Testing of NH_3/CH_3OH combustion mechanisms based on a large amount of experimental data

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Abstract

Ammonia (NH_3) is an attractive carbon-free fuel. Ammonia must be blended with other fuels, such as H_2 or organic compounds, to improve its combustion properties. Among these, methanol (CH_3OH) has become a popular additive for ammonia combustion due to its high reactivity and being a renewable fuel. This work aims to quantitatively evaluate the performance of detailed NH_3/CH_3OH combustion mechanisms using a comprehensive experimental data set. In our study, a large set of literature experimental data (2552 data points in 160 data series) on NH_3/CH_3OH combustion covering a wide range of conditions has been collected: ignition delay times measured in shock tubes and rapid compression machines, species concentration measurements carried out in jet-stirred reactors and flow reactors. The in-house developed Optima++ framework code was used to test the collected NH_3/CH_3OH combustion mechanisms. The performances of these combustion mechanisms were assessed based on an error function, which also considers the standard deviations (σ) of the experimental data. Mechanism Yin2024 was found to be the best-performing mechanism based on our experimental data collection.

Keywords: Carbon-free fuel; Ammonia/methanol; Combustion mechanism; Mechanism comparison

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1. Introduction

Global mobility has been substantially increased by the fast-paced globalization and the development of transportation technologies. Unfortunately, these developments have also made the transportation sector one of the biggest contributors to carbon emissions worldwide, worsening urban air quality and accelerating climate change. The need to find and use alternative fuels that can lessen the environmental impact of transportation is growing as the world shifts to a low-carbon economy. Because of its potential to aid in the decarbonization of the energy and transportation sectors, ammonia (NH_3) has received significant attention as a carbon-free fuel among the promising alternatives [1].

Ammonia is an efficient fuel with high energy density and knock resistance. However, its low reactivity causes slow combustion and harmful emissions. Its high auto-ignition temperature leads to incomplete combustion and NOx formation [2]. Methanol, a reactive and renewable fuel, enhances ammonia ignition and combustion properties [3]. Their blend improves efficiency and reduces emissions, making a more sustainable fuel solution.

Recently, several ammonia/methanol mechanisms have been proposed. However, these models were validated only against ammonia/methanol combustion experiments in a restricted range of experimental facilities or under narrow condition ranges. To compare the performances of these mechanisms accurately, a quantitative evaluation based on different experimental types is necessary.

In the present study, the performances of five ammonia/methanol mechanisms were investigated by using the experimental data from a large set of ammonia/methanol measurements.

2. Experimental data collection

A large set of experimental data on ammonia/methanol combustion has been collected. The so-called indirect measurements are widely used for testing, validating and optimizing combustion mechanisms. In the data collection of this study, ignition delay time measurements were carried out in shock tubes (IDT-ST) and rapid compression machines (IDT-RCM). Concentrations of species were measured in jet-stirred reactors (JSR) and flow reactors (FR). Table 1 shows the initial conditions for the collected data points according to different experimental types.

In total, 2552 data points in 160 dataseries were stored in 55 XML files using the ReSpecTh Kinetics Data (RKD) Format Specification v2.5 [4]. A "data series" contains those data points that were measured in the same apparatus in one experiment at similar conditions except for one that was systematically changed. An RKD-format data file contains all information required for the proper simulation of the experiments, including measured values and experimental conditions, which involves the exact ignition criteria for ignition delay time simulations, the volume of the experimental setup for JSR simulations, volume-time history profiles for IDT-RCM simulations, temperature profiles for FR simulations.

3. Methodology

All simulations were carried out with in-house developed Optima++ framework code [5], using the Cantera [6] and OpenSmoke++ [7] simulation packages. IDT-ST, IDT-RCM and JSR simulations were conducted with Cantera, while FR simulations were carried out using OpenSmoke++.

A systematical method [8] of assessments of the performance of combustion mechanisms was used in the present study. The method utilizes mean squared error *E*, which is defined as:

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

Here, N is the number of data series and N_i is the number of included data points in the i-th data series. Values Y_{ij}^{exp} and $\sigma\left(Y_{ij}^{\mathrm{exp}}\right)$ are the j-th data point and its estimated standard deviation, respectively, in the i-th data series. Value Y_{ij}^{sim} is the corresponding simulated result. If the experimental data is characterized by absolute error, then $Y_{ij} = y_{ij}$ was taken in Equation (1) for both the experimental data and the corresponding simulated results. We applied this method for concentration profile measurements. If, however, a relative error belongs to the data point, $Y_{ij} = \ln y_{ij}$ was taken. This option was used for ignition delay time measurements.

The computed mean squared error E given in Equation (1) is a suitable quantitative measure to evaluate the performance of a mechanism. Note that $E < 9$ means that the experimental data can be reproduced by the mechanism on average within three times of estimated standard deviation, and we consider it as a general indicator of the goodness for a mechanism.

4. The investigated mechanisms

The investigated mechanisms include Kaust2023[10], SJTU2024 [11], Yin2024 [9], Li2022 [12], and DUT2024 [13]. Mechanism Kaust2023 was proposed for the oxidation of NH_3/C1 fuel mixtures, including syngas, methanol and methane. Mechanisms DUT2024, Li2022 and Yin2024 were developed specifically for NH_3/methanol combustion. Additionally, SJTU2024, a kinetic model for the oxidation of NH_3, NH_3/H_2 and NH_3/CH_4, was also tested here.

Table 1. Summary of the experimental data on NH_3/methanol combustion sorted according to experiment types

EXP. type	T / K	p / atm	φ	Methanol % in fuel	Nr. data series	Nr. of data points	Reference
IDT-ST	1058-1980	1.3-13	0.5-2	0-4.1%	27	188	[15][16]
IDT-RCM	835-1100	19.7,39.5	0.5-2	0-5.7%	15	352	[12]
JSR	705-1215	1	0.5	0.19%-1.25%	41	934	[17]
FR	650-1250	49.35	0.1-0.7	0-5.7%	77	1078	[9][18]

Table 2. Mean squared errors of the investigated mechanisms

Mechanisms ID	Species	Reactions	Ref.	E_{IDT-ST}	$E_{IDT-RCM}$	E_{JSR}	E_{FR}	$E_{average}$
Yin2024	199	1288	[9]	15.4	13.0	56.2	10.9	23.9
SJTU2024	180	1409	[11]	7.8	20.0	51.7	25.4	26.2
Li2022	264	1801	[12]	11.2	25.4	51.5	24.9	28.3
Kaust2023	152	1388	[10]	12.7	102.2	55.5	27.7	49.5
DUT2024	60	400	[13]	28.8	96.1	71.3	34.1	57.6
Included data points/ data series				152/25	338/14	770/40	1041/77	2301/156
All data points/ data series				188/27	352/15	934/41	1078/77	2552/160

5. Discussion

Table 2 lists the number of species and reactions of the mechanisms and also shows the mean squared error function values of these models according to different experimental types. In this study, if the E value of a data point is extremely high (larger than 900 (30σ)) for any of the mechanisms, then we excluded the data point from the error calculation.

$E_{average}$ is the average of the type-specific errors. Mechanism Yin2024 is the best-performing model based on the filtered experimental dataset. Mechanism SJTU2024 is the best-performing mechanism for IDT-ST measurements with the E_{IDT} = 7.8, while Yin2024 is the best-performing mechanism for both IDT-RCM and FR measurements.

Figure 1 shows the percentages of the data points that were reproduced by the mechanisms within given multiples of experimental standard deviation. The mechanisms were ordered according to the decreasing percentage of the data points within 3 σ. The best-performing mechanism Yin2024 reproduced around 72% of data points with E < 9 (3 σ) and 16% of data points with E > 25 (3 σ).

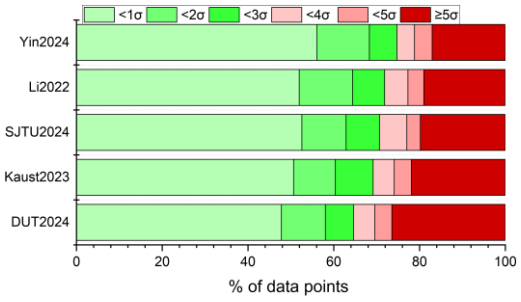

Figure 1. Stacked bar plot of the data points that were reproduced within given multiples of experimental standard deviations

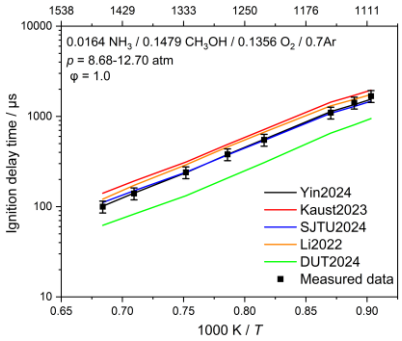

Figure 2. Ignition delay time measurements by Li et al. [15] in a shock tube.

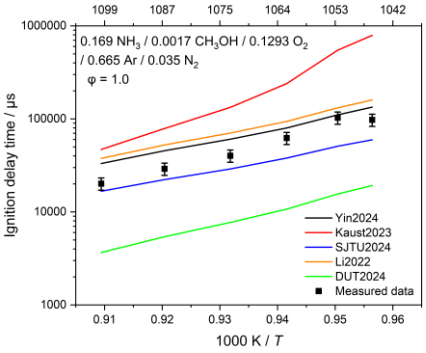

Figure 3. Ignition delay time measurements by Li et al. [12] in a rapid compression machine.

Figure 2 shows the simulation results of the mechanisms for a selected IDT-ST data series. Mechanisms SJTU2024 and Yin2024 reproduced the experimental data series well, while DUT2024 significantly underpredicted them in the whole temperature range.

For a selected IDT-RCM data series, there is a major disagreement for all the mechanisms, as shown in Figure 3. Kaust2023 significantly overpredicts

ignition delay times, while DUT2024 underpredicts them between 1032 K and 1100 K.

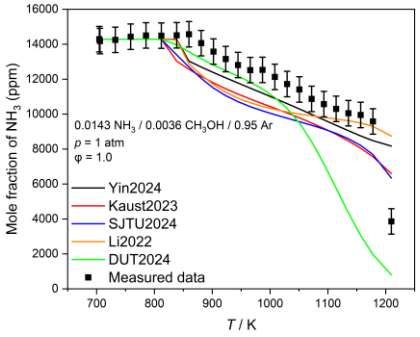

Figure 4. Simulation results of concentration profiles of NH_3 measured in a jet-stirred reactor by He et al. [17].

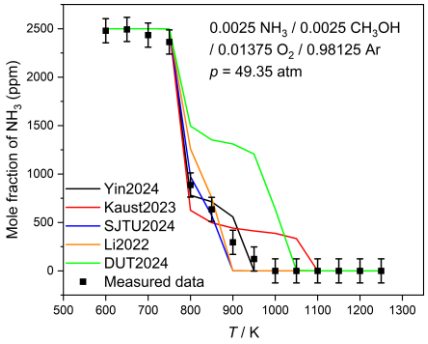

Figure 5. Simulation results of concentration profiles of NH_3 measured in a flow reactor by Yin2024 [9].

Figures 4 and 5 show the simulation results of the mechanisms for the concentration profiles of NH_3 measured in a jet-stirred reactor by He et al. [17] and a flow reactor by Yin2024 [9], respectively. For the JSR simulations, all the models underpredict the experimental data in the whole temperature range. DUT2024 largely underpredicts the JSR data between 1000 and 1200 K. For the case of FR measurements, the SJTU2024 mechanism well reproduced the measured NH_3 concentrations.

6. Conclusion

A large set of literature experimental data covering wide ranges of conditions on NH_3/CH_3OH combustion was collected: ignition delay times measured in shock tubes (188 data points in 27 data series) and rapid compression machines (352/15) and concentration measurements carried out in jet-stirred reactors (934/41) and flow reactors (1078/77). Five detailed reaction mechanisms were investigated using the collected experimental data. The simulation results of the mechanisms for several selected experimental data series were shown. The results show that Yin2024 is the best-performing mechanism based on the experimental data collection. Local sensitivity analysis for this model will be carried out in the future to identify the most important reactions on NH_3/methanol combustion.

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.

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