\sigma(Y_{fsd}^{exp})} \right)^2, \quad (3)$$

$$E_{fs} = \frac{1}{N_{fsd}} \sum_{d=1}^{N_{fsd}} E_{fsd}, \quad (4)$$

$$E_f = \frac{1}{N_{fs}} \sum_{s=1}^{N_{fs}} E_{fs} \quad (5)$$

It is assumed that the experimental data follow normal (Gaussian) distribution; therefore, the function E follows reduced chi-square distribution. $E = 1$ means that the average deviation between the model predictions and experimental data is equal to the standard deviation of the experimental data. In principle, the value of E can be smaller than 1, but in practice when a large number of data points is investigated, it rarely happens. A smaller E value means better mechanism performance. From this, it also follows that if $E \leq 4$ or ≤ 9 , then the model can reproduce the measurement results within their 2σ or 3σ uncertainty limits, on average, respectively.

In the above equations, the deviation between Y_{fsd}^{sim} and Y_{fsd}^{exp} was normalized by the standard deviation of the corresponding data point $\sigma(Y_{fsd}^{exp})$. To estimate this quantity, both the uncertainty reported by the experimenters ($\sigma_{exp,fsd}$) and the estimated statistical scatter ($\sigma_{fit,fs}$) were considered:

$$\sigma(Y_{fsd}^{exp}) = \sqrt{\sigma_{fit,fs}^2 + \sigma_{exp,fsd}^2}. \quad (6)$$

The statistical scatter ($\sigma_{fit,fs}$) was obtained by fitting a trendline to the data points of the corresponding data series. To find the optimal trendline and the corresponding $\sigma_{fit,fs}$, the code Minimal Spline Fit [94, 95] was used. The exact procedure of how $\sigma(Y_{fsd}^{exp})$ was determined for different types of experimental data series is discussed in the Supplementary Material (Part 4) in detail. The pointwise standard deviations of the utilized data points are given in the XML data files.

3.3. Local sensitivity analysis

Local sensitivity analysis [96] was applied to identify the most important parameters of a model. The current version of the built-in sensitivity analysis module of OpenSMOKE++ computes the first-order local sensitivity coefficients by numerically solving the system of sensitivity differential equations [97], while Optima++ uses the brute-force method for this purpose. Optima++ allows computing the sensitivity coefficients for both the Arrhenius parameters and the NASA coefficients of the thermodynamic data. In contrast, the sensitivity analysis of thermodynamic data is not available in OpenSMOKE++. In addition, Optima++ can perform the sensitivity analysis of each kind of model output investigated in this work (concentration, IDT, LBV), while with OpenSMOKE++, the sensitivities of IDT data cannot be analyzed directly. Therefore, all sensitivity analyses were carried out using Optima++ even though the numerical computation method of the sensitivity coefficients is more advanced in OpenSMOKE++. The brute-force method was used for sensitivity analysis successfully in our

previous publications for various types of experimental data [81–83,85, 86,88–92,98,99] and also in other papers for ignition delay time data [100–104].

To investigate the sensitivity of kinetic parameters, sensitivity coefficients were computed for the preexponential factor, A , of the rate coefficient of each reaction by applying a perturbation factor of +5%. In the case of thermodynamic properties, sensitivity coefficients were computed for the constant-pressure standard molar heat capacity ($c_{p,k}^\ominus$), standard molar enthalpy of formation ($\Delta_f H_k^\ominus$), and standard molar entropy ($S_k^\ominus$) for each species k at 300 K temperature. The procedure has been described in the work of Kovács et al. [92] in detail.

The local sensitivity coefficient s_{ij} describes how the i -th model output changes due to the perturbation of the j -th model parameter. To make the different sensitivity coefficients comparable to each other, normalized local sensitivity coefficients were computed as $sn_{ij} = p_j / Y_i \cdot s_{ij}$. The normalized sensitivity coefficients were also scaled into the $[-1,1]$ interval for each data point as follows:

$$\tilde{sn}_{ij} = \frac{sn_{ij}}{\max_j \{|sn_{ij}|\}}. \quad (7)$$

A sensitivity coefficient was considered significant if the absolute value of the corresponding scaled normalized sensitivity coefficient was larger than 0.1, that is, $|\tilde{sn}_{ij}| \geq 0.1$. In this case, the i -th model output was considered to be highly sensitive to the j -th model parameter. The limiting value, 0.1, was arbitrarily chosen because in our previous similar work [92] on a different combustion system (methanol/NO_x), it was found that using this value the results of sensitivity analysis are meaningful and can be interpreted well.

4. Results and discussion

4.1. Quantitative mechanism comparison

In this study, 18 detailed reaction mechanisms were investigated in the case of NH₃/H₂ fuel mixtures which were collected from the literature. More detailed information on these mechanisms can be found in the Supplementary Material (Part 5). Since five of the investigated mechanisms do not contain carbonaceous species, these models cannot be applied for modeling combustion systems containing CO. Hence, only 13 mechanisms were investigated in the case of NH₃/syngas fuel mixtures. In most publications in the literature, the performances of several mechanisms are assessed by the visual inspection of figures in which the experimentally measured results are plotted together with model predictions. Some representative plots of this type are shown in Fig. 1.

For the quantitative comparison of the performances of the investigated mechanisms, we would like to utilize as many data points as possible. It was not possible, however, to use all data points of the data collection for the comparison, because the simulations of some data points did not converge with one or more mechanisms. Not converging simulations occurred in two types of experiments: JSR concentration and LBV measurements, while the simulations of all ST-IDT and FR concentration measurements were successful.

In the case of LBV measurements, only very few simulations were identified that were unsuccessful with at least one mechanism (12 out of 843 data points in the NH₃/H₂ case and none of the 881 data points in the NH₃/syngas case). These 12 simulations were initiated from scratch, using different initial guesses of the solutions, and with different grid settings (number of grid points and gradient and curvature parameters), but they did not converge in any case. In these problematic simulations, the experimentally measured LBVs were always very small (2.1–7.5 cm/s). We also examined whether the consideration of the radiative heat transfer between the flame and the environment (radiative heat loss) affected the success of the simulations of these problematic data points. It was found that when the radiative heat loss was not considered, the simulations of all data points converged with each mechanism.

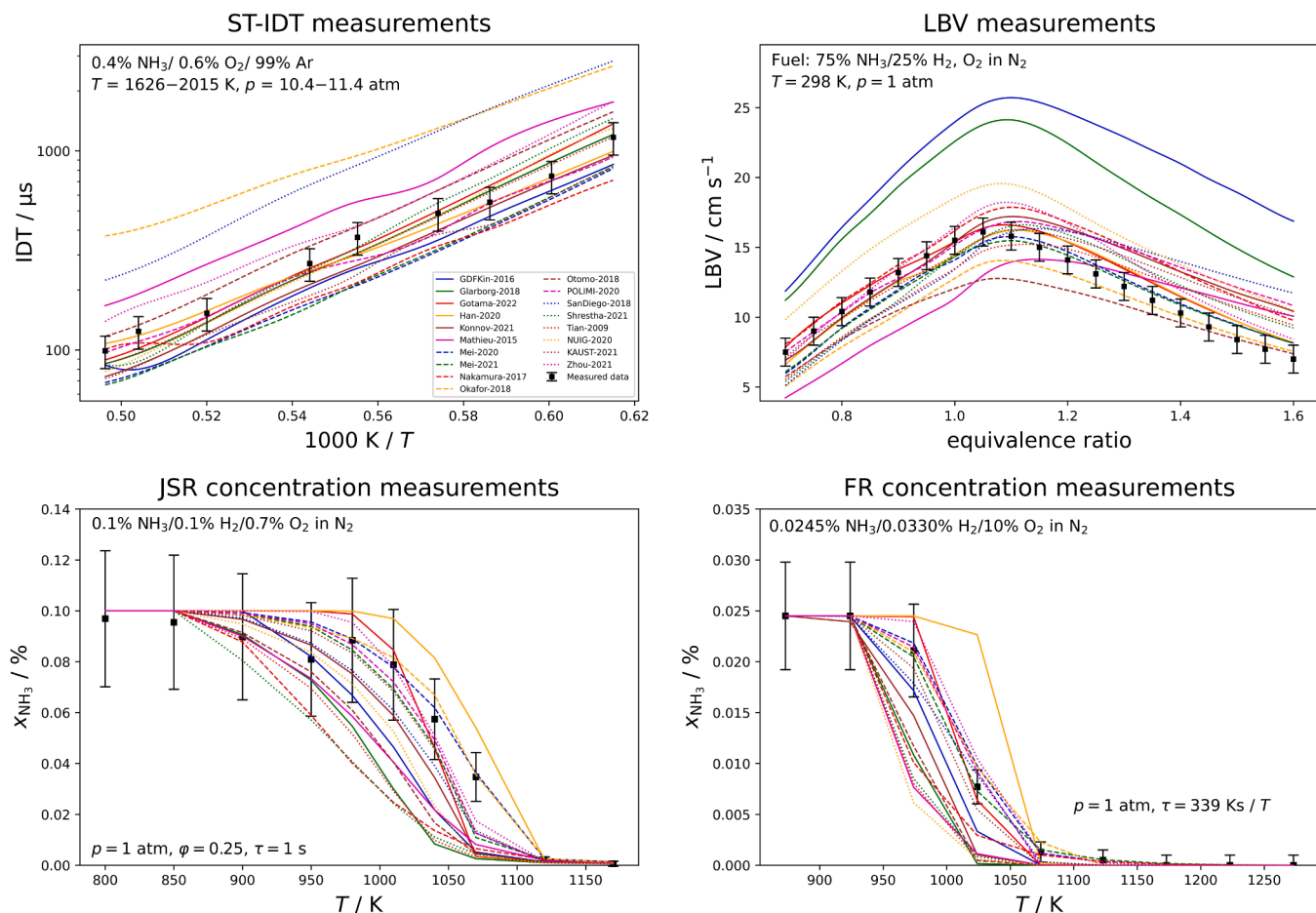


Fig. 1. Representative examples of the performances of the investigated mechanisms. Experimentally measured results (symbols) are plotted together with model predictions (lines). Error bars shown for the experimental data correspond to the 2σ limits. Source of experimental data: ST-IDT measurements of Mathieu et al. [38], LBV measurements of Han et al. [16], JSR concentration measurements of Zhang et al. [36], and FR outlet concentration measurement of Wargadalam et al. [68].

Radiative heat loss always decreases the temperature of the flame thus decreasing the reactivity of the system. Therefore, the reason for the failure of the simulations of the data points with very small LBVs (where the reactivity is relatively low) is that the reactivity decreases below a certain threshold due to the lower temperature calculated by considering the radiative heat loss and thus the flame cannot be stabilized in the simulations with certain mechanisms. This indicates a shortcoming of the corresponding model(s), and therefore these flame simulations were labeled as “failed” for those mechanism(s).

In the case of JSR experiments, some of the simulations in which constant heat exchange with the external environment was considered (experiments of Sabia et al. [58,59] on the oxidation of pure ammonia) did not converge with at least one mechanism. Different solver settings (numerical tolerances) were tested but convergence was not reached in any case. It was clear from the inspection of the time histories of the transient simulations that their failures were due to the presence of temperature and concentration oscillations in time (Fig. 2) during the simulations. These thermokinetic oscillations were also observed in simulations by Sabia et al. [58,59] using some of the investigated kinetic mechanisms but they were not detected in their original experiments. The experimental data of Sabia et al. investigated in this present work [58,59] cover the ϕ range 0.60–1.40 and T_{in} range 953–1313 K. In more recent experimental works of these authors [105,106], another temperature detector was used which was able to collect temperature values with ca. 300 times larger frequency than the old one. It was shown [105] that in several cases when the temperature data from the old equipment did not show oscillation, data from the new detector revealed the

Thermokinetic oscillation during a JSR simulation

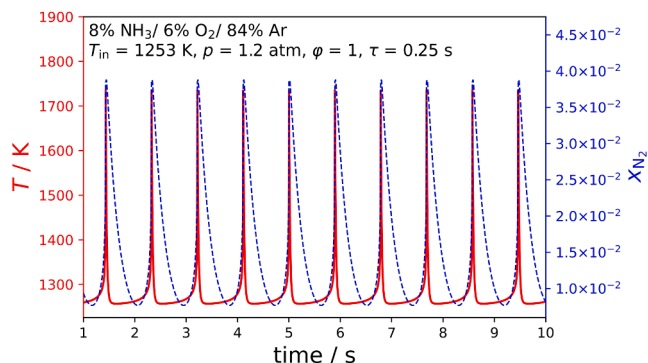


Fig. 2. Thermokinetic oscillation observed during a JSR simulation using the Gotama-2022 mechanism. Temperature (red solid line) and N_2 mole fraction (dashed blue line) values are plotted. The conditions are identical to those in a measurement of Manna et al. [58]. The simulation was carried out considering constant heat exchange with the environment (see the main text for details).

oscillation pattern. Experiments under the same conditions as in the previous works [58,59] were carried out with the new detector and oscillations were detected at $\phi = 0.55$ –1.00 and $T_{in} > 1250$ K (the upper T_{in} limit depended on ϕ) [106]. But it is important to note that periodic oscillations (like in the simulations) were observed experimentally only in a narrow range of conditions ($T_{in} = 1255$ –1260 K and $\phi = 0.55$ –0.58),

while in the remaining cases, the experimental oscillations were damped. In our investigations, the time-averages of the concentration values during an oscillation period were taken as simulation results because experimentally, the time-averages of the oscillating concentration values were measured [58,59,105,106].

The simulations were also performed without considering heat exchange with the environment (adiabatic assumption), and under these conditions, no oscillation was observed. Therefore, the occurrence of oscillation behavior in the investigated systems can be attributed to the introduction of constant heat exchange with the environment in addition to the kinetics of the system. The simulations were also carried out using the isothermal JSR model and concentration oscillations were not observed either.

Note that temperature and concentration oscillations were also detected in other combustion systems in JSRs, e.g., in the case of CH₄ oxidation [107–109]. Sabia et al. [108] and Lavadera et al. [107] found that oscillations can also be obtained numerically under adiabatic conditions, thus suggesting that heat exchange with the environment is in general not necessary for oscillations to occur, although in the systems investigated in the present work it was necessary. In addition, Lavadera et al. [107] and Stagni et al. [109] showed that concentration oscillations can also be observed in isothermal JSR simulations, which indicates that this dynamic behavior is first and foremost of kinetic nature. Stagni et al. [109] performed JSR experiments under “quasi-isothermal” conditions (high levels of dilution were applied) and concentration oscillations were detected confirming the results of the numerical simulations experimentally.

Some data points could not be reproduced within their 3σ uncertainty limits with any of the investigated mechanisms, that is, the E_{fsd} values of these data points were larger than 9 for all mechanisms. These data points may have very large systematic errors which were not considered, or they are related to experimental conditions that none of the mechanisms can describe satisfactorily. We could not identify which one was the real reason, but these data points were excluded from the quantitative comparison to ensure that the conclusions are unbiased.

Finally, another issue occurred during the analysis of the error function values after excluding those data for which $E_{fsd} > 9$ with all models. There still remained some data in the collection for which the E_{fsd} values were extremely high (i.e., thousands or ten thousands) with one or more (but not all) of the mechanisms. These data points can significantly increase the averaged E value of the corresponding mechanism, which would lead us to false impressions about the overall performance of the mechanism. However, in this case, the problem is with the mechanism and not the experiment; therefore, the number of data points with extremely high E_{fsd} values is also an indicator of the performance of the corresponding mechanism (in addition to the averaged E value).

Based on the previous arguments, two kinds of averaged error function values were computed for both (NH₃/H₂ and NH₃/syngas) data collections. One is denoted by E^{common} , and it was computed by excluding those data points for which the simulation failed or E_{fsd} was larger than 400 (extremely high, beyond 20σ) with at least one of the mechanisms. These data were excluded for all mechanisms, not only for the corresponding one. The advantage of this approach is that the models are compared using exactly the same data collection, but at the same time, we may exclude several valuable data because of the wrong behavior of only one or more (but not all) mechanisms. To avoid excluding these data for all mechanisms, another E value, denoted by E^{all} was computed for each mechanism. In this case, these problematic data points (failed or $E_{fsd} > 400$) were excluded for only the corresponding mechanism but kept for the others. Of course, the drawback of this approach is that the data collection based on which the models are compared may differ from mechanism to mechanism.

Finally, we would like to highlight that for both kinds of error functions, excluding the $E_{fsd} > 400$ data points means that the averaged E value slightly overestimates the accuracy of the corresponding

mechanism. Overall, the averaged E value and the number of $E_{fsd} > 400$ data points together characterize mechanism performance. However, as we shall see in the next subsections, the averaged E value and the number of $E_{fsd} > 400$ data points are usually well correlated, that is, a mechanism with a small averaged E value usually has a small number of $E_{fsd} > 400$ data points and vice versa.

4.1.1. NH₃/H₂ fuel mixtures

In the case of NH₃/H₂ fuel mixtures, 18 reaction mechanisms were investigated (Table 3). In the subsequent figures and tables on mechanism comparison, NUIG-2020 denotes the detailed kinetic mechanism of Wang et al. [101]. The SanDiego-2018 model is composed of the 2016/12/14 version of the hydrocarbon oxidation mechanism and the 2018/07/23 version of the nitrogen chemistry sub-mechanism of the Combustion Research Group at the University of California in San Diego [110]. Four of the investigated mechanisms do not contain the species He (Tian-2009, GDFKin-2016, Okafor-2018, Zhou-2021); therefore, those experiments in which the diluent gas was He were not used in the comparison in Table 3 (50 JSR, 138 FR, and 7 LBV data points).

In Table 3, the averaged error function values of the 18 investigated mechanisms are summarized for each type of experiment (E_{ST-IDT}^{all} , E_{JSR}^{all} , E_{FR}^{all} , E_{LBV}^{all}). These values were computed according to Eq. (1). After each of these error function values, the number of $E_{fsd} > 400$ data points (not counting those data for which $E_{fsd} > 9$ with all mechanisms) is shown in parentheses (“> 400” columns). The “ $E_{average}$ ” quantity is the un-weighted average of the type-specific error function values, that is, $E_{average} = (E_{ST-IDT} + E_{JSR} + E_{FR} + E_{LBV}) / 4$. The mechanisms are ordered in the table according to their $E_{average}^{all}$ values (first column highlighted in bold), from smallest (best performance) to largest (worst performance).

The aim of these investigations is to find the mechanisms that have the best overall performance under a wide range of experimental facilities. This is why $E_{average}$ was defined the abovementioned way: equal weight is given to each type of experiment irrespective of the number of available data series to avoid downweighting one type of experiment only because fewer data series are available in the literature for an experimental facility. For reference, the averaged error function values computed simply according to Eq. (1) considering all types of experiments are also shown (“ E_{total} ”, also highlighted in bold). In this case, the weight of a type of experiment depends on the number of the available data series. These arguments are well reflected in the E values of the KAUST-2021 model. It has a large E_{ST-IDT}^{all} value relative to the other best-performing models, which has a small effect on the computed E_{total}^{all} value due to the relatively small number of available ST-IDT data series (see Table 1), and therefore KAUST-2021 has the smallest E_{total}^{all} value. In contrast, the large E_{ST-IDT}^{all} value increases the $E_{average}^{all}$ value more significantly because each type of experiment has equal weight, and consequently, KAUST-2021 has only the third smallest $E_{average}^{all}$ value. Both the $E_{average}$ and the E_{total} quantities can be used for the characterization of mechanism performance depending on the purpose of the investigations.

The $E_{average}^{common}$ values (see Section 4.1) are also listed in the table (highlighted in bold). If we compare the two series of E values ($E_{average}^{all}$ and $E_{average}^{common}$), we see that the data point selection method does not change the order of the mechanisms significantly. For instance, the three best-performing models are the same (POLIMI-2020, Han-2020, and KAUST-2021) in both cases.

After the E^{all} and E^{common} values, the numbers of data points based on which these quantities were computed are shown for the corresponding mechanism in parentheses, respectively (“Dp.” columns). These numbers are the same for each mechanism in the case of the E^{common} values, as discussed in Section 4.1.

Finally, in the last two columns of the table, the numbers of data points for which the simulations were successful and failed with the corresponding mechanism are shown, respectively.

Table 3

Averaged error function values for the 18 investigated mechanisms in the case of NH_3/H_2 fuel mixtures excluding experiments containing He as diluent. See the main text of Sections 4.1 and 4.1.1 for the explanation of the quantities shown in the table.

Mechanism ID	Averaged error function values													Simulations	
	ST-IDT		JSR		FR		LBV		Overall					Successful	Failed
	$E_{\text{ST-IDT}}^{\text{all}}$	(>400)	$E_{\text{JSR}}^{\text{all}}$	(>400)	$E_{\text{FR}}^{\text{all}}$	(>400)	$E_{\text{LBV}}^{\text{all}}$	(>400)	$E_{\text{all average}}$	$E_{\text{all total}}$	(Dp.)	$E_{\text{common average}}$	(D.p.)		
POLIMI-2020 [34,111]	9.7	(0)	23.3	(74)	9.5	(10)	8.4	(1)	12.8	13.3	(3134)	10.0	(2650)	3574	1
Han-2020 [18]	5.9	(0)	28.9	(80)	10.2	(12)	7.1	(0)	13.0	14.3	(3127)	10.4	(2650)	3573	2
KAUST-2021 [36]	26.6	(0)	16.7	(64)	5.0	(9)	8.1	(0)	14.1	11.5	(3145)	10.1	(2650)	3573	2
Otomo-2018 [32]	5.8	(0)	24.6	(77)	9.7	(12)	19.6	(0)	14.9	17.8	(3129)	12.5	(2650)	3574	1
Mathieu-2015 [38]	5.7	(0)	22.6	(74)	9.2	(12)	24.9	(1)	15.6	19.1	(3122)	13.2	(2650)	3564	11
Tian-2009 [112]	9.1	(0)	27.4	(74)	9.3	(13)	19.1	(3)	16.2	18.6	(3128)	12.9	(2650)	3574	1
Mei-2020 [19]	33.8	(2)	23.0	(79)	10.1	(16)	5.1	(0)	18.0	14.0	(3122)	12.9	(2650)	3573	2
Gotama-2022 [37]	28.6	(14)	24.1	(55)	10.4	(17)	9.2	(0)	18.1	15.5	(3133)	14.0	(2650)	3574	1
Konnov-2021 [113]	23.3	(6)	27.3	(82)	11.8	(21)	13.0	(1)	18.8	17.9	(3109)	12.8	(2650)	3574	1
Zhou-2021 [79]	24.4	(0)	25.8	(59)	9.4	(14)	16.2	(5)	19.0	18.2	(3140)	15.7	(2650)	3574	1
Shrestha-2021 [41]	22.8	(0)	38.0	(111)	8.6	(12)	9.5	(1)	19.7	19.1	(3095)	13.5	(2650)	3572	3
Mei-2021 [42]	42.9	(1)	22.5	(70)	9.9	(17)	5.5	(0)	20.2	14.7	(3129)	12.8	(2650)	3573	2
SanDiego-2018 [110]	45.4	(0)	29.4	(74)	11.7	(16)	13.5	(1)	25.0	20.5	(3127)	20.9	(2650)	3573	2
Nakamura-2017 [31]	34.1	(0)	39.9	(109)	12.9	(14)	15.7	(0)	25.6	23.9	(3096)	21.3	(2650)	3575	0
NUIG-2020 [101]	16.9	(0)	30.6	(78)	14.8	(15)	40.8	(10)	25.8	29.8	(3116)	16.9	(2650)	3575	0
Glarborg-2018 [26]	9.5	(0)	30.5	(61)	8.6	(14)	77.1	(22)	31.4	41.6	(3122)	22.5	(2650)	3575	0
Okafor-2018 [114]	96.9	(45)	30.3	(72)	10.3	(19)	22.3	(6)	40.0	27.3	(3077)	38.8	(2650)	3575	0
GDFKin-2016 [115]	36.5	(0)	26.0	(74)	10.2	(14)	127.5	(157)	50.1	60.8	(2974)	47.3	(2650)	3575	0
All data points:	200		1545		987		843				3575		3575		
$E_{\text{fsd}} > 9$ with each model:	2		220		124		10				356		355		
	(1.0%)		(14.2%)		(12.6%)		(1.2%)				(10.0%)		(9.9%)		
All data series:	26		102		77		127				332		332		
All datasets:	26		27		20		127				200		200		

The results of Table 3 indicate that none of the investigated mechanisms has an $E_{\text{average}}^{\text{all}}$ value of less than 9, that is, they cannot reproduce the experimental data within their 3σ uncertainty limits, on average. This highlights the need for further mechanism development in ammonia combustion. The three best-performing mechanisms (in order according to the $E_{\text{average}}^{\text{all}}$ values) are POLIMI-2020, Han-2020, and KAUST-2021. POLIMI-2020 and KAUST-2021 were developed as comprehensive models for NH_3 oxidation and pyrolysis and NH_3 and NH_3/H_2 oxidation, respectively, and they were extensively validated against various types of experimental data (see Table A10 in the Supplementary Material), so their good overall performance is not

surprising. Han-2020 was primarily developed to describe the LBVs of $\text{NH}_3/\text{syngas}/\text{air}$ flames and validated against LBV and ST-IDT data on NH_3 and NH_3/H_2 oxidation. Hence, it is not surprising that it has very good performance for ST-IDT and LBV experiments.

It can be noticed that there are significant differences between the performances of the different models. The $E_{\text{average}}^{\text{all}}$ values range from about 13 to 50. Furthermore, the performance of a mechanism may vary significantly with the type of experiment. For example, the KAUST-2021 model performs very well in the case of flow reactor measurements with $E_{\text{FR}}^{\text{all}} = 5.0$, that is, well within the 3σ limits, while its $E_{\text{ST-IDT}}^{\text{all}}$ value is 26.6, which means that model predictions are beyond the 5σ uncertainty

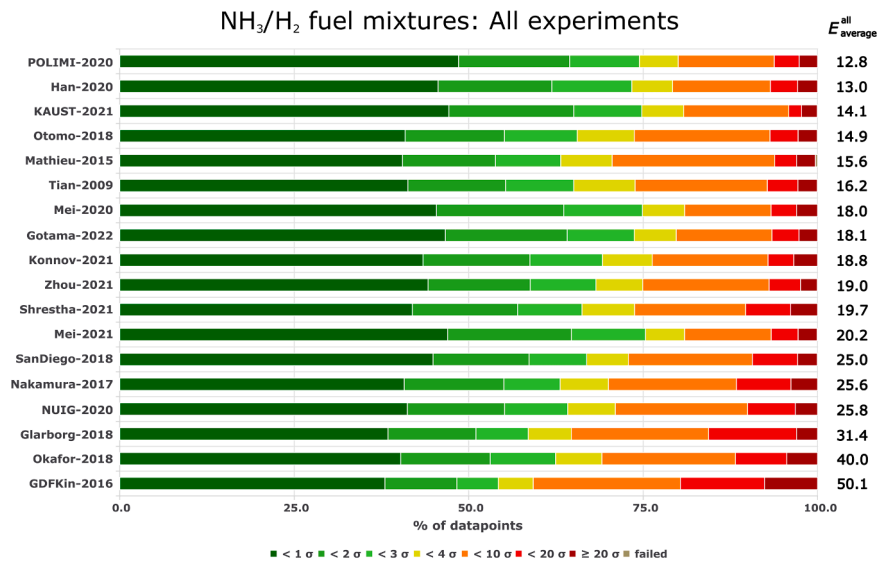


Fig. 3. Stacked bar chart of the frequencies of the data points when the mechanisms could reproduce them within given thresholds of their standard deviations (σ). 100% means all investigated data points in the case of NH_3/H_2 fuel mixtures (excluding those for which $E_{\text{fsd}} > 9$ for each mechanism), that is, 3219 data points. The mechanisms are ordered according to their $E_{\text{average}}^{\text{all}}$ values as in Table 3.

limits of the ST-IDT experimental data, on average.

Fig. 3 shows the distribution of the data points according to their error values, E_{fsd} , in a stacked bar chart. The frequencies of the data points that were reproduced by the mechanisms within a given threshold of the multiple of the estimated standard deviation are plotted. The ratios of the failed simulations are also shown, but due to the very small number of these data points (Table 3), the corresponding gray bars can hardly be seen in the figure for most of the mechanisms. In Fig. 3, we can observe the general trend that a mechanism with a smaller $E_{average}^{all}$ value usually has a smaller number of data points with larger E_{fsd} value and vice versa. For instance, KAUST-2021 has one of the smallest $E_{average}^{all}$ values, and it also has the smallest number of $E_{fsd} > 100$ (beyond 10σ) and one of the smallest numbers of $E_{fsd} > 400$ (beyond 20σ) data points. Moreover, the two models with the largest $E_{average}^{all}$ values, Okafor-2018 and GDFKin-2016, have the largest numbers of $E_{fsd} > 400$ data points. In the case of Okafor-2018, this is mainly due to the ST-IDT measurements, while for GDFKin-2016, LBV measurements contribute largely to the number of $E_{fsd} > 400$ data points. Nevertheless, this trend between $E_{average}^{all}$ and the distribution of the data points according to their E_{fsd} values is obviously not strictly monotonic.

In Table 3, those experiments in which He is used as the diluent gas were not included in the investigation because four of the mechanisms do not contain that species. The mechanism comparison results for the other 14 mechanisms including the experiments containing He (175 extra data points relative to Table 3) can be found in the Supplementary Material (Table A11). Also including those data in the mechanism comparison does not change the order of the models significantly; the three best-performing mechanisms (in order) are still POLIMI-2020 (12.6), Han-2020 (13.9), and KAUST-2021 (14.2) according to the $E_{average}^{all}$ values.

4.1.2. NH_3 /syngas fuel mixtures

Table 4 shows the computed averaged error function values for the investigated experiments with NH_3 /syngas fuel mixtures in the same way as Table 3, and the corresponding stacked bar chart is shown in Fig. 4. Here, the outlet concentration measurements in JSRs and FRs are treated together due to the small number of available data, and the averaged error function values computed for these experiments are denoted with E_{conc} . As five of the investigated 18 mechanisms do not contain carbon species, the performances of only 13 models were

investigated in this case.

It can be seen that all simulations were successful with each mechanism. The number of data points for which $E_{fsd} > 9$ with each mechanism is very low in the case of LBV measurements (around 1%), while it is a bit more in the case of concentration measurements (around 18%). The same is true for the numbers of the $E_{fsd} > 400$ data points; in the case of concentration measurements, Zhou-2021, Han-2020, and Konnov-2021 have the most data points of this type. The best three models are Shrestha-2021, Mei-2021, and Mei-2020, which also have a small number of $E_{fsd} > 400$ data points.

The Mei-2020 model was developed to describe the LBVs of NH_3 /syngas flames (see Table A10 in the Supplementary Material) and was validated against LBV measurements of NH_3 , NH_3/H_2 , and NH_3 /syngas oxidation, and ST-IDT measurements on syngas oxidation doped with NH_3 . The main development targets of Mei-2021 were the LBVs of NH_3/H_2 flames and it was validated against LBV data on NH_3 , NH_3/H_2 , and NH_3 /syngas oxidation along with burner stabilized flame (BSF) speciation data on NH_3/H_2 oxidation. It is an updated version of Mei-2020: the rate coefficients of six reactions were modified. Shrestha-2021 was developed primarily to model the LBVs of NH_3 and NH_3/H_2 flames, but it was validated against a large set of indirect experimental data containing various types of experiments and combustion systems. Therefore, the good performances of these three models are expected for the investigated LBV experiments, and their performances are also acceptable in the case of concentration measurements.

4.2. Local sensitivity analysis

Local sensitivity analysis was carried out on the best-performing models identified in Section 4.1. Three models were studied in the cases of both the NH_3/H_2 and NH_3 /syngas fuel mixtures. The sensitivities of the kinetic and thermodynamic parameters were investigated. For each set of investigated data points, the ratio of the number of data points that were highly sensitive to parameter j and the total number of investigated data points was computed for each parameter. These ratios are expressed in percentages and are called “frequency” values in this section. The larger the frequency value, the more sensitive the corresponding parameter, on average. The reactions are ordered according to these frequency values in the tables of this section.

For both fuel systems, the sensitivity analysis was carried out using all data points that were investigated in Section 4.1 except those for

Table 4

Averaged error function values for the investigated mechanisms in the case of NH_3 /syngas fuel mixtures. See the main text of Sections 4.1 and 4.1.1 for the explanation of the quantities shown in the table.

Mechanism ID	Averaged error function values								Simulations		
	Concentration		LBV		Overall					Successful	Failed
E_{conc}^{all}	(>400)	E_{LBV}^{all}	(>400)	$E_{average}^{all}$	E_{total}^{all}	(Dp.)	$E_{common}^{average}$	(Dp.)			
Shrestha-2021 [41]	10.6	(0)	9.7	(0)	10.2	10.0	(1076)	8.0	(1041)	1128	0
Mei-2021 [42]	12.9	(2)	9.6	(0)	11.3	10.7	(1074)	7.3	(1041)	1128	0
Mei-2020 [19]	16.8	(3)	9.4	(0)	13.1	11.8	(1073)	7.8	(1041)	1128	0
Han-2020 [18]	15.8	(9)	11.6	(0)	13.7	12.9	(1067)	13.8	(1041)	1128	0
Mathieu-2015 [38]	8.8	(0)	21.7	(0)	15.2	17.5	(1076)	13.4	(1041)	1128	0
Konnov-2021 [113]	17.1	(9)	18.2	(0)	17.6	17.8	(1067)	16.6	(1041)	1128	0
Zhou-2021 [79]	16.1	(11)	21.1	(2)	18.6	19.5	(1063)	17.8	(1041)	1128	0
NUIG-2020 [101]	20.0	(2)	18.3	(0)	19.1	18.8	(1074)	12.9	(1041)	1128	0
SanDiego-2018 [110]	7.9	(0)	30.7	(0)	19.3	23.3	(1076)	17.5	(1041)	1128	0
Tian-2009 [112]	25.6	(4)	39.7	(2)	32.6	35.1	(1070)	24.9	(1041)	1128	0
GDFKin-2016 [115]	12.2	(2)	70.7	(3)	41.5	51.9	(1071)	37.5	(1041)	1128	0
Glarborg-2018 [26]	8.8	(0)	82.5	(8)	45.7	58.8	(1068)	43.1	(1041)	1128	0
Okafor-2018 [114]	35.8	(6)	62.7	(4)	49.3	54.0	(1066)	36.5	(1041)	1128	0
All data points:	247		881				1128		1128		
$E_{fsd} > 9$ with each model:	45		7				52		52		
	(18.2%)		(0.8%)				(4.6%)		(4.6%)		
All data series:	42		80				122				
All datasets:	9		80				89		89		

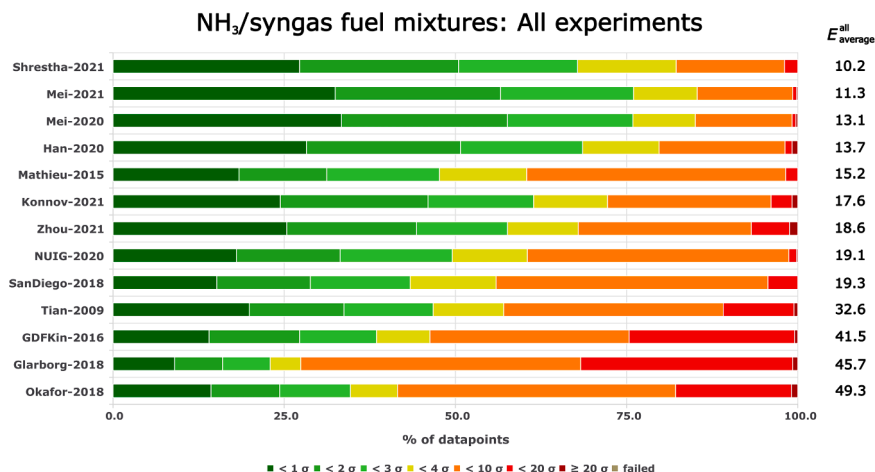


Fig. 4. Stacked bar chart of the frequencies of the data points when the mechanisms could reproduce them within given thresholds of their standard deviations (σ). 100% means all investigated data points in the case of NH₃/syngas fuel mixtures (excluding those for which $E_{fsd} > 9$ for each mechanism), that is, 1076 data points. The mechanisms are ordered according to their $E_{all}^{average}$ values as in Table 4.

which the E_{fsd} value was larger than 9 with each of the investigated mechanisms. In the case of NH₃/H₂ fuel mixtures, the numbers of the investigated data points are not the same for the three mechanisms in the case of LBV measurements because of the different numbers of failed flame simulations (see Section 4.1.1).

4.2.1. Kinetic parameters

4.2.1.1. NH₃/H₂ fuel mixtures. In the case of NH₃/H₂ fuel mixtures, the POLIMI-2020 model with the smallest $E_{all}^{average}$ value of 12.8 and the

Table 5

Sensitivity analysis results of the chemical kinetic parameters (preexponential factors, A) for experiments with NH₃/H₂ fuel mixtures. The 10-10 most sensitive reactions are shown for the three investigated mechanisms separately for shock tube ignition delay time (ST-IDT), concentration (JSR and FR), and laminar burning velocity (LBV) measurements.

POLIMI-2020			KAUST-2021			Shrestha-2021		
Reaction	Freq. ^a	$ \bar{s}t_{ij} ^b$	Reaction	Freq. ^a	$ \bar{s}t_{ij} ^b$	Reaction	Freq. ^a	$ \bar{s}t_{ij} ^b$
ST-IDT: 198 investigated data points								
H + O ₂ = OH + O	96.0%	0.861	H + O ₂ = OH + O	91.4%	0.771	H + O ₂ = OH + O	94.9%	0.801
NH ₃ + H = NH ₂ + H ₂	70.7%	0.281	NH ₂ + NO = N ₂ + H ₂ O (DUP1)	70.2%	0.234	NH ₃ + H = NH ₂ + H ₂	79.3%	0.290
NH ₂ + HO ₂ = NH ₃ + O ₂	67.7%	0.215	NH ₃ + H = NH ₂ + H ₂	69.7%	0.298	NH ₃ + NH ₂ = N ₂ H ₃ + H ₂	73.7%	0.318
NH ₂ + NH = N ₂ H ₂ + H	64.6%	0.197	NH ₃ + NH ₂ = N ₂ H ₃ + H ₂	69.7%	0.272	N ₂ H ₂ + M = NNH + H + M	69.7%	0.351
NH ₂ + NO = NNH + OH	41.9%	0.144	N ₂ H ₂ + M = NNH + H + M	69.7%	0.267	NH ₂ + H + M = NH ₃ + M (LP)	64.1%	0.345
NH ₂ + O ₂ = H ₂ NO + O	40.4%	0.148	NH ₂ + HO ₂ = NH ₃ + O ₂	63.1%	0.187	N ₂ H ₂ + H = NNH + H ₂	61.6%	0.174
N ₂ H ₂ + H = NNH + H ₂	40.4%	0.076	NH ₂ + NO = NNH + OH	63.1%	0.162	NH ₂ + NH ₂ = N ₂ H ₂ + H ₂	57.6%	0.132
N ₂ H ₂ = NNH + H (PLOG03) (DUP1)	38.4%	0.087	N ₂ H ₂ + H = NNH + H ₂	60.1%	0.137	NH ₂ + NO = NNH + OH	53.5%	0.266
N ₂ H ₂ = NNH + H (PLOG03) (DUP2)	35.4%	0.069	NH + O ₂ = HNO + O	56.6%	0.121	NH ₂ + O ₂ = H ₂ NO + O	49.5%	0.171
NH ₃ = NH ₂ + H (PLOG03)	32.3%	0.113	NH ₂ + NO = N ₂ + H ₂ O (DUP2)	52.5%	0.118	NH ₃ + OH = NH ₂ + H ₂ O	48.5%	0.117
Concentration measurements in JSRs and FRs: 2343 investigated data points								
H + O ₂ = OH + O	73.3%	0.451	H + O ₂ = OH + O	77.5%	0.496	H + O ₂ = OH + O	72.1%	0.414
NH ₂ + HO ₂ = NH ₃ + O ₂	71.5%	0.456	NH ₂ + NO = N ₂ + H ₂ O (DUP1)	73.0%	0.462	NH ₂ + NO = NNH + OH	52.0%	0.306
H + O ₂ + M = HO ₂ + M (LP)	56.1%	0.241	NH ₂ + HO ₂ = NH ₃ + O ₂	68.5%	0.379	NH ₂ + NO = N ₂ + H ₂ O	49.4%	0.312
NH ₂ + O ₂ = H ₂ NO + O	55.2%	0.239	NH ₂ + NO = NNH + OH	57.7%	0.228	NH ₃ + H = NH ₂ + H ₂	32.0%	0.119
NH ₂ + O ₂ = N ₂ + H ₂ O	54.8%	0.310	H + O ₂ + M = HO ₂ + M (LP)	57.1%	0.218	NH ₃ + NH ₂ = N ₂ H ₃ + H ₂	31.7%	0.240
NH ₂ + NO = NNH + OH	50.1%	0.211	NH ₂ + NO = N ₂ + H ₂ O (DUP2)	55.0%	0.173	NH ₂ + H + M = NH ₃ + M (LP)	30.0%	0.171
NH ₂ + HO ₂ = H ₂ NO + OH	40.4%	0.251	NH ₂ + HO ₂ = H ₂ NO + OH	49.0%	0.295	H + O ₂ + M = HO ₂ + M (LP)	28.5%	0.133
H ₂ NO + O ₂ = HNO + HO ₂	37.8%	0.133	NH ₃ + H = NH ₂ + H ₂	42.9%	0.134	NH ₂ + O ₂ = H ₂ NO + O	27.1%	0.146
NH ₃ + H = H ₂ + NH ₂	35.5%	0.122	NH ₃ + NH ₂ = N ₂ H ₃ + H ₂	36.1%	0.232	NH ₂ + HO ₂ = H ₂ NO + OH	25.1%	0.082
NH ₂ + NH = N ₂ H ₂ + H	28.0%	0.085	NH ₂ + O ₂ = H ₂ NO + O	35.1%	0.107	H ₂ NO + O ₂ = HNO + HO ₂	24.8%	0.091
LBV: 835 investigated data points			LBV: 834 investigated data points			LBV: 834 investigated data points		
H + O ₂ = OH + O	100.0%	0.998	H + O ₂ = OH + O	100.0%	0.997	H + O ₂ = OH + O	99.8%	0.995
NH ₂ + NH = N ₂ H ₂ + H	95.6%	0.216	NH ₂ + NO = NNH + OH	93.4%	0.235	NNH = N ₂ + H	74.3%	0.179
NH ₂ + NO = NNH + OH	76.0%	0.145	H + O ₂ + M = HO ₂ + M (LP)	72.9%	0.151	NNH + O ₂ = N ₂ + HO ₂	68.1%	0.160
NH ₂ + O = HNO + H (DUP1)	74.3%	0.123	NH ₂ + O = HNO + H (DUP1)	69.3%	0.109	NH ₂ + NO = NNH + OH	64.0%	0.140
H ₂ + O = H + OH	71.3%	0.143	NH ₂ + H = NH + H ₂	64.1%	0.106	H ₂ + OH = H + H ₂ O	50.5%	0.123
H + O ₂ + M = HO ₂ + M (LP)	69.9%	0.149	NH ₂ + NH = N ₂ H ₂ + H	57.2%	0.106	N ₂ H ₂ + H = NNH + H ₂	41.4%	0.076
NH + H = N + H ₂	32.0%	0.085	NH ₂ + NO = N ₂ + H ₂ O (DUP1)	54.2%	0.172	N ₂ H ₂ + M = NNH + H + M	39.8%	0.079
H ₂ + OH = H + H ₂ O	24.0%	0.091	H ₂ + O = OH + H (DUP2)	48.7%	0.110	NH ₂ + NH = N ₂ H ₂ + H	32.5%	0.078
HNO + H = NO + H ₂	20.6%	0.066	NH ₂ + NO = N ₂ + H ₂ O (DUP2)	31.1%	0.090	H + O ₂ + H ₂ O = HO ₂ + H ₂ O (LP)	23.0%	0.062
HNO = H + NO (PLOG02)	20.2%	0.053	H ₂ + OH = H + H ₂ O	23.0%	0.092	NO + H + M = HNO + M (LP)	21.7%	0.058

^aFrequency value: number of data points for which the reaction has $|\bar{s}t_{ij}| \geq 0.1$ normalized by the total number of data points.

^bAverage of the $|\bar{s}t_{ij}|$ values over all included data points for each reaction.

LP: low pressure limit reactions, PLOG: reactions parameterized by PLOG formalism, DUP: DUPLICATE reactions.

KAUST-2021 with the smallest $E_{\text{total}}^{\text{all}}$ value of 11.5 were selected for further model analyses (Table 3). The Shrestha-2021 model has a wet CO submechanism, and it is the best-performing model in the case of NH_3 /syngas fuel mixtures (Table 4); therefore, it was investigated by sensitivity analysis in the case of NH_3 /syngas systems (see Section 4.2.1.2). To compare the important model parameters of the Shrestha-2021 mechanism between the NH_3/H_2 and NH_3 /syngas cases, it was selected as the third model studied by sensitivity analysis in the case of NH_3/H_2 fuel mixtures even though it is not among the three best-performing models for these experiments.

As each of the investigated three mechanisms contains the species He, those experiments were also included in the sensitivity analysis in which the diluent gas is He. Table 5 shows the results of the sensitivity analysis of the kinetic parameters for the three investigated mechanisms. The results are shown separately for ST-IDT, concentration (JSR and FR), and LBV measurements.

In almost all cases, simulation results are most sensitive to reaction $\text{H} + \text{O}_2 = \text{OH} + \text{O}$, which is a major chain-branching step of H_2 oxidation. In laminar burning velocity experiments, this reaction is of particular importance ($|\tilde{s}_{ij}|$ value is around 1.0 for each mechanism). The low-pressure limit of the termolecular, chain termination reaction of hydrogen oxidation, $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$ also has large sensitivity in the case of concentration and LBV measurements. However, its role is less emphasized in Shrestha-2021 than in the other two mechanisms. In the case of LBV measurements, other H/O reactions also appear in the list but with a $|\tilde{s}_{ij}|$ value of less than 0.2: $\text{H}_2 + \text{O} = \text{H} + \text{OH}$ (chain-branching), $\text{H}_2 + \text{OH} = \text{H} + \text{H}_2\text{O}$ (chain propagation).

Other important reactions are contained in the NH_3 oxidation subsets of the mechanisms. Most of these are the reactions of the species NH_3 , NH_2 , and/or NNH . In the initiation step of NH_3 oxidation, reactive H/O radicals consume NH_3 , and a H radical is abstracted by NH_3 to form NH_2 [26]. The most sensitive reaction of this type is $\text{NH}_3 + \text{H} = \text{H}_2 + \text{NH}_2$. Its sensitivity is the largest in the case of ST-IDT experiments. However, in the case of LBV measurements, reactions of NH_3 do not appear in Table 5, which indicates that later phases of NH_3 oxidation are more important for LBV predictions.

NH_2 may react with NO in two possible channels: one forming $\text{NNH} + \text{OH}$, and the other resulting in $\text{N}_2 + \text{H}_2\text{O}$. At least one of these channels appears in the list of most sensitive reactions for all types of experiments for each investigated mechanism. As highlighted in the work of Glarborg et al. [26], model predictions are usually very sensitive to the branching ratio of the two channels in NH_3 oxidation experiments.

The reaction $\text{NH}_2 + \text{HO}_2 = \text{NH}_3 + \text{O}_2$ is present in each of the three mechanisms, although in POLIMI-2020 it is written in the opposite direction, that is, $\text{NH}_3 + \text{O}_2 = \text{NH}_2 + \text{HO}_2$. This reaction shows large sensitivity to the model outputs in the case of ST-IDT and concentration measurements for POLIMI-2020 and KAUST-2021 but not in the case of Shrestha-2021. To study the role of this reaction in more detail, rate-of-production and element flux analyses were applied at some selected representative experimental conditions. Program Optima++ computed the reaction rates and the fluxes for elements H, O, and N, and these fluxes were visualized by program FluxViewer++ [116].

It was found that the reaction is dominant in the initial phase of the overall reaction (when NH_3 and O_2 concentrations are the largest) and it proceeds much faster in the direction $\text{NH}_3 + \text{O}_2 \rightarrow \text{NH}_2 + \text{HO}_2$ than in the opposite way. Fig. 5 shows partial H flux diagrams for two selected initial fuel mixture compositions, 100% NH_3 and 50-50% NH_3/H_2 , respectively. All other experimental conditions are the same in the two cases: $T = 2000 \text{ K}$, $p = 10 \text{ atm}$, $\varphi = 1.0$, and Ar / O_2 ratio equals 28.23. The H fluxes are shown at $t = 0.1\tau_{\text{ign}}$, that is, at the beginning of the reaction. It can be seen in both cases that there is no noticeable H flux between NH_3 and HO_2 in the simulations with Shrestha-2021, while significant H flux can be observed from NH_3 to HO_2 using KAUST-2021. Table 6 lists the five globally fastest reactions along with their relative rates ("Rel. rate") in both experiments for both mechanisms at $t = 0.1\tau_{\text{ign}}$. In each case, the fastest reaction is the consumption of NH_3 by the OH radical (100% relative rate); therefore, the rates of the other reactions are given relative to this reaction. The $\text{NH}_3 + \text{O}_2$ reaction is among the five fastest reactions in the case of KAUST-2021. It is the third and second fastest NH_3 -consuming reaction in the "100% NH_3 " and "50-50% NH_3/H_2 " cases, respectively. The reaction does not appear in the top 5 lists for Shrestha-2021, moreover, its relative rates are less than 1% in both cases (not shown in the table).

Program FluxViewer++ can also prepare videos from a series of flux diagrams during a simulation. Two videos of the same simulations as in Fig. 5 in the time frame $t = 0 - 1.2\tau_{\text{ign}}$ are available as Supplementary files. In those videos, the relative rate of the reaction (in percentages, like in Table 6) and the rank of the reaction according to the reaction rates (in parentheses) are listed next to each reaction equation. The videos show that in the KAUST-2021 model, the $\text{NH}_3 + \text{O}_2$ reaction is relatively fast during the initial phase of the reaction. As the concentrations of NH_3 and O_2 decrease, its relative rate decreases, and between $t = 0.4 - 0.5\tau_{\text{ign}}$, the reaction becomes faster in the opposite direction ($\text{NH}_2 + \text{HO}_2 \rightarrow \text{NH}_3 + \text{O}_2$). However, the relative rate of the opposite

H fluxes between some selected species

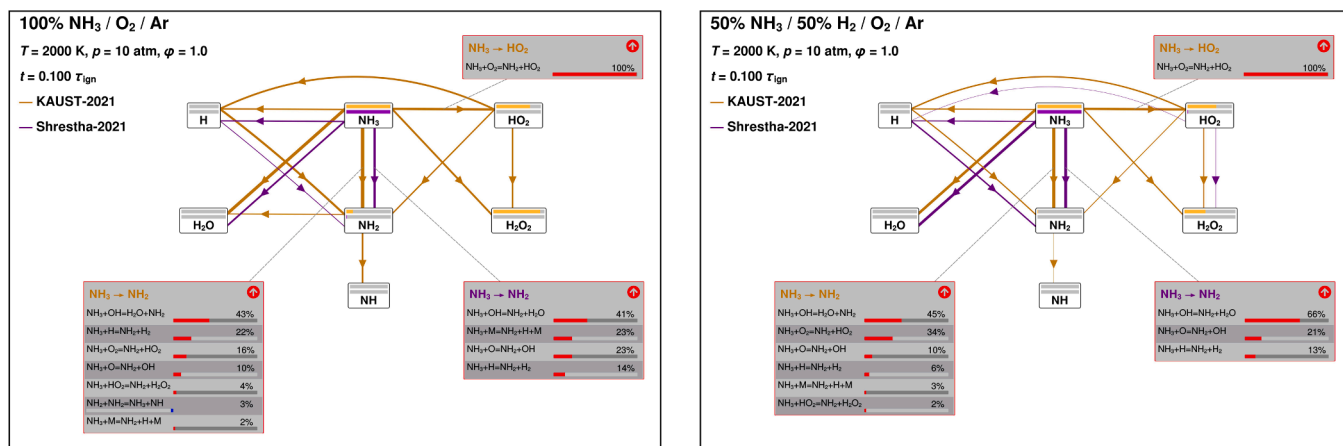


Fig. 5. H flux diagrams for some selected species under two selected experimental conditions at $t = 0.1\tau_{\text{ign}}$ using the KAUST-2021 and Shrestha-2021 mechanisms. The widths of the arrows are proportional to the logarithms of the H fluxes between the corresponding species and the direction of an arrow shows the direction of the corresponding overall flux. The boxes show the reactions that contribute to the corresponding arrow (H flux) along with the percentages indicating their individual contributions.

Table 6

The five globally fastest reactions for the two conditions given in Fig. 5. The $\text{NH}_3 + \text{O}_2 = \text{NH}_2 + \text{HO}_2$ reaction is highlighted in bold.

100% NH_3 / O_2 / Ar				50% NH_3 / 50% H_2 / O_2 / Ar			
KAUST-2021		Shrestha-2021		KAUST-2021		Shrestha-2021	
Reaction	Rel. rate	Reaction	Rel. rate	Reaction	Rel. rate	Reaction	Rel. rate
$\text{NH}_3 + \text{OH} = \text{NH}_2 + \text{H}_2\text{O}$	100%	$\text{NH}_3 + \text{OH} = \text{NH}_2 + \text{H}_2\text{O}$	100%	$\text{NH}_3 + \text{OH} = \text{NH}_2 + \text{H}_2\text{O}$	100%	$\text{NH}_3 + \text{OH} = \text{NH}_2 + \text{H}_2\text{O}$	100%
$\text{NH}_3 + \text{H} = \text{NH}_2 + \text{H}_2$	50%	$\text{NH}_3 + \text{M} = \text{NH}_2 + \text{H} + \text{M}$	56%	$\text{H} + \text{O}_2 = \text{OH} + \text{O}$	100%	$\text{H}_2 + \text{OH} = \text{H} + \text{H}_2\text{O}$	99%
$\text{NH}_3 + \text{O}_2 = \text{NH}_2 + \text{HO}_2$	36%	$\text{NH}_3 + \text{O} = \text{NH}_2 + \text{OH}$	56%	$\text{H}_2 + \text{OH} = \text{H} + \text{H}_2\text{O}$	88%	$\text{H} + \text{O}_2 = \text{OH} + \text{O}$	92%
$\text{NH}_2 + \text{HO}_2 = \text{H}_2\text{NO} + \text{OH}$	32%	$\text{H} + \text{O}_2 = \text{OH} + \text{O}$	40%	$\text{NH}_3 + \text{O}_2 = \text{NH}_2 + \text{HO}_2$	76%	$\text{H}_2 + \text{O} = \text{OH} + \text{H}$	49%
$\text{NH}_3 + \text{O} = \text{NH}_2 + \text{OH}$	23%	$\text{NH}_3 + \text{H} = \text{NH}_2 + \text{H}_2$	35%	$\text{H}_2 + \text{O} = \text{OH} + \text{H}$	59%	$\text{NH}_3 + \text{O} = \text{NH}_2 + \text{OH}$	31%

reaction does not exceed 1% of the rate of the fastest reaction during the simulations. In the Shrestha-2021 model, the rate of the $\text{NH}_3 + \text{O}_2 = \text{NH}_2 + \text{HO}_2$ reaction does not become significant in either direction. Flux diagrams and reaction rates are not shown for POLIMI-2020 for the better visualization of the figures but the observations for that model are similar to those for KAUST-2021.

To identify the reason for the different behavior of Shrestha-2021 relative to the other two models regarding the $\text{NH}_3 + \text{O}_2 = \text{NH}_2 + \text{HO}_2$ reaction, the Arrhenius plots of the corresponding rate coefficients were prepared in the temperature range 500–2500 K (Fig. 6). This temperature range covers the conditions of the experiments investigated in this work (see Table 1). First, it can be observed that the rate coefficients have very strong temperature dependence; they change around 20 orders of magnitude in the investigated temperature interval. Second, the rate coefficients in KAUST-2021 and POLIMI-2020 are 4–6 orders of magnitude larger than that in Shrestha-2021, which explains why these reactions are much faster and more sensitive in the simulations with the former two models.

Other competing reactions of NH_2 include reactions with H/O radicals ($\text{H}/\text{O}/\text{OH}$) and with NH_x species ($x = 1, 2, 3$) [26]. The latter type of reaction may lead to the formation of N_2 -amines such as N_2H_2 and N_2H_3 . Some of these reactions can also be found in Table 5, together with the reaction of NH_2 and molecular oxygen (O_2) forming nitroxide (H_2NO).

In previous publications related to ammonia combustion, sensitivity analysis has been carried out for some selected experimental conditions [16,37,38,41,47,74]. Our comprehensive sensitivity analysis results are in good accordance with those results in the literature obtained for specific sets of experimental data.

4.2.1.2. NH_3 /syngas fuel mixtures. In the case of NH_3 /syngas fuel mixtures, the three best mechanisms, Shrestha-2021, Mei-2021, and Mei-

2020 (Table 4) were selected for the sensitivity analysis.

Table 7 shows the results of sensitivity analysis for the Mei-2020 and Mei-2021 models in the case of the kinetic parameters. The rate parameters of six reactions were updated in Mei-2021 relative to Mei-2020. Among these reactions, the reaction $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ shows large sensitivity to the simulation results, on average, and in the case of concentration measurements, the reaction $\text{NH} + \text{NO} = \text{N}_2\text{O} + \text{H}$ is also among the most sensitive ones. These reactions are highlighted in bold in the table. The results also show that the most important reactions are identical in the two models, which is not surprising given that only a few rate parameters are different in the two mechanisms, but structure of the models is identical.

Reaction $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$, which is the major CO oxidation pathway in the presence of H atoms, is the only sensitive reaction that contains carbonaceous species.

Table 8 summarizes the sensitivity analysis results obtained with the Shrestha-2021 model for NH_3/H_2 and NH_3 /syngas fuel mixtures, respectively. The experimental conditions are similar in the two sets of experimental data. As can be seen in the table, the four most sensitive reactions are identical in the two cases, only their order varies slightly. The most important reaction is $\text{H} + \text{O}_2 = \text{OH} + \text{O}$, followed by three reactions from the NH_3 oxidation submechanism. Besides these reactions, only H/O reactions and the CO oxidation reaction by OH have $|\tilde{s}_{ij}|$ values above 0.1.

Although the Shrestha-2021 model contains reactions in which C-chemistry and N-chemistry are directly coupled, these reactions were found to be unimportant in the case of NH_3/CO oxidation. Hence, the oxidation mechanisms of CO and NH_3 are coupled through the H/O radical pool, but not through direct C/N reactions. These observations agree with sensitivity analysis results in the literature [16–19] obtained for smaller sets of experimental data.

4.2.2. Thermodynamic parameters

4.2.2.1. NH_3/H_2 fuel mixtures. Table 9 shows the overall results of the sensitivity analysis of thermodynamic parameters for the three investigated mechanisms for LBV measurements. Results for the 0D experiments (ST-IDT, JSR, FR) are shown in the Supplementary Material (Table A12).

In these experiments, H_2 and H have very large sensitivities in all cases. N_2 is the diluent gas in almost all LBV experiments. The results indicate that the simulation results are relatively sensitive to the constant pressure heat capacity and enthalpy of formation of N_2 , but N_2 is not among the ten most sensitive species in the case of entropies for any of the mechanisms. We note that the enthalpy of formation of N_2 is zero at 298.15 K by definition, and the temperature dependence of its constant pressure heat capacity is known with low uncertainty. The thermodynamic data of H_2O also show relatively large sensitivity, although H_2O is not present in any of the initial gas mixtures. It is not surprising that the simulation results are relatively sensitive to the thermodynamic data of NH_3 , NH_2 , H, O, and OH in each investigated mechanism.

4.2.2.2. NH_3 /syngas fuel mixtures. Results can be found in Table 10 for the standard enthalpies of formation in the case of LBV measurements.

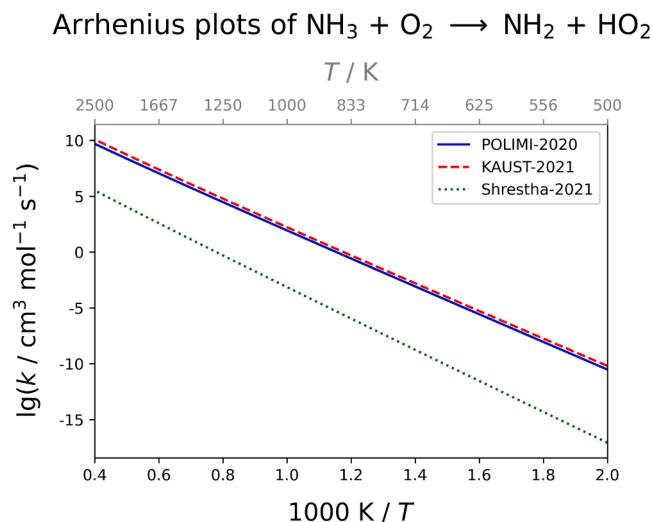


Fig. 6. Arrhenius plots of the rate coefficients of the reaction $\text{NH}_3 + \text{O}_2 \rightarrow \text{NH}_2 + \text{HO}_2$ in the POLIMI-2020, KAUST-2021, and Shrestha-2021 models in the temperature range 500–2500 K.

Table 7

Comparison of the overall sensitivity analysis results of the chemical kinetic parameters (preexponential factors, A) for experiments with NH₃/syngas fuel mixtures with the Mei-2020 and Mei-2021 mechanisms. The 10-10 most sensitive reactions are for concentration (JSR and FR) and laminar burning velocity (LBV) measurements. Reactions whose rate parameters were changed in Mei-2021 relative to Mei-2020 are highlighted in bold.

Mei-2021			Mei-2020		
Reaction	Freq. ^a	$ \bar{s}\tilde{n}_{ij} ^b$	Reaction	Freq. ^a	$ \bar{s}\tilde{n}_{ij} ^b$
Concentration measurements (JSR and FR): 202 investigated data points					
H + O ₂ + M = HO ₂ + M (LP)	92.1%	0.590	H + O ₂ + M = HO ₂ + M (LP)	92.6%	0.601
H + O₂ = OH + O	76.2%	0.397	H + O₂ = OH + O	77.7%	0.427
NH ₂ + NO = N ₂ + H ₂ O (DUP1)	73.3%	0.425	NH ₂ + NO = N ₂ + H ₂ O (DUP1)	71.3%	0.405
NH + NO = N₂O + H (DUP1)	53.0%	0.350	NH + NO = N₂O + H	52.5%	0.302
NH ₂ + NO = N ₂ + H ₂ O (DUP2)	48.0%	0.149	NH ₂ + NO = N ₂ + H ₂ O (DUP2)	49.0%	0.140
NO + O + M = NO ₂ + M (LP)	48.0%	0.138	NH ₂ + NO = NNH + OH	46.5%	0.132
NH ₂ + NO = NNH + OH	47.5%	0.143	CO + OH = CO ₂ + H	42.6%	0.252
CO + OH = CO ₂ + H	41.1%	0.273	NO + O + M = NO ₂ + M (LP)	40.6%	0.104
NH + O = NO + H	39.1%	0.099	NH + O = NO + H	38.6%	0.118
NH + NO = N₂O + H (DUP2)	37.6%	0.092	NH ₂ + OH = NH + H ₂ O	34.2%	0.112
LBV measurements: 874 investigated data points					
H + O₂ = OH + O	100.0%	0.956	H + O₂ = OH + O	100.0%	0.957
H + O ₂ + M = HO ₂ + M (LP)	91.9%	0.218	H + O ₂ + M = HO ₂ + M (LP)	91.2%	0.211
NH ₂ + NO = NNH + OH	89.5%	0.201	NH ₂ + NH = N ₂ H ₂ + H	85.6%	0.233
NH ₂ + NH = N ₂ H ₂ + H	81.8%	0.209	NH ₂ + NH = N ₂ H ₂	81.6%	0.190
NH ₂ + NH = N ₂ H ₂	78.0%	0.164	NH ₂ + NO = NNH + OH	79.5%	0.162
CO + OH = CO ₂ + H	70.6%	0.312	CO + OH = CO ₂ + H	70.6%	0.311
H ₂ + O = H + OH	43.0%	0.105	H ₂ + O = H + OH	38.1%	0.099
NH ₂ + NO = N ₂ + H ₂ O (DUP1)	40.4%	0.102	NH ₂ + OH = NH + H ₂ O	36.2%	0.089
NH ₂ + OH = NH + H ₂ O	32.7%	0.081	NH ₂ + NO = N ₂ + H ₂ O (DUP1)	25.6%	0.076
H ₂ + OH = H ₂ O + H	24.7%	0.082	H ₂ + OH = H ₂ O + H	24.3%	0.081

^a: Number of data points for which the reaction has $|\bar{s}\tilde{n}_{ij}| \geq 0.1$ normalized by the total number of data points.

^b: Average of the $|\bar{s}\tilde{n}_{ij}|$ values over all included data points for each reaction.

LP: low pressure limit reactions, DUP: DUPLICATE reactions.

The results for the other thermodynamic properties (heat capacity, entropy) and those for the zero-dimensional experiments are summarized in the Supplementary Material (Tables A13 and A14, respectively).

Simulation results are relatively sensitive to the thermochemical data of CO and CO₂ in each mechanism, which data are known with low uncertainty. Other than that, the trends are similar to those in the case of NH₃/H₂ fuel mixtures.

Note that the thermochemical data in Mei-2021 and Mei-2020 are identical, and the data of almost all species are from the Glarborg-2018 model [26]. Exceptions are the parameters of HNO and NH₂ whose thermodynamic parameters were recalculated by the authors of

Mei-2020 [19] using quantum chemistry tools because they found discrepancies between the data from different sources, and they included the recalculated results in both Mei-2020 and Mei-2021. Consequently, it is not surprising that the sensitivity analysis results for Mei-2020 and Mei-2021 are very similar.

5. Conclusions

A comprehensive quantitative comparison of 18 detailed reaction mechanisms was performed using a large amount of experimental data for the combustion of NH₃/H₂ fuel mixtures including shock tube

Table 8

Comparison of the sensitivity analysis results of the chemical kinetic parameters (preexponential factors, A) of the Shrestha-2021 mechanism for NH₃/H₂ and NH₃/syngas laminar burning velocity (LBV) measurements. The 10-10 most sensitive reactions are shown for both cases.

Shrestha-2021 (NH ₃ /H ₂)			Shrestha-2021 (NH ₃ /syngas)		
LBV measurements: 834 investigated data points			LBV measurements: 874 investigated data points		
T = 298–476 K p = 0.50–10.00 atm φ = 0.40–1.80			T = 298–443 K p = 1.00–10.00 atm φ = 0.70–1.70		
Reaction	Freq. ^a	$ \bar{s}\tilde{n}_{ij} ^b$	Reaction	Freq. ^a	$ \bar{s}\tilde{n}_{ij} ^b$
H + O ₂ = OH + O	99.8%	0.995	H + O ₂ = OH + O	99.9%	0.977
NNH = N ₂ + H	74.3%	0.179	NH ₂ + NO = NNH + OH	77.6%	0.139
NNH + O ₂ = N ₂ + HO ₂	68.1%	0.160	NNH = N ₂ + H	74.1%	0.185
NH ₂ + NO = NNH + OH	64.0%	0.140	NNH + O ₂ = N ₂ + HO ₂	71.2%	0.167
H ₂ + OH = H + H ₂ O	50.5%	0.123	H + O ₂ + H ₂ O = HO ₂ + H ₂ O (LP)	57.2%	0.120
N ₂ H ₂ + H = NNH + H ₂	41.4%	0.076	CO + OH = CO ₂ + H (DUP3)	51.0%	0.202
N ₂ H ₂ + M = NNH + H + M	39.8%	0.079	H + OH + M = H ₂ O + M	50.0%	0.099
NH ₂ + NH = N ₂ H ₂ + H	32.5%	0.078	NH ₂ + NH = N ₂ H ₂ + H	45.7%	0.085
H + O ₂ + H ₂ O = HO ₂ + H ₂ O (LP)	23.0%	0.062	OH + H ₂ = H + H ₂ O	29.6%	0.092
NO + H + M = HNO + M (LP)	21.7%	0.058	H ₂ + O = H + OH (DUP2)	25.5%	0.082

^a: Number of data points for which the reaction has $|\bar{s}\tilde{n}_{ij}| \geq 0.1$ normalized by the total number of data points.

^b: Average of the $|\bar{s}\tilde{n}_{ij}|$ values over all included data points for each reaction.

LP: low pressure limit reactions, DUP: DUPLICATE reactions.

Table 9

Comparison of the overall sensitivity analysis results of the thermodynamic data for laminar burning velocity (LBV) experiments with NH_3/H_2 fuel mixtures. The 10-10 most sensitive species of the three investigated mechanisms are shown for each thermodynamic property separately.

LBV measurements								
POLIMI-2020			KAUST-2021			Shrestha-2021		
835 investigated data points			834 investigated data points			834 investigated data points		
Species	Freq. ^a	$ \widetilde{sn}_{ij} ^b$	Species	Freq. ^a	$ \widetilde{sn}_{ij} ^b$	Species	Freq. ^a	$ \widetilde{sn}_{ij} ^b$
Constant-pressure standard molar heat capacity at 300 K								
H ₂	100.0%	0.994	H ₂	100.0%	0.984	H ₂	99.8%	0.965
H	99.8%	0.807	H	99.6%	0.891	H	99.5%	0.850
OH	94.0%	0.305	N ₂	92.2%	0.293	N ₂	93.0%	0.308
N ₂	92.3%	0.294	NH ₃	80.9%	0.284	H ₂ O	85.0%	0.332
H ₂ O	87.8%	0.330	NH ₂	77.8%	0.236	NH ₃	84.4%	0.370
NH ₃	81.8%	0.290	OH	51.4%	0.199	NH ₂	81.4%	0.335
NH ₂	78.0%	0.231	O	46.9%	0.108	HO ₂	76.6%	0.259
O ₂	38.7%	0.124	H ₂ O	46.6%	0.127	OH	72.2%	0.193
O	7.4%	0.039	NH	33.5%	0.074	HNO	60.3%	0.157
HO ₂	3.5%	0.032	O ₂	23.1%	0.081	NO	52.6%	0.136
Standard enthalpy of formation at 300 K ($\widetilde{ssn}_{ij}$ values instead of $\widetilde{sn}_{ij}$ values)								
H ₂ O	100.0%	0.920	H ₂ O	100.0%	0.818	H ₂ O	99.8%	0.957
H ₂	100.0%	0.744	H ₂	100.0%	0.766	H ₂	99.8%	0.722
O ₂	100.0%	0.413	O ₂	100.0%	0.394	O ₂	99.8%	0.343
H	99.8%	0.835	H	99.8%	0.939	H	99.4%	0.825
N ₂	94.0%	0.191	N ₂	92.8%	0.205	N ₂	95.2%	0.205
OH	84.0%	0.193	NH ₃	82.1%	0.298	NH ₃	81.9%	0.247
NH ₃	83.2%	0.284	NH ₂	71.2%	0.189	NH ₂	70.5%	0.241
NH ₂	71.1%	0.188	O	45.9%	0.102	HO ₂	68.0%	0.136
O	5.6%	0.040	OH	38.5%	0.138	OH	53.8%	0.126
NH	0.1%	0.026	NH	18.2%	0.056	NO	40.5%	0.089
Standard molar entropy at 300 K								
H ₂	100.0%	0.949	H ₂	100.0%	0.876	H ₂	99.8%	0.875
H	99.8%	0.953	H	99.6%	0.977	H	99.5%	0.938
H ₂ O	99.5%	0.601	H ₂ O	90.8%	0.270	H ₂ O	96.9%	0.572
OH	96.2%	0.387	NH ₃	81.8%	0.328	NH ₃	84.8%	0.412
NH ₃	88.1%	0.352	NH ₂	81.3%	0.286	NH ₂	84.4%	0.401
NH ₂	85.0%	0.298	O	65.8%	0.156	HO ₂	83.6%	0.331
O ₂	47.9%	0.169	OH	56.8%	0.233	OH	75.3%	0.237
O	17.6%	0.063	NH	46.6%	0.097	HNO	71.8%	0.195
NH	10.3%	0.050	O ₂	25.8%	0.102	NO	66.3%	0.184
HO ₂	7.4%	0.046	NaH ₃	11.6%	0.045	O	50.8%	0.118

^a: Number of data points for which the thermodynamic property has $|\widetilde{sn}_{ij}| \geq 0.1$ or $|\widetilde{ssn}_{ij}| \geq 0.1$ ^c normalized by the total number of data points.

^b: Average of the $|\widetilde{sn}_{ij}|$ or $|\widetilde{ssn}_{ij}|$ ^c values over all included data points for each thermodynamic property.

^c: Refer to Kovács et al. [92] for the definition of the $\widetilde{ssn}_{ij}$ values (scaled semi-normalized sensitivity coefficients).

Table 10

Comparison of the overall sensitivity analysis results of the thermodynamic data for laminar burning velocity (LBV) experiments with $\text{NH}_3/\text{syngas}$ fuel mixtures (874 investigated data points). The 10-10 most sensitive species of the three investigated mechanisms are shown for the standard enthalpies of formation.

LBV measurements: 874 investigated data points								
Mei-2021			Mei-2020			Shrestha-2021		
Species	Freq. ^a	$ \widetilde{ssn}_{ij} ^b$	Species	Freq. ^a	$ \widetilde{ssn}_{ij} ^b$	Species	Freq. ^a	$ \widetilde{ssn}_{ij} ^b$
Standard enthalpy of formation at 300 K								
O ₂	100.0%	0.542	O ₂	100.0%	0.574	O ₂	96.1%	0.487
H	96.8%	0.853	H	96.2%	0.848	H	91.5%	0.791
H ₂ O	92.7%	0.468	H ₂ O	93.5%	0.500	H ₂	91.2%	0.527
NH ₃	92.0%	0.370	NH ₃	93.4%	0.395	H ₂ O	88.1%	0.554
H ₂	91.9%	0.417	H ₂	92.4%	0.434	CO	85.9%	0.457
CO ₂	89.4%	0.424	CO ₂	89.2%	0.447	CO ₂	85.7%	0.461
CO	89.4%	0.420	CO	89.2%	0.442	N ₂	81.1%	0.161
N ₂	82.4%	0.158	N ₂	83.1%	0.166	NH ₃	77.8%	0.192
OH	66.2%	0.435	OH	70.8%	0.436	OH	71.6%	0.355
NH ₂	53.5%	0.144	HNO	65.9%	0.126	NH ₂	58.8%	0.182

^aNumber of data points for which the thermodynamic property has $|\widetilde{ssn}_{ij}| \geq 0.1$ ^c normalized by the total number of data points.

^bAverage of the ^c values over all included data points for each thermodynamic property.

^cRefer to Kovács et al. [92] for the definition of the $\widetilde{ssn}_{ij}$ values (scaled semi-normalized sensitivity coefficients).

ignition delay time measurements, concentration measurements in jet stirred and flow reactors, and laminar burning velocity measurements. The investigated data collection contained 3770 data points in 350 data series. The same investigations were performed with 13 reaction mechanisms in the combustion of NH_3 /syngas fuel mixtures (1128 data points in 122 data series). The data were encoded in RKD format XML files. Framework code Optima++ read the data files, organized the simulations, and processed the results. The simulations were performed with the OpenSMOKE++ program package.

In the case of NH_3/H_2 fuel mixtures, the POLIMI-2020, Han-2020, and KAUST-2021 models have the best performance, but even these mechanisms cannot reproduce the experimental data within their 3σ uncertainty limits, on average. In the case of NH_3 /syngas fuel mixtures, the same is true for the three best-performing mechanisms, Shrestha-2021, Mei-2021, and Mei-2020. For the same collection of data, the performances of the investigated mechanisms are very different. For the NH_3/H_2 fuel mixtures, the best-performing model, POLIMI-2020, has an averaged E value of 12.8 (between the 3σ and 4σ average uncertainties), while for the worst model, it is 50.1 (beyond the 7σ average uncertainty). It was also found that the performances of the investigated mechanisms are usually very different for different types of experiments. For example, the KAUST-2021 mechanism can reproduce the flow reactor experiments very well ($E = 5.0$), but its performance is much worse for the ignition delay times measured in shock tubes ($E = 26.6$). These results highlight the need for the cross-analysis of the mechanisms via sensitivity analysis to identify the sources of these deviations.

Local sensitivity analysis was carried out on the kinetic and thermodynamic parameters of the best-performing mechanisms. In the absence of CO, simulation results are most sensitive to the chain-branching step of H_2 oxidation, $\text{H} + \text{O}_2 = \text{OH} + \text{O}$. The chain termination reaction of hydrogen oxidation, $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$ also has large sensitivity in the majority of experiments. Other important reactions are contained in the NH_3 oxidation subsets of the mechanisms. Most of these are the reactions of the species NH_3 , NH_2 , and/or NNH . The most important reactions and thermodynamic properties were similar in all reaction mechanisms investigated by sensitivity analysis. The most sensitive thermodynamic properties belong to the H/O radical species (H , O , OH , HO_2), NH_3 , NH_2 , O_2 , and H_2 . In the case of NH_3 /syngas fuel mixtures, the major CO oxidation reaction, $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$ also shows relatively large sensitivity to the simulation results. The same is true for the thermochemical data of CO and CO_2 . Reactions in which C-chemistry and N-chemistry are directly coupled were found to be unimportant by the investigation of the Shrestha-2021 model. Hence, the oxidation mechanisms of CO and NH_3 are coupled through the H/O radical pool but not through direct C/N reactions. These observations are in agreement with the literature results obtained for smaller sets of experimental data. The authors believe that the results presented in this work will facilitate further mechanism development for neat NH_3 , NH_3/H_2 , and NH_3 /syngas combustion systems.

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Supplementary Material

The Supplementary Material document has the following content: (1) supplementary information about the utilized experimental data in a tabulated form; (2) discussion of experimental data on NH_3/H_2 and NH_3 /syngas oxidation not investigated in this study and justification for their exclusion; (3) discussion of the simulation of the investigated ST-IDT experiments; (4) discussion of the estimation of the standard deviation for different kinds of experimental data; (5) supplementary

information about the investigated mechanisms; (6) quantitative comparison of the performance of the investigated mechanisms including the experiments containing He; (7) sensitivity analysis results not shown in the main paper.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All data used are available in the ReSpecTh.hu web site.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.jaecs.2023.100127](https://doi.org/10.1016/j.jaecs.2023.100127).

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