A compact kinetic reaction mechanism for the oxidation of NH_3/H_2 mixtures

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Introduction

- **In this poster we present the development and validation of our recently proposed compact NH_3 reaction mechanism [1].**
- **The potential of ammonia as a zero-carbon fuel and hydrogen carrier** has stimulated scientific interest in its application as a fuel in combustion systems**.**
- **However, the use of ammonia** as a fuel source for energy applications presents **notable challenges due to its low flammability and the potential for high emissions [2].**
- **Blending NH_3 with H_2 offers the prospect of improving combustibility, albeit with a notable increase in NOx emissions, especially under fuel-rich conditions [3].**
- The **design** of burners, turbines, and engines is **aided by computational fluid dynamics (CFD)** simulations, which **require small-sized mechanisms**.
- According to a **recent review** of the performance of ammonia combustion mechanisms [4], **the San Diego 2018 mechanism** [5], 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 to develop a small and robust kinetic mechanism for CFD simulations of NH_3/H_2 flames by optimising the rate parameters of the San Diego 2018 NH_3 mechanism against experimental data using the Optima++ code [6-8].**

Experimental Data Collection

- **A large collection of LBV and concentration data measured in JSRs**, previously compiled from the literature [4] was downloaded **in ReSpecTh Kinetic Data (RKD) format** XML files [9] **from the** Reaction Kinetic branch **ReSpecTh database** [10-11] .
- In addition, **concentration data from burner-stabilised stagnation flames (BSSF)** [12], and **recently published LBV data** were **collected**.
- All newly collected data were coded in RKD files [9] and will be available in the **ReSpecTh database** [10-11].
- See ECM manuscript for corresponding publications.

Method / Measured Quantity	No. of data series	No. Of data points	H_2 content in fuel mixture (%)	Pressure range (atm)	Temperature range (K)	Equivalence ratio (φ)
LBV	179	1283	0-100	1.0–36.6	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

- **The Optima++ code with the FOCTOPUS algorithm [6-8]** minimizes the following error function:

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

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
$Y_{fsd}^{\mathrm{exp/sim}}$: experimental data and simulation result
$\sigma_{fsd}^{\mathrm{exp}}$: 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 contribution of different experimental types: (LBV: 1/179, JSR: 1/47, BSSF:1/7)
- **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 [13].

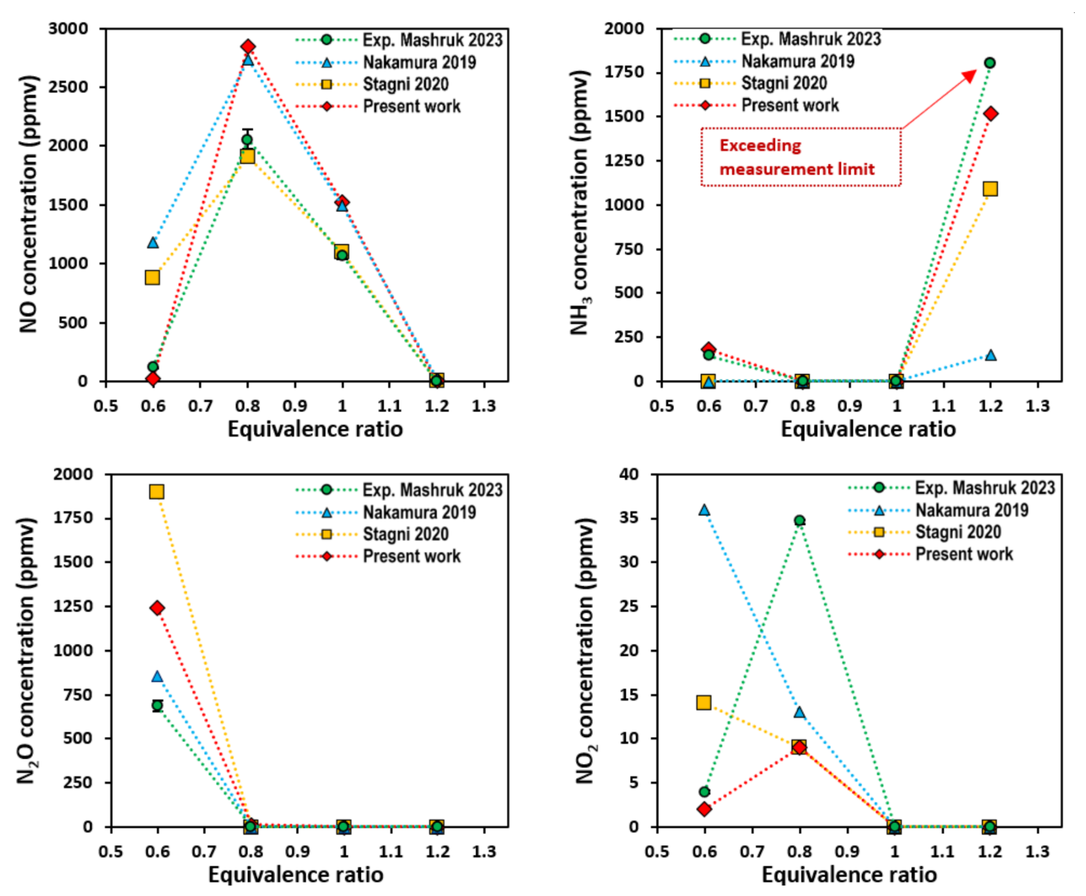
Results

#	Mechanism	N_{spec}	N_{reac}	$\sqrt{E_{\mathrm{LBV}}}$	$\sqrt{E_{\mathrm{JSR}}}$	$\sqrt{E_{\mathrm{BSSF}}}$	$\sqrt{E_{\mathrm{Overall}}}$
1	Zhu 2024	39	312	2.97	1.11	2.27	2.25
2	Han 2023	32	171	2.24	1.63	3.70	2.67
3	Present work	21	64	1.97	2.72	3.24	2.70
4	Jian 2024	32	233	3.23	1.80	3.79	3.06
5	Otomo 2018	32	213	3.67	2.03	3.65	3.21
6	X. Zhang 2021	34	224	2.45	2.78	4.59	3.41
7	Stagni 2023	31	203	3.46	1.75	4.69	3.51
8	Gotama 2022	32	165	3.28	2.91	4.59	3.67
9	Nakamura 2019	34	229	3.75	2.87	4.71	3.85
10	Stagni 2020	31	203	3.32	3.31	4.90	3.91
11	Liu 2024	35	238	3.96	2.39	5.19	4.01
12	Glarborg 2022	34	227	6.42	2.55	4.45	4.74
13	Glarborg 2023	34	228	6.52	2.54	4.45	4.79
14	He 2023	34	221	7.37	2.46	4.45	5.17
15	Z. Zhang 2024	34	224	8.46	1.14	4.50	5.57
16	Mei 2021	35	239	4.02	1.65	9.84	6.21
17	Wang 2022	32	140	2.53	2.64	10.13	6.22
18	Tamaoki 2024	33	228	3.29	2.14	10.17	6.29
19	Meng 2023	39	269	10.14	3.11	4.62	6.68
20	Klippenstein 2018	33	108	10.28	3.03	4.73	6.76
21	Glarborg 2018	33	211	10.29	3.03	4.73	6.77
22	San Diego 2018	21	64	3.36	2.43	13.94	8.40

- **The performance of the initial and optimized San Diego 2018 models were compared with 19 recent models (refs→ECM paper).**
- **Significantly improved accuracy** of the optimised mechanism **(present work, PW)** vs. the San Diego 2018 (SD) model **in predicting the LBVs** ($\sqrt{E}$: 3.36→1.97)
- PW is currently **the most accurate model for LBV** simulations with **the shortest computational time**.
- **For BSSF simulations of 70/30 vol% NH_3/H_2 mixtures, the accuracy of the model improved greatly** ($\sqrt{E}$: 13.91→3.24).
- **Except for Zhu 2024, all models perform poorly for BSSF data.**
- The model **performance for JSR concentrations (with at least 10% of H_2) slightly deteriorated** upon optimisation (2.43→2.72) but $\sqrt{E}$ **remained below 3**.

#	Mechanism	$\sqrt{E_{\mathrm{JSR}}}$ NH_3	H_2	O_2	H_2O	N_2	NO	N_2O	$\sqrt{E_{\mathrm{BSSF}}}$ NH_3	H_2	O_2	H_2O	NO	NO_2	N_2O
1	Zhu 2024	2.1	0.8	0.8	1.4	0.6	0.4	0.5	0.9	0.9	1.3	1.9	0.7	1.5	5.2
2	Han 2023	2.5	0.8	0.6	1.3	0.9	0.7	2.8	1.1	5.4	0.7	3.9	6.3	3.0	1.0
3	Present work	4.0	2.3	2.9	3.3	2.7	1.3	1.5	0.7	5.6	0.8	3.9	1.5	3.6	3.2
4	Jian 2024	2.2	2.6	1.0	1.3	2.8	0.5	0.5	1.8	5.1	0.7	4.0	2.8	2.2	6.5
5	Otomo 2018	2.9	1.4	2.5	2.3	2.4	0.5	1.0	0.8	5.3	0.8	3.8	5.4	1.9	4.1
6	X. Zhang 2021	3.5	2.8	1.3	3.1	3.5	1.1	3.0	1.3	5.6	0.7	3.8	3.9	2.8	8.7
7	Stagni 2023	2.0	1.3	0.8	1.8	2.1	0.6	2.7	1.5	5.4	0.7	4.0	3.3	2.7	9.4
8	Gotama 2022	2.9	3.7	2.1	2.4	1.2	1.2	5.0	1.0	5.6	0.7	3.8	5.1	3.1	8.1
9	Nakamura 2019	3.9	3.6	0.9	4.2	3.0	0.6	1.4	2.7	5.3	0.7	4.0	2.7	2.7	9.4
10	Stagni 2020	2.0	1.3	0.5	1.6	1.5	0.7	8.1	1.1	5.7	0.7	3.8	7.2	2.8	7.6
11	Liu 2024	2.7	1.4	1.4	2.7	1.1	1.2	4.3	1.5	5.5	0.7	3.9	6.2	3.2	9.6
12	Glarborg 2022	3.1	2.4	1.2	2.8	3.2	1.4	2.9	2.1	5.3	0.8	4.1	1.8	2.2	9.0
13	Glarborg 2023	3.1	2.4	1.2	2.8	3.2	1.4	2.9	2.2	5.3	0.8	4.0	1.8	2.2	9.0
14	He 2023	3.2	2.7	1.1	2.7	3.1	1.0	2.4	2.9	4.1	0.8	3.9	2.5	2.3	9.3
15	Z. Zhang 2024	2.1	0.6	1.1	1.5	0.6	0.5	0.4	3.1	4.1	0.7	4.0	2.9	2.4	9.2
16	Mei 2021	2.3	1.7	2.0	1.6	1.8	0.6	0.8	17.1	6.1	9.4	10.4	1.8	3.6	11.6
17	Wang 2022	3.6	3.5	2.7	3.0	2.0	1.5	0.9	17.2	8.2	9.3	10.9	5.1	3.8	10.5
18	Tamaoki 2024	2.9	1.2	2.3	1.8	2.3	1.8	2.3	17.2	8.2	9.3	10.8	5.7	3.8	10.5
19	Meng 2023	4.1	2.4	1.6	4.1	3.6	1.3	3.4	2.9	5.1	0.8	4.1	2.5	2.4	9.3
20	Klippenstein 2018	4.1	2.4	1.6	4.1	3.6	1.3	2.8	2.9	5.1	0.8	4.2	2.9	2.2	9.6
21	Glarborg 2018	4.1	2.4	1.6	4.1	3.6	1.3	2.8	2.9	5.1	0.8	4.1	2.9	2.2	9.6
22	San Diego 2018	2.8	3.1	1.1	3.1	1.0	0.7	3.4	24.9	10.1	12.3	15.8	9.7	5.5	10.7

- **The Zhu 2024** model shows **outstanding performance** for all species in JSR and BSSF simulations, **except for NO_2 in BSSF**.
- **The prediction for all species concentrations improved greatly** upon optimization of the San Diego 2018 model **in BSSF**.
- The **PW** model can **accurately predict NO and N_2O JSR data**, but improvement is needed for other species, especially for NH_3 and H_2O.
- **The PW model accurately predicts NO emissions and NH_3 slip in BSSF**, while improvement is needed for H_2, H_2O and NO_2.



- **Validation in Reynolds Averaged Navier Stokes (RANS) CFD simulations of a swirl burner** against experimental data of **Mashruk et al.** [14]
- **All models predict N_2O emission qualitatively well.**
- **Stagni 2020 is the most accurate for NO peak conc.**
- Both the **Stagni 2020 and Nakamura 2019** models give **qualitatively incorrect** predictions **at lean conditions:** they fail to predict the very small NO emission, the non-zero NH_3 emission and the low NO_2 emission at φ=0.6.
- **The PW model predicts all four emissions qualitatively well over the whole φ range.**
- **The PW model is the most computationally efficient** , as it runs ~2 faster than the other two models.

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, which implies that the deficiencies in its chemistry cannot be compensated by** the rates of other reaction routes.
- **In CFD swirl burner simulations, it ran faster than other models and qualitatively captures all major emissions.**

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