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Implications of the Chemical Kinetics of Ammonia on Combustion Behaviour

**Presentation to U.S. DOE National Energy Technology Laboratory
Research & Innovation Center - Thermal Sciences
Pittsburgh**

Contributions from Rob Barlow, Peter Glarborg, Andrea Gruber, Gaetano Magnotti, Heinz Pitsch, Martin Richter and others are gratefully acknowledged.

R. P. Lindstedt
27/08/2024

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Background

Ammonia is the current “hot” topic when it comes to alternative fuels. It is also a **“terrible” fuel with exceptionally low reactivity, prone to unacceptable emissions of oxides of nitrogen** and typically requiring hydrogen enhancement to use even in a laboratory environment.

The aim of the current talk is to explore:

- What are the challenges?
- Current state of chemical mechanisms.
- Comments on what criteria are sensible.
- Some – not extensive - current uncertainties in key fundamental rate parameters.
- What role for validation data and what types?
- How can we move this forward?

Challenges from the July 2024 TNF Review

Andrea Gruber

- What is the pressure effect on **NO and N₂O formation** in premixed and non-premixed flames? Which **minimal set of elementary reactions** are needed to accurately predict this?
- What is the **origin of ammonia slip** observed in experiments (less so in simulations) of ammonia flames, either premixed or non-premixed, at globally fuel-rich conditions? Is there a chemical kinetics pathway that leads to ammonia slip even at idealized adiabatic-flame conditions or ammonia slip is just the result of **local extinction and/or wall heat loss / quenching**?
- *Are presently available chemical kinetics schemes able to **accurately predict HCN formation** in ammonia-methane flames? Which minimal set of elementary reactions are needed to accurately predict this?*

*Background for this: in a set of **high-pressure experiments** that we recently conducted for a customer on lab-scale GT combustor fired with a methane-ammonia blend, we measured (FTIR) **100-200 ppm HCN in the exhaust gases** at certain operating conditions!*

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Background Ammonia Chemistry

Work on ammonia in a combustion context can arguably be divided into three time periods based on the discovery of Selective Non-Catalytic Reduction (SNCR) of nitric oxide (NO):

1. The pre-SNCR era leading up to 1975.
2. The SNCR era spanning the period from 1975 to 2011.
3. The post-SNCR era spanning the period from 2011 onwards.

The above is, of course, highly approximate and only serves to illustrate the rather intermittent progress made.

The dividing dates stem from the original SNCR patent by Lyon (US3900554A) in 1975 and the study of SNCR by Klippenstein et al. (2011)¹.

¹ Klippenstein et al., The role of NNH in NO formation and control, *Combust. Flame* 158 (2011) 774-789.

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Background Ammonia Chemistry

Taking a big risk in attempting to attribute motivation:

- The pre-SNCR era was driven by curiosity.
- The SNCR era by a desire to understand how it works, to determine applicability limits and process optimization.
- The current era is aimed at figuring out if and how we can use ammonia as a hydrogen rich fuel.
- The stoichiometric reaction is simple: $2\text{NH}_3 + 1.5\text{O}_2 = 3\text{H}_2\text{O} + \text{N}_2$

Property	NH ₃ -O ₂	NH ₃ -Air	CH ₄ -Air
T [K]	2845	2070	2226
N ₂	0.225	0.688	0.709
H ₂ O	0.559	0.304	0.183
O ₂	0.027	0.0013	0.0046
OH	0.054	0.0014	0.0029
NO	0.0079	0.00072	0.0020
N ₂ O	2.15*10 ⁻⁷	3.39*10 ⁻⁸	---
CO	---	---	0.0090
CO ₂	---	---	0.0850

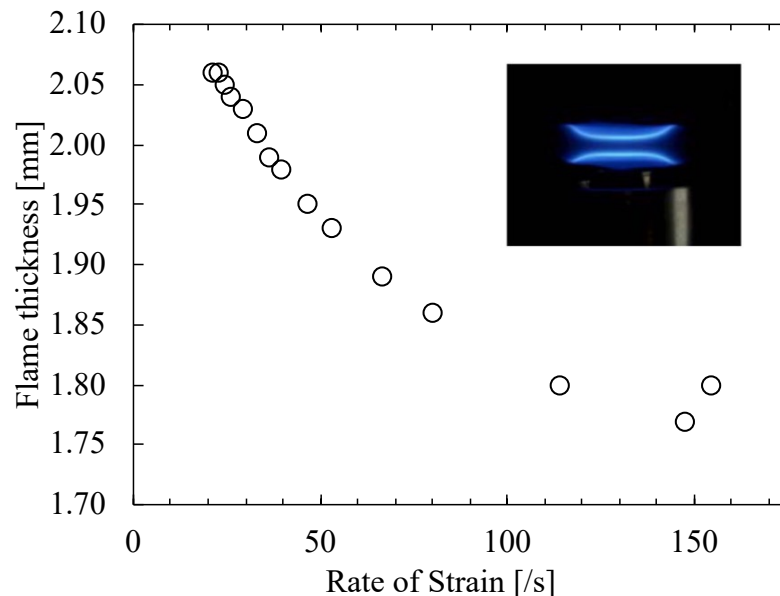
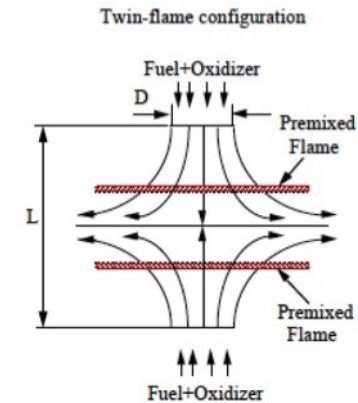
Table shows chemical equilibrium products for stoichiometric ammonia combustion compared to methane at atmospheric pressure¹.

¹Kobayashi et al. (2019) point out that NO levels in flames can reach 4000 ppm even with 5% NH₃ added.

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There are (at least) three main challenges:

1. Oxides of nitrogen present a significant problem with **the chemistry of ammonia is particularly complex** as it can be used to reduce NO through the SNCR chemistry as well as providing unacceptable levels if not mitigated.
2. How to model the poor reaction dynamics as the hydrogen content is reduced – this will lead to increased/intense turbulence-chemistry interactions.
3. A direct consequence is that the accuracy of the applied chemistry matters to an even higher degree than for hydrocarbon-based fuels.



Laminar flame thicknesses based on the 5 to 95 % temperature rise in **opposed jet back-to-back stoichiometric ammonia-air flames**.

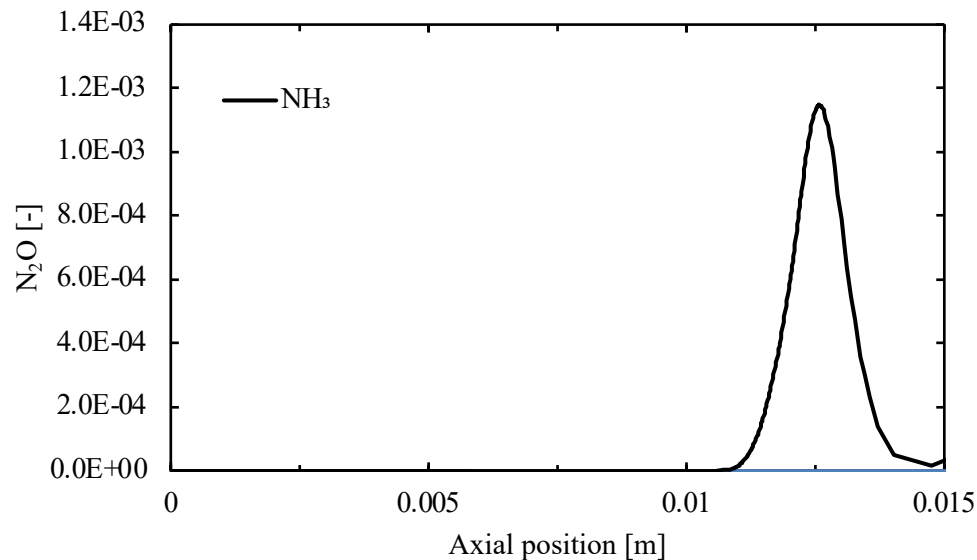
Accounting for the low burning velocities (peak around 7 cm/s) a characteristic chemical timescale (τ_c) for **ammonia** combustion around **27 ms**.

The corresponding **methane** flame timescale is around **1.3 ms**.

Likely strong impact on combustion regimes and properties.

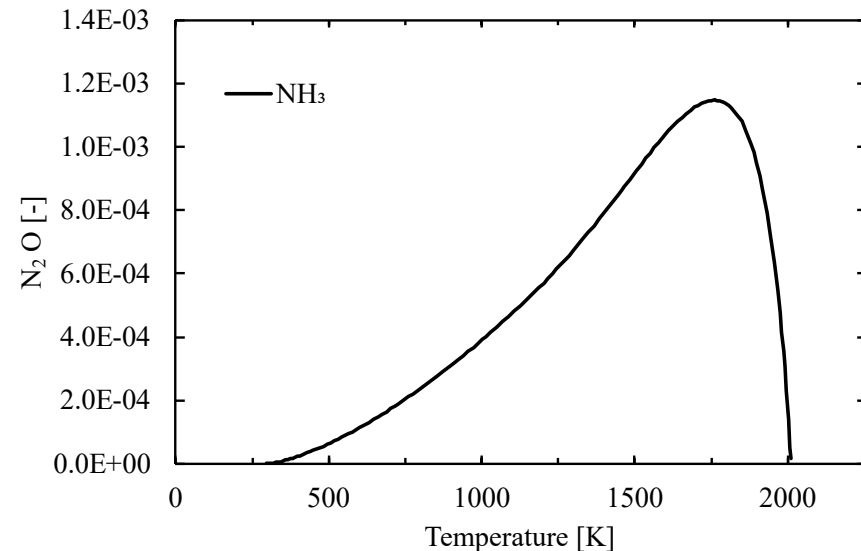
Nitrous oxide can become an issue.

Nitrous oxide has a greenhouse gas potential that is around 300 times that of carbon dioxide and is formed in large concentrations as an intermediate.



In the opposed jet geometry, the flame is pushed towards the stagnation plane due to the low burning velocity even at the exceptionally low rate of strain of 81 /s.

The nitrous oxide formation start at low temperatures in a manner that is consistent with nitric oxide.



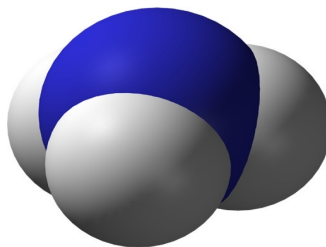
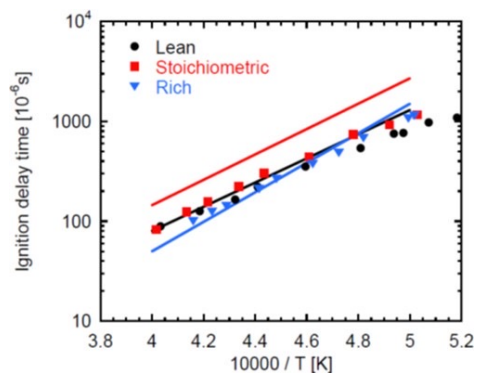
Can local extinction and incomplete combustion give rise to nitrous oxide emissions?



NH₃ oxidation modeling status 2018

Shock tube IDT

(Mathieu and Petersen, 2015)

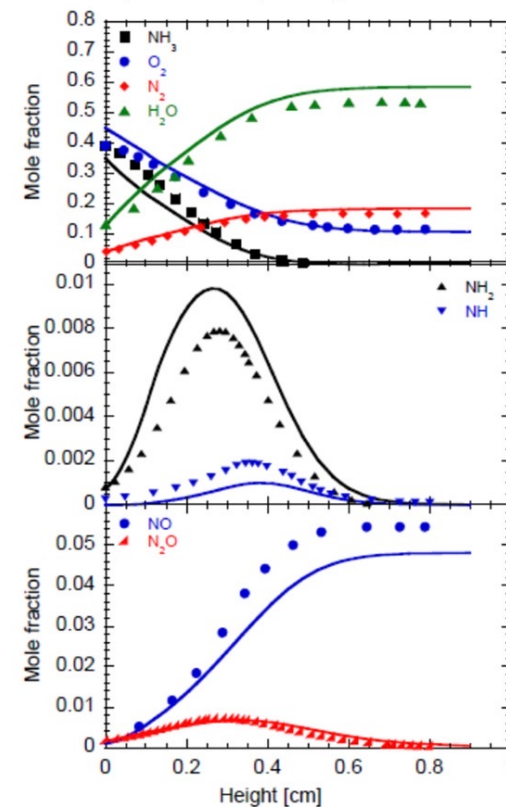


Model:

Glarborg et al. (2018)

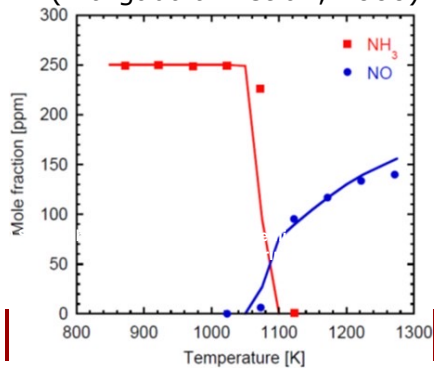
Flame structure

(Bian et al., 1986)



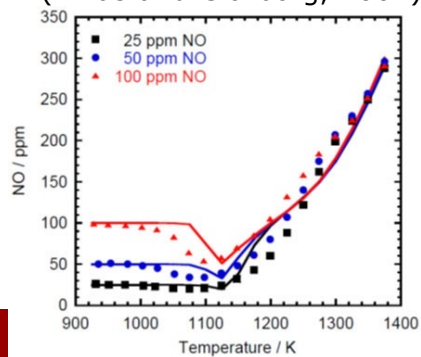
reactor: CO/NH₃

(Wargadalam et al., 2000)



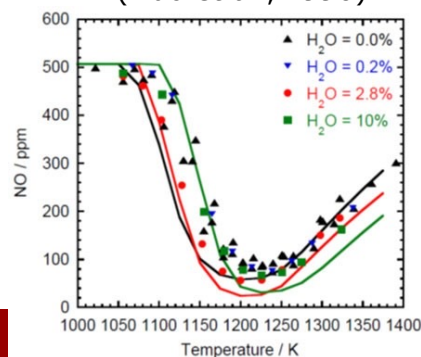
NH₃+trace NO

(Vikas and Glarborg, 2004)



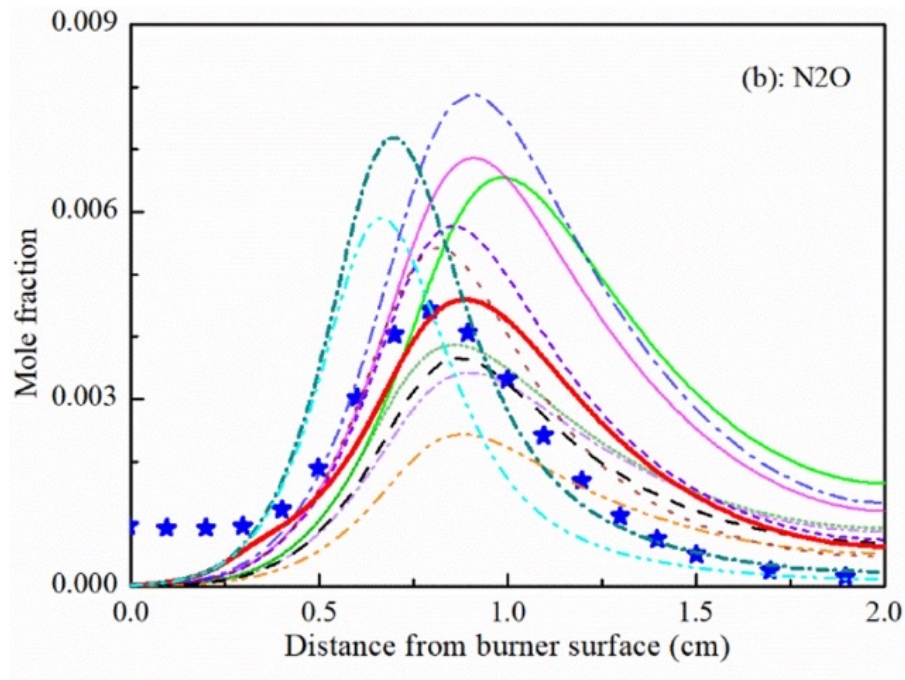
Thermal DeNO_x

(Duo et al., 1990)

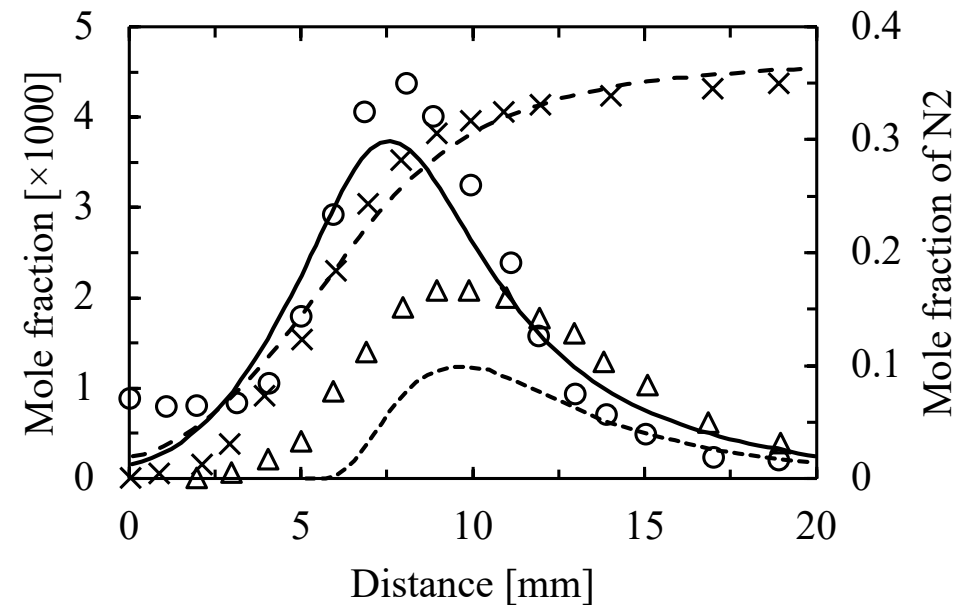


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Progress in modelling nitrous oxide?

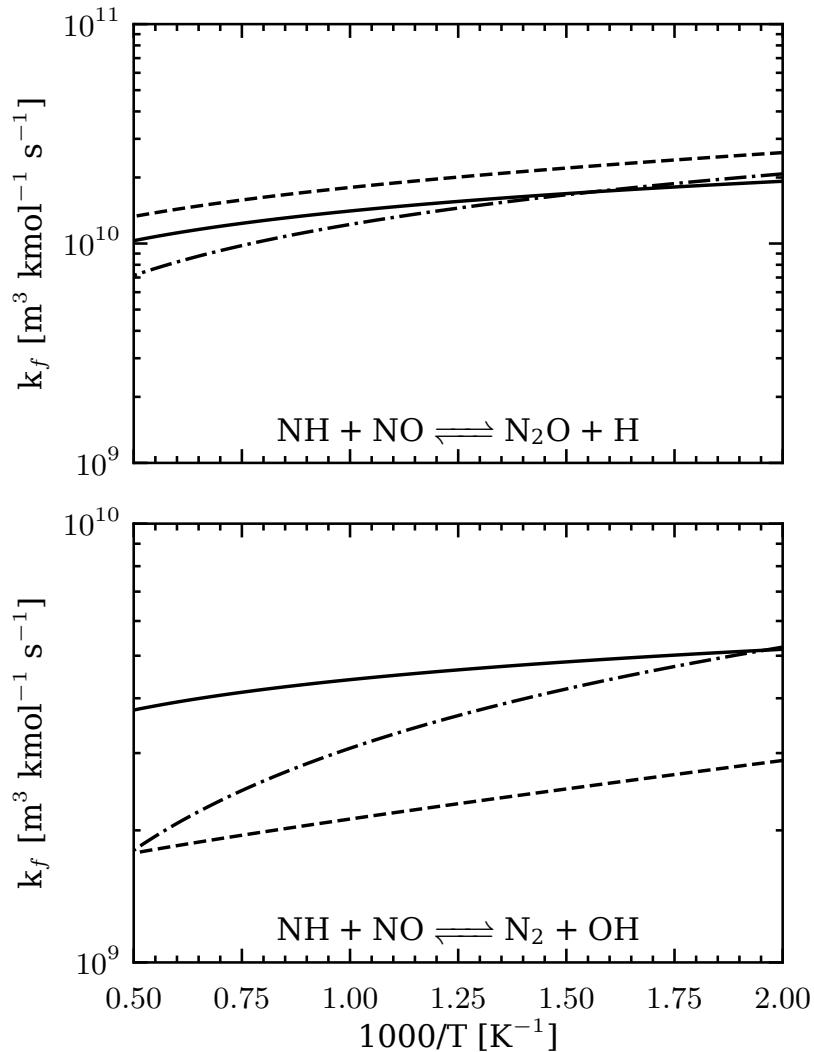


Experimental results from Vandooren et al. (1994) flame showing spatial distribution of N_2O (*) in a burner stabilized $NH_3/NO/Ar$ flame ($0.461 NH_3/0.472 NO/0.067 Ar$; $P = 7200 Pa$) computed by a wide range of chemical kinetic mechanisms as presented by Han et al. (2020).

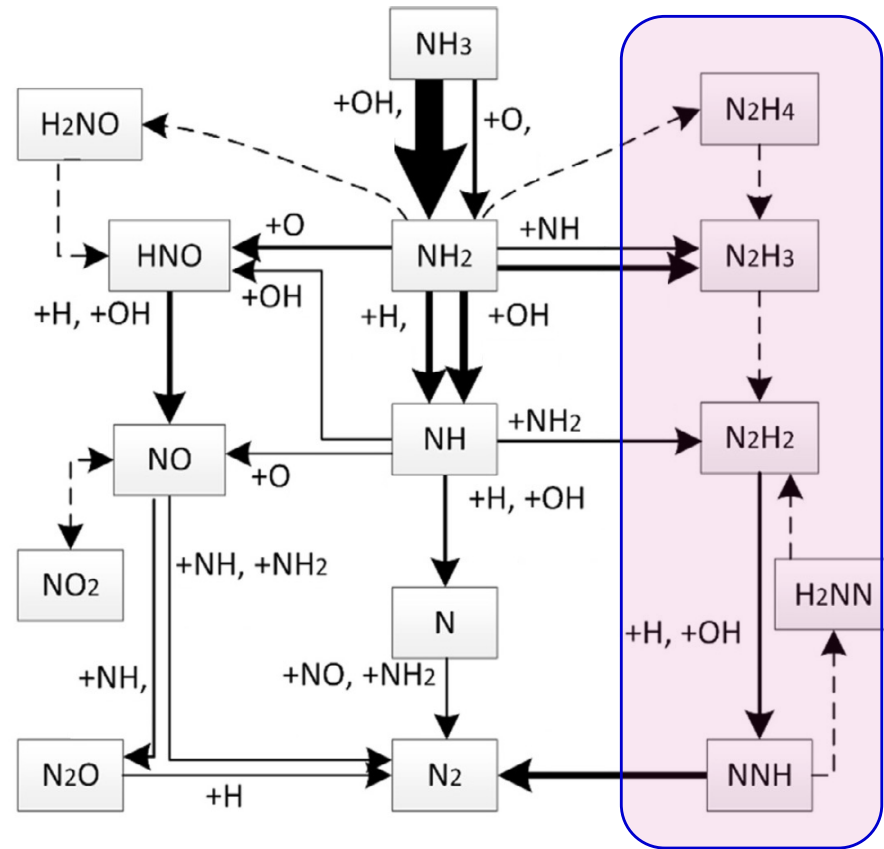


Computations by Lindstedt et al. (1995) of the same flame showing NH_2 (Δ), N_2O (o) and N_2 (\times).

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Overall ammonia chemistry

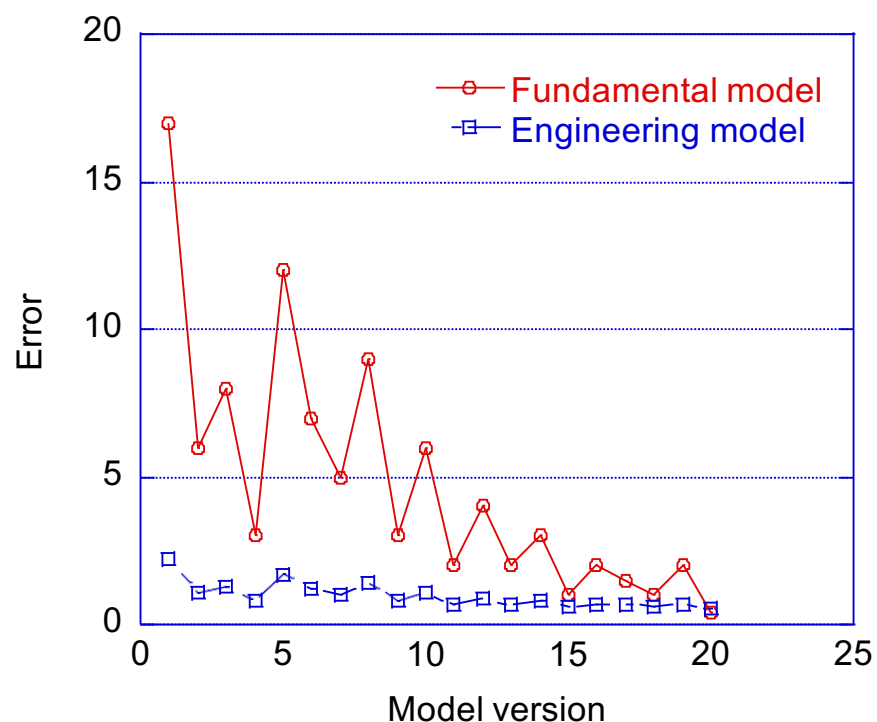


“quite uncertain”
 Glarborg et al. (2018)
 Gao et al. (2023)

Left: Key reaction steps in N₂O formation. Right: **Adapted from Rob Barlow**, originally from Han et al., *Combust. Flame* 213 (2020) 1–13; Gao et al., *Proc. Combust. Inst.* 39 (2023) 571–579.



First-principles versus engineering models



First-principles model

- Scientifically solid
- Represents the present understanding of the chemistry
- Often lower accuracy compared to engineering models

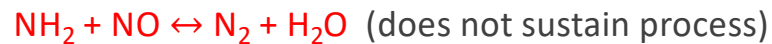
Engineering model

- Optimized to improve agreement
- Often impressive predictive capabilities (within optimized regime)
- Tends to disguise scientific issues

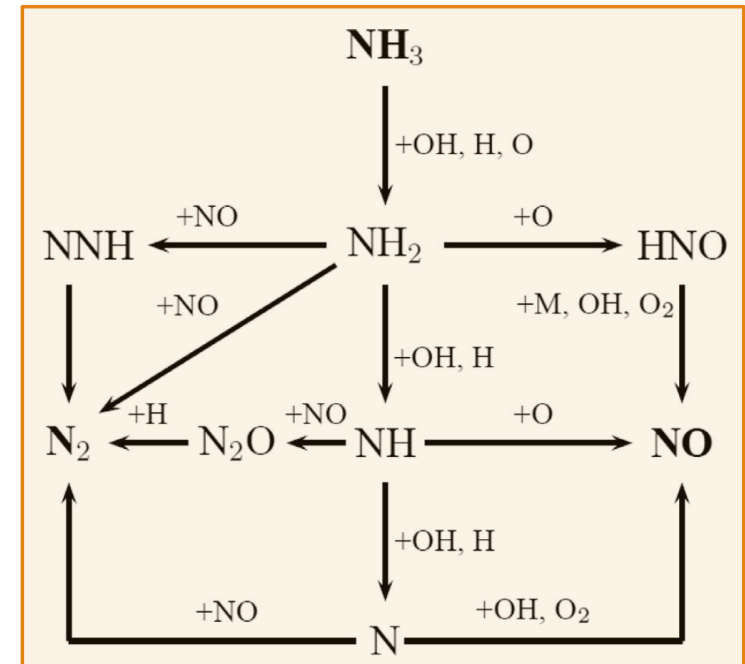
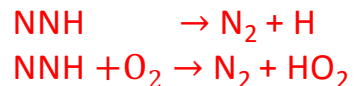
Slide adapted from Rob Barlow

Thermal DeNO_x (SNCR)

- Key step has two product channels:



- Effective in narrow temperature range centered around 1250 K (too slow below 1100 K; $\text{NH}_2 \rightarrow \text{HNO} \rightarrow \text{NO}$ above 1400 K)
- Early work done with low NH₃ levels (additive, not fuel)
- The two crucial steps controlling the SNCR behaviour are linked to the NNH radical as shown by Greenblatt et al. (2023).

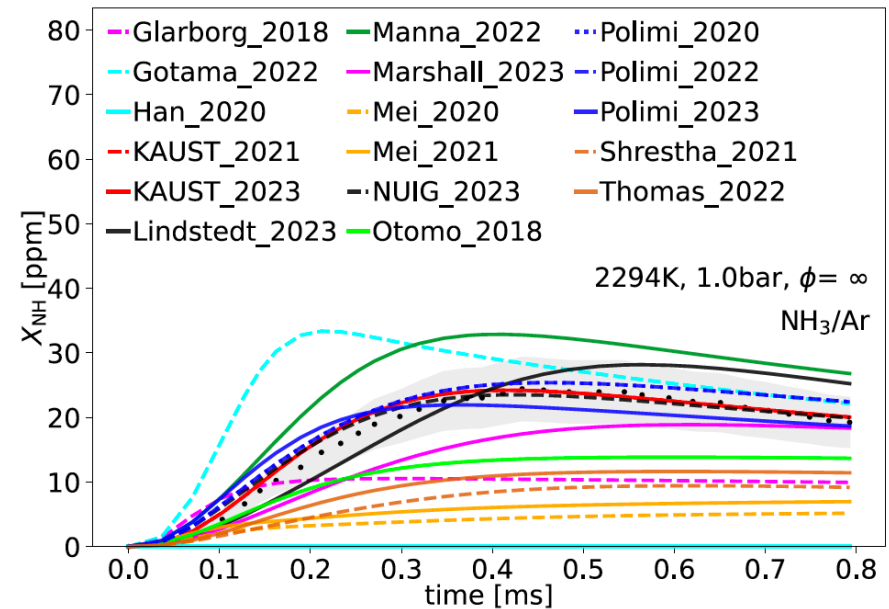
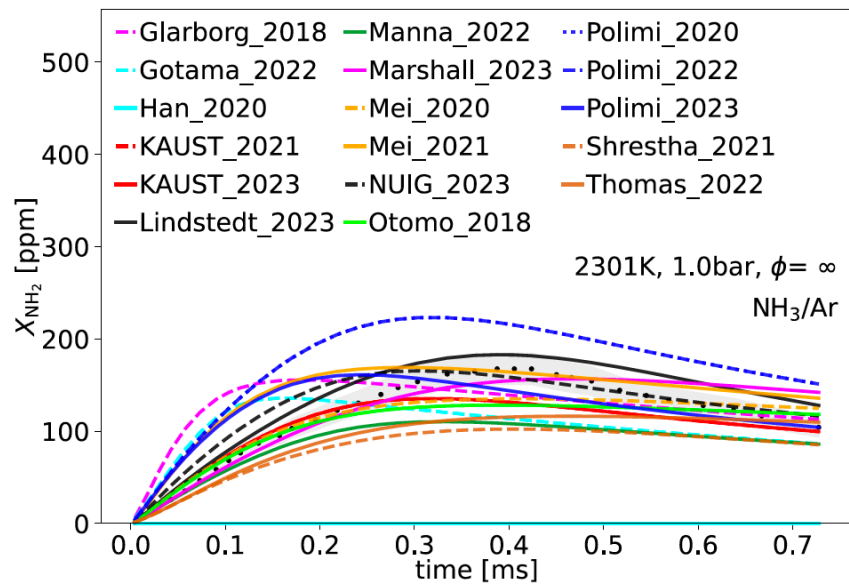


Glarborg et al., Prog. Energy Combust. Sci. 67 (2018) 3168

The two steps are intrinsically linked and cannot be independently specified if the SNCR performance of a model is to be maintained.

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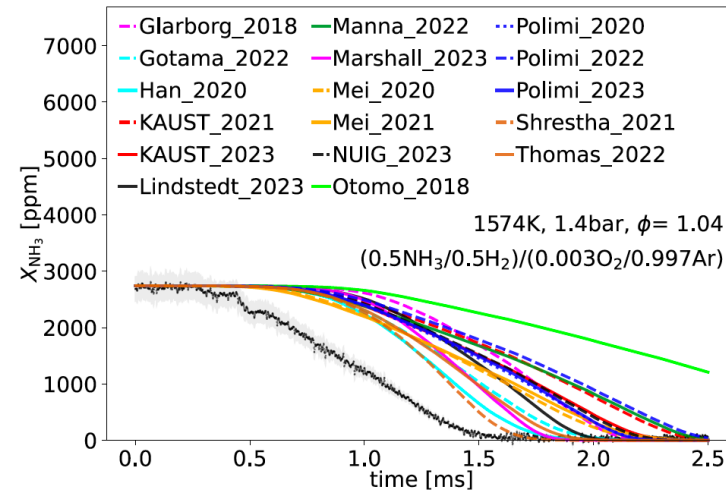
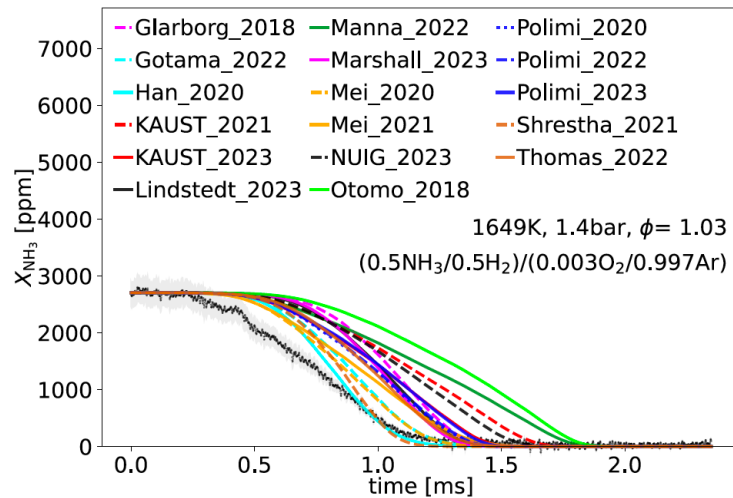
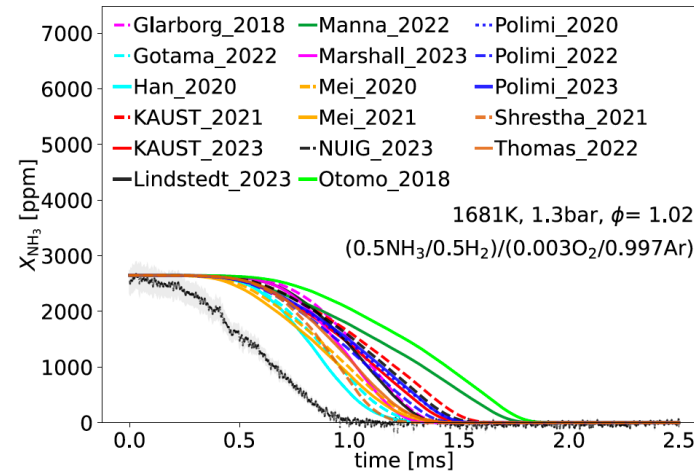
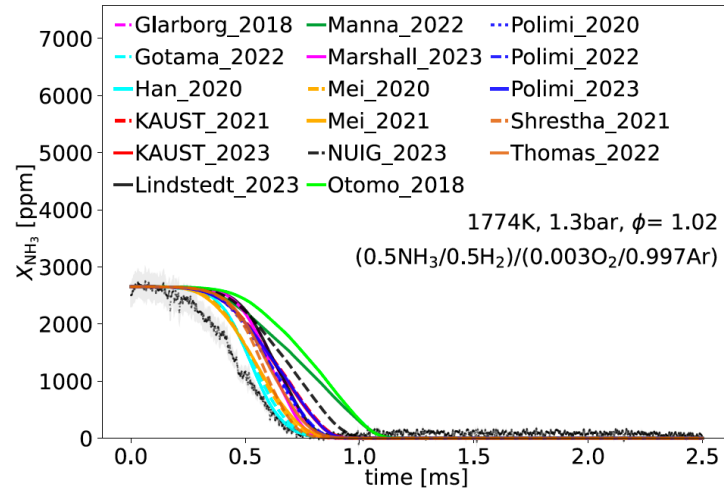
Graphs provided by Heinz Pitsch and correspond to Girhe et al. (2024) accepted for publication (Combust. Flame) Experimental data from Davidson et al. (1990).



The NH₂ chemistry, crucial for SNCR, is better reproduced than the subsequent NH pathways.
The NH radical plays an important role in N₂O formation.

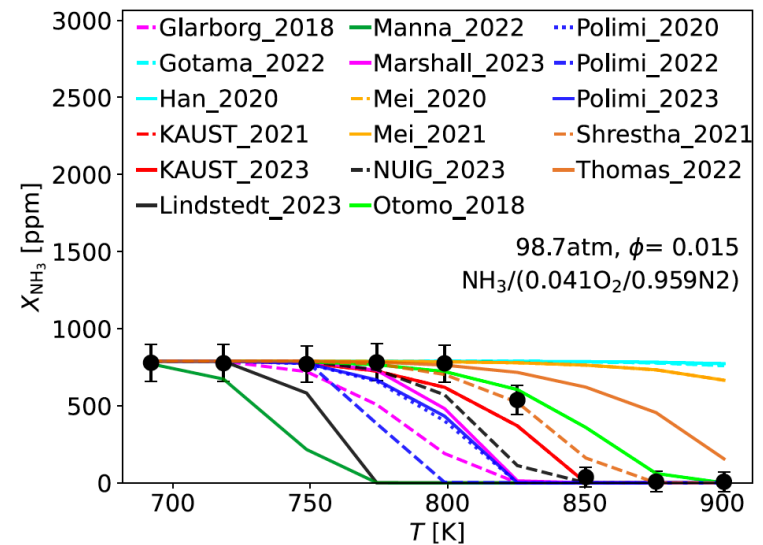
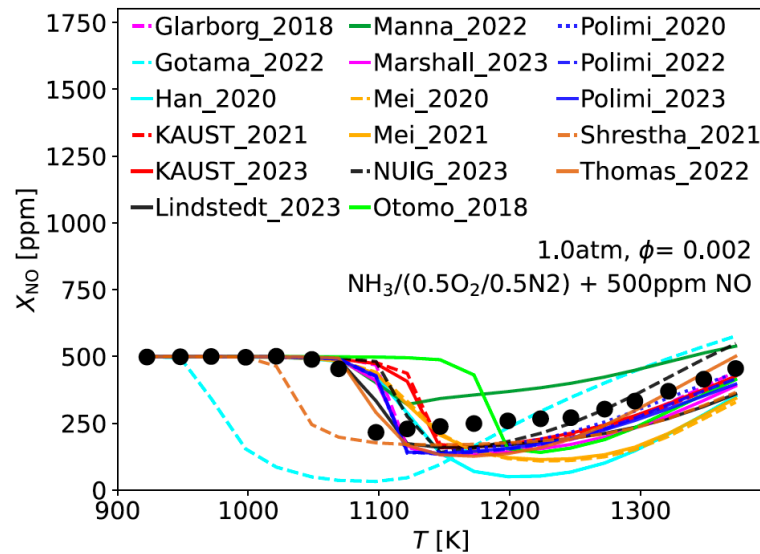
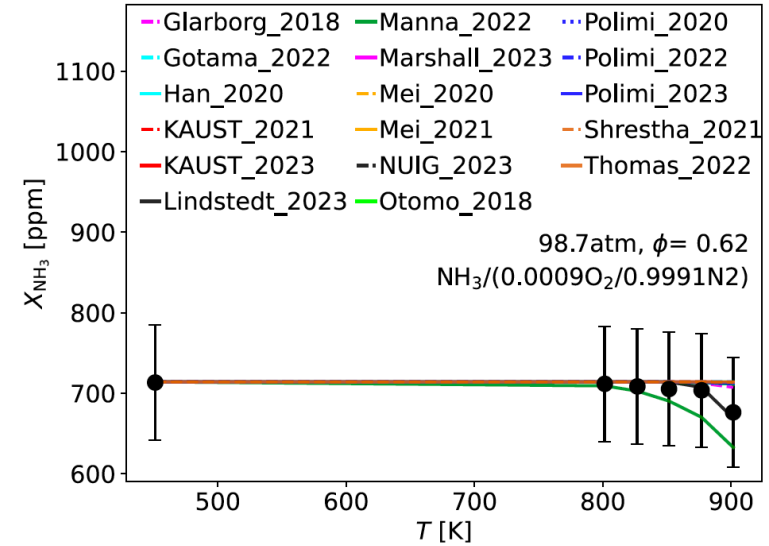
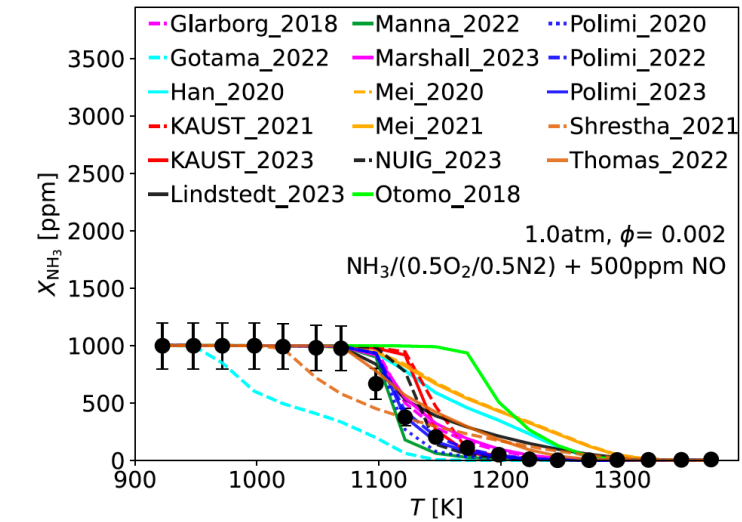
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Graphs provided by Heinz Pitsch and correspond to Girhe et al. (2024) accepted for publication (Combust. Flame). Experimental data from Altuarifi et al. Proc. Combust. Inst. (2023).



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Graphs provided by Heinz Pitsch and correspond to Girhe et al. (2024) accepted for publication (Combust. Flame). Experimental data from (left) Kasuya et al., Chem. Eng. Sci. 50 (1995) 1455-1466 and (right) Song et al., Fuel 181 (2016) 358-365.



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Thermal DeNOx (SNCR)

Rate comparisons:

Top: $\text{NNH} = \text{N}_2 + \text{H}$

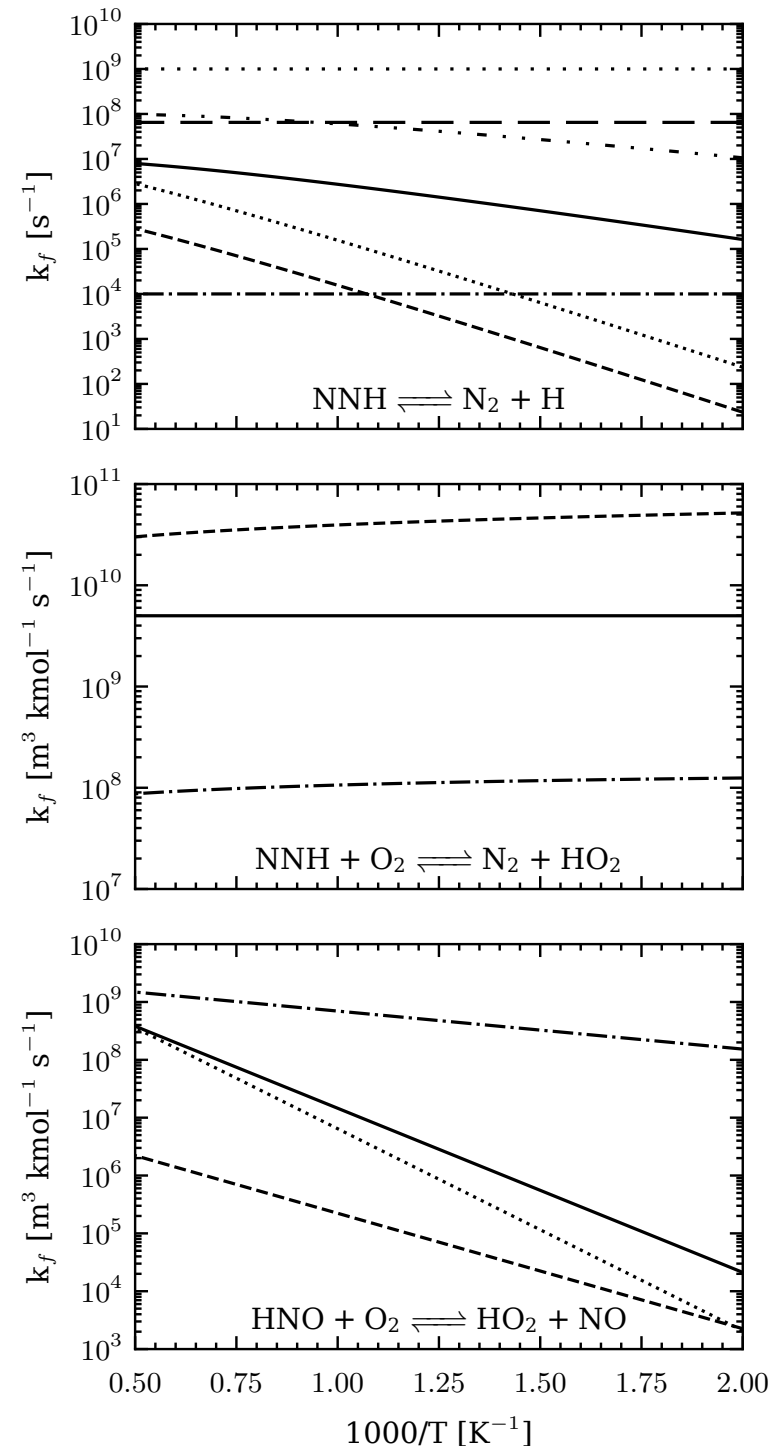
Lindstedt et al. (1994) (solid line); Miller and Bowman (dot-dashed line); Vandooren et al. (1991) (dotted line), Bozzelli and Dean (1995) (dot-dot-dash line); Miller and Glarborg (1999) (long dashed line) and Klippenstein et al. (2011) (sparse dotted line).

Middle: $\text{NNH} + \text{O}_2 = \text{N}_2 + \text{HO}_2$

GRI-Mech 3.0 (solid line), Klippenstein et al. (2011) (dashed line) and Dean and Bozzelli (dot-dashed line).

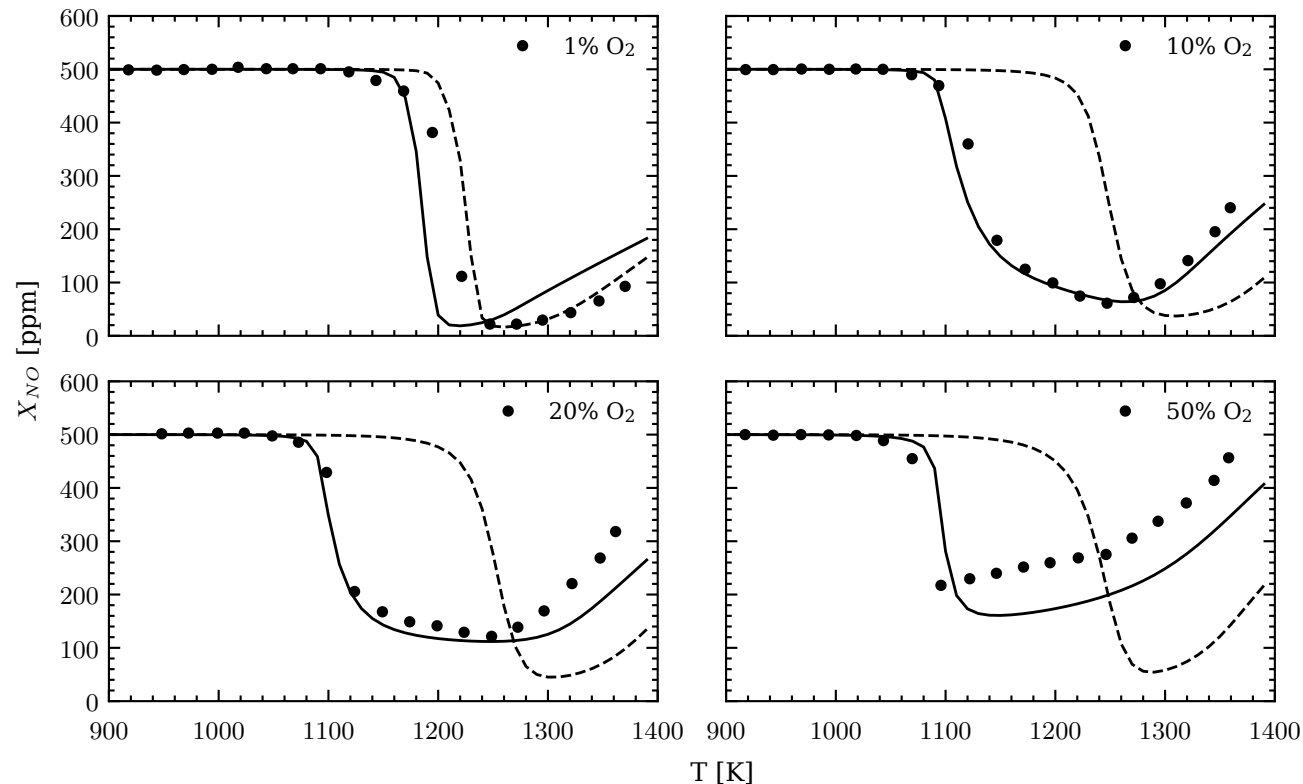
Bottom: $\text{HNO} + \text{O}_2 = \text{HO}_2 + \text{NO}$

GRI-Mech 3.0 (solid line), Bryukov et al. (1993) (dashed line), Fujii et al. (1981) (dot-dashed line) and Dean and Bozzelli (2000) (dotted line).



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Thermal DeNO_x (SNCR)

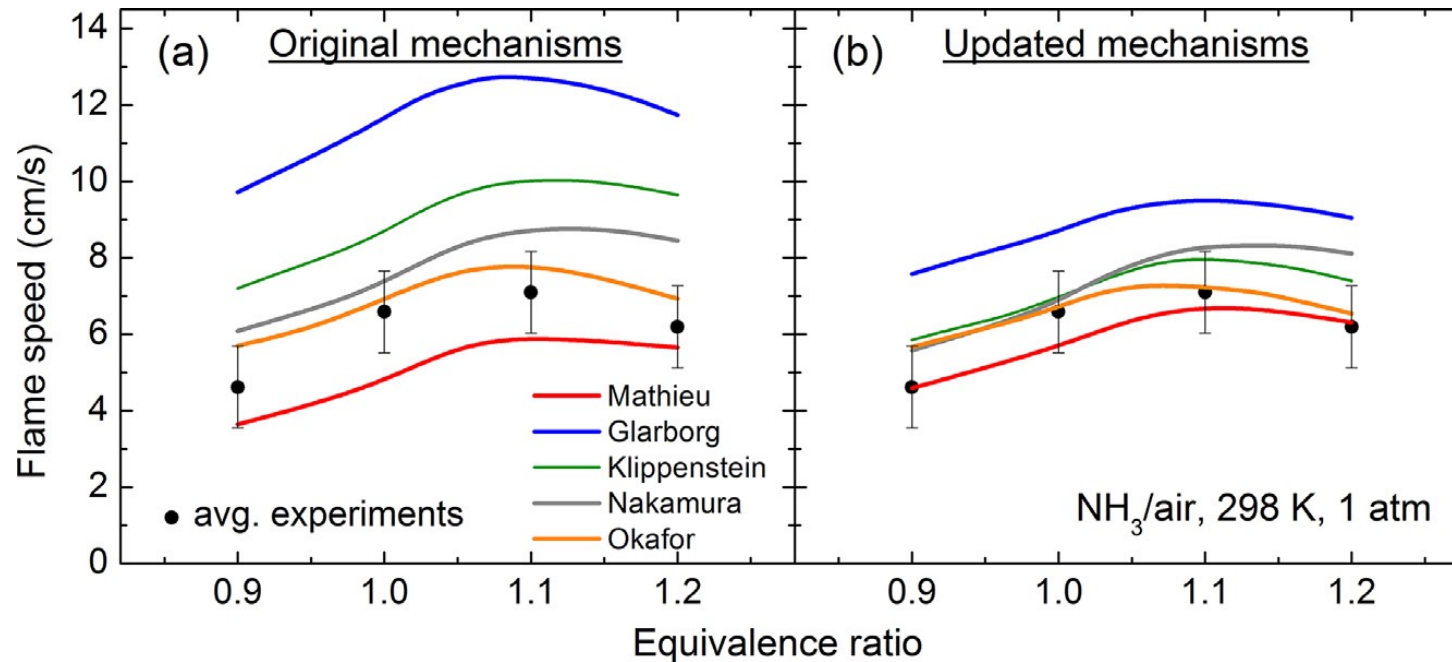


Flow reactor calculations comparing the impact on the SNCR behaviour of an inappropriate balancing of the NNH destruction reactions. From Greenblatt et al. (2023).

Experimental data from Kasuya et al. (1995) showing the impact of O₂ on the SNCR behaviour with inlet concentrations: NH₃ = 1000 ppm, NO = 500 ppm, O₂ = 1, 10, 20 and 50%, H₂O = 5% with a residence time (s) = 88.0/T(K) at a pressure of 101 kPa and mole fractions balanced with N₂.

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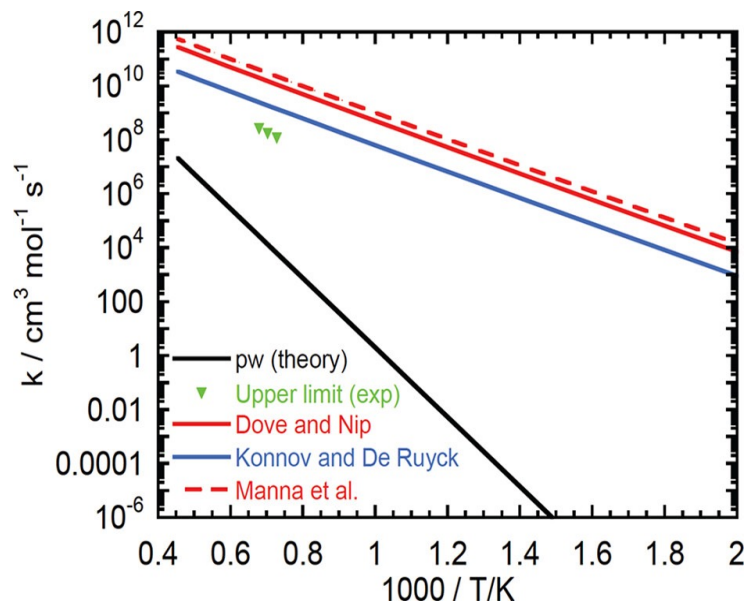
Importance of pyrolysis reactions – a key feature of ammonia combustion dynamics Alturaifi et al. (2022)



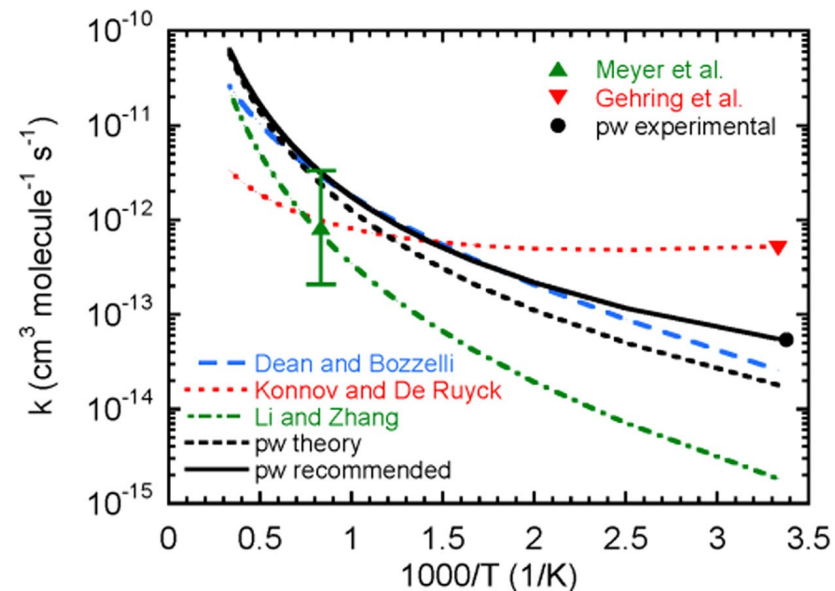
Prediction of NH₃ / air laminar flame speed showing the effect of updating selected detailed chemical kinetics mechanisms with the NH₃ pyrolysis sub-mechanism of Alturaifi et al. (2022). Experiments were averaged at each equivalence ratio from the studies of Takizawa et al. (2008), Hayakawa et al. (2015), Mei et al. (2019) and Han et al. (2019).

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The $\text{N}_2\text{H}_4/\text{N}_2\text{H}_3$ system is critical for hydrazine combustion with an impact on ammonia.



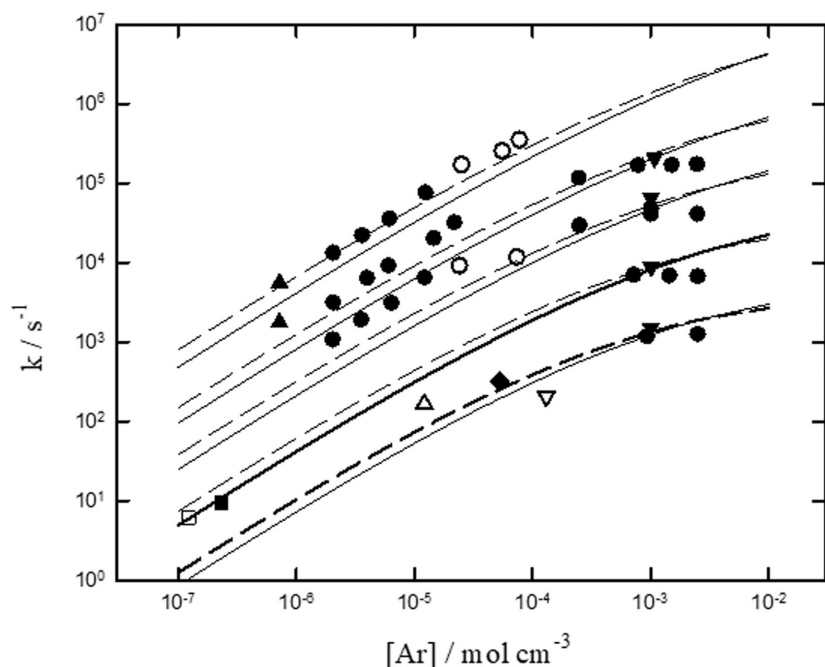
Arrhenius plot for the reaction $\text{NH}_3 + \text{NH}_2 \rightleftharpoons \text{N}_2\text{H}_3 + \text{H}_2$ (Marshall and Glarborg, *J. Phys. Chem. A* 127 (2023) 2601-2607). The calculated value, assumed to be an upper limit, is compared to estimates from Dove and Nip (1979), Konnov and De Ruyck (2001) and Manna et al. (2020). Also shown is upper limit values derived from modeling the flow reactor results of Benes et al. (2021).



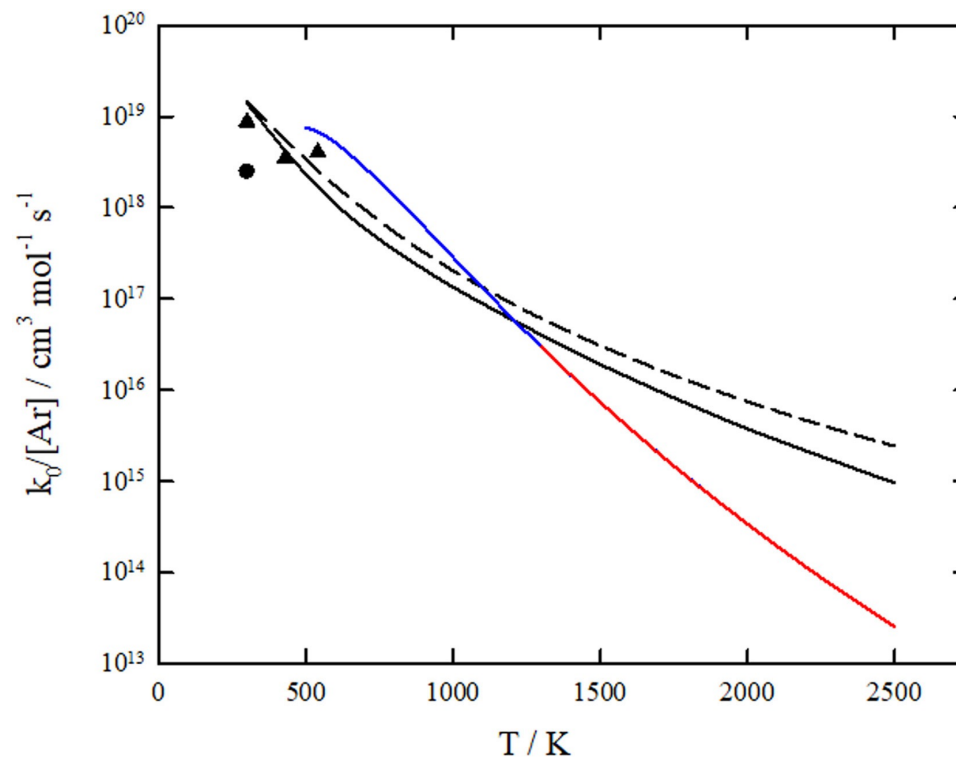
Arrhenius plot of some evaluations of the rate coefficient for $\text{NH}_2 + \text{N}_2\text{H}_4$ (Gao et al., *Proc. Combust. Inst.* 39 (2023) 571-579). ▲ Meyer et al. (1969), ▼ Gehring et al. (1971), dotted red line Konnov and De Ruyck [6], green dash-dot line Li and Zhang (2006), blue dashed line Dean and Bozzelli (2000), dashed black line present quantum calculations, ● Gao et al. (2023) measurement and solid black line their recommendation.

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A key reaction: $\text{N}_2\text{H}_4 (+ \text{Ar}) \rightarrow \text{NH}_2 + \text{NH}_2 (+ \text{Ar})$ from Cobos et al. *Combust Flame* 257 (2023) 112374.



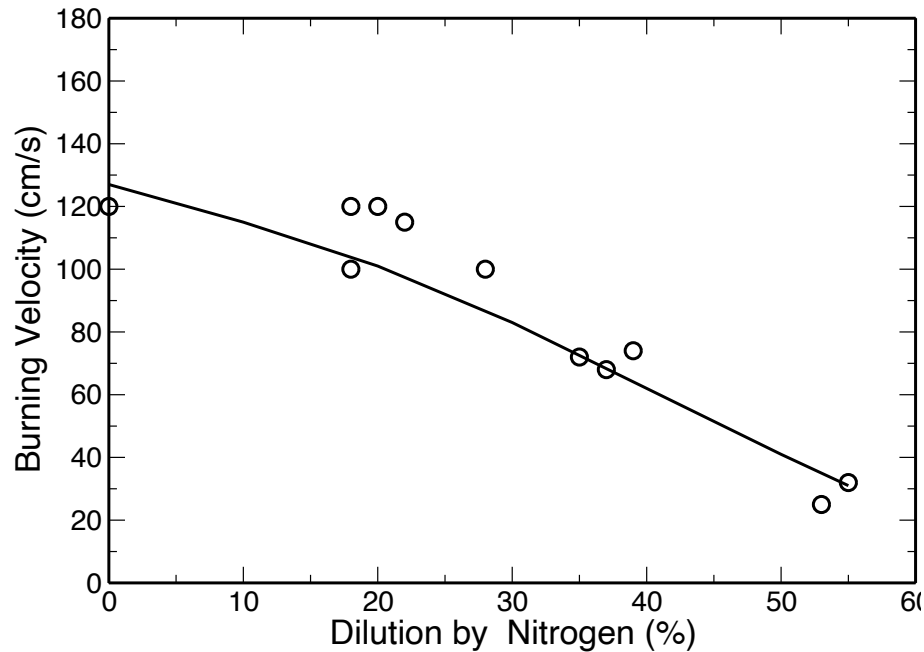
Falloff curves for $\text{N}_2\text{H}_4 (+ \text{Ar}) \rightarrow \text{NH}_2 + \text{NH}_2 (+ \text{Ar})$. Representations from bottom to top, for 1110, 1200, 1300, 1400 and 1550 K. Theoretical curves: (dashed line) Klippenstein et al. (2009); (solid line) Cobos et al. (2023).



Limiting low-pressure rate constants k_0 for $\text{N}_2\text{H}_4 (+ \text{Ar}) \rightarrow \text{NH}_2 + \text{NH}_2 (+ \text{Ar})$. Red curve and blue curves experimental data and theoretical calculations by Klippenstein et al. (2009) with $\langle \Delta E \rangle_{\text{down}} / hc = 150 (T/300 \text{ K})^{0.85} \text{ cm}^{-1}$ (dashed black line) and from Cobos et al. (2023) with $\langle \Delta E \rangle_{\text{total}} / hc = -100 \text{ cm}^{-1}$ (solid black line).

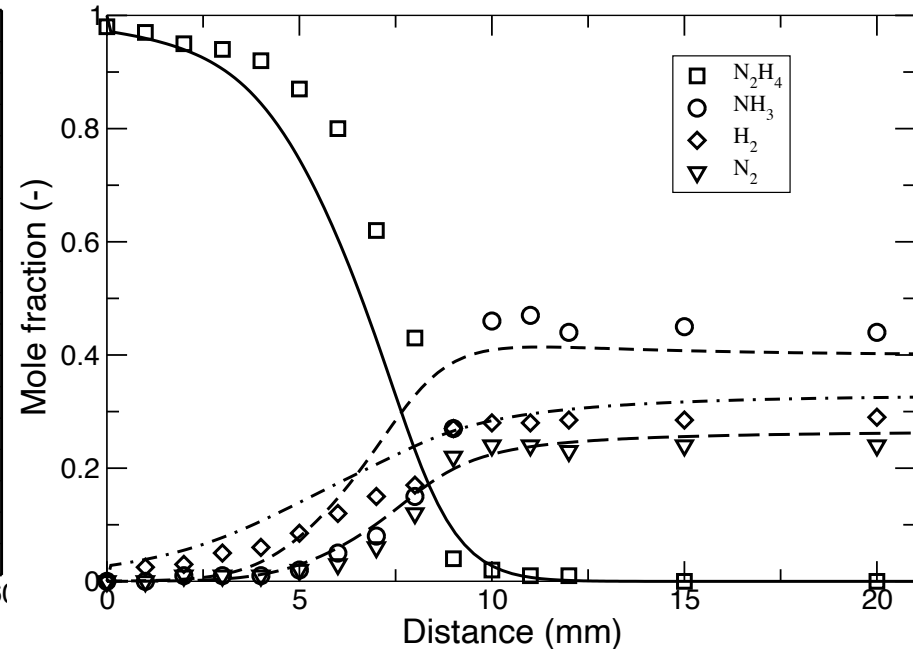
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Hydrazine decomposition flames (no oxidant) are exceptionally sensitive to the N_2H_4/N_2H_3 system Cobos et al. (2023) amongst others.



Burning velocities of N_2 diluted hydrazine decomposition flames. Circles: mixtures with N_2 at 1 atm pressure and an initial temperature of 383 K (Greenblatt and Lindstedt 2025 to appear).

Experimental data from Karpov and Sokolik, Russ. J. Phys. Chem. 38 (1964) 903 (c.f., Konnov and De Ruyck 2001).



Hydrazine decomposition flame structure. Experimental results from MacLean and Wagner (1967). Initial temperature 353 K, pressure 14 Torr (0.0184 atm). Computations Greenblatt and Lindstedt (2025).

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Some critical reaction steps

- The pyrolysis chemistry has a huge impact due to the scarcity of H radicals during the combustion of NH_3 – in particular in the absence of additional H_2 as part of the fuel stream. How much H_2 is appropriate?
- Girhe et al. (2024) recommend that the reaction $\text{NH}_2 + \text{NH} = \text{N}_2\text{H}_3$ be studied further. The lack of stabilisation reported by Klippenstein et al., J. Phys. Chem. A 113 (2009) 10241 could usefully be confirmed.
- Greenblatt et al. (2023) adopts the NNH chemistry for decomposition and oxidation according to Klippenstein et al. (2011). This is not universal and good SNCR results can be obtained using very different rate combinations. The uncertainties in the reaction $\text{NNH} + \text{O}_2$ could usefully be further established. The same applies to the reaction $\text{HNO} + \text{O}_2$.
- Gao et al. (2023) makes a forceful argument that the that the pyrolysis chemistry of N_2H_3 is in urgent need of clarification.
- How accurate is the low-pressure limit for the reaction $\text{N}_2\text{H}_4 (+ \text{M}) = \text{NH}_2 + \text{NH}_2 (+ \text{M})$? The reaction has been studied by Cobos et al. (2023) and Klippenstein et al. (2009) amongst others. Computed results can be exceptionally sensitive to both chaperon efficiencies (c.f., Glarborg et al. 2021) and the actual value (e.g., in Ar bath gas).

Model improvements

Reaction mechanism performance (Girhe et al. 2024)

Kinetic model	Species concentration					Thermal DeNO _x	Mean	Ignition delay time	Laminar burning velocity	Overall mean
	Pyrolysis	Oxidation								
		High <i>T</i>	Intermediate <i>T</i>	Low <i>T</i>						
NUIG_2023	0.741	0.778	0.841	0.894	0.909	0.833	0.842	0.888	0.854	
KAUST_2023	0.734	0.763	0.903	0.890	0.910	0.840	0.820	0.897	0.852	
KAUST_2021	0.734	0.759	0.887	0.890	0.901	0.834	0.823	0.894	0.851	
Polimi_2023	0.687	0.769	0.850	0.883	0.908	0.819	0.822	0.888	0.843	
Polimi_2020	0.715	0.737	0.848	0.885	0.906	0.818	0.817	0.892	0.842	
Mei_2021	0.673	0.759	0.848	0.850	0.921	0.810	0.818	0.882	0.837	
Polimi_2022	0.715	0.736	0.848	0.869	0.906	0.815	0.801	0.892	0.836	
Thomas_2022	0.636	0.769	0.848	0.834	0.898	0.797	0.814	0.889	0.833	
Mei_2020	0.633	0.736	0.851	0.811	0.917	0.790	0.819	0.891	0.833	
Manna_2022	0.708	0.720	0.887	0.848	0.910	0.814	0.823	0.833	0.823	
Lindstedt_2023	0.707	0.689	0.832	0.865	0.898	0.798	0.821	0.841	0.820	
Shrestha_2021	0.678	0.685	0.815	0.797	0.712	0.737	0.818	0.890	0.815	
Gotama_2022	0.589	0.748	0.825	0.845	0.731	0.748	0.804	0.880	0.810	
Marshall_2023	0.718	0.712	0.829	0.840	0.892	0.798	0.793	0.831	0.807	
Glarborg_2018	0.624	0.699	0.809	0.816	0.892	0.768	0.823	0.810	0.801	
Han_2020	0.095	0.752	0.843	0.831	0.859	0.676	0.810	0.899	0.795	
Otomo_2018	0.652	0.591	0.808	0.858	0.819	0.746	0.805	0.818	0.790	

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Summary

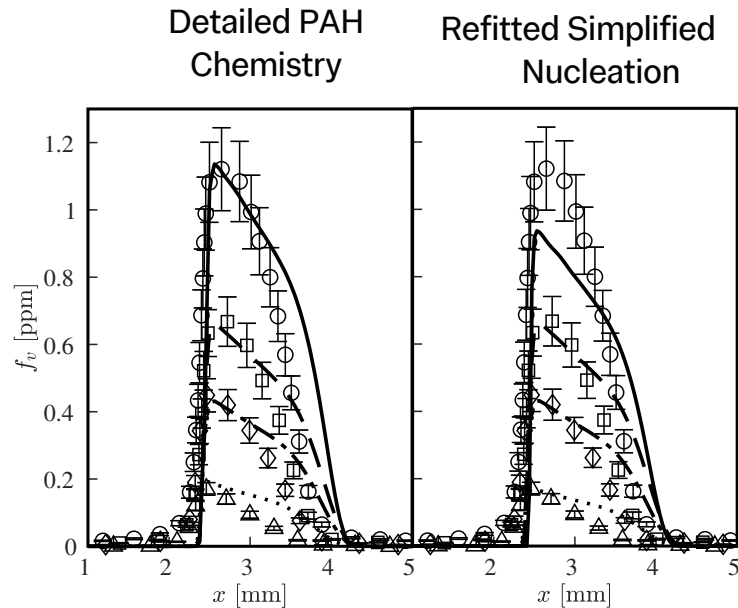
- An exceptionally wide range of chemical mechanisms have been produced. Some of these are not based on best available data and/or not subject to comprehensive validation.
- Accurate validation data remains essential and not all data sets available appear to have been subject to a thorough accuracy assessment.
- Inaccurate validation data poses a problem when assessing model performance. Put simply – to assess model performance vs questionable data is at best futile and at worst misleading.
- **Accurate speciation data is king** and the prospects for fundamental “chemistry experiments” featuring time resolved shock tube data are gradually improving.
- Stirred reactor data can be affected by imperfect mixing, heat losses and, if mixtures are not sufficiently dilute, heat release effects. Still such data also has a major role provided conditions are well-defined. Flow reactor data may also suffer some of these disadvantages.
- Flames are not suitable for determining chemical kinetic data. There is, however, a major role for accurate flame data use in the context of validation. This opens the possibility of assessing the overall performance of a model under more complex conditions.

Can current state of the art provide guidance?

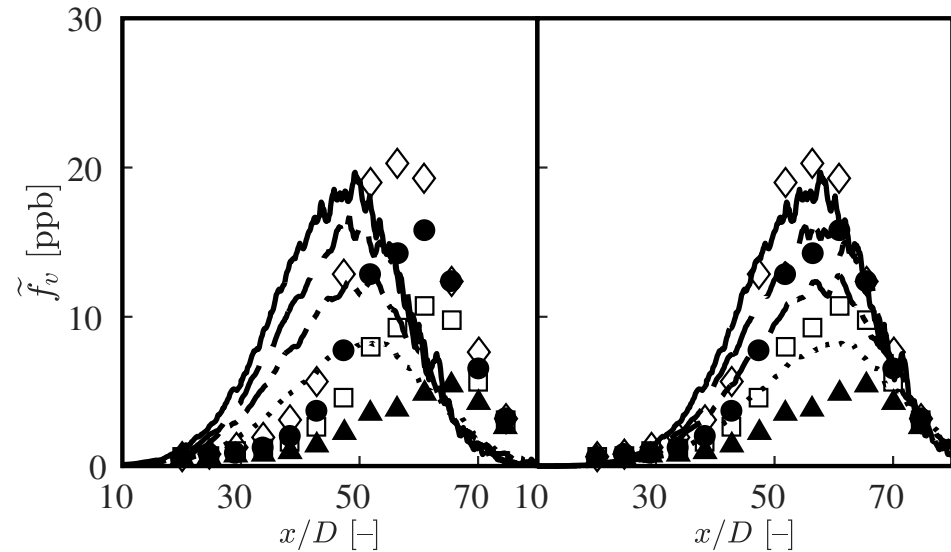
- The impact of ammonia addition on soot formation has attracted much attention and some quite esoteric attempts to explain the observed reduction.
- The explanation appears quite straightforward in that to a leading order the reduction in H radical concentrations changes the dynamics of soot inception and growth. Provided these aspects are well reproduced accurate predictions are possible (Greenblatt et al. 2024).
- Experiments on laminar and turbulent flames featuring identical $\text{NH}_3/\text{C}_2\text{H}_4/\text{N}_2$ fuel blends are recently made available [1,2] by researchers from KAUST and the University of Sydney.
- Turbulent calculations for ammonia-soot flames are relevant - especially for the low Damköhler number processes associated with soot formation.
- The impact of ammonia addition to hydrogen mixtures has been studied experimentally at the University of Sydney (Masri and co-workers) and computationally at Imperial (Greenblatt et al. 2024).

[1] Bennett et al., Combust. Flame 220 (2020). [2] Boyette et al., Combust. Flame 226 (2021).

Impact of ammonia on soot formation



(○) (—) C₂H₄:N₂:NH₃ = 75:25:0 (□) (- - -) C₂H₄:N₂:NH₃ = 75:19:6
 (◇) (- · - ·) C₂H₄:N₂:NH₃ = 75:12.5:12.5 (△) (· · ·) C₂H₄:N₂:NH₃ = 75:0:25

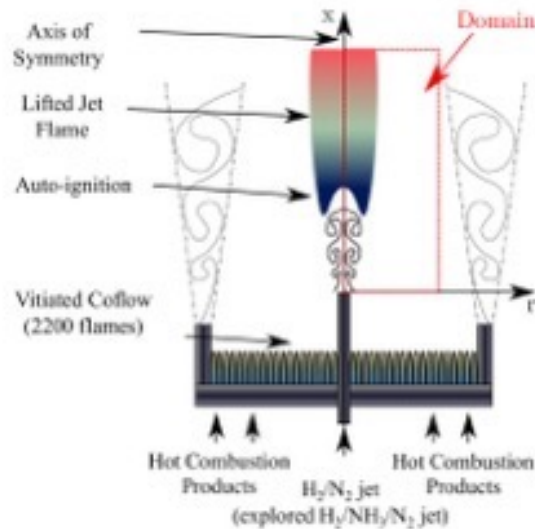


Predicted and measured (Boyette et al. 2021) axial profiles of mean soot volume fractions for turbulent partially premixed C₂H₄/NH₃ flames at Re ~ 12,400 with 0 to 25% ammonia substitution. Profiles shifted by x/D = 8.5 in the right panel.

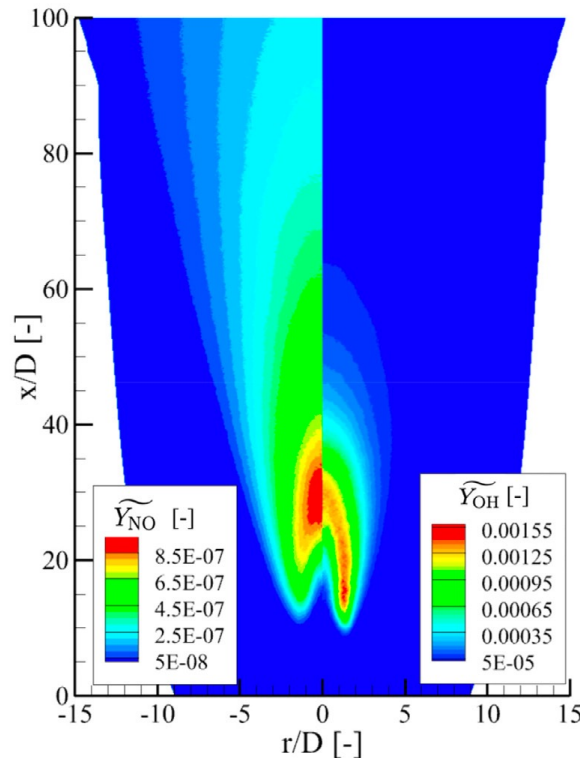
- The reduction of soot with ammonia addition is captured in laminar flames.
- Refitted simplified nucleation based on the mole fraction of NH₃ provides adequate prediction of soot.
- **The H radical is of key importance.**
- Computations using the simplified nucleation rate and a fully coupled 84-dimensional transported joint probability density functional method.
- Correct profile width captured – reflects reproduction of Turbulence-Chemistry-Soot-Radiation Interactions.

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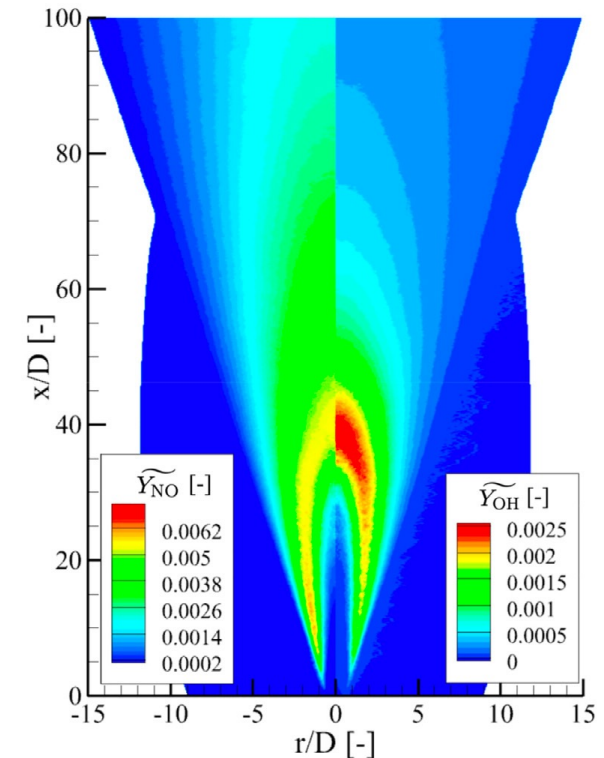
Impact of ammonia flame stabilisation



- The revised Cabra geometry used computationally has also been used experimentally by Masri and co-workers (2024).
- The replacement of a fuel stream with 25.7% H₂ with 5.37% H₂ and 20% NH₃ requires ~ **550 K** increase in coflow temperature to compensate the loss in reactivity.



(a) Mean NO and OH mass fractions for Case 1 (fuel stream with 25.37% H₂) at a coflow temperature of 1045 K.



(b) Mean NO and OH mass fractions for Case 4 (fuel stream with 5.37% H₂ and 20% NH₃) at a coflow temperature of 1600 K.

- The peak NO levels increase ~ 7000 times and the flame structure becomes much broader (Greenblatt et al. 2024). Computations using a fully coupled transported PDF method.

What can the community do in collaboration?

- Is there scope for a chemical kinetic data evaluation/advisory group featuring contributions from practitioners and dedicated to recommend the best chemical kinetic data currently available (c.f., Baulch et al. 1992, 1994, 2005)?
- If so, the development of accurate ammonia mechanisms can usefully be considered in two parts: pyrolysis and oxidation. Perhaps with a further focus on high pressure.
- As an example, the success of the TNF workshop series has to a large extent relied upon accurate experimental data. Can an experimental data evaluation group be convened that assesses the accuracy of validation data sets and their appropriate use?
- Is there any prospect for the exceptionally useful formal accuracy assessments (e.g., developed by Girhe et al. 2024) to be made available to model developers to help analyse their efforts?
- Overall, can a framework evolve to account for new and more comprehensively evaluated data sets for the benefit of the community?