A Comprehensive Analysis of NO_2 Formation and Kinetics in 70/30 vol% NH_3/H_2 Flames

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Introduction

- Ammonia (NH_3) is considered a zero-carbon fuel and hydrogen (H_2) carrier due to its good infrastructure and high hydrogen density [1].
- Harnessing NH_3 as a fuel presents challenges due to low flammability and high emissions, but blending NH_3 with H_2 improves combustibility while increasing NOx emissions, especially in fuel-rich conditions [1,2].
- Nitrogen dioxide (NO_2), a key combustion by-product that typically peaks under mildly lean conditions, not only poses environmental risks but also promotes nitric oxide (NO) formation through secondary reactions, intensifying overall NO_x emissions [3].
- This study investigates the kinetic pathways governing NO_2 formation in 70/30 vol% NH_3/H_2 flames under atmospheric conditions, with a focus on the key elementary reactions and reactive radicals that significantly influence NO_2 chemistry.

Methodology

The methodology employs a premixed laminar burner-stabilised stagnation flame model in ANSYS-CHEMKIN-Pro [4] to simulate 76 literature-based kinetic mechanisms, using a normalised error metric to quantitatively identify the top-performing models that best match experimental measurements.

$$\text{Normalised Error} = \frac{F_i - A_i}{\sigma}$$

Where F_i is the value predicted by the simulations, A_i is the experimentally measured value, and σ represents the uncertainty corresponding to one standard deviation.

Experimental Data

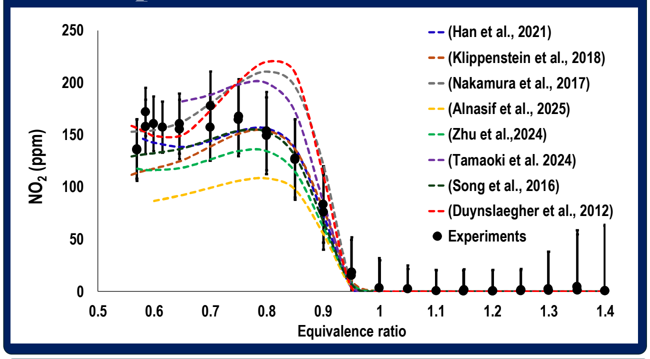
#	Equivalence Ratio (Φ)	V_{in} (cm/s)	Plate Temperture (K)	Ref.
1-9	0.6-1.4	25.53-30.86	493.50-504.00	[5]

Normalised Error Results

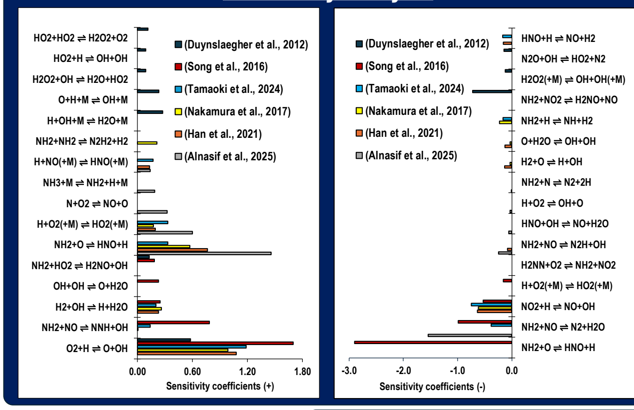
● → Bad ● → Satisfied ● → Good ● → Excellent

#	Mechanism	0.6	0.7	0.8	0.9	1
1	(Nakamura & Shindo, 2019)	-0.240	0.078	1.519	1.262	-0.107
2	(Nakamura et al., 2017)	-0.240	0.078	1.519	1.262	-0.107
3	(Duynslaegher et al., 2012)	-0.452	-0.127	1.771	0.976	-0.111
4	(Han et al., 2021)	-0.698	-1.008	0.067	-0.075	-0.110
5	(Capriolo et al., 2021)	-0.792	-1.061	0.028	-0.053	-0.107
6	(Song et al., 2016)	-1.079	-0.964	-0.017	-0.247	-0.108
7	(Jian et al. 2024)	-1.251	-1.198	-0.123	-0.034	-0.107
8	(Abian et al., 2015)	-1.464	-1.568	-0.468	-0.328	-0.110
9	(Glarborg, 2022)	-1.467	-1.213	-0.132	-0.088	-0.106
10	(Houshfar-mid temperature et al., 2012)	-1.488	-1.595	-0.547	-0.823	-0.112
11	(Xu et al., 2023)	-1.534	-1.423	-0.395	-0.176	-0.108
12	(Meng et al., 2023)	-1.593	-1.191	-0.012	0.117	-0.106
13	(Klippenstein et al., 2018)	-1.645	-1.170	0.016	0.086	-0.106
14	(Zhu et al.,2024)	-1.707	-1.544	-0.518	-0.402	-0.109
15	(T. Wang et al., 2018)	-1.709	-1.960	-0.929	-0.372	-0.102
16	(Mei, Zhang, et al., 2021)	-1.739	-1.690	-0.668	-0.276	-0.107
17	(Alzueta et al., 2001)	-1.768	-1.277	0.038	0.392	-0.101
18	(Glarborg et al., 2018)	-1.783	-1.421	-0.288	-0.087	-0.107
19	(He et al.,2023)	-1.784	-1.450	-0.411	-0.229	-0.108
20	(Bertolino et al., 2021)	-1.800	-1.614	-0.482	-0.045	-0.108
21	(Esarte et al., 2011)	-1.831	-1.764	-0.320	0.591	-0.095
22	Zhang et al. 2024	-1.903	-1.492	-0.425	-0.149	-0.108
23	(Valkó et al., 2022)	-1.915	-1.391	-0.082	0.277	-0.107
24	(Y. Zhang et al., 2017)	-2.023	-1.834	-0.829	-0.789	-0.110
25	(Klippenstein et al., 2011)	-2.031	-1.881	-0.698	-0.349	-0.110
26	(Arunthanayothin et al., 2021)	-2.042	-1.695	-0.473	0.080	-0.107
27	(Stagni et al., 2020)	-2.044	-1.695	-0.474	0.080	-0.107
28	(Alzueta MU, 2016)	-2.049	-1.818	-0.367	0.553	-0.096
29	(Kovács et al., 2021)	-2.085	-1.402	-0.157	0.025	-0.109
30	(X. Zhang et al., 2021)	-2.086	-1.824	-0.819	-0.451	-0.107
31	(Kovács et al., 2020b)	-2.152	-1.462	-0.218	-0.021	-0.109
32	(Han et al.,2023)	-2.167	-2.054	-0.784	-0.099	-0.109
33	(Shmakov et al., 2010)	-2.176	-1.933	-0.599	0.030	-0.111
34	(Gotama et al., 2022)	-2.292	-2.016	-0.736	-0.182	-0.109
35	(Mei, Ma, et al., 2021)	-2.383	-2.209	-1.297	-0.769	-0.109
36	(Dagaut et al., 2008)	-2.424	-2.200	-0.885	-0.132	-0.103
37	(Thomas et al., 2022)	-2.466	-2.214	-1.193	-0.682	-0.110
38	(Konnov, 2009)	-2.483	-1.761	-0.385	0.000	-0.104
39	(Coda Zabetta & Hupa, 2008)	-2.527	-2.317	-0.962	-0.191	-0.107
40	(Liu et al. 2024)	-2.561	-2.123	-0.820	-0.145	-0.108
41	(Alnasif et al., 2025)	-2.833	-2.365	-1.210	-0.579	-0.110
42	(Lamoureux et al., 2016)	-2.892	-2.221	-0.846	-0.040	-0.101
43	(De Persis et al., 2020)	-2.923	-2.228	-0.840	-0.053	-0.101
44	(Nozari & Karabeyoǧlu, 2015)	-3.073	-2.344	-1.233	-0.921	-0.111
45	(Lamoureux et al., 2010)	-4.346	-3.469	-1.966	-0.410	-0.107
46	(Saxena & Williams, 2007)	-4.465	-3.787	-2.578	-1.105	-0.111
47	(Tamaoki et al. 2024)	-6.146	0.321	1.225	0.271	-0.109
48	(Otomo et al., 2018)	-6.146	0.273	1.083	0.143	-0.109
49	(Da Rocha-Otomo et al., 2019)	-6.146	0.163	1.119	0.380	-0.108
50	(Xiao et al., 2017)	-6.146	-0.797	0.299	0.244	-0.109
51	(Sun et al., 2022)	-6.146	-0.901	0.284	0.808	-0.109
52	(Da Rocha-Mathieu et al., 2019)	-6.146	-0.967	0.044	0.048	-0.109
53	(Mathieu & Petersen, 2015)	-6.146	-1.016	0.063	0.125	-0.108
54	(T. Faravelli, 2017)	-6.146	-1.398	-0.585	-0.540	-0.110
55	(Song et al., 2019)	-6.146	-1.432	-0.484	-0.328	-0.109
56	(Mendiara & Glarborg, 2009)	-6.146	-1.594	-0.611	-0.436	-0.111
57	(Houshfar-Low temperature et al., 2012)	-6.146	-1.723	-0.790	-0.511	-0.111
58	(POLIMI, 2014)	-6.146	-1.809	-0.379	0.592	-0.089
59	(Z. Wang et al., 2021)	-6.146	-1.938	-0.696	-0.219	-0.110
60	(Han et al., 2019)	-6.146	-1.956	-0.733	-0.216	-0.109
61	(K. Zhang et al., 2011)	-6.146	-2.047	-0.950	-0.472	-0.110
62	(Mei et al., 2019)	-6.146	-2.118	-1.274	-1.033	-0.111
63	(Shrestha et al., 2018)	-6.146	-2.129	-1.249	-1.032	-0.111
64	(Tian et al., 2009)	-6.146	-2.140	-1.038	-0.596	-0.111
65	(Mével et al., 2009)	-6.146	-2.234	-0.961	-0.035	-0.108
66	(Kovaleva et al., 2022)	-6.146	-2.444	-1.258	-0.450	-0.108
67	(Shrestha et al., 2021)	-6.146	-2.516	-1.479	-0.646	-0.109
68	(Da Rocha-Okafor et al., 2019)	-6.146	-3.193	-2.425	-1.884	-0.113
69	(UCSanDiego, 2018)	-6.146	-3.196	-2.053	-0.845	-0.109
70	(Jiang et al., 2020)	-6.146	-3.198	-2.050	-0.852	-0.109
71	(Gregory P. Smith et al., 2000)	-6.146	-5.361	-1.202	-1.635	-0.112
72	(Marques et al., 2009)	-6.146	-5.361	-4.087	0.060	-0.103
73	(Aranda et al., 2013)	-6.146	-5.361	-4.087	-2.102	-0.113
74	(Houshfar-High temperature) et al., 2012)	-6.146	-5.361	-4.087	-2.102	-0.113
75	(Li et al., 2019)	-6.146	-5.361	-4.087	-2.102	-0.113
76	(Okafor et al., 2019)	-6.146	-5.361	-4.087	-2.102	-0.113

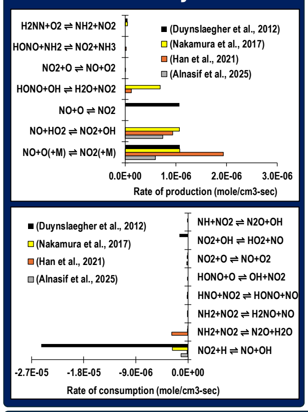
NO_2 Concentration Vs. Equivalence ratios



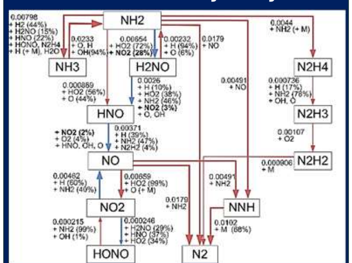
Sensitivity Analysis



ROP Analysis



Reaction Pathway Analysis



Arrows show chemical transformations: percentages indicate reactant contributions; numbers show net reaction rates (kmol/m³·s) scaled by line thickness. Red arrows represent fuel-NO_x pathways; blue arrows denote NO_2 reburn routes.

Conclusions

This study assessed NO_2 kinetics in a 70/30 (% vol.) NH_3/H_2 fuel blend over an equivalence ratio range of ϕ = 0.6–1.0 using 76 kinetic mechanisms. The key findings are as follows:

- The Han et al. (2021) mechanism exhibited the highest accuracy in capturing NO_2 chemistry.
- NO_2 formation is primarily promoted by O and HO_2 radicals, whereas its consumption is largely controlled by H and NH_2 species.
- NO_2 plays a significant role in reburn chemistry, facilitating the production of H_2NO, HNO, and NO, thereby influencing the broader nitrogen reaction network.

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