



Testing of Reaction Mechanisms for the Combustion of NH₃/H₂ Mixtures Using a Large Amount of Experimental Data

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Introduction

- Ammonia (NH₃) is a promising circular carbon-free fuel** because it can be used in a sustainable and recyclable loop for energy production.
- However, it has some unfavorable combustion properties; therefore, **it is usually blended with other fuels** in practical applications. One of the most often used co-fuels is hydrogen (H₂).
- Accurate chemical kinetic models are needed that can describe the combustion of fuel mixtures containing NH₃ under typical conditions of industrial applications.
- In this work **we compare the performance of 18 recently published reaction mechanisms against a large amount of experimental data on the combustion of NH₃/H₂ fuel mixtures.**

Experimental data and simulations

- Experimental data were utilized from **31 publications** from the literature:

Exp. type ^a	XML/Ds./Dp. ^b	T / K	p / atm	φ
ST-IDT ^c	26/26/200	1022–2489	1.01–41.65	0.50–2.00
JSR ^d	32/113/1651	500–1452	1.00–1.20	0.01–1.50
FR ^e	24/89/1141	451–1973	1.00–98.69	0.00–2.44
LBV ^f	129/129/850	298–476 ^g	0.50–10.00	0.40–1.80
Overall:	211/357/3842			

^a: Type of experiment

^b: Number of XML data files/datasets/data points

^c: Shock tube ignition delay time measurements

^d: Concentration measurements in jet stirred reactors

^e: Concentration measurements in flow reactors

^f: Laminar burning velocity measurements

^g: Cold side temperatures of the flames

1 Experimental data were encoded in **ReSpecTh Kinetics Data (RKD) 2.3 format XML files [1]**.

2 Program **Optima++ [2]** reads the XML data file, sets up the simulation environment and calls the **OpenSMOKE++ [3]** simulation code to carry out the simulation.

3 All simulations were carried out with OpenSMOKE++ [3] using a **0D (ST-IDT, JSR, FR) or a 1D model (LBV)**.

Error function

- Quantitative assessment of mechanism performance** based on the evaluation of an **averaged error function**:

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

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

○ N_{XML} : Number of XML data files

○ N : Number of datasets

○ N_i : number of data points in the i -th dataset

○ N_{ds} : Number of datasets in the XML of the i -th dataset

○ y_{ij}^{exp} : measured value of the j -th experimental data point in the i -th dataset

○ y_{ij}^{sim} : simulation result for the j -th experimental data point in the i -th dataset

○ $\sigma(Y_{ij}^{\text{exp}})$: standard deviation of y_{ij}^{exp}

$E = 9 \rightarrow 3\sigma$ error on average

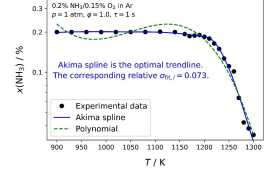
Estimation of the standard deviation of experimental data

- To estimate $\sigma(Y_{ij}^{\text{exp}})$, both the **uncertainty reported by the experimenters** ($\sigma_{\text{exp},ij}$) and the **estimated statistical scatter** of dataset i ($\sigma_{\text{fit},i}$) were considered as follows:

$$\sigma(Y_{ij}^{\text{exp}}) = \sqrt{\sigma_{\text{fit},i}^2 + \sigma_{\text{exp},ij}^2}$$

- $\sigma_{\text{fit},i}$ was obtained by **fitting a trendline** (spline or polynomial function) to the data points of the i -th dataset.

- To find the optimal trendline and the corresponding $\sigma_{\text{fit},i}$, code **Minimal Spline Fit [4]** was used:



Experimental data: Osipova et al. [5] JSR measurements

Reaction mechanisms investigated

Mechanism ID	Species	Reactions	Ref.
Tian-2009	31	191	[6]
Mathieu-2015	33	159	[7]
GDFKin-2016	22	124	[8]
Nakamura-2017	34	229	[9]
SanDiego-2018 ^a	21	64	[10]
Otomo-2018	32	213	[11]
Glarborg-2018	34	221	[12]
Okafor-2018	25	101	[13]
POLIMI-2020 ^b	31	203	[14]
NUIG-2020 ^c	37	231	[15]
Han-2020	32	163	[16]
Mei-2020	34	237	[17]
Konnov-2021	36	295	[18]
KAUST-2021	34	262	[19]
Shrestha-2021	33	262	[20]
Mei-2021	35	239	[21]
Zhou-2021	32	187	[22]
Gotama-2022	32	165	[23]

^a: 2016/12/14 hydrocarbon + 2018/07/23 nitrogen chemistry mechanisms

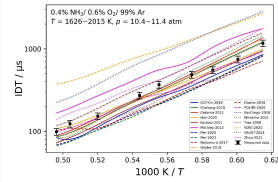
^b: NH₃ mechanism (Version 2003, March 2020)

^c: The detailed kinetic mechanism of the authors

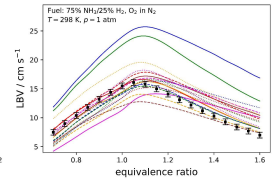
Visual mechanism comparison

- The investigated models have very different performances. Selected examples:

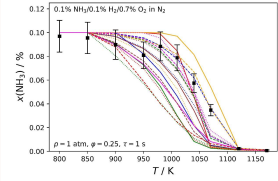
ST-IDT measurement by Mathieu et al. [7]



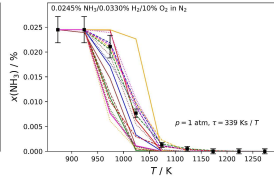
LBV measurement by Han et al. [24]



JSR measurement by Zhang et al. [19]



FR measurement by Wargadalam et al. [25]



A quantitative method is needed to assess the goodness of mechanisms on a large set of data.

Quantitative mechanism comparison

- Comparison of the investigated mechanisms by computing their averaged error function values for each type of experiment ($E_{\text{ST-IDT}}$, E_{JSR} , E_{FR} , and E_{LBV}) and all experimental data (E_{average})

- Smaller E value $\rightarrow$ better mechanism performance**

E :	< 4	< 9	< 16	< 25	< 36	< 49	< 100
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Mechanism ID	$E_{\text{ST-IDT}}$	E_{JSR}	E_{FR}	E_{LBV}	E_{average}	Failed simulations
KAUST-2021	17.52	5.12	2.91	6.88	8.11	32
POLIMI-2020	10.38	8.61	6.86	7.04	8.22	1
Han-2020	11.69	11.35	8.87	5.14	9.26	5
Shrestha-2021	11.21	17.31	6.23	7.29	10.51	10
Gotama-2022	19.29	10.32	8.27	5.35	10.81	110
Otomo-2018	9.52	8.60	6.58	18.70	10.85	2
Tian-2009	9.09	11.56	7.89	14.90	10.86	2
Konnov-2021	10.53	16.61	8.24	8.96	11.08	64
Mei-2021	28.55	5.03	8.96	5.99	12.13	3
Mei-2020	28.55	5.94	9.09	5.23	12.20	1
Mathieu-2015	23.77	9.18	6.51	22.10	15.39	11
NUIG-2020	15.45	15.34	10.45	23.36	16.15	17
Zhou-2021	40.54	8.28	8.43	13.66	17.73	2
Nakamura-2017	26.99	25.83	7.53	11.49	17.96	200
SanDiego-2018	48.44	10.06	10.66	11.08	20.06	2
Glarborg-2018	10.27	13.19	4.71	53.18	20.34	114
Okafor-2018	121.69	11.34	10.91	22.24	41.54	0
GDFKin-2016	28.28	12.80	7.64	127.56	44.07	50

Further mechanism development is necessary!

Sensitivity analysis

- Brute force **local sensitivity analysis** was applied to identify the most important parameters of the best-performing models.
- The sensitivities of the **kinetic parameters** (Arrhenius preexponential factors) of each reaction and the **thermodynamic properties** ($c_p^\ominus$, $\Delta_f H^\ominus$, $S^\ominus$) of each species were investigated.
- Main conclusion:** Although the investigated models have different parameter sets, the most important reactions and thermodynamic properties are similar.
- The **10 most sensitive reactions for ST-IDT experiments** in POLIMI-2020 and KAUST-2021 mechanisms:

POLIMI-2020	KAUST-2021
O ₂ + H = OH + O	O ₂ + H = OH + O
NH ₃ + H = NH ₂ + H ₂	NH ₂ + NO = N ₂ + H ₂ O
NH ₂ + HO ₂ = NH ₃ + O ₂	NH ₂ + NO = NNH + OH
NH ₂ + NO = NNH + OH	NH ₂ + HO ₂ = NH ₃ + O ₂
NH ₂ + NH = N ₂ H ₂ + H	NH ₂ + HO ₂ = H ₂ NO + OH
NH ₂ + O ₂ = H ₂ NO + O	NH ₂ + NO = N ₂ + H ₂ O
NH ₃ + OH = H ₂ O + NH ₂	NH ₃ + H = NH ₂ + H ₂
NH ₂ + NO = N ₂ + H ₂ O	N ₂ H ₂ + M = NNH + H + M
NH ₃ = NH ₂ + H	NH ₃ + NH ₂ = N ₂ H ₃ + H ₂
O + OH + M = HO ₂ + M	N ₂ H ₂ + H = NNH + H ₂

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