Compact kinetic model for the combustion of NH_3/H_2 mixtures

Tibor Nagy[1,*], Ali Alnasif[2,3], András György Szanthoffer[4,5], Máté Papp[4,6], Tamás Turányi[2], Agustin Valera-Medina[2]

[1] Institute of Materials and Environmental Chemistry, HUN-REN Research Centre for Natural Sciences (TTK), Budapest, 1117, Hungary
[2] College of Physical Sciences and Engineering, Cardiff University, Cardiff CF24 3AA, United Kingdom
[3] Engineering Technical College of Al-Najaf, Al-Furat Al-Awsat Technical University, Najaf, 31001, Iraq
[4] Institute of Chemistry, Eötvös University (ELTE), Budapest, 1117, Hungary
[5] Hevesy György PhD School of Chemistry, ELTE Eötvös Loránd University, Budapest, 1117, Hungary
[6] HUN-REN–ELTE Research Group on Complex Chemical Systems, Budapest, 1117, Hungary
* nagy.tibor@ttk.hu

Introduction

- **Ammonia's potential as a zero-carbon fuel and hydrogen carrier** has ignited scientific interest in its application as a fuel in combustion systems**.**
- **However, harnessing ammonia** as a fuel source for energy applications presents **notable challenges due to its low flammability and the potential for high emissions** (Valera-Medina et al., 2018)**.**
- **Blending NH_3 with H_2 presents a prospect for enhancing combustibility, albeit with a notable increase in NOx emissions, particularly in fuel-rich conditions** (Alnasif et al., 2023)**.**
- The **development** of burners, turbines, and engines is **assisted by computational fluid dynamics (CFD)** simulations, which **require small-sized mechanisms**.
- According to a **recent review** of the performance of ammonia combustion mechanisms (Szanthoffer et al., 2023), **the San Diego 2018 mechanism** (University of California**; SD18**), which has an **exceptionally small size (21 species, 64 reactions), shows fair performance** in predicting laminar burning velocities (LBV) and concentration data measured in jet-stirred reactors (JSR) under a wide range of conditions.
- **The current study aims at developing a small and robust combustion kinetic mechanism for CFD simulations of NH_3/H_2 mixtures by optimizing the rate parameters of the San Diego 2018 NH_3 mechanism against LBV data and species concentration data measured in JSRs and in burner-stabilized stagnation flames (BSSF) using the Optima++ code (Turányi et al., 2012; Papp et al., 2024; respecth.hu).**

Experimental Data Collection

- **Large collection of LBV and concentration data measured in JSRs**, which was compiled previously from the literature (Szanthoffer et al, 2023), were downloaded **from the** Reaction Kinetic branch **ReSpecTh database**.
- In addition, **concentration data from burner-stabilized stagnation flames (BSSF)** (Hayakawa et al., 2021), and **recently publish LBV data** were **collected**.
- The data were encoded in ReSpecTh Kinetic Data (RKD) format XML files and will be available in the ReSpecTh database.

Method / Measured Quantity	No. of data series	No. Of data points	H_2 content in fuel mixture (%)	Pressure range (atm)	Tempera-ture range (K)	Equiva-lence ratio
LBV	185	1311	0-100	0.5–10	295-584	0.2–2.0
JSR conc	47	538	10-70	1	800–1300	0.15-1.5
BSSF conc	7	119	30	1	298	0.57–1.4
Overall	239	1968	0-100	0.5-10	295-1300	0.15-2.0

Optimization method

- **FOCTOPUS algorithm** [2] in **code Optima++** [1,3] minimizes the following error function:

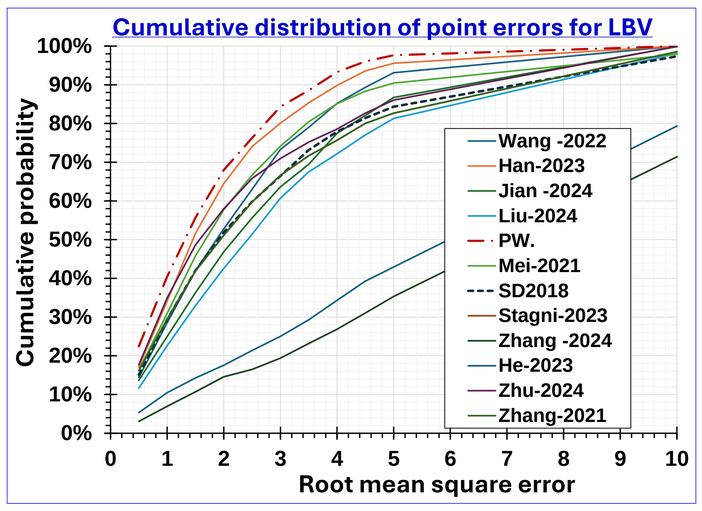
$$E(\mathbf{P}) = \frac{1}{N}\sum_{f=1}^{N_f}\sum_{s=1}^{N_{fs}}\frac{w_{fsd}}{N_{fsd}}\sum_{d=1}^{N_{fsd}}\left(\frac{Y_{fsd}^{\mathrm{sim}}(\mathbf{P}) - Y_{fsd}^{\exp}}{\sigma_{fsd}^{\mathrm{exp,tot}}}\right)^2$$

f,s,d: data file index, data series index, data points index
P: vector of model parameters
N: the total number of the data series
$N_{f/s/d}$: the number of the data files/series/points
$Y_{fsd}^{exp/sim}$: experimental data and simulation result
σ_{fsd}^{exp}: standard deviation of exp. data *d* in data series *s* in data file *f*
w_{fsd} : weigths to equalize an data collection which may contain different number of data series of each experiment type.

- $\sqrt{E}$ measures the RMS deviation between the model and the experimental results, with respect to σ^{exp}. A mechanism is typically considered accurate if $\sqrt{E} < 3$.
- **Weights to balance** the initial errors from differ. exper. types
- **Sensitivity** analysis found **all the 64 rate coefficients important**.
- The **initial model missing important chemistry**, which can be **compensated by unphysical rate coefficients**.
- Thus, **one order of magnitude prior uncertainty range** was employed for parameter tuning .
- For the simulations, we used Cantera 2.6 [4].

Results

Mechanism	$N_{spec}(C_0)$	$N_{Reac}(C_0)$	$\sqrt{E_{LBV}}$	$\sqrt{E_{BSSF}}$	$\sqrt{E_{JSR}}$	$\sqrt{E}$	Ref.
Present work	21	64	1.97	3.24	2.72	2.70	-
Han-2023	32	171	2.24	3.70	1.63	2.67	[6]
Wang-2022	32	140	2.53	10.13	2.64	6.22	[7]
Zhu-2024	39	312	2.97	failed	1.11	failed	[8]
Jian-2024	32	233	3.23	3.79	1.80	3.06	[9]
SanDiego-2018	21	64	3.36	13.94	2.43	8.40	[10]
Zhang-2021	34	224	2.45	4.59	2.78	3.41	[11]
Stagni-2023	31	203	3.46	4.69	1.75	3.51	[12]
Liu-2024	35	238	3.96	5.19	2.39	4.01	[13]
Mei-2021	35	239	4.02	failed	1.65	failed	[14]
He-2023	34	221	7.37	4.45	2.46	5.17	[15]
Zhang-2024	34	224	8.46	4.50	1.14	5.57	[16]



- The **optimized San Diego 2018 mechanism (" Present work") is the smallest mechanism and it features the shortest computational time for flame simulations.**
- **It gives the most accurate prediction for laminar burning velocities of NH_3/H_2** mixtures (including pure NH_3 and H_2) on average (**1.97σ**). It can predict the 85% of available LBV data within 3 sigma experimental uncertainty.

$\sqrt{E}$ for Concentrations in Burner Stabilized Stagnition Flame								
Mechanism	NH_3	H_2	O_2	H_2O	NO	NO_2	N_2O	Overall
Present work	0.7	5.6	0.8	3.9	1.5	3.6	3.2	3.2
Han-2023	1.1	5.4	0.7	3.9	6.3	3.0	1.0	3.7
Wang-2022	17.2	8.2	9.3	10.9	5.1	3.8	10.5	10.1
Zhu-2024	failed	failed	failed	failed	failed	failed	failed	failed
Jian-2024	1.8	5.1	0.7	4.0	2.8	2.2	6.5	3.8
SanDiego-2018	24.9	10.1	12.3	15.8	9.7	5.5	10.7	13.9
Zhang-2021	1.3	5.6	0.7	3.8	3.9	2.8	8.7	4.6
Stagni-2023	1.5	5.4	0.7	4.0	3.3	2.7	9.4	4.7
Liu-2024	1.5	5.5	0.7	3.9	6.2	3.2	9.6	5.2
Mei-2021	failed	failed	failed	failed	failed	failed	failed	failed
He-2023	2.9	4.1	0.8	3.9	2.5	2.3	9.3	4.4
Zhang-2024	3.1	4.1	0.7	4.0	2.9	2.4	9.2	4.5

- **For BSSF simulations of 70/30 vol% NH_3/H_2 mixtures**, which are the closest in combustion characteristics to methane, the optimized mechanism showed **the best overall performance** (**3.24σ**).
- It **predicts** the concentration of the most important pollutant, **NO the most accurately**.
- Its accuracy for **H_2, H_2O, NO_2 and N_2O** still **should be improved**.

$\sqrt{E}$ for Concentrations in Jet-Stirred Reactor								
Mechanism	NH_3	H_2	O_2	H_2O	N_2	NO	N_2O	Overall
Present work	4.0	2.3	2.9	3.3	2.7	1.3	1.5	2.7
Han-2023	2.5	0.8	0.6	1.3	0.9	0.7	2.8	1.6
Wang-2022	3.6	3.5	2.7	3.0	2.0	1.5	0.9	2.6
Zhu-2024	2.1	0.8	0.8	1.4	0.6	0.4	0.5	1.1
Jian-2024	2.2	2.6	1.0	1.3	2.8	0.5	0.5	1.8
SanDiego-2018	2.8	3.1	1.1	3.1	1.0	0.7	3.4	2.4
Zhang-2021	3.5	2.8	1.3	3.1	3.5	1.1	3.0	2.8
Stagni-2023	2.0	1.3	0.8	1.8	2.1	0.6	2.7	1.8
Liu-2024	2.7	1.4	1.4	2.7	1.1	1.2	4.3	2.4
Mei-2021	2.3	1.7	2.0	1.6	1.8	0.6	0.8	1.6
He-2023	3.2	2.7	1.1	2.7	3.1	1.0	2.4	2.5
Zhang-2024	2.1	0.6	1.1	1.5	0.6	0.5	0.4	1.1

- **For JSR concentrations**, the optimized model **performs worse than most of the other mechanisms.**
- Nevertheless, it can predict these data **within 3σ accuracy on average**.
- Its performance **for NH_3 and H_2O should be improved**.

Concluding remarks

- The **accuracy** of the San Diego 2018 mechanism could be **greatly improved for laminar burning velocities and for concentrations in burner stabilized stagnation flames**, and it is on par with best-performing mechanisms.
- However, its **performance for concentrations in JSR, and for NO_2 concentration in BSSF need to be improved**.
- **It implies that its chemistry misses pathways** that can not be replaced by altering the rates of other reaction routes, thus **its chemistry need to be extended for further improvements.**

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