An Optimised Reaction Mechanism for Predicting Laminar Flame Speed in NH_3 and NH_3/H_2 Flames

Ali Alnasif[a,b], András György Szanthoffer[c,d], Máté Papp[c,e], T. Turányi[c], Syed Mashruk[a], Agustin Valera-Medina[a*], T. Nagy[f*]

[a] *College of Physical Sciences and Engineering, Cardiff University, Cardiff, CF24 3AA, United Kingdom*

[b] *Engineering Technical College of Al-Najaf, Al-Furat Al-Awsat Technical University, Najaf, 31001, Iraq*

[c] *Institute of Chemistry, Eötvös Loránd University (ELTE), Budapest, 1117, Hungary*

[d] *Hevesy György PhD School of Chemistry, Eötvös Loránd University (ELTE), Budapest, 1117, Hungary*

[e] *HUN-REN−ELTE Research Group on Complex Chemical Systems, Budapest, 1117, Hungary*

[f] *Institute of Materials and Environmental Chemistry, HUN-REN Research Centre for Natural Sciences, Budapest, 1117, Hungary*

* ValeraMedinaA1@cardiff.ac.uk, nagy.tibor@ttk.hu

MariNH3 — Clean, green ammonia engines for maritime

Introduction

- Ammonia (NH_3) is considered a zero-carbon fuel and hydrogen (H_2) carrier due to its good infrastructure and high hydrogen density.
- Harnessing ammonia 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.
- Addressing these challenges requires a detailed analysis of NH_3 chemistry using a kinetic reaction mechanism.
- The study aims to develop a kinetic reaction mechanism for NH_3/O_2 and $NH_3/H_2/O_2$ flame chemistry, ensuring efficient CFD simulation under complex engine chamber conditions and turbulent flow dynamics.

Methodology

The methodology involves tuning the Arrhenius parameters of the rate constants within predefined uncertainty limits [1] using the Optima++ code [2]. This tuning is applied to the most influential reactions affecting flame speed under various operational conditions. The aim is to align the results with experimental observations from previous studies while considering their associated uncertainties. The process is detailed in the following steps.

1. Experimental data were encoded in **ReSpecTh Kinetics Data** (RKD) **2.3 format** XML files [3].
2. Program **Optima++** [2] reads the XML data file, sets up the simulation environment and calls the **Cantera** [4] simulation code to carry out the simulation.
3. All simulations were carried out with Cantera [4] using a **a 1D model** (LBV).

Experimental data

Exp. type	XML/Ds./Dp.	T / K	p / atm	φ
LBV	185/3381/1311	295-584.1	0.50–36.6	0.2–2.0

Error function

Quantitative evaluation of mechanism performance using an average error function.

$$E(\mathbf{P}) = \frac{1}{N_s}\sum_{s=1}^{N_s}\frac{1}{N_{sd}}\sum_{d=1}^{N_{sd}}\left(\frac{Y_{sd}^{\mathrm{sim}}(\mathbf{P}) - Y_{sd}^{\mathrm{exp}}}{\sigma_{sd}^{\mathrm{exp,tot}}}\right)^2$$

s,d: data series index, data points index
P: vector of model parameters
N: the total number of the data series
$N_{s/d}$: the number of the data series/points

$Y_{sd}^{\mathrm{exp/sim}}$: experimental data and simulation result
$\sigma_{sd}^{\mathrm{exp}}$: standard deviation of exp. data *d* in data series *s*

$\sqrt{E}$ measures the RMS deviation between the model and the experimental results, with respect to σ^{exp}.

A mechanism is typically considered accurate if $\sqrt{E} < 3$.

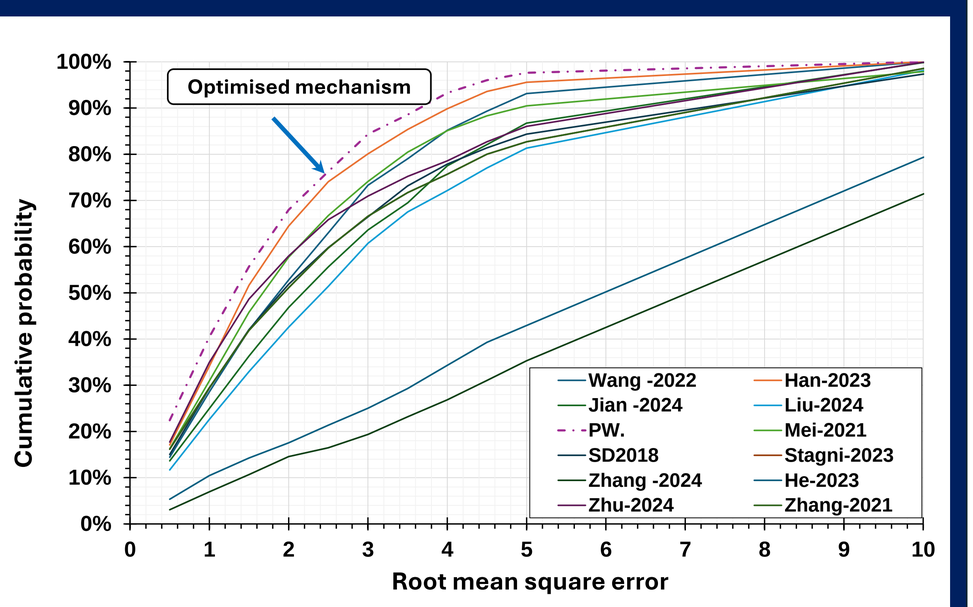
Reaction mechanisms investigated

	$N_{spec}(C_0)$	N_{Reac}	Max sqrt E_{sd}	$\sqrt{E}$	Ref.
Present	21	64	9.0	2.17	-
Han2023	32	171	9.9	2.39	[5]
CEU2022	32	140	8.7	2.75	[6]
Zhu2024	39	312	10.3	3.15	[7]
Jian2024	32	233	11.1	3.36	[8]
SD2018	21	64	16.5	3.77	[9]
Zhang2021	34	224	13.4	3.75	[10]
Stagni2023	31	203	13.4	3.75	[11]
Liu2024	35	238	18.3	3.98	[12]
Mei2021	35	239	34.2	4.39	[13]
He2023	34	221	24.9	7.72	[14]
Zhang2024	34	224	28.2	8.92	[15]

Quantitative mechanism comparison

$\sqrt{E}$	Wang 2022	Han 2023	Jian 2024	Liu 2024	Present work	Mei 2021	SD2018	Stagni 2023	Zhang 2024	He 2023	Zhu 2024	Zhang 2021
0.5	14%	17%	14%	12%	22%	16%	15%	16%	3%	5%	18%	16%
1.0	29%	34%	25%	23%	40%	31%	29%	29%	7%	10%	35%	29%
1.5	42%	52%	36%	33%	56%	46%	42%	42%	11%	14%	49%	42%
2.0	53%	64%	47%	43%	68%	58%	52%	51%	15%	18%	58%	51%
2.5	63%	74%	56%	51%	76%	67%	60%	60%	16%	21%	66%	60%
3.0	73%	80%	64%	61%	84%	74%	66%	67%	19%	25%	71%	67%
3.5	79%	85%	69%	68%	89%	80%	73%	72%	23%	29%	75%	72%
4.0	85%	90%	77%	72%	93%	85%	78%	76%	27%	34%	79%	76%
4.5	89%	94%	82%	77%	96%	88%	81%	80%	31%	39%	83%	80%
5.0	93%	96%	87%	81%	98%	90%	84%	83%	35%	43%	86%	83%
10.0	100%	100%	100%	98%	100%	98%	97%	99%	71%	79%	100%	99%
15.0	100%	100%	100%	100%	100%	99%	100%	100%	93%	97%	100%	100%
20.0	100%	100%	100%	100%	100%	99%	100%	100%	98%	100%	100%	100%
25.0	100%	100%	100%	100%	100%	99%	100%	100%	100%	100%	100%	100%
30.0	100%	100%	100%	100%	100%	99%	100%	100%	100%	100%	100%	100%
35.0	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
N_failed	0	0	0	0	0	1	0	0	0	0	0	0

Distribution function



References

[1] Nagy, T. & Turányi, T. Uncertainty of Arrhenius parameters. Int J Chem Kinet 43, 359–378 (2011).
[2] Máté Papp et al. Optima++ v2.5: A general C++ framework for performing combustion simulations and mechanism optimization. available at http://respecth.hu/ (2024).
[3] Varga, T., Olm, C., Busai, Á. & Zsély, I. G. ReSpecTh Kinetics Data Format Specification v2. 0. Preprint at (2017).
[4] Goodwin, D. G., Moffat, H. K. & Speth, R. L. Cantera: An object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes. Preprint at (2018).
[5] Han, X. et al. Effect of H2 and O2 enrichment on the laminar burning velocities of NH3+H2+N2+O2 flames: Experimental and kinetic study. Applications in Energy and Combustion Science 15, (2023).
[6] Wang, S. et al. Applying heat flux method to laminar burning velocity measurements of NH3/CH4/air at elevated pressures and kinetic modeling study. Combust Flame 236, (2022).
[7] Zhu, Y. et al. The combustion chemistry of ammonia and ammonia/hydrogen mixtures: A comprehensive chemical kinetic modeling study. Combust Flame 260, (2024).
[8] Jian, J. et al. An experimental, theoretical, and kinetic modeling study of post-flame oxidation of ammonia. Combust Flame 261, (2024).
[9] Mechanical and Aerospace Engineering (Combustion Research) & University of California at San Diego. Chemical-Kinetic Mechanisms for Combustion Applications. https://web.eng.ucsd.edu/mae/groups/combustion/mechanism.html (2018).
[10] Zhang, X., Moosakutty, S. P., Rajan, R. P., Younes, M. & Sarathy, S. M. Combustion chemistry of ammonia/hydrogen mixtures: Jet-stirred reactor measurements and comprehensive kinetic modeling. Combust Flame 234, (2021).
[11] Stagni, A. et al. Low- and intermediate-temperature ammonia/hydrogen oxidation in a flow reactor: Experiments and a wide-range kinetic modeling. Chemical Engineering Journal 471, (2023).
[12] Liu, B. et al. Experimental and chemical kinetic study for the combustion of ammonia-hydrogen mixtures. Fuel 371, 131850 (2024).
[13] Mei, B., Zhang, J., Shi, X., Xi, Z. & Li, Y. Enhancement of ammonia combustion with partial fuel cracking strategy: Laminar flame propagation and kinetic modeling investigation of NH3/H2/N2/air mixtures up to 10 atm. Combust Flame 231, (2021).
[14] He, X., Li, M., Shu, B., Fernandes, R. & Moshammer, K. Exploring the Effect of Different Reactivity Promoters on the Oxidation of Ammonia in a Jet-Stirred Reactor. Journal of Physical Chemistry A 127, 1923–1940 (2023).
[15] Zhang, Z. et al. An experimental and kinetic modelling study on the oxidation of NH3, NH3/H2, NH3/CH4 in a variable pressure laminar flow reactor at engine-relevant conditions. Combust Flame 265, 113513 (2024).

This work was supported by the Engineering and Physical Sciences Research Council, grant number EP/W016656/1.

The partnership — University of Nottingham UK | CHINA | MALAYSIA; UKRI Science and Technology Facilities Council; University of Birmingham; University of Brighton; Cardiff University; Prifysgol Caerdydd

Funded by UKRI Engineering and Physical Sciences Research Council