A compact kinetic reaction mechanism for NH_3/H_2 flames

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1. INTRODUCTION

Ammonia's potential as a zero-carbon fuel and hydrogen (H_2) carrier has attracted 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. Blending NH_3 with H_2 presents a prospect for enhancing combustibility, albeit with a notable increase in NOx emissions, particularly in fuel-lean conditions. To address these challenges and underscore the underlying factors, a comprehensive understanding and analysis of the chemical kinetics of NH_3 combustion are necessary. The current study focuses on developing a compact and robust kinetic model for smooth Computational Fluid Dynamics (CFD) simulations of NH_3/H_2 flames by optimising the rate parameters of the San Diego 2018 mechanism against a large experimental data collection. This mechanism was selected due to its exceptionally small size (21 species and 64 reactions) and its fair overall performance [1]. The results of the present work are available in a journal publication [2].

2. METHODS

The Optima++ code [3] was used to tune the Arrhenius parameters (**P**) of rate constants within loose uncertainty limits (f=1), to minimize the experimental uncertainty ($\sigma_{fsd}^{\exp}$)- normalized mean square deviation (E, Eq. (1)) of simulation results from a large collection of laminar burning velocity (LBV) data, concentration data from jet-stirred reactors (JSRs, Zhang et al., Osipova et al.), and concentration data from burner-stabilised stagnation flames (BSSFs, Hayakawa et al.) of 70/30 NH_3/H_2 mixtures (see Table 1).

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

Table 1: Optimisation targets

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

If $\sqrt{E}\leq 1$, $\sqrt{E}\sim 2$, $\sqrt{E}<3$ the model is considered perfect, accurate and satisfactory, respectively.

3. RESULTS

The results in Table 2 show the greatly improved accuracy of the optimized mechanism (Present work, PW) vs. the San Diego 2018 (SD) model in predicting the LBVs ($\sqrt{E}$: 3.36→1.97) and BSSF concentrations

(13.91→3.24). Actually, PW is currently the most accurate model for LBV simulations while featuring the shortest computational time. In BSSF simulations of 70/30 vol% NH_3/H_2 mixtures, it predicts NO emission accurately, while improvement is needed for other species. The performance of the SD model in predicting JSR concentrations slightly deteriorated upon optimization (2.43→2.72) but $\sqrt{E}$ error value stayed below 3, and PW model can also predict NO and N_2O emissions accurately.

Table 2: Performance of mechanisms in predicting experimental data.

#	Mechanism	N_{spec}	N_{reac}	$\sqrt{E_{LBV}}$	$\sqrt{E_{JSR}}$	$\sqrt{E_{BSSF}}$	$\sqrt{E_{Overall}}$	$\sqrt{E_{JSR}}$ NH_3	H_2	O_2	H_2O	N_2	NO	N_2O	$\sqrt{E_{BSSF}}$ NH_3	H_2	O_2	H_2O	NO	NO_2	N_2O
1	Zhu 2024	39	312	2.97	1.11	2.27	2.25	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	32	171	2.24	1.63	3.70	2.67	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	21	64	1.97	2.72	3.24	2.70	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	32	233	3.23	1.80	3.79	3.06	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	32	213	3.67	2.03	3.65	3.21	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	34	224	2.45	2.78	4.59	3.41	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	31	203	3.46	1.75	4.69	3.51	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	32	165	3.28	2.91	4.59	3.67	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	34	229	3.75	2.87	4.71	3.85	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	31	203	3.32	3.31	4.90	3.91	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	35	238	3.96	2.39	5.19	4.01	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	34	227	6.42	2.55	4.45	4.74	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	34	228	6.52	2.54	4.45	4.79	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	34	221	7.37	2.46	4.45	5.17	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	34	224	8.46	1.14	4.50	5.57	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	35	239	4.02	1.65	9.84	6.21	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	32	140	2.53	2.64	10.13	6.22	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	33	228	3.29	2.14	10.17	6.29	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	39	269	10.14	3.11	4.62	6.68	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	33	108	10.28	3.03	4.73	6.76	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	33	211	10.29	3.03	4.73	6.77	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	21	64	3.36	2.43	13.94	8.40	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

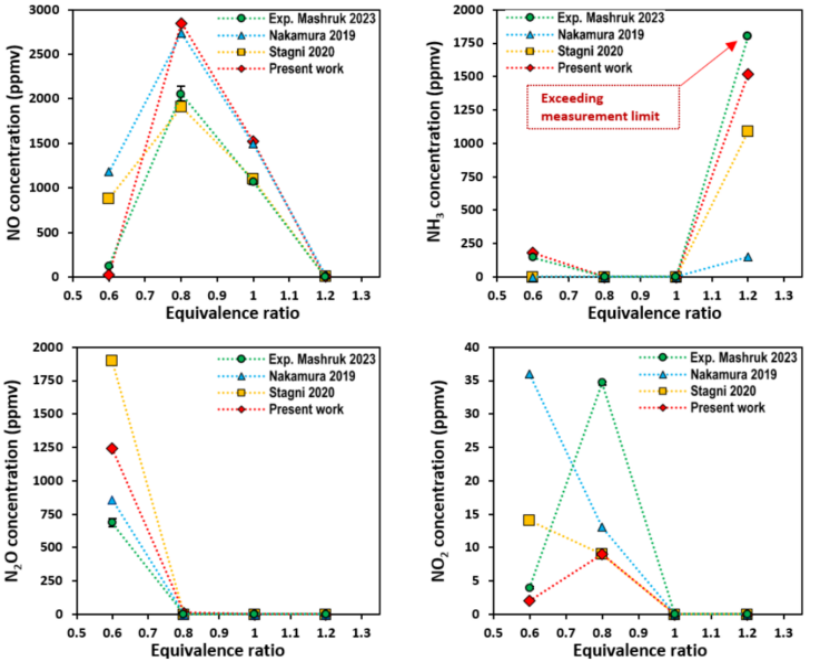

Figure 1: Validation in CFD RANS simulations of a swirl burner.

The PW model was validated in Reynolds Averaged Navier Stokes (RANS) CFD simulations of a swirl burner against experimental data of Mashruk et al. [4] (Fig. 1). It gave improved predictions for all four main emission species and twice faster simulations as the Nakamura 2019 and Stagni 2020 models.

4. CONCLUSIONS

A model with good qualitative and often good quantitative predictions for LBV and NOx emissions has been developed. However, its structural deficiencies limit its accuracy for the prediction of other combustion features.

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