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Research Article

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Posted Date: October 27th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-11222349/v1>

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Additional Declarations: No competing interests reported.

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Abstract

The present work investigates the transient and steady-state combustion behavior of ammonia and ammonia/hydrogen fuels under MILD combustion conditions in diffusion-controlled configurations. Numerical simulations were performed through one-dimensional counterflow flamelets in both steady and unsteady Hot-Oxidizer Diluted-Fuel (HODF) conditions. Particular attention is devoted to the transient ignition stage, in order to clarify how the reaction zone is established and how the final reactive structure emerges as a function of fuel dilution and hydrogen blending. The analysis shows that ignition is initially triggered on the lean side for all conditions, whereas the subsequent evolution depends strongly on the local reactivity: weakly diluted cases develop localized and stratified reaction structures that propagate toward richer conditions, while highly diluted cases evolve toward broader and more distributed igni-diffusive regimes consistent with MILD combustion. Steady-state regimes are then used to classify the stabilized combustion regimes and to identify the corresponding transition trends in terms of temperature and heat-release distributions. At low and moderate dilution, the dominant reactive region remains closely associated with the stoichiometric mixture fraction, while under highly diluted conditions a progressive

spatial decoupling develops. Additional analysis of nitrogen chemistry identifies the dominant routes controlling NO formation and shows how dilution, hydrogen enrichment, strain rate, oxidizer preheating, and molecular transport redistribute the relative importance of the main NH_3 -NO conversion pathways.

Keywords: MILD, Ignition, flamelet, Ammonia, Hydrogen

1 Introduction

Decarbonization of the energy sector has intensified interest in carbon-free fuels such as hydrogen and ammonia for power generation (Turner (2004); Jensen et al. (2007); Chai et al. (2021); Valera-Medina et al. (2018); Klerke et al. (2008); Lan et al. (2012); Morlanés et al. (2021)). Although hydrogen is considered as the most promising solution for clean energy production (Hanley et al. (2018)), significant technical and economic barriers (production, storage, distribution) impede a rapid transition to a purely hydrogen-based economy (Ball and Weeda (2015)). In this context, ammonia NH_3 has emerged as a promising complementary energy carrier (Valera-Medina et al. (2018); Klerke et al. (2008); Lan et al. (2012); Morlanés et al. (2021)). Ammonia is a carbon-free molecule with a high hydrogen density and a well-established global production and transportation infrastructure. It can be easily liquefied at moderate pressure, enabling efficient storage and bulk transport of hydrogen in chemically bound form. These attributes make ammonia an attractive energy vector for future low-carbon combustion systems (Sabia and de Joannon (2026); Tornatore et al. (2022)). However, ammonia combustion presents several challenges that must be overcome for its use in propulsion or power generation (Hayakawa et al. (2017)). Pure ammonia has low reactivity, with high autoignition temperature and slow flame speed (Shrestha et al. (2021); Lhuillier et al. (2020)), and extremely narrow flammability limits. Therefore, ignition and stable flame propagation are difficult under conventional combustion conditions. Furthermore, ammonia can rapidly oxidize to form nitrogen oxides (NO_x) (Kurata et al. (2019)). It is therefore crucial to identify and develop optimized combustion technologies and strategies to enable clean and stable ammonia utilization. One strategy to enhance ammonia's reactivity is to blend it with more reactive fuels such as hydrogen or hydrocarbon fuels. This approach can significantly improve flame stability and reduce ignition delay. Both hydrogen and methane addition to ammonia has been shown to increase the burning velocity and widen the flammability range (Valera-Medina et al. (2017); Zitouni et al. (2021)). These studies underscore that ammonia's combustion properties can be improved by blending, but drawbacks are present: blending with hydrocarbons introduces CO_2 emissions and it generally tends to produce higher NO_x emissions than pure ammonia combustion under comparable conditions (Kurata et al. (2017); Rocha et al. (2019)). Another strategy is to employ non-conventional combustion technologies. In particular, MILD combustion (Moderate or Intense Low-Oxygen Dilution) has shown to be a great solution for a wide palette of fuels (Ariemma et al. (2022); de Joannon et al. (2024)). MILD combustion is characterized by highly preheated and highly diluted reactants (Cavaliere and de Joannon

(2004); Sabia et al. (2021)) , typically obtained by mixing with recirculating combustion products. Under these conditions, chemical time scales become longer and the interaction between mixing and finite-rate chemistry becomes increasingly important, leading to combustion structures that differ substantially from conventional flame-like regimes Parente et al. (2016).

Under MILD conditions, the stabilization of deflagrative or/and diffusive structures is prevented while igni-diffusive structures occur throughout the mixture wherever local temperature and concentration conditions become favourable. This distributed combustion regime offers multiple advantages: the absence of hot flame zones leads to lower peak temperatures and extremely uniform temperature field, which drastically reduce thermal NOx formation (Ariemma et al. (2021)). At the same time, the continuous entrainment of burned gases preheats and dilutes the incoming reactants, making the system highly resistant to thermo-acoustic instabilities and capable of sustaining combustion even for low-calorific or low-reactivity fuels that would quench in a normal flame (Feser et al. (2020)). These unique features make MILD combustion a compelling approach for ammonia and other alternative fuels that are challenging to burn in classical modes. Ammonia combustion under MILD conditions has proven to be a promising solution (Sorrentino et al. (2019)). Studies by Ariemma et al. and others have shown that ammonia can be oxidized stably in a MILD regime with low NOx emissions (Ariemma et al. (2022, 2025)). Methane blends were also investigated by the same authors. Their experiments showed that even as low as 10–30% methane addition yielded significantly enlarged stability limits compared to the pure ammonia case. Hydrogen/Ammonia blends under MILD conditions were further investigated by the same authors (Ariemma et al. (2025)). They highlighted how total conversion of fuel mixtures can be achieved independently of fuel blend composition, whereas NOx emissions are generally higher than those from either pure ammonia or pure hydrogen. Other works have explored ammonia MILD combustion in diffusion flames: Sorrentino et al. (2021) carried out numerical studies of one-dimensional counterflow flames in both Hot-Fuel-Diluted-Fuel (HFDF) and Hot-Oxidant-Diluted-Fuel (HODF) configurations. Their analysis confirmed that high dilution and preheat levels fundamentally alter the combustion structure of NH_3 , leading to the distributed ignition behavior typical of MILD regimes. These studies confirm that ammonia (and its blends) can be effectively burned in MILD combustion systems, achieving high stability and low emissions outcomes that would not be achievable in conventional flame regimes.

Despite the progress, a key knowledge gap remains: transient behaviour of ammonia-fueled MILD combustion, particularly under diffusion-controlled conditions. Nearly all existing studies on ammonia MILD combustion have focused on steady-state conditions, however, practical operation of any combustion system involves transient events such as ignition, extinction, and load adjustments. Therefore, understanding these transient phenomena is crucial for safe and reliable burner design. To date, only a few works have explored such aspects: Ku et al. (2018) investigated extinction limits of nonpremixed ammonia flames under diluted oxidizer conditions, Colson et al. (2021) studied ammonia/methane counterflow flames across varying compositions, and Sorrentino et al. (2021) identified the regime transitions for ammonia diffusion flames. Previously mentioned works provided valuable data on reactivity

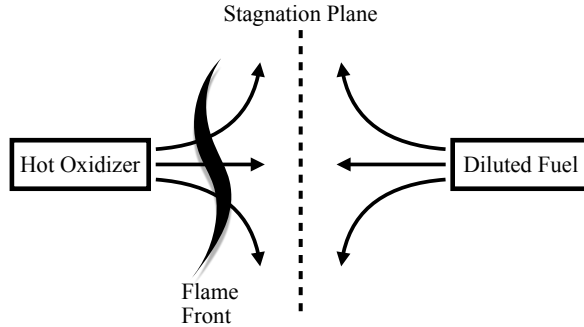


Fig. 1: Hot-Oxidizer Diluted-Fuel (HODF) configuration.

and stability, but only under steady/quasi-steady conditions. Detailed analysis of the ignition process and flame stabilization dynamics for ammonia in MILD conditions is still missing, especially regarding MILD reactive structures. Understanding reactive structures formation under highly diluted and/or preheated reactants is relevant to processes in systems like gas turbine combustion chambers (Sidey and Mastorakos (2016); Nemitallah et al. (2018)), and, in particular, in furnaces, gasification, and incineration applications (Kwiatkowski et al. (2013); Kwiatkowski and Mastorakos (2016); Song et al. (2013)), where low-heating-value fuels burn in an environment of hot combustion products. Transient studies in similar configurations with conventional fuels have shown complex behaviours – for example, numerical simulations by Sidey and Mastorakos (2018) revealed the formation of ignition kernels and unsteady flame propagation in a hot coflow mixing layer – but no analogous data exist for ammonia or ammonia/hydrogen mixtures under HODF MILD conditions. In light of this gap, the present study is undertaken to investigate the transient ignition and combustion behaviour of ammonia and an ammonia/hydrogen blend in a MILD combustion regime in HODF conditions. Specifically, we analyse a diffusion-controlled, hot-oxidant ignition configuration to characterize how ammonia and NH_3/H_2 mixtures ignite, propagate, and stabilize when exposed to a hot, diluted oxidizer stream. Using detailed chemistry and transient simulations, we examine the ignition dynamics and transient evolution of the reactive structures in ammonia/hydrogen counterflow flamelets, together with the nitrogen-oxides pathways associated with the resulting steady states. This work aims to fill the existing knowledge gap on ammonia’s performance in MILD combustion. The findings provide new fundamental insight into the ignition kinetics and stability limits of ammonia-based fuels under MILD conditions, and will help with the design and optimization of future carbon-free combustion systems that can utilize ammonia and ammonia/hydrogen mixtures in a stable-low-emission combustion.

2 Numerical Methodology

Ammonia-hydrogen/air igniting counterflow diffusion flamelets were computed with the 1D reactive flow solver CHEM1D (van Oijen (2012)). To mimic MILD conditions, simulations were carried out in a Hot-Oxidizer Diluted-Fuel (HODF) configuration,

pictured in Fig. 1. Fuel inlet temperature was fixed to 300 K, while oxidizer inlet temperature was set to 1400, 1600, or 1800 K. All simulations were performed at atmospheric pressure, with the fuel stream diluted by nitrogen at levels ranging from 0% to 93% N₂. Different fuel compositions were investigated including pure ammonia, pure hydrogen and blends of the two. Three strain rates were examined and kept constant across all simulations: 50, 150, 500 s⁻¹.

To account for the presence of fuel-bounded nitrogen in ammonia, Angelilli et al. (2024) proposed a generalized mixture fraction formulation. Later on, Guo et al. (2025) found little or no difference between the generalized and classic Bilger formulation of the mixture fraction. Therefore, Bilger mixture fraction formulation is used for all fuel mixtures (Ballatore et al. (2025)) in the present work.

A comparison among various chemical kinetic models is presented in Appendix A, showing consistent qualitative trends in the selected ignition and reactive-structure indicators. Based on this assessment, the mechanism by Manna et al. (2023) was selected for the main analysis, as it has been explicitly validated for MILD combustion conditions, including high dilution levels ranging from 86% to 99%, making it particularly suitable for the present study. To assess the impact of molecular transport modelling, diffusion terms in the scalar transport equations were treated using both the unity-Lewis-number approximation and a mixture-averaged diffusion model.

All simulated conditions are summarized in Tab. 1 for clarity. In total, 252 1D transient simulations were performed.

2.1 Post-processed metrics and diagnostic quantities

The computed counterflow flamelets are post-processed with an in-house Python code to characterize reactive structures and nitrogen-chemistry pathways across the investigated parameter space. For each operating condition, results are analysed in mixture-fraction space using temperature $T(Z)$ and heat-release rate $\dot{q}(Z)$ profiles, together with derived scalar indicators. The maximum temperature rise is defined as $\Delta T_{\max} = \max_Z [T(Z) - T_{\text{frozen}}(Z)]$, where T_{frozen} denotes the reference (non-reacting) temperature field obtained by suppressing chemical source terms while retaining transport. The location of peak heat release is quantified by the mixture fraction at maximum heat release, $Z(\dot{q}_{\max}) = \arg \max_Z \dot{q}(Z)$, and is compared to the stoichiometric mixture fraction Z_{st} . Similarly for the location of the maximum temperature rise $Z(\Delta T_{\max})$. The displacement $Z(\Delta T_{\max}) - Z_{st}$ is used as a compact marker of the rich/lean positioning of the dominant reactive zone and of the departure from classical diffusion-flame behaviour under strongly diluted MILD conditions.

Oxidizer preheating effects are assessed by varying the oxidizer inlet temperature T^{ox} and analysing the resulting changes in $\Delta T_{\max}$ and $Z(\dot{q}_{\max}) - Z_{st}$ as functions of dilution level X_{N_2} and fuel blending ratio X_{H_2} . Strain-rate sensitivity is quantified by repeating selected conditions at different imposed strain rates a and evaluating the same indicators. Transport-model sensitivity is examined by comparing the mixture-averaged formulation to the unity-Lewis-number approximation, with the analysis focusing on differences in the same reactive-structure indicators.

T^{ox} [K]	Strain rate [s ⁻¹]	X_{H_2} [%]	X_{N_2} [%]	Transport model
1400	50			Mixture-averaged
1600	50			Mixture-averaged
1800	50			Mixture-averaged
1600	150	0, 5, 10, 50, 75, 100	0, 50, 70, 80, 85, 90, 93	Mixture-averaged
1600	500			Mixture-averaged
1600	50			Unity-Lewis

Table 1: Simulated conditions for HODF counterflow diffusion flamelets.

For nitrogen oxides, one-dimensional domain integrals are used to provide a scalar measure of the amount of a given NO_x species within the counterflow domain,

$$I_{\text{NO}_x} = \int_{-L/2}^{L/2} \rho Y_{\text{NO}_x} dx, \quad (1)$$

where L is the domain length, ρ is the density, and Y_{NO_x} is the mass fraction of the selected species (e.g. NO , NO_2 , N_2O). In addition, elementary-reaction rates of progress are post-processed to quantify pathway contributions to net production/consumption of selected nitrogen species and to construct species-to-species reaction graphs and pathway representations. The detailed definitions and procedures employed to (i) compute rates of progress and (ii) construct the directed weighted graphs and ranked pathway sets are provided in the appendices (Secs. ??–C).

3 Ignition and Reactive-Structure Evolution

The present section focuses on the transient development of the counterflow flamelets, with the aim of clarifying how ignition occurs and how the reaction zone evolves toward its final state. Particular attention is devoted to the temporal evolution of key reactive-structure indicators, such as the mixture fraction at maximum heat release, $Z(\dot{q}_{\text{max}})$, and the maximum temperature rise, ΔT_{max} , together with their position relative to the stoichiometric mixture fraction Z_{st} , following previous works from literature (Sorrentino et al. (2021, 2019); de Joannon et al. (2009)). These quantities are used to track the emergence and evolution of reactive structures, allowing us to distinguish between localized ignition fronts and more distributed igni-diffusive regimes.

3.1 Transient evolution of the reactive structure

Figure 2 compares the transient evolution of pure-ammonia flamelets at $T = 1600\text{K}$ and $a = 50\text{s}^{-1}$ for two dilution levels, $X_{N_2} = 0\%$ and $X_{N_2} = 90\%$. The top panel reports the temporal evolution of $Z(\dot{q}_{\text{max}})$, while the lower panels show selected snapshots (t_1 , t_2 , t_3) of heat release rate and species mass fractions in mixture-fraction space. Vertical dashed lines denote the stoichiometric mixture fraction Z_{st} , whereas solid lines indicate the instantaneous position of $Z(\dot{q}_{\text{max}})$. For each snapshot, the corresponding temperature T_q and equivalence ratio ϕ_q at $Z(\dot{q}_{\text{max}})$ are also reported.

A marked difference emerges in the evolution of $Z(\dot{q}_{\max})$. In both cases, autoignition is first established on the lean side of the stoichiometric mixture fraction, where the hot oxidizer stream initially promotes chemical activation. The subsequent evolution, however, differs substantially depending on the dilution level. In the undiluted flamelet, the higher local NH_3 concentration leads to stronger heat release once ignition is triggered, producing higher temperatures and a more intense radical pool. This enhances the local reactivity and allows the reaction zone to propagate rapidly toward richer conditions. Once the rich region is reached, $Z(\dot{q}_{\max})$ exhibits a pronounced stratification, with the formation of a three-peak heat-release structure: two peaks remain approximately fixed in mixture-fraction space, corresponding to the primary diffusive oxidation zone and consistent with the OH distribution, while a third peak progressively moves toward the fuel side. The latter can be interpreted as an autoignition kernel propagating in the rich region, sustained by the combined effect of elevated temperature and residual oxygen availability. Its presence is consistent with the transient evolution of HO_2 and with the appearance of oxygenated nitrogen intermediates such as HNO , which indicate that active oxidation chemistry is taking place even on the rich side. The sudden jump observed in $Z(\dot{q}_{\max})$ can therefore be explained by the moment at which the peak associated with the main reaction front becomes comparable to, and eventually overtakes, the travelling rich-side peak.

By contrast, for $X_{N_2} = 90\%$, the reduced fuel concentration leads to weaker heat release, lower local temperatures, and a less developed radical pool. As a result, the reactive front evolves much more gradually, and $Z(\dot{q}_{\max})$ remains significantly lower throughout the transient, indicating delayed and weaker reactivity. In this case, the heat-release field becomes broader and less stratified, and the multi-peak structure collapses into a single distributed peak. The lower temperatures do not allow the formation of a secondary rich-side autoignitive kernel, so the reaction zone remains confined to leaner mixture fractions and does not propagate deeply into the fuel-rich side. This explains both the absence of a sharp transition in the temporal evolution of $Z(\dot{q}_{\max})$ and the fact that, under highly diluted conditions, $Z(\dot{q}_{\max})$ does not cross the stoichiometric mixture fraction.

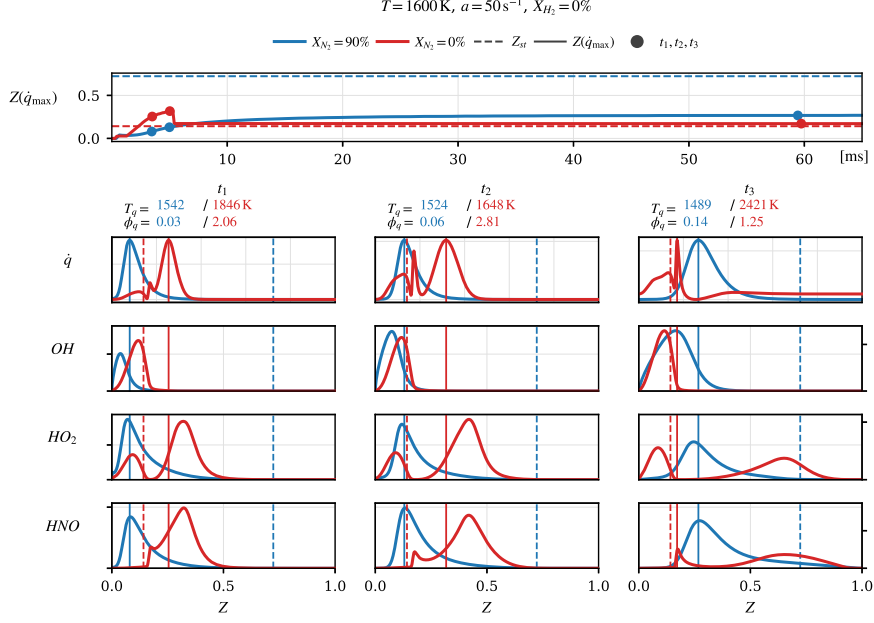


Fig. 2: Transient evolution of pure-ammonia flamelets at $T = 1600\text{K}$ and $a = 50\text{s}^{-1}$ for $X_{N_2} = 0\%$ (red) and $X_{N_2} = 90\%$ (blue). Top: evolution of $Z(\dot{q}_{\max})$. Bottom: snapshots at t_1 – t_3 of $\dot{q}$ and selected species in mixture-fraction space. Dashed lines indicate Z_{st} , solid lines $Z(\dot{q}_{\max})$, and markers the selected times; Temperature T_q and equivalence ratio ϕ_q at $Z(\dot{q}_{\max})$ are reported for each snapshot.

Overall, the comparison indicates that strong dilution suppresses the formation of secondary ignition structures and weakens the propagation of localized reaction fronts, leading to a broader and less spatially confined reactive zone characteristic of MILD combustion.

3.2 Ignition delay time and location

To characterize both the temporal and spatial onset of ignition, two quantities are extracted from each transient solution. The ignition delay time, τ_{ign} , is defined as the first instant at which the maximum temperature rise reaches $\Delta T_{\max} = 10\text{K}$,

$$t_{\text{ign}} = \min\{t : \Delta T_{\max}(t) \geq 10\text{K}\}.$$

The corresponding mixture fraction at maximum heat release is denoted as the most reactive mixture fraction,

$$Z_{mr} = Z(\dot{q}_{\max}, t_{\text{ign}}).$$

Figure 3 reports the ignition-delay behaviour of the baseline configuration, corresponding to $T^{ox} = 1600\text{K}$, $a = 50\text{s}^{-1}$, and the mixture-averaged transport model.

The left panel shows the absolute ignition-delay time, while the right panel reports the hydrogen-induced speed-up factor, defined as the ratio between the ignition delay of the pure-ammonia case and that of the corresponding ammonia-hydrogen blend at the same dilution level.

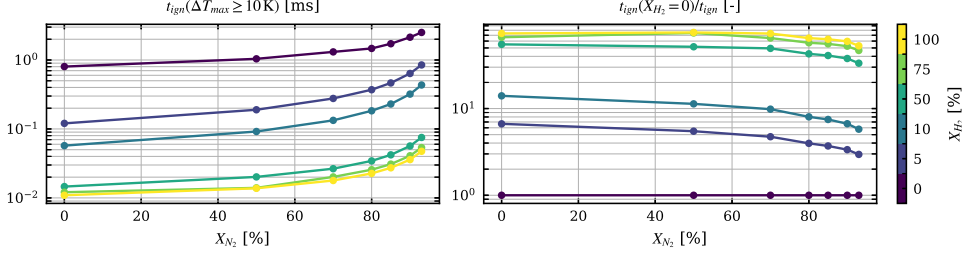


Fig. 3: Ignition-delay time of the baseline case, $T^{ox} = 1600\text{K}$, $a = 50\text{s}^{-1}$, with mixture-averaged transport model. Left: absolute ignition-delay time. Right: hydrogen speed-up factor, $t_{ign}(X_{H_2} = 0)/t_{ign}$, evaluated at the same dilution level.

As expected, increasing dilution progressively lengthens the ignition delay, whereas hydrogen addition accelerates ignition across the entire range of investigated conditions. This effect is particularly pronounced at low and moderate dilution: the addition of only 5% hydrogen reduces the ignition delay by approximately one order of magnitude, while further enrichment up to pure hydrogen produces an additional reduction of roughly one order of magnitude.

At the highest dilution levels, however, the relative ignition-promoting effect of hydrogen becomes progressively weaker, as highlighted by the reduction of the speed-up factor. Although hydrogen still shortens the absolute ignition delay, its ability to compensate for the loss of reactivity caused by dilution becomes less effective.

Oxidizer preheating and strain rate mainly affect ignition in the highly diluted regime. Reducing T^{ox} increases ignition delay for all conditions. A similar trend is observed with strain rate. Higher strain increases ignition delay, particularly for highly diluted pure ammonia, due to reduced residence time and stronger depletion of reactive intermediates such as HO_2 . Hydrogen-enriched mixtures are less sensitive, leading to a larger hydrogen speed-up with increasing strain.

Figure 4 reports the temporal evolution of $Z(\dot{q}_{\max})$, and respective Z_{mr} location, at fixed strain rate, $a = 50\text{s}^{-1}$, and oxidizer temperature, $T^{ox} = 1600\text{K}$, for all the investigated hydrogen blending and dilution levels. For all hydrogen fractions, Z_{mr} shifts toward higher mixture-fraction values as dilution increases, consistently with the progressive reduction in mixture reactivity and changing of the stoichiometry with dilution. The figure also highlights the effect of dilution on the stabilization of the main oxidation zone. At low dilution levels, the dominant heat-release region stabilizes on the rich side, in agreement with the trends previously discussed for the transient flame structure. As dilution increases, the stabilized value of $Z(\dot{q}_{\max})$ progressively

decreases, until a condition is reached where the main oxidation zone remains on the lean side and no transition toward rich conditions is observed.

Hydrogen addition influences the sharpness of this transition. In particular, low hydrogen blending levels tend to smooth and delay the shift between the two regimes. It is worth noting that, at low and moderate dilution, the absence of a sudden jump in $Z(\dot{q}_{\max})$ does not necessarily imply the absence of a rich-side autoignitive kernel. In several of these cases, such a kernel is still present and propagates toward richer mixture fractions. However, its associated heat release remains lower than that of the main oxidation zone, so that the absolute heat-release maximum continues to be controlled by the latter. As a result, the trajectory of $Z(\dot{q}_{\max})$ remains comparatively smooth even though secondary reactive structures are developing in the rich region.

Overall, Fig. 4 confirms that dilution is the primary parameter controlling whether the dominant oxidation zone ultimately stabilizes on the rich or lean side, while hydrogen blending modulates the abruptness of this transition and the relative importance of secondary rich-side ignition structures.

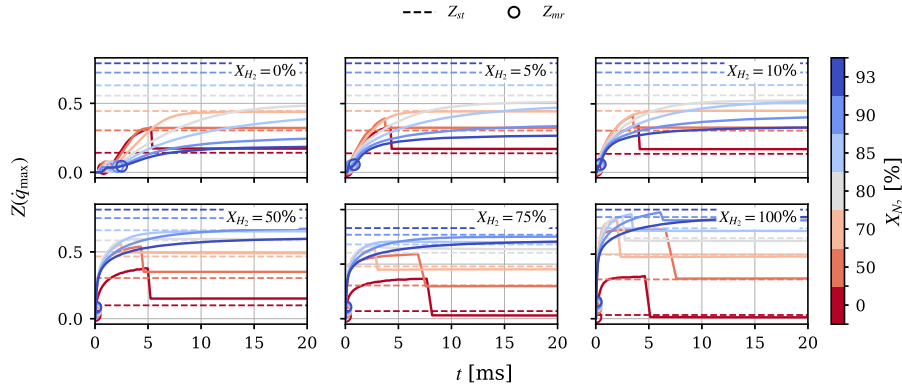


Fig. 4: Evolution of the mixture fraction at maximum heat-release, $Z(\dot{q}_{\max})$, as a function of time for multiple H_2 blending levels and N_2 dilution levels. Z_{st} (dashed) and Z_{mr} (marked) are shown for reference.

4 Steady-State Reactive Structures and Regime Transition

The steady-state results are presented in this section to provide a complementary interpretation of the reactive structures identified during the transient evolution. These results allow a clearer classification of the different combustion regimes and their dependence on dilution level and hydrogen blending.

4.1 Reactive Structure Topology

Reactive structures obtained under steady-state conditions for the HODF configuration are shown in Figs. 5 and 6. All results shown here correspond to a fixed strain rate of 50 s^{-1} , oxidizer temperature $T^{ox} = 1600 \text{ K}$, and mixture-averaged transport model. As expected, the stoichiometric mixture fraction, here indicated by a dashed line, increases with dilution for all blends. Temperature profiles show that the location (in mixture-fraction space) of the maximum temperature rise, defined as $\Delta T = T - T_{frozen}$ and highlighted by markers in Fig. 5, closely follows the stoichiometric mixture fraction up to a given dilution level (e.g., $\approx 70\% \text{ N}_2$ for pure ammonia). At higher dilution, the peak ΔT progressively shifts away from stoichiometric conditions.

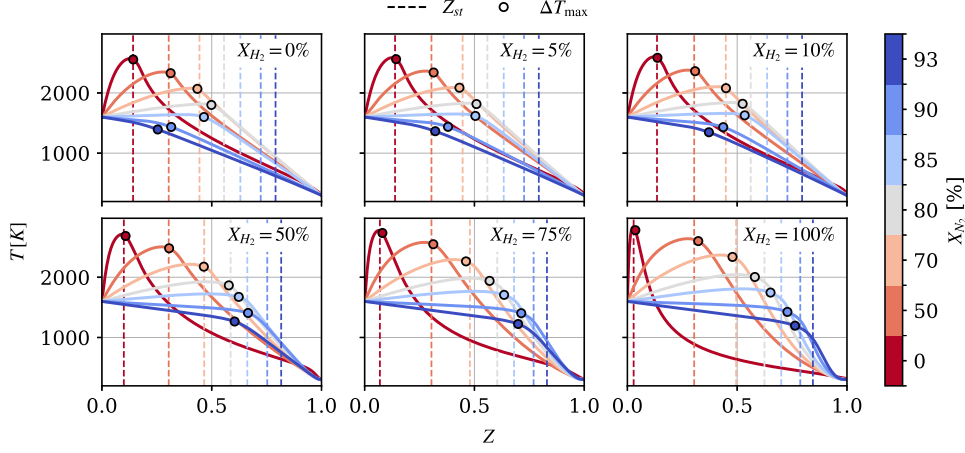


Fig. 5: Temperature profiles vs mixture fraction (Z) for multiple H_2 blending levels and N_2 dilution levels. Strain = 50 s^{-1} .

The effects of dilution and hydrogen enrichment are more clearly reflected in the heat-release profiles. As shown in Fig. 6, the pure ammonia cases exhibit a characteristic double peak structure (Sorrentino et al. (2021)), with one peak on the rich side and a second on the lean side. A region of negative heat-release is also observed, indicative of endothermic (pyrolytic) reactions. As dilution increases up to an intermediate level (approximately $70\% \text{ N}_2$), the magnitude of the dominant peak increases, whereas the secondary peak and the negative heat-release region progressively weaken. For higher dilution levels, both the secondary peak and the negative heat-release zone vanish, leaving a single heat-release peak whose intensity decreases with further dilution.

More pronounced effects are observed as hydrogen content increases. In the heat-release profiles, hydrogen addition modifies both the relative intensity and the topology of the peaks: the primary peak decreases, while the secondary peak becomes relatively more evident. At intermediate blending levels ($X_{\text{H}_2} \approx 50\%$), a triple-peak structure appears, indicating the existence of multiple reaction zones in the flamelet. At higher

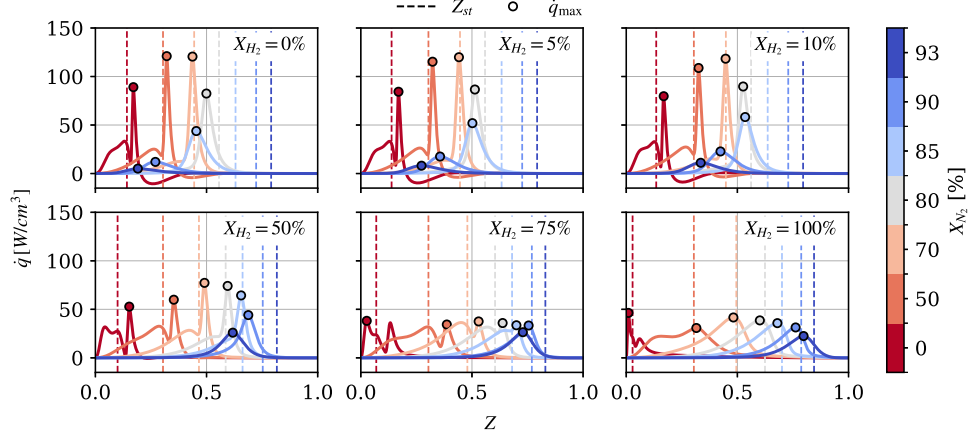


Fig. 6: Heat-release profiles vs mixture fraction (Z) for multiple H_2 blending levels and N_2 dilution levels. Strain = 50 s^{-1} .

hydrogen blending ratios, the dominant heat-release peak shifts from the rich side to the lean side.

Effects of intermediate dilution levels previously identified for pure ammonia are still observed in the blends. In particular, fuel dilution up to approximately $\approx 70\%$ tends to enhance the rich-side peak while reducing the lean-side one. This behavior is especially pronounced at $X_{H_2} = 75\%$, where the two peaks have comparable magnitudes. As dilution increases, the enhancement of the rich-side peak causes a rapid change in peak hierarchy, with the dominant heat-release peak shifting from the lean side to the rich side, aligning the trend with that observed at other hydrogen contents. Finally, hydrogen addition tends to reduce the sensitivity of peak heat-release levels to dilution, yielding more uniform profiles across the investigated dilution range.

4.2 Stoichiometric Decoupling and Transition Criterion

The behavior previously described is summarized more clearly in Fig.7, which compares the locations of the maximum temperature rise, $Z(\Delta T_{\max})$, and maximum heat release, $Z(\dot{q}_{\max})$, with the stoichiometric mixture fraction. Under weakly and moderately diluted conditions, both closely follow Z_{st} , indicating a reactive structure still predominantly anchored to stoichiometric conditions. Beyond a critical dilution level the reactive-zone locations depart from the stoichiometric trajectory.

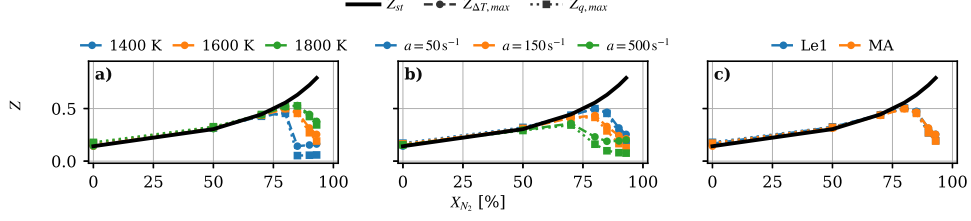


Fig. 7: Mixture fraction locations of the stoichiometric point Z_{st} , maximum temperature rise $Z(\Delta T_{max})$ and maximum heat-release rate $Z(\dot{q}_{max})$ as a function of dilution level for selected reference case ($X_{H_2} = 0$, $T^{ox} = 1600$ K, $a = 50$ s $^{-1}$). Black lines denote Z_{st} while coloured lines show $Z(\Delta T_{max})$ and $Z(\dot{q}_{max})$ for the different pre-heating, strain rate and transport model cases.

The corresponding displacement of Z_{st} therefore results from the inlet elemental composition and does not necessarily imply an equivalent displacement of the chemically most active region. At sufficiently high dilution, Z_{st} remains mathematically well defined but becomes progressively less representative of the location of maximum chemical activity. The resulting decoupling between stoichiometry and the reactive-zone position is therefore characteristic of the transition from a stoichiometrically anchored diffusion structure toward a more distributed, kinetically controlled MILD regime.

To quantify this transition, the following normalized displacement is introduced:

$$D_T = \frac{|Z(\Delta T_{max}) - Z_{st}|}{Z_{st}}.$$

The transition dilution is identified as the first dilution level for which

$$D_T \geq k,$$

with $k = 0.05$ adopted here as the reference threshold. Figure 8 reports the resulting transition dilution for all hydrogen blending levels and for two threshold values, together with the actual normalized drift, D_T , for the baseline configuration. The departure of $Z(\Delta T_{max})$ from Z_{st} is accompanied by the disappearance of the secondary heat-release peak and of the endothermic region, together with the development of a broader and less localized reactive structure. The agreement between these independent indicators supports the use of D_T as a quantitative marker of the transition toward MILD combustion in the present configuration.

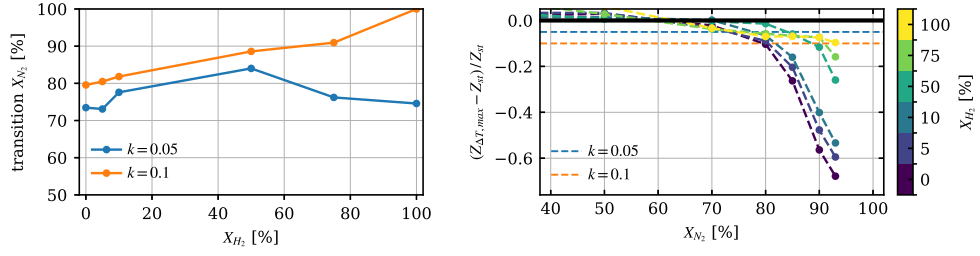


Fig. 8: Left: transition dilution levels versus fuel hydrogen fraction X_{H_2} for $k = 0.05$ and 0.10 . Right: normalised drift, $|Z(\Delta T_{\max}) - Z_{st}|/Z_{st}$, versus dilution for each hydrogen level.

The two threshold values provide complementary information on the progressive decoupling of the reactive zone from stoichiometric conditions. The lower threshold, $k = 0.05$, identifies the onset of the departure from Z_{st} and is reached at nearly the same dilution level over a wide range of hydrogen fractions. By contrast, the larger threshold, $k = 0.10$, requires a more pronounced separation and shifts progressively toward higher dilution as X_{H_2} increases. Hydrogen enrichment therefore does not substantially delay the initial onset of the decoupling, but reduces the rate at which the separation from Z_{st} develops. Therefore, $k = 0.10$ provides a more conservative indicator of MILD departure from stoichiometric location.

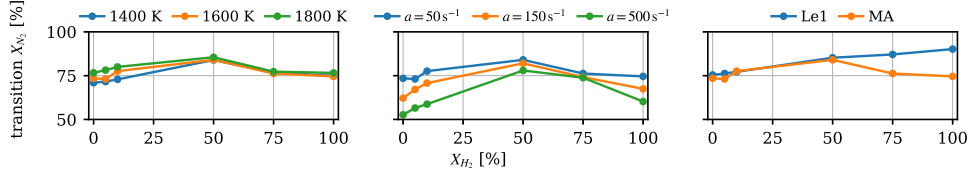


Fig. 9: Transition dilution levels $X_{N_2}(D_T \geq k)$, with $k = 0.05$, for the different preheating, strain rate and transport model cases.

The trends obtained from this criterion are consistent with the previous reactive-structure analysis, as highlighted in Fig. 9. Increasing oxidizer preheating generally shifts the transition toward slightly higher dilution levels while increasing strain promotes an earlier departure from Z_{st} . This behavior is consistent with the reduced residence time at higher strain, which penalizes the comparatively slow chemistry of strongly diluted mixtures and favors the loss of a localized stoichiometrically anchored reaction structure.

With increasing hydrogen content, the transition dilution becomes only weakly dependent on fuel composition, remaining around $X_{N_2} \simeq 75\text{--}80\%$ for the mixture-averaged transport model. Although hydrogen enrichment increases chemical reactivity and tends to keep $Z(\Delta T_{\max})$ closer to stoichiometric conditions, the high diffusivity of H_2 promotes diffusion toward the lean side, thereby modifying the local fuel and radical distributions. As a consequence, the chemically active region becomes progressively decoupled from the mixture-fraction coordinate and from Z_{st} , while Z_{st} continues to shift toward the fuel-stream endpoint as dilution increases more rapidly than $Z(\Delta T_{\max})$. A finite separation between the reactive peak and Z_{st} can therefore develop at comparable dilution levels, leading to an approximately constant transition dilution at high hydrogen fractions. This interpretation is supported by the comparison between mixture-averaged and unity-Lewis-number transport. When $Le = 1$, preferential diffusion is suppressed and the radical pool remains more localized around the stoichiometric region. Under these conditions, the transition dilution increases more clearly with hydrogen enrichment.

Hydrogen enrichment therefore has two competing effects: enhanced chemical reactivity tends to preserve the stoichiometric anchoring of the reaction zone, while molecular diffusion promotes its displacement toward lower Z .

4.3 Nitrogen-Oxides formation pathways

Variations of the NO_x domain integrals, I_{NO_x} , computed at a fixed strain rate of 50 s^{-1} are shown in Fig. 10. Results are compared for different oxidizer preheating temperatures as a function of fuel dilution level and hydrogen fraction. Two distinct dilution-dependent regimes are observed for NO. At moderate dilution ($X_{N_2} \lesssim 70\%$), NO increases with hydrogen content and reaches its maximum for pure H_2 . This behaviour is consistent with the role of H_2 in enhancing the H/OH radical pool and accelerating the conversion of NH_x intermediates, therefore promoting NO formation (Mashruk et al. (2024)). In addition, increasing oxidizer preheating generally raises NO, in line with the strong temperature sensitivity of nitrogen-chemistry pathways and the tendency of hotter conditions to favour NO production, particularly for hydrogen-enriched mixtures (Shi et al. (2022)).

At higher dilution ($X_{N_2} \gtrsim 70\%$), the trend reverses: NO decreases with increasing hydrogen fraction and attains its lowest values for pure H_2 . This reduction reflects both the decreasing availability of fuel-bound nitrogen as NH_3 is progressively replaced by H_2 , and the emergence of more distributed and cooler reaction zones typical of MILD conditions, which suppress NO_x formation (Shi et al. (2022); Wang et al. (2022)).

Across the entire parameter space, NO_2 remains negligible. The highest values occur for pure ammonia at the lowest preheating temperature, whereas increasing T^{ox} drives NO_2 toward near-zero levels, consistent with its rapid conversion/consumption at elevated temperatures (Yang et al. (2023)).

Finally, N_2O exhibits trends broadly opposite to NO. Peak N_2O integrals are obtained at low preheating and high dilution, where reduced temperatures limit N_2O oxidation and favor its persistence (Mashruk et al. (2021, 2022)). The region of enhanced N_2O is confined to a narrow high-dilution band (typically $X_{N_2} \gtrsim 80\%$), with the maximum occurring at modest hydrogen enrichment (around $X_{H_2} \sim 10\%$).

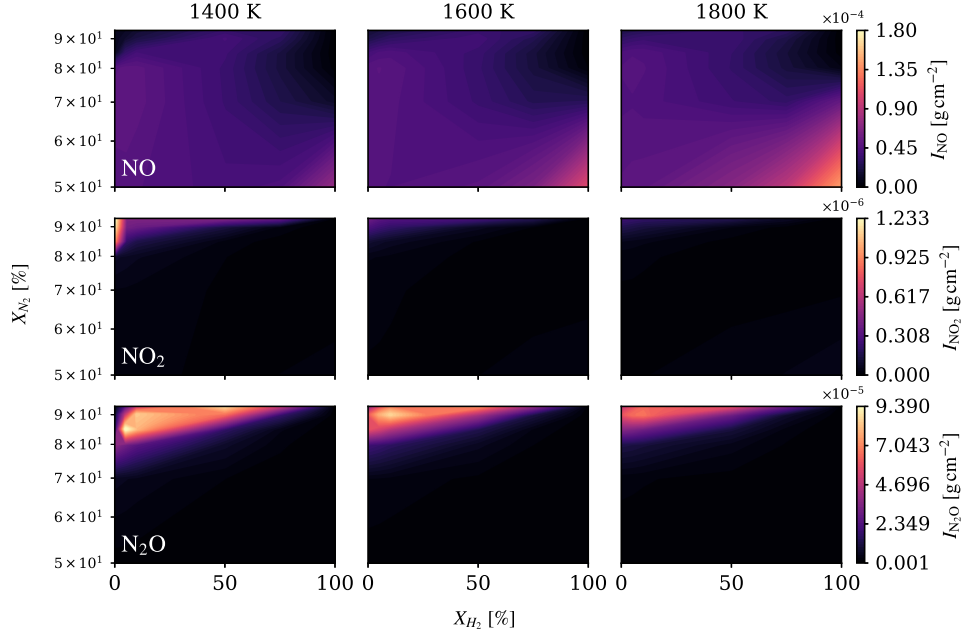


Fig. 10: Domain integral maps of NOx emission: contour plots of I_{NO} , I_{NO_2} , and $I_{\text{N}_2\text{O}}$ as functions of X_{H_2} and X_{N_2} for different oxidizer preheating temperatures. Strain = 50 s^{-1} .

and shifting toward ammonia-rich mixtures as T^{ox} increases. This behavior is consistent with kinetic evidence indicating that key N_2O -forming routes (involving NH_2 and NO_2) yield less N_2O at higher temperatures, so that hotter conditions suppress N_2O formation and/or enhance its consumption (Glarborg (2023)) .

To complement the integral-based analysis of NO_x emissions, the main kinetic routes contributing to NO formation were further examined. The pathways considered in the present work are summarized in Table 2. Based on this pathway grouping, Fig. 11 reports the contributions of the different route families to the net NO source term at $T^{\text{ox}} = 1600 \text{ K}$, as a function of dilution level and hydrogen fraction.

At $T^{\text{ox}} = 1600 \text{ K}$, Fig. 11 shows that the net NO source term is governed primarily by the HNO- and NH-mediated pathways over most of the investigated dilution range, whereas the NNH route remains of secondary importance. By contrast, the thermal, N_2O , and deNOx contributions are negative over nearly the entire parameter space, indicating that these channels act predominantly as net NO-consumption routes. Only under the most highly diluted conditions does the thermal contribution become positive. Thermal (Zeldovich) and deNOx pathways exhibit a strong coupling. When deNOx activity increases, enhancing NO consumption, less NO is available to participate in the thermal pathway. As a result, the thermal contribution to NO consumption is reduced, effectively favoring net NO formation through thermal pathway.

Table 2: Summary of NO_x pathways contributing to NO formation (reaction numbers in parentheses refer to the kinetic mechanism).

Pathway	Reactions (reaction #)
Zeldovich (thermal NO)	$\text{NO} + \text{N} \rightarrow \text{O} + \text{N}_2$ (45) $\text{N} + \text{OH} \rightarrow \text{NO} + \text{H}$ (44) $\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$ (43)
N ₂ O route	$\text{NO} + \text{NH} \rightarrow \text{N}_2\text{O} + \text{H}$ (57) $\text{N}_2\text{O} + \text{O} \rightarrow \text{NO} + \text{NO}$ (230)
NNH route	$\text{NNH} + \text{O} \rightarrow \text{NH} + \text{NO}$ (94)
HNO route	$\text{HNO} + \text{OH} \rightarrow \text{NO} + \text{H}_2\text{O}$ (202) $\text{HNO} \rightarrow \text{H} + \text{NO}$ (199) $\text{HNO} + \text{O} \rightarrow \text{NO} + \text{OH}$ (200) $\text{HNO} + \text{H} \rightarrow \text{NO} + \text{H}_2$ (201) $\text{HNO} + \text{O}_2 \rightarrow \text{NO} + \text{HO}_2$ (204) $\text{HNO} + \text{N} \rightarrow \text{NO} + \text{NH}$ (205)
NH oxidation route	$\text{NH} + \text{O}_2 \rightarrow \text{NO} + \text{OH}$ (53) $\text{NH} + \text{O} \rightarrow \text{NO} + \text{H}$ (47) $\text{NH} + \text{OH} \rightarrow \text{NO} + \text{H}_2$ (51)
NO ₂ interconversion	$\text{NO}_2 \rightarrow \text{NO} + \text{O}_2$ (222) $\text{NO}_2 + \text{H} \rightarrow \text{NO} + \text{OH}$ (219) $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$ (218) $\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$ (221)
deNO _x	$\text{NH}_2 + \text{NO} \rightarrow \text{NNH} + \text{OH}$ (78) $\text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O}$ (77)

For low-dilution and weakly hydrogen-enriched mixtures ($X_{\text{H}_2} = 0\text{--}10\%$), the absolute magnitude of all pathway contributions is largest. As dilution increases, these contributions progressively decrease and tend toward zero at the highest X_{N_2} levels. Hydrogen addition further reduces the overall intensity of the pathway contributions and makes the pathway structure more compact, although the HNO- and NH-mediated routes remain dominant as long as ammonia is present in the fuel. In the pure-hydrogen case, fuel-nitrogen chemistry essentially disappears, and only the thermal contribution survives.

Overall, these results indicate that dilution progressively suppresses the pathways responsible for NO formation, but at the same time it also weakens the deNO_x channels. Therefore, the net effect of dilution on NO_x emissions cannot be assessed solely from the pathway decomposition, since both production and consumption routes are reduced simultaneously. A clearer answer to this point is provided by Fig. 12, which reports the production-to-consumption ratio as a function of dilution level and hydrogen fraction. For lean-hydrogen mixtures ($X_{\text{H}_2} < 75\%$), the overall NO ratio remains close to unity over the whole dilution range, indicating that dilution alone does not strongly alter the balance between production and consumption. By contrast, for highly hydrogen-enriched mixtures, dilution clearly promotes a reduction in net NO formation, as the ratio decreases from values close to 2 toward values approaching 1.

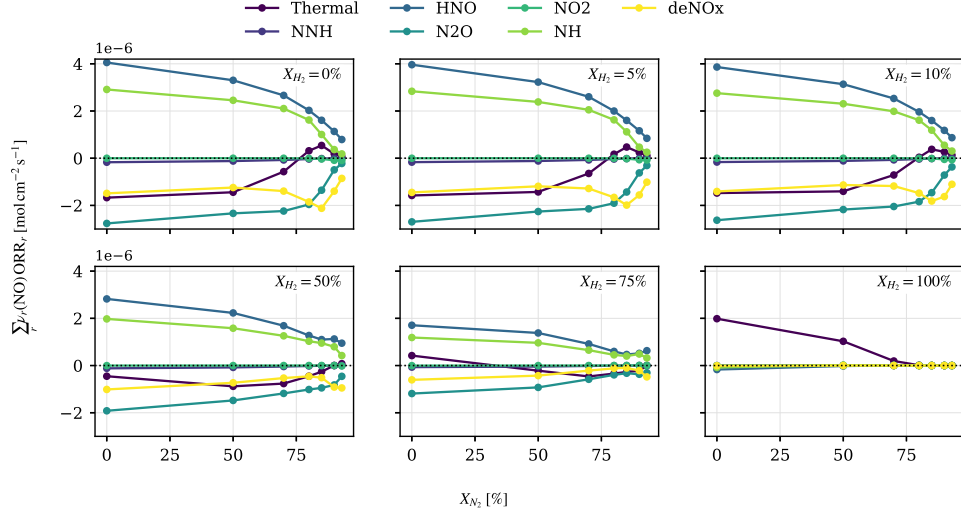


Fig. 11: Pathway contributions to the net NO source term as a function of dilution level, X_{N_2} , for different hydrogen blending conditions, X_{H_2} , in the 1600 K flamelet set.

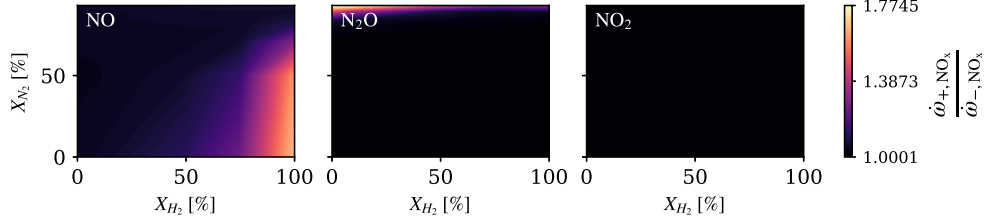


Fig. 12: Maps of the production-to-consumption ratio, $\dot{\omega}_+/\dot{\omega}_-$, for NO, N_2O , and NO_2 as a function of hydrogen blending, X_{H_2} , and dilution level, X_{N_2} , for the 1600 K flamelet set.

This confirms that, in these cases, dilution is effective in shifting the balance toward a weaker net NO formation. An opposite behavior is observed for N_2O . In this case, the production-to-consumption ratio becomes larger under highly diluted, low-hydrogen conditions, where lower temperatures favor N_2O formation.

4.4 Graph-based analysis of NH_3 -to-NO conversion pathways

To complement the pathway-group decomposition based on integrated rates of progress (Fig. 11), a graph-based analysis was carried out to identify the dominant directed routes connecting NH_3 to NO. For each flamelet, the normalized rates of progress were projected onto a reduced nitrogen-chemistry graph. The graph nodes are restricted to the main nitrogen-containing species involved in fuel-N conversion, while non-nitrogen

radicals affect the elementary rates but are not explicitly represented in the network. The most relevant simple paths were ranked according to the path weight p , which provides a relative measure of the importance of each conversion sequence within the reduced nitrogen-chemistry graph.

Results are presented in Fig. 13, in terms of main NH_3 -NO conversion pathways as a function of dilution level, X_{N_2} , for different hydrogen blending conditions, X_{H_2} , in the $T^{\text{ox}} = 1600$ K case. The four main pathway trends are presented here and summarized in Tab. 3.

Path ID	Pathway
P1	$\text{NH}_3 \rightarrow \text{NH}_2 \rightarrow \text{NH} \rightarrow \text{NO}$
P2	$\text{NH}_3 \rightarrow \text{NH}_2 \rightarrow \text{NH} \rightarrow \text{HNO} \rightarrow \text{NO}$
P3	$\text{NH}_3 \rightarrow \text{NH}_2 \rightarrow \text{HNO} \rightarrow \text{NO}$
P4	$\text{NH}_3 \rightarrow \text{NH}_2 \rightarrow \text{H}_2\text{NO} \rightarrow \text{HNO} \rightarrow \text{NO}$

Table 3: Top 4 main pathways $\text{NH}_3 \rightarrow \text{NO}$

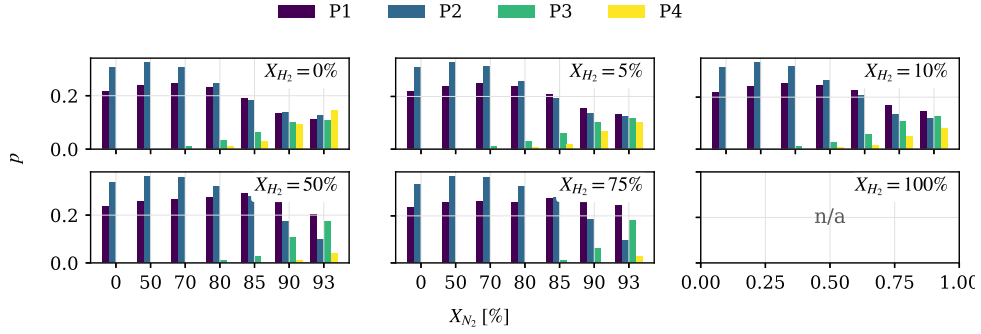
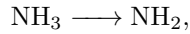


Fig. 13: Dominant NO-formation pathways, for different dilution conditions and different hydrogen blending levels for the baseline case.

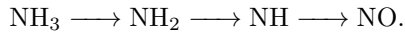
Across all ammonia-containing cases, the conversion of fuel nitrogen to NO is organized around a robust common backbone initiated by



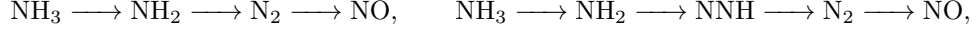
followed by competition among a limited number of oxidative branches. At low and moderate dilution, the dominant pathways are consistently



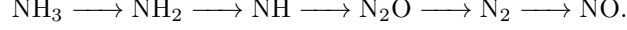
and



These two branches remain the first- and second-ranked routes over most of the parameter space at $X_{N_2} \leq 70\%$, as shown in Fig. 13, independently of oxidizer temperature and strain rate. In this regime, the pathway set is not fully collapsed onto only two channels, since secondary contributions through N_2 , NNH , and N_2O are still present, for instance through



and



Therefore, under weakly diluted conditions the nitrogen-conversion network is structured but still distributed, with the $NH_2/NH/HNO$ sequence providing the dominant framework for NO formation.

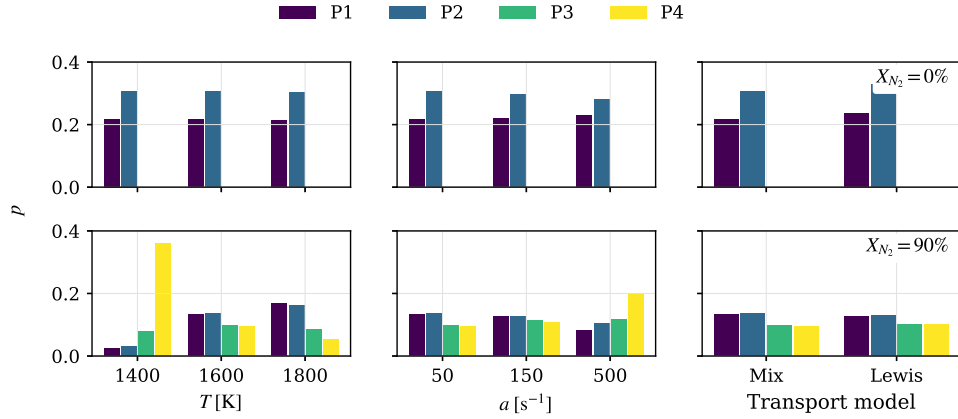
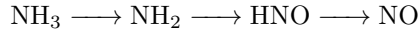
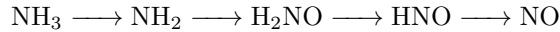


Fig. 14: Comparison of the relative contribution of the selected reaction pathways to the formation of NO under different oxidizer preheating temperature, strain rate, and transport model for two selected dilution levels ($X_{N_2} = 0, 90\%$).

Increasing dilution progressively redistributes the normalized pathway flux. For pure ammonia and weakly hydrogen-enriched mixtures ($X_{H_2} \leq 10\%$), the transition occurs between $X_{N_2} = 80\%$ and 93% , where oxygenated intermediates become increasingly important. In this range, the routes



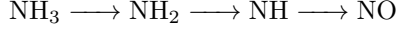
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gain relative weight and may become dominant at the highest dilution levels. This trend is particularly evident in the low-temperature, lean-hydrogen cases. For example,

at $T^{ox} = 1400$ K and $X_{H_2} = 0\%$, the leading path changes from the NH-based branches at $X_{N_2} \leq 80\%$ to $NH_3 \longrightarrow NH_2 \longrightarrow H_2NO \longrightarrow HNO \longrightarrow NO$ at $X_{N_2} = 85\%–93\%$. A similar, although less pronounced, tendency is also observed at 1600 K, whereas at 1800 K the direct NH-based channels remain more competitive even under strong dilution. These results indicate that high dilution promotes a more oxygenated nitrogen-conversion network, especially when the oxidizer preheating level is lower.

Hydrogen enrichment modifies this redistribution in a systematic way. For intermediate and high hydrogen fractions ($X_{H_2} = 50\%–75\%$), the pathway set becomes more compact, and the direct route



progressively overtakes the HNO-mediated branch as dilution increases. At $X_{N_2} \geq 85\%$, the direct NH-to-NO channel is generally the first-ranked path, while



remains the main secondary route and the H_2NO -mediated branch is either weak or absent. This behavior is especially clear for $X_{H_2} = 75\%$, where the graph often collapses onto only two or three relevant channels.

The effects of oxidizer preheating, strain rate, and molecular transport, presented in Fig. 14, mainly modify the relative weighting of the same dominant pathway skeleton rather than introducing qualitatively new conversion routes. Their influence becomes most evident under highly diluted, ammonia-rich conditions, where lower oxidizer temperatures and higher strain rates increase the relative prominence of HNO- and H_2NO branches. The transport model produces comparatively smaller changes in the pathway hierarchy, although it can alter the relative weighting of individual branches through its effect on the radical pool distribution.

Overall, the graph-based analysis shows that NO formation in the present HODF flamelets is governed by a compact and persistent nitrogen-chemistry backbone,



followed by competition among direct oxidation to NO, oxidation through HNO, and, under the most diluted lean-hydrogen conditions, oxidation through $H_2NO \longrightarrow HNO$. The investigated parameters do not introduce fundamentally different NO-formation mechanisms; instead, they control how concentrated or distributed the normalized pathway flux becomes.

5 Conclusions

The ignition and reactive-structure evolution of ammonia/hydrogen blends under hot and highly diluted conditions was investigated through transient one-dimensional flamelets. The effects of nitrogen dilution, hydrogen enrichment, oxidizer temperature,

strain rate, and molecular transport were analyzed together with the corresponding nitrogen-chemistry pathways. The main conclusions can be summarized as follows.

- Ignition is initially promoted on the lean side of the mixing layer, where the hot oxidizer provides favorable thermal conditions. Increasing nitrogen dilution systematically increases the ignition delay, whereas hydrogen enrichment strongly enhances reactivity and shortens the ignition time.
- At low and moderate dilution, the transient reactive structure remains relatively localized and may exhibit multiple heat-release regions, including secondary rich-side structures. Increasing dilution suppresses these secondary features and promotes a broader, weaker, and more spatially distributed reactive region characteristic of igni-diffusive MILD behavior.
- The dominant reactive region remains closely associated with the stoichiometric mixture fraction at low and moderate dilution. Under highly diluted conditions, however, a progressive separation develops between the reactive-zone location and Z_{st} , indicating a loss of stoichiometric anchoring. For the baseline configuration, the transition occurs approximately in the 75–80% X_{N_2} range. A threshold of $k = 0.05$ identifies the onset of the displacement, whereas $k = 0.10$ provides a more conservative indication of a pronounced departure from stoichiometric anchoring.
- Hydrogen enrichment introduces competing kinetic and transport effects. Its enhanced chemical reactivity tends to preserve the anchoring of the reactive region with stoichiometric conditions, whereas molecular diffusion under mixture-averaged transport promotes a displacement toward leaner mixture fractions. Consequently, the dependence of the transition dilution on hydrogen content remains relatively weak for the lower displacement threshold but becomes more evident when a larger drift is required.
- The nitrogen-chemistry analysis shows that dilution and hydrogen enrichment modify both the magnitude and the relative importance of the pathways involved in NO formation and consumption. The integrated reaction-rate analysis identifies HNO- and NH-mediated routes as the dominant contributors over much of the investigated parameter space, while the graph-based analysis reveals an always present nitrogen conversion backbone initiated by $NH_3 \rightarrow NH_2$, followed by competition among NH-, HNO-, and, under strongly diluted ammonia-rich conditions, H2NO-mediated branches.

Overall, the results indicate that the conventional stoichiometric mixture fraction becomes progressively less representative of the location of the dominant reactive region under strongly diluted MILD conditions. The loss of stoichiometric anchoring therefore provides a useful indicator for identifying changes in combustion topology.

Appendix A Chemical-kinetic mechanism comparison

A mechanism-sensitivity analysis was performed to assess the robustness of the main flamelet trends and to support the selection of the kinetic mechanism adopted in the main manuscript. Following Girhe et al. (Girhe et al. (2024)), seven alternative ammonia mechanisms with different curve matching (CM) scores were considered together with MANNA (Manna et al. (2023)), which is used as the reference mechanism. The MANNA mechanism was specifically validated under highly diluted ammonia-combustion conditions, making it particularly suitable for the present analysis of MILD reactive structures. Their main characteristics are summarized in Tab. A1. All simulations were performed for pure ammonia fuel ($X_{H_2} = 0$), $T_{ox} = 1600K$, and $a = 50s^{-1}$, at $X_{N_2} = 0, 70$, and 90% , representing low-dilution, near-transition, and highly diluted MILD conditions, respectively.

Mech	Year	Species	Reactions	CM score (Girhe et al. (2024))
GLARBORG (Glarborg et al. (2018))	2018	33	211	0.861
NUIG (Zhu et al. (2024))	2023	39	306	0.902
MEI (Mei et al. (2021))	2021	35	238	0.894
POLIMI (Stagni et al. (2023))	2023	31	203	0.895
KAUST21 (Zhang et al. (2021))	2021	34	262	0.897
KAUST23 (Zhang et al. (2023))	2023	32	243	0.898
MANNA (Manna et al. (2023))	2023	34	273	0.873
THOMAS (Thomas et al. (2023))	2022	33	262	0.892

Table A1: Selected kinetic mechanisms used for the comparative assessment.

Figure A1 compares the ignition-delay time and the locations of the main reactive-structure indicators ($Z(\Delta T_{max})$, $Z(\dot{q}_{max})$). All mechanisms reproduce the same qualitative increase of τ_{ign} with nitrogen dilution, confirming the inhibiting effect of dilution on ammonia ignition. The absolute ignition times remain mechanism dependent. At low and moderate dilution, KAUST21 and KAUST23 are generally close to MANNA, with POLIMI also showing comparable behavior at intermediate dilution. Larger discrepancies appear for GLARBORG, MEI, NUIG, and THOMAS, particularly as dilution increases.

Despite these quantitative differences, all mechanisms reproduce the progressive departure of the dominant reactive region from the stoichiometric mixture fraction. As shown in Fig. A1, the resulting values of $Z(\Delta T_{max})$ and $Z(\dot{q}_{max})$ differ in magnitude among mechanisms, but the same qualitative displacement with increasing dilution is retained.

The corresponding steady temperature and heat-release profiles are reported in Fig. A2. The temperature distributions show comparatively weak mechanism sensitivity in the undiluted and low-diluted cases, whereas larger differences emerge at $X_{N_2} = 90\%$.

The heat-release distributions exhibit a stronger kinetic sensitivity. Differences are observed both in peak magnitude and in the location of the dominant reactive region,

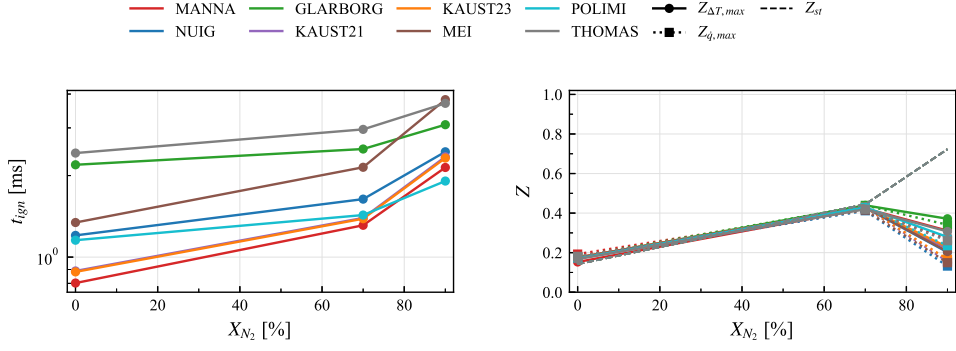


Fig. A1: Comparison of ignition-delay (left) and mixture-fraction-location diagnostics (right) for the pure-ammonia case, $X_{H_2} = 0$, $T_{ox} = 1600K$, and $a = 50s^{-1}$, using different kinetic mechanisms.

with the largest discrepancies occurring under the highly diluted condition. In this regime, where the heat release is weaker and spatially broadened, differences in the underlying kinetic description lead to appreciable variations in $Z(\dot{q}_{max})$. KAUST21, KAUST23, and POLIMI remain generally closest to the MANNA prediction, while GLARBORG, MEI, NUIG, and THOMAS show larger quantitative deviations.

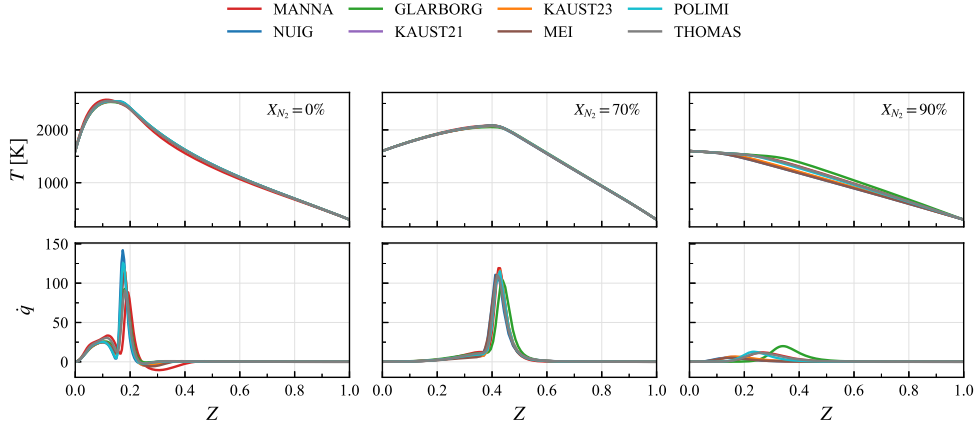


Fig. A2: Steady mixture-fraction profiles of temperature and heat-release rate for the pure-ammonia mechanism comparison at $T_{ox} = 1600K$ and $a = 50s^{-1}$, for the selected dilution levels.

Overall, the comparison shows that the absolute ignition delay and reactive-zone localization are mechanism dependent, particularly under highly diluted conditions. However, the principal qualitative trends are consistently reproduced across the tested mechanisms. This supports the use of MANNA as the reference mechanism, further justified by its previous validation under highly diluted ammonia-combustion conditions directly relevant to the regime investigated here.

Appendix B CHEM1D Solver

The set of conservation equations solved in CHEM1D is expressed as (Ramaekers (2011)):

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho u_x)}{\partial x} = -\rho K \quad (\text{B1a})$$

$$\frac{\partial(\rho Y_k)}{\partial t} + \frac{\partial(\rho u_x Y_k)}{\partial x} = -\frac{\partial(\rho V_{x,k} Y_k)}{\partial x} + W_k \dot{w}_k - \rho K Y_k \quad (\text{B1b})$$

$$\frac{\partial \rho K}{\partial t} + \rho u_x \frac{\partial K}{\partial x} = \frac{\partial}{\partial x} \left(\mu \frac{\partial K}{\partial x} \right) + \rho_p a^2 - \rho K^2 \quad (\text{B1c})$$

$$\frac{\partial \rho h}{\partial t} + \frac{\partial \rho u_x h}{\partial x} = \frac{\partial q}{\partial x} - \rho K h \quad (\text{B1d})$$

In the above, ρ_p is the density of the products mixture, a is the applied strain rate, K is the local stretch rate, h is the specific absolute enthalpy and q is the specific heat flux. The caloric equation of state and the ideal gas law are used to close the system of equations, where a low Mach-number approximation is used for the density-pressure coupling. The applied strain rate a is a setup parameter in CHEM1D and is defined as the velocity gradient at the products boundary:

$$a = - \left(\frac{du_x}{dx} \right)_p \quad (\text{B2})$$

The influence of the y -component (flame-tangential) of the flow on the transport of scalars is taken into account by introducing the local stretch rate Ramaekers (2011):

$$K(x) = \frac{\partial u_y}{\partial y} \quad (\text{B3})$$

The two aforementioned parameters, K and a , are linked to each other by the relation $K_{x \rightarrow \infty} = a$, which is a consequence of the continuity equation.

Appendix C Pathways analysis of NH_3 conversion

C.1 From elementary reaction rates to a directed weighted network

For a given operating condition, the chemistry provides $\{\text{ORR}_r\}_{r=1}^{N_r}$. The sign of ORR_r determines the net direction of each elementary step: if $\text{ORR}_r > 0$ the forward direction is net-active (reactants $\rightarrow$ products), whereas if $\text{ORR}_r < 0$ the backward direction

is net-active (products $\rightarrow$ reactants). The nonnegative reaction intensity is defined as $m_r = |\text{ORR}_r|$.

A subset of N main species $\mathcal{S}$ is selected to focus the analysis on chemically relevant intermediates and products. For each reaction r , reactants and products are considered in the net direction implied by ORR_r , and only species belonging to $\mathcal{S}$ are retained. Let $\mathcal{R}_r \subseteq \mathcal{S}$ and $\mathcal{P}_r \subseteq \mathcal{S}$ denote the sets of main-species reactants and products, respectively. For $i \in \mathcal{R}_r$ and $j \in \mathcal{P}_r$, let $\nu_{i,r}^{(R)}$ and $\nu_{j,r}^{(P)}$ be the corresponding stoichiometric coefficients in the net direction. Define the reactant- and product-side stoichiometric sums

$$S_r^{(R)} = \sum_{i \in \mathcal{R}_r} \nu_{i,r}^{(R)}, \quad S_r^{(P)} = \sum_{j \in \mathcal{P}_r} \nu_{j,r}^{(P)}. \quad (\text{C4})$$

Since the present analysis focuses on fuel-nitrogen conversion toward NO, the graph is restricted to a selected set of nitrogen-containing species,

$$\mathcal{S}_N = \{\text{NH}_3, \text{NH}_2, \text{NH}, \text{NNH}, \text{HNO}, \text{H}_2\text{NO}, \text{N}_2, \text{N}_2\text{O}, \text{NO}, \text{NO}_2\}.$$

Non-nitrogen species, such as H, O, OH, and O₂, influence the corresponding elementary reaction rates but are not represented as graph nodes.

The reaction intensity m_r is distributed across all reactant-product pairs according to stoichiometric shares,

$$\Delta A_{ij}^{(r)} = m_r \left(\frac{\nu_{i,r}^{(R)}}{S_r^{(R)}} \right) \left(\frac{\nu_{j,r}^{(P)}}{S_r^{(P)}} \right), \quad i \in \mathcal{R}_r, j \in \mathcal{P}_r, \quad (\text{C5})$$

and the adjacency matrix $A \in \mathbb{R}^{N \times N}$ is obtained by summation over all reactions,

$$A_{ij} = \sum_{r=1}^{N_r} \Delta A_{ij}^{(r)}. \quad (\text{C6})$$

A node-wise net production rate is computed for each main species $i \in \mathcal{S}$ as

$$\dot{\omega}_i = \sum_{r=1}^{N_r} \nu_{i,r} \text{ORR}_r, \quad (\text{C7})$$

where $\nu_{i,r}$ is the net stoichiometric coefficient of species i in reaction r .

To facilitate comparisons across operating conditions affected by global rate scaling (e.g. dilution), a per-case normalization can be introduced by defining

$$\widetilde{\text{ORR}}_r = \frac{\text{ORR}_r}{S}, \quad (\text{C8})$$

with a positive scale factor S selected according to the intended comparison. One convenient choice enforces $\sum_{i,j} \tilde{A}_{ij} = 1$ for the graph built from $\widetilde{\text{ORR}}_r$,

$$S = \sum_{i=1}^N \sum_{j=1}^N A_{ij}, \quad \Rightarrow \quad \sum_{i,j} \tilde{A}_{ij} = 1. \quad (\text{C9})$$

For visualization, the graph is sparsified by removing weak edges. Denoting $A_{\max} = \max_{i,j} A_{ij}$, only edges satisfying

$$A_{ij} \geq f_{\text{edge}} A_{\max} \quad (\text{C10})$$

are shown, where $f_{\text{edge}} \in (0, 1)$ is a prescribed fraction.

C.2 Pathway extraction between a start and a target species

The adjacency matrix A is interpreted as defining outgoing branching fractions of conversion intensity from each species. The row-normalized branching matrix P is

$$P_{ij} = \begin{cases} \frac{A_{ij}}{\sum_{k=1}^N A_{ik}}, & \text{if } \sum_{k=1}^N A_{ik} > 0, \\ 0, & \text{otherwise.} \end{cases} \quad (\text{C11})$$

A directed path from a start species s to a target species t is a sequence

$$\pi = (v_0 = s, v_1, \dots, v_m = t), \quad (\text{C12})$$

such that $A_{v_q v_{q+1}} > 0$ for all $q = 0, \dots, m-1$. Paths are restricted to be simple (no repeated nodes) and are limited to a maximum depth $m \leq m_{\max}$.

Each path is scored by the product of the branching fractions along its edges,

$$p(\pi) = \prod_{q=0}^{m-1} P_{v_q v_{q+1}}, \quad (\text{C13})$$

where $p(\pi)$ provides a relative measure of the importance of the pathway under the branching structure of the reduced nitrogen-conversion graph. Larger values of $p(\pi)$ therefore identify sequences that are more strongly favored by the net reaction activity. The pathway score should not be interpreted as a strictly conserved nitrogen flux from NH_3 to NO , but rather as a metric for ranking competing conversion sequences within the reduced network.

Candidate paths are generated by iterative expansion from s , prioritizing partial paths with larger intermediate scores. Expansion is terminated when either the depth exceeds $m_{\max}$ or the partial-path score falls below a prescribed minimum $p_{\min}$. Completed paths are ranked by $p(\pi)$ and the top- K highest-scoring paths are retained for analysis and visualization.

Acknowledgements. The authors gratefully acknowledge the partial financial support of the European Union, NextGenerationEU - in the framework of the National Sustainable Mobility Center - MOST, CN00000023, Italian Ministry of University and Research Decree n. 1033, 17/06/2022, Spoke 12, CUP B43C22000440001. This research was partly funded by the Italian Ministry of Environment and Energy Security through Ricerca di Sistema Elettrico Nazionale (RdS), the “National Electricity System Research” programme 2025-2027 triennial implementation plan Objective: Decarbonization - Theme 1.3 Integrated Project on Hydrogen Technologies and End-uses.

Declarations

Author Contribution. All authors conceptualised the study. B.C. conducted the numerical study and wrote the paper. G.S., P.S., R.R. and M. de J. supervised and reviewed the manuscript.

Funding. The authors have no funding sources to declare.

Code Availability. Available upon request.

Data Availability. Available upon request.

Conflict of Interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Consent for Publication. Consent for publication has been obtained from all authors. This manuscript does not include any identifiable personal data that requires separate consent.

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