



Evolution of ammonia reaction mechanisms and modeling parameters: A review

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ABSTRACT

Ammonia (NH_3) has been suggested as a fuel to attain zero carbon emissions. However, dealing with ammonia needs careful studies to reveal its limits as a suitable and promising fuel for broad applications within large power requirements. Chemical reaction mechanisms, widely employed in the modeling of these applications, are still under development. Therefore, this review is aimed to shed light on the current mechanisms available in the literature, highlighting modeling parameters that directly affect reaction rates which in turn govern the performance of each reaction mechanism. The key findings denote that most of the reaction mechanisms have poor performance when predicting combustion characteristics of ammonia flames such as laminar flame speed, ignition delay time, and nitrogen oxide emissions (NOx). In addition, none of the mechanisms have been optimised efficiently to predict properly experimental measurements for all these combustion characteristics. For example, Duynslaeger's mechanism perfectly predicted the laminar flame speed at lean and stoichiometric conditions, while Nakamura's reaction mechanism worked properly at rich conditions for the estimation of laminar flame speed. Although the aforementioned mechanisms achieved good estimation in terms of laminar flame speed, they showed poor performance against NO mole fractions. Similarly, Glarborg's (2018) mechanism properly estimated NO mole fractions at lean and stoichiometric flames while Wang's mechanism performed well in rich conditions for such emissions. Other examples are presented in this manuscript. Finally, the prediction performance of the assessed mechanisms varies based on operating conditions, mixing ratios, and equivalence ratios. Most mechanisms dealing with blended NH_3 combinations gave good predictions when the concentration of hydrogen was low, while deteriorating with increasing hydrogen concentrations; a result of the shift in reactions that require more research.

Introduction

The global demand for energy will increase substantially over the following decades. The International Energy Agency (IEA) has predicted that the demand will triple in the next 10 years, whilst it is envisaged that five times more energy will be required by the middle of the century. This factor, combined with the accelerated rise in carbon dioxide concentration in the atmosphere, has posed one of the most complex and critical challenges for humanity. The increase in energy requirements has always been accompanied by a sharp rise in emissions, which in turn have led to climatic changes and related consequences. Climate change, as explained by the Intergovernmental Panel on Climate Change (IPCC), has been mainly triggered by emissions such as carbon dioxide,

increasing global temperatures between 0.8 and 1.2 °C. It is estimated that by 2050, the situation will lead to an average increase above 1.5 °C [1], with speculations that now consider a potential increment of 2.0°C, a point at which the impacts on climate and environment might not be reversible. Thus, the consequence of human activities and pollution will have a direct impact on living standards and economic performance across regions [2]. In this context, it is important to use alternative carbonless fuels to mitigate the carbon imprint on the environment and attain zero carbon emissions.

Ammonia (NH_3) is a promising solution to climate change and environmentally friendlier energy generation. Due to its high energy density, vast infrastructure, safe utilization, and longstanding storage, ammonia has been gaining attention for researchers and industries as a

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promising alternative fuel for the replacement of fossil sources [3,4]. However, the high ignition energy, potential high NO_x production and low laminar burning velocity are obstacles that can restrict the utilization of this fuel in broader thermal applications [3–6]. Therefore, it is necessary to study the chemical interaction of NH₃ and its radicals in combustion environments, highlighting the parameters/reactions that affect the combustion performance of blends with NH₃. Parameters such as laminar flame speed, NO_x and ignition delay time are among the most important when evaluating this fuel, thus they can be used as a key finding to improve our understanding when dealing with NH₃ [7]. Therefore, the combustion mechanism of NH₃ is the right starting point to shed light on the complexities of using the chemical for combustion systems, not only under standard atmospheric conditions, but also under elevated pressure, temperature, and a variety of equivalence ratios. The key findings can be used to regulate NO_x formation or improve the laminar flame speed or ignition delay time.

The significance of this review lies in the comprehensive analysis of kinetic reaction mechanisms utilized for NH₃ oxidation, as reported in the existing literature, and their ability to accurately predict the combustion characteristics of ammonia as a fuel. These characteristics include laminar flame speed, ignition delay time, and speciation in various experimental setups such as jet-stirred and flow reactors and burner-stabilized flames. It is essential for kinetic reaction mechanisms to faithfully reproduce experimental measurements across a diverse range of operational conditions, encompassing temperature and pressure variations, as well as equivalence ratio and mixing ratios of binary fuels (e.g., NH₃/H₂). However, a majority of the published kinetic mechanisms encountered challenges in reproducing experimental measurements accurately under varying operational conditions, and where a model would perform well, it might not be ideal for other applications, hence making a big challenge for designers, engineers and users to select the adequate mechanism. This parameter, combined with the vast number of available mechanisms, makes this review critical for coherent progression of the subject.

Other examples exist in the literature. According to Otomo's investigation [8], the kinetic models proposed by Dagaut et al. [9], Mathieu and Petersen [10], despite successfully reproducing experimental shock tube ignition delay times, significantly overestimate the laminar flame speeds of NH₃. Similarly, Klippenstein et al. [11,12], Tian et al. [13], and Song et al. [14] provide inadequate estimations for laminar flame speed. Regarding the kinetics of the interaction between H₂ and NH₃ chemistry, most of the existing kinetic mechanisms exhibit insufficient mechanistic coupling between the H₂ oxidation pathway and the NH₃ oxidation pathway. This deficiency becomes particularly evident under fuel-rich conditions and elevated pressures, leading to underestimation of the burning velocity of NH₃/H₂ flames in certain circumstances. In an attempt to address this issue, Gotama et al. [15] conducted a study aimed at enhancing the model by incorporating direct coupling between the H₂ oxidation pathway and the NH₃ oxidation pathway. Although his model appropriately resolves several flame parameters, it does not provide accurate results for some emissions. And the list continues.

Within the field of chemistry, the kinetic reaction mechanisms exhibit discernible differences that are effectively highlighted through sensitivity analysis. A comprehensive investigation conducted by Da Rocha et al. [16] reported the difference in the prediction of laminar flame speed for 10 tested mechanisms [8–11,14,17–21]. This investigation was carried out under stoichiometric conditions at a temperature of 298 K and a pressure of 1 bar. Each tested mechanism yielded distinct estimations for the sensitivity coefficient pertaining to the most influential reactions influencing the laminar flame speed of NH₃/air flames. While the dominant role of the reaction H+O₂ O+OH was evident in all analyzed mechanisms, most of the kinetic models that provided accurate estimations for experimental measurements [8,10,18,20] emphasized the substantial impact of the reaction H + NO + M HNO + M in promoting flame speed within NH₃/air mixtures. This reaction was found to be the second most significant. However, certain mechanisms, such as

those proposed by Konnov [17] and Dagaut et al. [9], as well as the mechanism of Glarborg et al. [21], failed to acknowledge the importance of this reaction as it was not listed among the ten most influential reactions. Furthermore, Glarborg's mechanism demonstrated a low sensitivity value for the mentioned reaction. Conversely, the mechanisms developed by Konnov [17], Klippenstein et al. [11], and Glarborg et al. [21] considered the reaction NH₂ + NO \rightleftharpoons NNH + OH to be one of the most critical, characterized by a high sensitivity value.

The impacts caused by ammonia blends combustion have also been at the core of research programs. The investigation conducted by Alnasif et al. [22] shed light on the disparities among the mechanisms in estimating NO mole fractions. The study revealed that the tested reaction mechanisms exhibited varying performances due to their proposed NO-chemistry. Despite numerous efforts to enhance the performance of kinetic mechanisms [7,21,23–26] by considering a range of operational conditions for improving the prediction performance in reproducing the experimental measurements for NH₃/H₂ flames, they showed poor estimation quality for NO mole fraction across all equivalence ratios (φ). The sensitivity analysis conducted by Glarborg et al. [27] and Nakamura et al. [28] show distinct trends in estimating the most influential kinetic reactions involved in the formation and consumption of NO mole fractions. Although both kinetic models shared some common reactions, their estimated sensitivity coefficients differed significantly. Glarborg et al. [reference] identified the kinetic reactions NH₂+O \rightleftharpoons HNO+H, 2NH₂(+M) \rightleftharpoons N₂H₄(+M), NH₂+NH \rightleftharpoons tHNNH+H, H₂+OH \rightleftharpoons H+H₂O, and NH₂+H \rightleftharpoons NH+H₂ as reactions with high to moderate local sensitivity coefficients for NO mole fractions in an NH₃/H₂ mixture containing 70% NH₃ and 30% H₂, under atmospheric conditions and a φ value of 0.8. In contrast, the mentioned reactions were absent in the mechanism proposed by Nakamura et al. [28], which instead highlighted reactions such as N₂O+O \rightleftharpoons 2NO, HNO+O \rightleftharpoons NO+OH, NH+O₂ \rightleftharpoons HNO+O, N+OH \rightleftharpoons NO+H, H₂+OH \rightleftharpoons H+H₂O, and HNO+OH \rightleftharpoons NO+H₂O as having the largest positive local sensitivities.

According to investigations by Miller and Bowman [29], the chain-branching reaction NH₂+NO \rightleftharpoons NNH+OH and the chain termination reaction NH₂+NO \rightleftharpoons N₂+H₂O are identified as the primary channels governing the kinetics of NO reduction, Fig. 1. This finding aligns with what was previously established [8,22,26]. Both of these reactions highlight the significant role of NH₂ in the thermal De-NO_x process. The production rate of O and OH radicals in reaction NH₂+NO \rightleftharpoons NNH+OH plays a crucial role in determining the self-sustaining nature of the De-NO_x mechanism [11,29]. This production rate can be controlled by adjusting the branching ratio. Decreasing

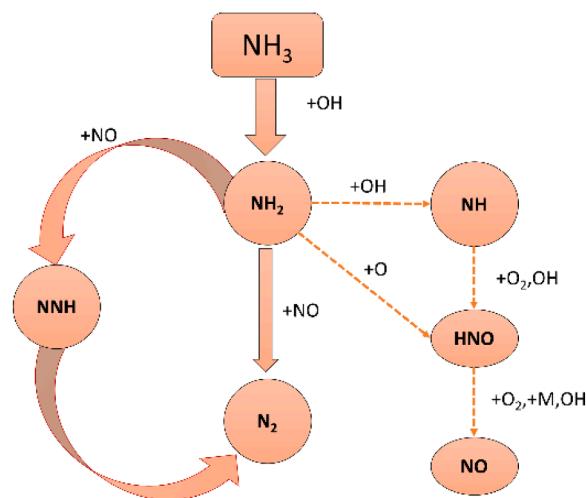


Fig. 1. Chemical reaction pathway of Thermal De-NO_x process. The dashed lines represent pathways that are predominantly significant at high temperatures.

the branching ratio in the reaction $\text{NH}_2 + \text{NO} \rightleftharpoons \text{NNH} + \text{OH}$ can result in a slower reaction, potentially hindering the formation of H/O radicals. This, in turn, may lead to a continuous production of NO. On the other hand, increasing the branching ratio can enhance the production rate of NNH, thereby facilitating the generation of OH and O radicals through reaction steps such as $\text{NNH} \rightleftharpoons \text{N}_2 + \text{H}$, $\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$, and $\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{OH} + \text{OH}$. Simultaneously, NH₂ radicals will react with O/H radicals to generate NO, and the reduction reaction will be replaced, resulting in $\text{NH}_2 + \text{OH} \rightleftharpoons \text{NH} + \text{H}_2\text{O}$, $\text{NH}_2 + \text{O} \rightleftharpoons \text{HNO} + \text{H}$, and in the end $\text{HNO} + \text{OH} \rightleftharpoons \text{NO} + \text{H}_2\text{O}$ [21]. Therefore, the branching ratio plays a crucial role in determining the reactivity of NH₃, and experiments and theories[30,31] have revealed that the process shows to be temperature dependent.

Since the existing mechanisms yield varying estimations in response to changes in operating conditions, such as fuel composition (in the case of binary fuels) or combustion characteristics (e.g., laminar flame speed, ignition delay time, and speciation), it becomes evident that each mechanism has been developed to accommodate specific conditions of interest. While published mechanisms include sub-mechanisms for NH₃ and NO, it does not imply that these mechanisms are suitable for all operating conditions. The limitations of these mechanisms may stem from the absence of specific reaction pathways or the need to update the kinetic rates of reactions. According to the study conducted by Da Rocha et al. [16], the kinetic mechanisms developed by Mathieu and Petersen [10] and Otomo et al. [8] demonstrate accurate predictions of the ignition delay time for NH₃/O₂ mixtures with 98% dilution in Ar under high-pressure conditions (1.4, 11, and 30 bar). Additionally, both kinetic models exhibit flame speeds that closely match experimental measurements across different equivalence ratios and atmospheric conditions for NH₃/air flames.

The performance of kinetic reaction mechanisms has also been examined in binary fuels consisting of NH₃/H₂. In the investigations conducted by Alnasif et al. [32], the team focused on a mixture composition of 70% NH₃ and 30% H₂ at atmospheric conditions and various equivalence ratios (ranging from 0.6 to 1.4). It was observed that the Duynslaeger et al. mechanism [19] accurately reproduces experimental measurements under lean conditions. However, its accuracy deteriorates under rich conditions. At these conditions, Nakamura et al. mechanism [28] was employed, hence providing a good estimation of flame speed. The accuracy of the Duynslaeger mechanism has also been evaluated in the study conducted by Da Rocha et al. [16]. This study involved a comprehensive analysis of numerous experimental measurements [33–35], which were utilized to assess the performance of the mechanism. The findings revealed that the Duynslaeger mechanism tends to overpredict the behavior of fuels with low H₂ content while underpredicting its performance as the H₂ content exceeds 40%. Furthermore, in the investigations conducted by same study [16], it was observed that under stoichiometric conditions, with varying H₂ content ranging from 5% to 100%, the kinetic mechanisms developed by Klippenstein et al. [11] and Song et al. [14] demonstrated good prediction accuracy, aligning well with the corresponding experimental measurements.

Recently, Szanthoffer et al. [36] conducted a comprehensive study focusing on the chemical kinetic modeling of binary fuel mixtures, specifically NH₃/H₂ and NH₃/Syngas, under various combustion conditions. The research aimed to investigate the combustion behavior of these fuel mixtures by utilizing a wide range of experimental measurements obtained from different combustion systems [10,14,15,23,25,26,33,37–57]. These measurements included shock tube ignition delay time (ST-IDT) measurements, concentration measurements in jet stirred reactors (JSR) and flow reactors (FR), as well as laminar burning velocity (LBV) measurements. The experimental data used in the study were collected from the literature. The collected experimental data were subsequently employed to assess the effectiveness of specific kinetic reaction mechanisms [8,10,13,15,20,21,23,25,26,28,42,44,47,58–62]. To accomplish this evaluation, the data set was subjected to function-alization, which entailed utilizing the Optima++ simulation framework

code supported by the OpenSMOKE++ simulator. This approach enabled the accurate description of the combustion characteristics of the investigated combustion systems. Importantly, the framework facilitated the testing of a given mechanism against a substantial number of data points in a single run, streamlining the analysis process. Furthermore, the study aimed to identify the model parameters that significantly influence the simulation outputs. Based on the unweighted averaged error function “E_{average}”, which was used as a criterion for the characterization of mechanism performance calculations, the study found that none of the investigated kinetic mechanisms were found to have an E_{average} value less than 9.0, indicating their inability to replicate the experimental measurements within their 3σ uncertainty limits consistently. Based on their E_{average} values, the top three performing mechanisms are POLIMI-2020 [25], Han-2020 [42], and KAUST-2021 [26]. POLIMI-2020 and KAUST-2021 were specifically developed as comprehensive models for NH₃ oxidation and pyrolysis and NH₃ and NH₃/H₂ oxidation, respectively. These models underwent extensive validation against various experimental datasets. Furthermore, it is worth noting that there are significant variations in the performance of the different models. This discrepancy is evident in the range of E_{average} values, spanning from approximately 13.0 to 50.0. This discrepancy can be attributed to the fact that a mechanism's performance can vary significantly depending on the type of experiment conducted. For instance, the KAUST-2021 model demonstrates excellent performance in flow reactor measurements with an E_{FR} value of 5.0, which falls well within the 3σ limits. However, its E_{ST-IDT} value is 26.6, indicating that the model's predictions exceed the 5σ uncertainty limits of the ST-IDT experimental data, on average.

The above statements denote the complexity of these reaction mechanisms. Establishing a reliable kinetic model that accurately predicts experimental outcomes is a challenging task. The accuracy of predictions is inherently dependent on the quality and precision of the experimental measurements. As a result, chemical kinetic models constantly require refinement and updates to incorporate new observations from experiments[7,23]. Consequently, this review focuses on the evolution of different reaction mechanisms and modeling parameters, taking into consideration the intricate nature of ammonia combustion mechanisms. By addressing these key aspects, this review aims to make a valuable contribution to the dissemination of research, theories, and advancements in the field of ammonia combustion chemistry, so users can distinguish fundamental concepts employed for the creation of these mechanisms to provide them with a more informed guidance for final selection.

Currently available mechanisms

Significant efforts have been made to develop and refine chemical kinetic models for the analysis of ammonia (NH₃) combustion under various conditions. These models play a crucial role in understanding the complex chemical reactions involved in NH₃ combustion and assessing its performance in different scenarios. One key area of focus has been the development of chemical kinetic mechanisms specifically tailored for NH₃ combustion. These mechanisms consist of a detailed set of chemical reactions that accurately describe the conversion of NH₃ to its combustion products. Researchers have worked on refining these mechanisms to ensure they capture the intricacies of NH₃ combustion, considering factors such as temperature, pressure, equivalence ratio, and atmospheric conditions. Another area of interest is the applicability of these kinetic models to analyze binary-fuel blends, such as NH₃-hydrogen (H₂) mixtures. The behavior of NH₃-H₂ blends can differ from pure NH₃ combustion, and the chemical kinetic models need to accurately capture these differences. This part of the review aims to shed light on the chemical kinetic mechanisms developed and used for NH₃ combustion, and their performance in terms of equivalence ratio, atmospheric conditions, elevated pressure, and temperature, as well as the accuracy of their applicability in the analysis of binary-fuel blends (i.e., NH₃-H₂).

Efforts have been dedicated to studying flame kinetics in fuels containing NH₃ [63,64]. Extensive numerical investigations have been conducted to enhance our understanding of NH₃ kinetics, encompassing various conditions and compositions [65–68]. Miller et al. first published a detailed kinetic mechanism for NH₃ oxidation [68]. This model was developed based on NH₃ combustion experiments reported in the literature and provides an overview of nitrogen compounds (see Fig. 2). The proposed model demonstrates favorable accuracy in predicting ammonia reactions under different pressures, temperatures, and equivalence ratios. Over the years, Miller's kinetic mechanism [68] has been updated through numerous studies that correlate a wide range of NH₃-fueled flame conditions [45,57,69].

Several campaigns were initiated to refine Miller's NH₃ oxidation mechanism [70,71]. In one study [70], the NH₃ oxidation mechanisms were improved for a diverse set of experiments involving burner-stabilized premixed flames. The investigation revealed crucial reactions for NO formation in pure NH₃ flames and NH₃ blended with hydrogen (H). Additionally, the study highlighted the role of the Zeldovich mechanism [72] and its impact on NO formation levels in NH₃ flames with high concentrations of H₂. Allen et al. [73] established a model for NH₃ oxidation and utilized flow reactor experiments to enhance their kinetic mechanism. Another study conducted by [71] aimed to establish a kinetic reaction mechanism for NH₃ oxidation in the presence of H₂, carbon monoxide (CO), and methane (CH₄). The objective was to accurately characterize key reactions and improve the prediction of experimental outcomes. This study employed H/N/O sub-mechanisms; augmenting NH₃ flame predictions based on Miller's studies.

Numerous efforts have been made to develop a kinetic mechanism that accurately predicts NO_x formation in NH₃ flames under different conditions. Konnov's kinetic model [17] has been widely used in studies due to its superior performance compared to other mechanisms [74]. Originally designed for small hydrocarbon fuels, Konnov's mechanism incorporated the presence of NH₃. Duynslaeger et al. [19] further modified Konnov's mechanism to enhance its accuracy in estimating mole fraction profiles of key radicals such as NH₂ and N₂O. Their experimental study utilized burner-stabilized flames of NH₃/O₂/H₂ mixtures to adjust reactions, particularly those involving nitrous oxide (N₂O) and amidogen radical (NH₂) present in Konnov's kinetic mechanism. Bian et al. [75] established a kinetic model for H₂/O₂/air flames with NH₃ or NH₃+NO seeding to investigate species profiles and elucidate the primary pathways leading to NO and N₂O formation. Their kinetic model was experimentally validated using measurements obtained from flat flames at low pressure. Their findings revealed that the reactions NH₂+O = NO+H₂ and NH+NO = N₂O+H play pivotal roles in

NO and N₂O production, respectively. They also observed that N₂O is a long-lived species concentrated in the burnt gas region, particularly in lean flames. Furthermore, they identified amidogen (NH₂) as the key radical involved in the generation of NO and N₂O in NH₃-seeded flames. They attributed the temperature dependency of the reaction NH+O₂ = NO+OH as one of the factors contributing to the decrease in NH₃ efficiency in reducing NO at temperatures above 1400 K.

Research efforts have focused on enhancing various kinetic mechanisms for NH₃ oxidation, whether as a standalone fuel or when blended with other fuel agents. These efforts involved utilizing existing published mechanisms and employing sensitivity analysis to identify key reactions in NH₃ combustion. Tian et al. [13] developed a kinetic reaction model based on the work of Skreiber et al. [71], investigating NH₃-CH₄-O₂-Ar blends in premixed flames under low-pressure conditions. Mendiara and Glarborg [18] conducted oxy-fuel combustion experiments to establish a kinetic model for NH₃ oxidation, building upon the models proposed by Tian [13] and Skreiber [71]. Their work successfully captured experimental measurements and highlighted the inhibitory effects of NH₂+O = HNO and NH₂+H = NH reactions due to low concentrations of O and H radicals. Mathieu et al. [10] conducted shock tube experiments to study NH₃ combustion and developed a comprehensive NH₃/NOx/H₂ model based on Dagaut's Mechanism [9]. This model accurately predicted NOx measurements and ignition delay time. Xiao et al. [76] established a reduced kinetic model for NH₃-CH₄ combustion in gas turbine conditions. While some of the reduced mechanisms performed well in 2D computational simulations, they exhibited instability and had limitations in predicting NOx emissions under other specific conditions.

Kinetic reaction mechanisms for binary flames using ammonia as the primary fuel blended with CH₄ or H₂ have been also investigated as these doping agents are either heavily used in industry (CH₄) or promise a net zero scenario (H₂) for flame enhancement purposes. However, accurately estimating NH₃ oxidation in high NH₃ concentration flames remains challenging due to the third body effects caused by ammonia. Despite the development and validation of mechanisms incorporating Hydrocarbon/Hydrogen (H₂) oxidation sub-mechanisms, further improvements are needed in this regard. The GRI-Mech 3.0 [77] and San Diego [58] mechanisms, commonly used for natural gas flames with NH₃ and NO, show inconsistencies with experimental results when compared against flame structure data [78]. Other researchers, such as Lamoureux et al. [59,79] and De Persis et al. [80], have focused on identifying key reactions for NO formation/consumption in high-pressure premixed flames under lean-to-stoichiometric conditions. Shrestha et al. [7] utilized the kinetic model proposed by Lamoureux et al. [59] as a base mechanism to develop a new kinetic mechanism for

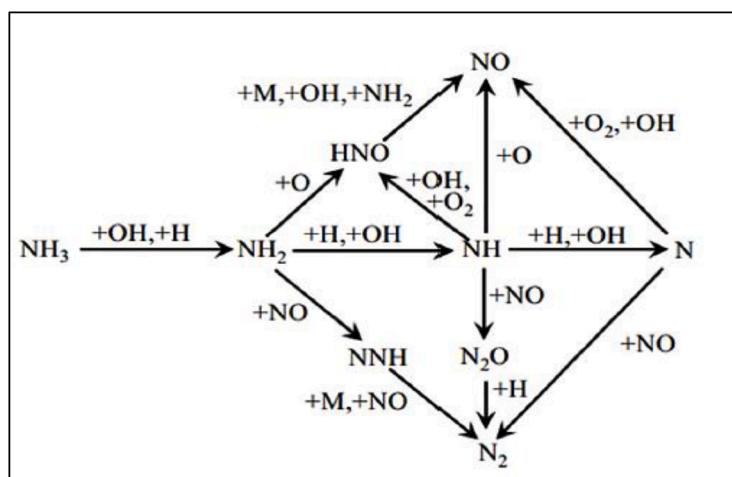


Fig. 2. NO pathways diagram generated by Miller mechanism demonstrating the most important reactions paths to NO and N₂ in NH₃/O₂ flames. Reproduced from Ref. [68] with permission from Taylor & Francis.

NH_3 oxidation. They used various experimental techniques from the literature to investigate NO formation/consumption pathways in pure NH_3 and NH_3/H_2 flames. Their findings highlighted the involvement of reactive radicals (H , OH , and O) in hydrogen abstraction from NH_3 , leading to the formation of amidogen radical (NH_2), which further decomposes to NH . NH_2 and NH are highly reactive species, playing a crucial role in the system's reactivity through their interactions with O , H , OH , and NO .

Recent studies have focused on improving the accuracy of NH_3 kinetic models and their blends. Despite these improvements, there are still discrepancies between the generated modeling data and experimental measurements across a wide range of operating conditions are needed. Mei et al. [43] constructed a mechanism for NH_3 combustion, updating rate constants to enhance performance. They utilized published works [7,81] and incorporated information from [7,82–85] to optimize the kinetic mechanism. Their study investigated the impact of oxygen enrichment, equivalence ratio, and initial pressure on laminar burning velocity. The optimized mechanism successfully reproduced the laminar burning velocity, ignition delay time, and speciation data. Oxygen enrichment positively affected flame propagation by increasing adiabatic flame temperature and key radical concentrations. NH_3 reactions with O , OH , O_2 , and NO dominated at lean flame conditions, while reactions with hydrogenated species played a crucial role in rich flames. Li et al. [86] established a detailed kinetic mechanism for $\text{NH}_3/\text{H}_2/\text{CH}_4$ combustion, combining three published mechanisms. While the mechanism accurately predicted ignition delay times, it overestimated laminar burning velocity under rich conditions. Glarborg et al. [21] developed a chemical kinetic mechanism for nitrogen chemistry in combustion based on the work conducted by [11,87–89], and validating it against experimental data from the literature. The mechanism provided proper predictions for NO formation and consumption over a wide range of conditions. Otomo et al. [90] improved the mechanism for NH_3 oxidation by incorporating elementary reactions. Their model successfully predicted the laminar flame speed of NH_3/H_2 blends. N_2H_2 was found to be influential in promoting NH_3 combustion, particularly under rich conditions.

Klippenstein et al. [24] conducted a study to investigate the effect of pressure on prompt NO production. They compared their model predictions with experimental results from the literature and explored the role of reactions involving $\text{NCN}+\text{H}$ and $\text{NCN}+\text{OH}$. The developed mechanism showed good agreement between predicted values and available literature data. They also emphasized the significance of the reaction $\text{NCN}+\text{OH}$, which produces $\text{NCO}+\text{NH}$.

Nakamura et al. [28] developed a proposed model to improve the estimation of ignition delay times for highly diluted $\text{NH}_3/\text{O}_2/\text{Ar}$ blends at elevated temperatures. The mechanism included four steps, (1) adoption of $\text{H}_2/\text{NHx}/\text{N}_2\text{O}/\text{NO}_2/\text{NNH}$ chemistry similar to the one investigated by Mathieu and Petersen [10], H_2/CO chemistry proposed by Keromnes et al. [91], the NHx/HCN chemistry updated by Dagaut et al. [92], N_2O chemistry proposed by [93], and NO_2 chemistry as determined by Dayma and Dagaut [94], and Sivaramakrishnan et al. [95]; (2) adoption of N_2Hx chemistry based on the newly published work of Konnov [96]; (3) consideration of a set of thermochemical properties studied by Bugler et al. [97]; (4) finally, the last step of improvement was to update the values of rate parameters based on various published work from the literature. The results reported that the developed model gave a better estimation of species such as NH_3 , O_2 , and H_2O . The authors also mentioned that profiles of NO and N_2O at the post-flame zone were well predicted, but the mechanism overestimated the NO and N_2O profiles at the reaction zone. In addition, further improvements on the NH_3 chemical kinetics bases are still necessary to avoid the disparities between measured and modeled mole fractions.

Zhang et al. [98] developed a kinetic model that incorporated updated thermodynamic and kinetic data to describe the pyrolysis and oxidation of H_2/NOx and Syngas/NOx. They employed a hierarchical approach, incorporating subsets during the development process. The Zeldovich mechanism [72] was used to account for thermal NOx formation at high temperatures, while Mathieu and Petersen were used for NH_3 sub-mechanism of NH_3 chemistry [14]. The primary objective of their study was to analyze NO formation/consumption and provide a predictive strategy for reproducing NO measurements under practical gas turbine conditions. The study revealed a temperature-dependent

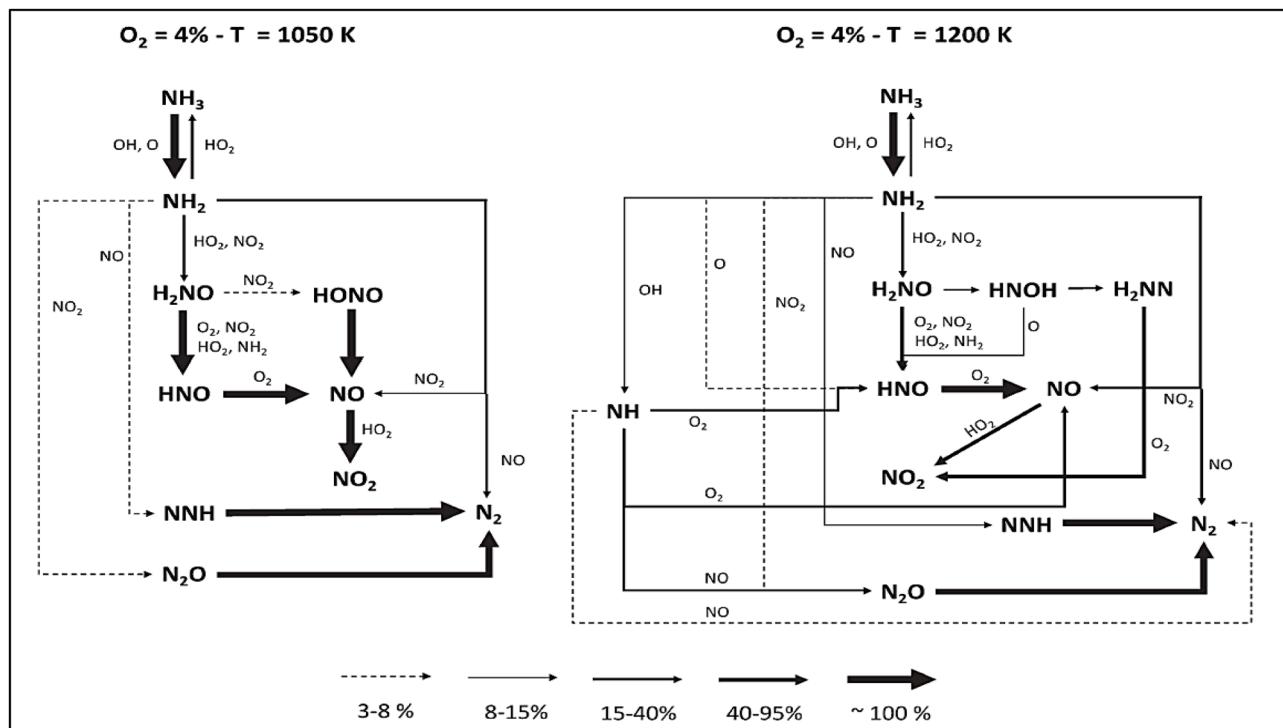


Fig. 3. The reaction flux analysis for identifying the most important reactions for NO formations in NH_3/O_2 flames. Reproduced from Ref. [25] with permission from Reaction Chemistry & Engineering.

Table 1

Chemical kinetic mechanisms from the literature.

No.	Kinetic model	No. of Reaction	no. of species	optimization factors	Refs.
1	(Bowman 1971)	16	N/A	Improved mechanism for H ₂ /O ₂ /N ₂ flames considering NO formation/consumption. Equivalence ratio (N/A); Temperature (2150–2800 K); Pressure (2.2 ± 0.3 atm.).	[111]
2	(Dean et al. 1982)	31	N/A	Improved mechanism for NH ₃ combustion at lower temperatures. Equivalence ratio (N/A); Temperature (1279 - 1323 K); Pressure (120 kPa).	[39]
3	(Dean et al. 1983)	68	N/A	Improved mechanism for NH ₃ combustion under rich conditions. Equivalence ratio (1.28–1.81); Temperature (1200–2239 K); Pressure (1 atm.).	[112]
4	(Miller et al. 1983)	98	N/A	A kinetic reaction mechanism for NH ₃ /O ₂ and NH ₃ /H ₂ /O ₂ flames considering NO/N ₂ formation, flame speed, and flame structure of the proposed fuel mixtures. Equivalence ratio (wide range); Temperature (wide range K); Pressure (1–10 atm.).	[68]
5	(Dasch et al. 1984)	42	N/A	Improved mechanism for NH ₃ oxidation under lean and stoichiometry conditions considering NO Formation. Equivalence ratio (0.5–1.1); Temperature (2000–2700 K); Pressure (1 atm.).	[113]
6	(Bian et al. 1990)	73	20	A kinetic mechanism for H ₂ /O ₂ /Ar flames seeded with NH ₃ /NH ₃ +NO under low pressure considering the formation of NO and N ₂ O. Equivalence ratio (N/A); Temperature (1500–2256 K); Pressure (35 Torr).	[114]
7	(Davidson et al. 1990)	21	N/A	Improved mechanism for NH ₃ pyrolysis. Equivalence ratio (N/A); Temperature (2000–3200 K); Pressure (0.8–1.1 atm.).	[115]
8	(Lindstedt et al. 1994)	7,5,4	10	Reduced mechanism for NH ₃ oxidation considering NO and N ₂ O formation/destruction. Equivalence ratio (N/A); Temperature (2000–3200 K); Pressure (0.8–1.1 atm.).	[116]
9	(Lindstedt et al. 1994)	95	21	A detailed kinetic mechanism for NH ₃ combustion considering the kinetics of NH ₃ /H ₂ /O ₂ , NH ₃ /NO/H ₂ /O ₂ , and NH ₃ /O ₂ flames. Equivalence ratio (0.12–1.9); Temperature (1200–2900 K); Pressure (2666.4–4600 Pa).	[70]
10	(Lindstedt et al. 1995)	419	67	Improved mechanism for NH ₃ combustion considering hydrocarbon radicals effect. Equivalence ratio (N/A); Temperature (800–1400 K); Pressure (7.2–101 kPa).	[117]
11	(Allen et al. 1997)	125	N/A	Improved chemical kinetic mechanism for CO/N ₂ O/H ₂ O/N ₂ under higher pressure and intermediate temperatures considering nitrogen chemistry and 5 major reactions of NH ₃ . Equivalence ratio (N/A); Temperature (950–1123 K); Pressure (3–15 atm.).	[73]
12	(Miller et al. 1999)	29	17	Improved kinetic mechanism for thermal De-NOx process. Equivalence ratio (N/A); Temperature (300–2000 K); Pressure (1 atm.).	[118]
13	(GRI, 2000)	325	53	A kinetic reaction mechanism for CH ₄ combustion considering NO formation at high pressure and temperatures and for a full range of equivalent ratios. Equivalence ratio (0.1–5); Temperature (1000–2500 K); Pressure (0.0013–10 atm.)	[77]
14	(Konnov et al. 2000)	50	28	Detailed N/H mechanism developed considering NH ₃ pyrolysis. Equivalence ratio (1.2); Temperature (2000–3200 K); Pressure (1 atm.)	[119]
15	(Konnov et al. 2001)	238	31	Detailed kinetic model of H/N/O for the formation of nitric oxide (NO) from N ₂ via N ₂ H ₃ in rich hydrogen blends at low temperatures. Equivalence ratio (1.2); Temperature (1000–1800 K); Pressure (1 atm.)	[120]
16	(Skreiberg et al. 2004)	520	73	Improved mechanism for NH ₃ oxidation under fuel-rich conditions and moderate temperatures. Equivalence ratio (N/A); Temperature (300–1330 K); Pressure (1 atm.)	[121]
17	(Dagaut et al., 2008)	250	41	A kinetic reaction mechanism for nitrogen chemistry optimized for NO _x formation/consumption considering prompt-NO and fuel-NO mechanisms in the presence of HCN chemistry. Equivalence ratio (N/A); Temperature (800–3000 K); Pressure (0.033–10 atm.)	[9]
18	(Konnov, 2009)	1207	127	Optimized kinetic reaction mechanism for NO _x formation considering role of prompt-NO in the presence of NCN chemistry. Equivalence ratio (N/A); Temperature (1000–1800 K); Pressure (0.75–20 atm.)	[17]
19	(Mendiara and Glarborg, 2009)	779	79	A kinetic reaction model for NH ₃ /CH ₄ /CO ₂ oxidation optimized for speciation concentrations and NO _x formation. Equivalence ratio (0.13–1.55); Temperature (1173–1773 K); Pressure (1 atm.)	[122]
20	(Tian et al., 2009)	703	84	A kinetic reaction model for NH ₃ /CH ₄ /O ₂ /Ar optimized for speciation concentrations and NO _x formation. Equivalence ratio (1); Temperature (300 K); Pressure (4 kPa)	[13]
21	(Mével et al. 2009)	203	32	Optimized kinetic mechanism of H ₂ /N ₂ O/Ar flames for the delay time considering NH ₃ /Air chemistry. Equivalence ratio (0.5–2); Temperature (1300–2000 K); Pressure (300 kPa)	[123]
22	(Lamoureux et al., 2010)	883	119	A kinetic reaction mechanism for CH ₄ /O ₂ /N ₂ and C ₂ H ₂ /O ₂ /N ₂ combustion optimized for speciation concentrations and NO _x formation/consumption considering prompt-NO mechanism in the presence of NCN chemistry under rich and stoichiometric conditions. Equivalence ratio (1–1.25); Temperature (1575–1830 K); Pressure (5.3 kPa)	[79]
23	(Klippenstein et al., 2011)	202	31	A kinetic reaction mechanism for nitrogen-chemistry optimised for NO _x formation considering NNH chemistry as a key intermediate in thermal DeNOx. Equivalence ratio (N/A); Temperature (1200 K); Pressure (38–78 Torr)	[11]
24	(Zhang et al., 2011)	701	88	A kinetic mechanism for CH ₃ NO ₂ /O ₂ /Ar mixtures and C ₂ H ₂ /O ₂ /N ₂ combustion optimised for speciation concentrations and NO _x formation/consumption. Equivalence ratio (1–2); Temperature (N/A); Pressure (4.655 kPa)	[124]
25	(Houshfar et al. 2011)	198	35	Reduced mechanism for the oxidation of biomass volatiles updated for nitrogen-containing species (NH ₃ and HCN) for NO _x emission prediction. Equivalence ratio (0.8–3.3); Temperature (700–1400 °C); Pressure (N/A)	[125]
26	(Duynslaeger et al., 2012)	80	19	Reduced kinetic mechanism of NH ₃ /H ₂ /O ₂ /A combustion optimized for NO _x formation. Equivalence ratio (0.9–1.1); Temperature (500–2000 °C); Pressure (60–120 mbar).	[19]
27	(Løvås et al. 2013)		36	Reduced chemical mechanism for gas-phase biomass at low to high-temperature ranges considering NH ₃ and HCN kinetics. Equivalence ratio (0.8–3.3); Temperature (200–1400 °C); Pressure (1 atm.)	[126]
28	(Nozari and Karabeyoglu, 2015)	91	21	Reduced kinetic reaction mechanism for NH ₃ /H ₂ /Air combustion optimized for laminar flame speed and NO _x formation. Equivalence ratio (0.5); Temperature (400 °C); Pressure (17 bar)	[127]
29	(Mathieu and Petersen, 2015)	278	54	A kinetic reaction mechanism of NH ₃ oxidation optimized for IDTs). Equivalence ratio (0.5–2); Temperature (1560–2455 K); Pressure (0.14–3.00 MPa)	[10]
30	(Lamoureux et al., 2016)	934	123	A kinetic reaction mechanism for CH ₄ /NO _x optimized for speciation measurements and NO _x formation considering NCN chemistry for prompt NO process. Equivalence ratio (0.8–1.25); Temperature (273.15 K); Pressure (0.1 MPa)	[59]
31	(Xiao et al., 2016)	276	55	Reduced kinetic model for NH ₃ /CH ₄ combustion improved for simulation studies under gas turbine operation conditions. Equivalence ratio (N/A); Temperature (1000–1800 K); Pressure (1–12.5 atm.)	[128]

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Table 1 (continued)

32	(Song et al., 2016)	204	32	A kinetic reaction mechanism of NH ₃ oxidation optimized for speciation concentrations and NOx formation. Equivalence ratio (0.24–1.04); Temperature (450–925 K); Pressure (30–100 bar)	[14]
33	(Nakamura et al., 2017)	232	33	A kinetic reaction model for NH ₃ oxidation optimized for ignition characteristics and species measurements (NH ₃ , O ₂ , NO, N ₂ O, and H ₂ O) at atmospheric pressure, low temperatures, and equivalence ratios in the range of (0.8–1.2). Equivalence ratio (0.8–1.2); Temperature (1400 K); Pressure (1 atm.)	[28]
34	(Zhang et al., 2017)	251	44	A kinetic mechanism for H ₂ /NOx and Syngas/NOx combustion optimized for speciation measurements and NOx formation considering oxidation and pyrolysis concepts. Equivalence ratio (0.167–3); Temperature (298–2800 K); Pressure (1–100 atm.)	[98]
35	(Glarborg et al., 2018)	231	39	A kinetic mechanism for nitrogen chemistry improved for speciation measurements and NOx formation/destruction under a wide range of operation conditions and considering updating the thermochemistry data of nitrogen compounds. Equivalence ratio (0.13–1.55); Temperature (900–2125 K); Pressure (0.046–1.1 atm.)	[21]
36	(Shrestha et al., 2018)	1081	124	A kinetic reaction mechanism for NH ₃ and NH ₃ /H ₂ oxidation updated for NOx formation/destruction. Equivalence ratio (0.4–2.4); Temperature (1000–3000 K); Pressure (1–15 atm.)	[7]
37	(Otomo et al., 2018)	213	32	A kinetic mechanism for NH ₃ oxidation optimized comprehensively for flame speed and ignition delay time. Equivalence ratio (0.6–2); Temperature (N/A); Pressure (1.4–30 atm.)	[8]
38	(UC San Diego, 2018)	41	20	A kinetic reaction model for CH ₄ combustion optimized for NOx formation considering NH ₃ chemistry. Equivalence ratio (N/A); Temperature (300–5000 K); Pressure (N/A)	[58]
39	(Klippenstein et al., 2018)	211	33	A kinetic reaction mechanism for nitrogen chemistry improved for NOx formation considering a prompt-NO process. Equivalence ratio (0.8–1.2); Temperature (N/A); Pressure (0.1–1.5 MPa)	[24]
40	(Wang et al. 2018)	308	48	Reduced skeletal mechanism of CH ₄ /H ₂ /N ₂ for the formation of NO from CH ₄ /H ₂ flames at atmospheric and elevated pressures (0.1–4.0 MPa). Equivalence ratio (0.6–1.4); Temperature (1000–2600 K); Pressure (1–40 bar)	[129]
41	(Han et al., 2019)	177	35	Proposed kinetic model for NH ₃ /air, NH ₃ /H ₂ /air, NH ₃ /CO/air, and NH ₃ /CH ₄ /air flames optimized for LBV. Equivalence ratio (0.6–1.8); Temperature (413 K); Pressure (1 atm.)	[42]
42	(Mei et al., 2019)	265	38	Updated model reaction mechanism for NH ₃ /O ₂ /N ₂ flames improved for laminar flame propagation under wide ranges of equivalence ratios and oxygen enrichment ratios. Equivalence ratio (0.6–1.5); Temperature (298 K); Pressure (1–5 atm.)	[43]
43	(Li et al., 2019)	957	128	A comprehensive kinetic reaction model for NH ₃ /H ₂ /CH ₄ mixture combustion developed for speciation measurements and NOx formation. Equivalence ratio (0.5–2); Temperature (1000–2000 K); Pressure (0.1–5 MPa)	[130]
44	(Okafor et al., 2019)	356	59	Reduced reaction mechanism for combustion of CH ₄ /NH ₃ flames optimized for LBV and speciation concentrations of NH ₃ , NO, and CO. Equivalence ratio (0.7–1.3); Temperature (298 K); Pressure (0.1–0.5 MPa)	[20]
45	(Song et al. 2019)	2361	153	Updated mechanism for net CH ₄ and CH ₄ /NOx (NO and NO ₂) in biogas oxidation considering intermediate species of HONO, CH ₃ NO ₂ and HCN. Equivalence ratio (0.5–2); Temperature (650–1200 K); Pressure (107 kPa)	[103]
46	(Da Rocha, et al. 2019)	66	22	A reduced kinetic reaction mechanism based on Mathieu and Petersen's kinetic model is optimized for combustion characteristic prediction of computational simulation in the presence of fluid mechanics considering time consumption. Equivalence ratio (0.5–1.5); Temperature (1564–2489 K); Pressure (1.4–30 bar)	[16]
47	(Stagni et al., 2020)	51	21	A reduced kinetic reaction mechanism based on Okafor's kinetic model is optimized for combustion characteristic prediction of computational simulation in the presence of fluid mechanics considering time consumption. Equivalence ratio (0.5–1.5); Temperature (1564–2489 K); Pressure (1.4–30 bar)	[25]
		72	24	A reduced kinetic reaction mechanism based on Otomo's kinetic model is optimized for combustion characteristic prediction of computational simulation in the presence of fluid mechanics considering time consumption. Equivalence ratio (0.5–1.5); Temperature (1564–2489 K); Pressure (1.4–30 bar)	
		210	31	Optimized kinetic reaction mechanism for oxidation and pyrolysis of NH ₃ updated for speciation measurements and NOx formation. Equivalence ratio (0.01–0.375); Temperature (500–2000 K); Pressure (1 atm.)	
48	(De Persis et al., 2020)	647	103	A kinetic reaction mechanism for CH ₄ oxidation optimized for NO formation. Equivalence ratio (0.7–1.2); Temperature (1841–2251 K); Pressure (0.1–0.7 MPa)	[80]
49	(Jiang et al. 2020)	60	19	Improved H ₂ /O ₂ /N ₂ mechanism for NOx formation/consumption considering NH ₃ combustion. Equivalence ratio (0.6–1.3); Temperature (750–1750 K); Pressure (1.4–30 atm.)	[99]
50	(Bertolino et al., 2021)	264	38	Optimized detailed kinetic mechanism for NH ₃ pyrolysis and oxidation chemistry considering pressure-dependent reactions, and covering ignition delay times, laminar flame speed, and speciation for a wide range of operational conditions. Equivalence ratio (0–∞); Temperature (0–3000 K); Pressure (0–100 bar)	[131]
51	(Mei et al., 2021a)	265	38	An improved kinetic model for NH ₃ /NO flames covering laminar burning velocity (LBV) and speciation. Equivalence ratio (1.1–1.9); Temperature (298 K); Pressure (1 atm.)	[132]
52	(Han et al., 2021)	298	36	Improved kinetic reaction mechanism for NH ₃ /N ₂ O/Air flames considering updating the H/N/O kinetic mechanism and for the reactions which are most important for NH ₃ flame propagation and self-igniting. Equivalence ratio (0.4–2); Temperature (298 K); Pressure (1 atm.)	[133]
53	(Mei et al., 2021)	257	40	A kinetic reaction mechanism for partially cracked NH ₃ /air mixtures optimized for laminar flame propagation. Equivalence ratio (0.7–1.4); Temperature (298 K); Pressure (1–10 bar)	[44]
54	(Shrestha et al., 2021)	1099	125	Developed kinetic reaction mechanism for NH ₃ and NH ₃ /H ₂ oxidation under different mixing ratios of H ₂ in fuel ranging from (0–30%) considering laminar propagating flame and NO formation/consumption. Equivalence ratio (0.6–1.8); Temperature (298–473 K); Pressure (1–10 bar)	[23]
55	(Wang et al., 2021)	444	91	Updated kinetic mechanism for combustion of NH ₃ +CH ₃ OH and NH ₃ +C ₂ H ₅ OH mixtures for optimization of LBV, IDTs, and speciation measurements considering various mixing ratios. Equivalence ratio (0.7–1.8); Temperature (298–448 K); Pressure (1 atm.)	[134]
56	(Zhang et al., 2021)	263	38	Improved comprehensive kinetic mechanism for combustion of NH ₃ /H ₂ mixtures updated for speciation data (NH ₃ , H ₂ O, NO, and N ₂ O) under various mixing ratios (H ₂ content in the fuel ranging from 0 to 70 vol%). Equivalence ratio (0.25–1); Temperature (800–1280 K); Pressure (1 atm.)	[26]
57	(Arunthanayothin et al., 2021)	2444	157	Updated mechanism for NH ₃ /CH ₄ flames optimised for speciation measurements and NOx formation. Equivalence ratio (0.5–2); Temperature (600–2000 K); Pressure (1 atm.)	[106]

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Table 1 (continued)

58	(Gotama et al., 2022)	119	26	A kinetic mechanism for NH ₃ /H ₂ combustion and improved for the LBV under rich-fuel range (up to 1.8). Equivalence ratio (0.8–1.8); Temperature (298 K); Pressure (0.1–0.5 MPa)	[15]
59	(Glarborg et al. 2022)	50	12	Improved mechanism for NH ₃ pyrolysis. Equivalence ratio (N/A); Temperature (0–3500 K); Pressure (0.1–100 atm.)	[135]
60	(Kovaleva et al. 2022)	354	59	Improved mechanism for NH ₃ /CH ₄ oxidation considering NO formation/consumption. Equivalence ratio (0.6–1.4); Temperature (298 K); Pressure (1 atm.)	[110]
61	(Sun et al. 2022)	486	66	Improved mechanism for NH ₃ /NO/NO ₂ /O ₂ and CH ₄ /NH ₃ /NO/NO ₂ /O ₂ flames. Equivalence ratio (N/A); Temperature (600–1200 K); Pressure (0.1 MPa).	[136]

conversion rate of NO to NO₂. Initially, increasing temperature promoted the conversion, reaching maximum reactivity at around 800 K. However, further temperature increase inhibited the conversion. The role of HO₂ radicals in the transformation mechanism of NO to NO₂ was analyzed kinetically. At lower temperatures, the reactivity of the H+O₂ (+ M) ⇌ HO₂ (+ M) reaction was significant, leading to an enhanced rate of NO to NO₂ conversion. As temperature rose, the importance of the H+O₂ (+ M) ⇌ HO₂ (+ M) reaction diminished compared to the H+O₂ ⇌ O+OH reaction. Consequently, the concentration of HO₂ radicals decreased, resulting in a lower rate of the NO₂+OH ⇌ NO+HO₂ kinetic reaction. Additionally, the presence of additional H atoms generated by the H+O₂ ⇌ O+OH and H₂+OH ⇌ H+H₂O reactions facilitated the NO₂+H ⇌ NO+OH reaction, promoting the conversion of NO₂ back to NO.

In another study by Song et al. [14], a model reaction for NH₃ oxidation was developed at elevated pressures (3.0–10.0 MPa) and temperatures up to 925 K. The authors improved the mechanism by focusing on high-pressure kinetic reactions and highlighted the role of the nitroxide radical (H₂NO) as an intermediate under the studied conditions. Jiang et al. [99] expanded San Diego's short nitrogen mechanism by incorporating ammonia oxidation chemistry, resulting in a mechanism consisting of 60 reactions and 19 chemical species. Rate parameters were improved based on newly published data, leading to a reduced model that addressed time consumption in reactive flow simulations while maintaining acceptable accuracy limits ($\pm 20\%$). Wang et al. [100] optimised a kinetic model to predict the laminar burning velocities (LBV) of NH₃/Syngas/air, NH₃/CO/air, and NH₃/H₂/air flames under elevated pressures. The researchers reported that the proposed model successfully predicted LBV and ignition delay time, aligning with experimental measurements conducted within the same study.

Stagni et al. [25] conducted a comprehensive investigation aiming to establish a kinetic mechanism for NH₃ oxidation. The study encompassed a wide range of investigations under lean conditions, utilizing both jet-stirred and flow reactors, thereby covering a broad operating temperature range from 500 K to 2000 K. They adopted a hierarchical and modular approach in developing their model, similar to the methodology presented in [101]. The study incorporated previously published works [102–105] that considered pyrolysis conditions, high-temperature oxidation, as well as intermediate and low temperatures. By employing reaction flux analyses, the researchers elucidated various dynamic conversion mechanisms from NH₃ to the final products. Notably, they identified key reaction pathways to NO formation under two representative conditions (see Fig. 3). The evaluation of NH₃ decomposition, H-abstraction, and the decomposition of the HNO intermediate were highlighted in their investigation. The study highlighted the decisive role of H₂NO at low temperatures (below 1200 K), where the reaction between H₂NO and HO, NO₂, and NH₂ resulted in H-abstraction, controlling the reactivity. Furthermore, the reaction 'NH₂+O=HNO+H' played a significant role in HNO formation as an intermediate species, particularly at higher temperatures, ultimately influencing NO/N₂ ratios and flame propagation.

Arunthanayothin et al. [106] formulated a comprehensive kinetic model for CH₄/NH₃ combustion and validated it for a broad range of operating conditions. Their sensitivity analysis demonstrated the role of NH₃ in the promotion of CH₄ reactivity at low temperatures due to NO

formation, which acts as a reactivity enhancer. Conversely, at high temperatures, the effect did not exhibit any significant change. A kinetic mechanism for NH₃ and NH₃/H₂ oxidation was proposed by Zhang et al. [107]. They employed the suggested mechanism of Mei et al. [43] as a core mechanism. Numerous experimental measurements were utilized for validation purposes under atmospheric pressure and a range of temperatures (800–1280 K). The research group reported that their kinetic mechanism accurately captured the experimental data used for validation. Wang et al. [108] established a kinetic mechanism named CEU-NH₃ for reproducing the laminar burning velocity and ignition delay time of NH₃-CH₃OH/air and NH₃-C₂H₅OH/air blends. Building upon the mechanism by Han et al. [109] as a baseline for their model, the simulation results of ignition delay time and species profiles demonstrated proper agreement with the data resulting from their experimental work as well as the data from the literature. They reported that the kinetic interaction between C and N-containing species was insignificant and had no effect on the promotion of the laminar burning velocities of NH₃ mixtures. Instead, this case presents a different perspective in terms of ignition delay times (IDTs), where two reactions of C-N species were found to have large A-factor sensitivities.

Gotama et al. [15] formulated a kinetic model, namely 'H₂-recovery,' for NH₃/H₂ combustion at rich equivalence ratios under various high-pressure conditions. The core mechanism proposed by Han et al. [42] served as the foundation for the developed model. Similar to previous studies, the research group updated the rate parameters of 11 reactions based on published work from the literature. The kinetic analysis conducted in their study demonstrated that the constructed mechanism satisfactorily reproduces and measures the LBV of NH₃/H₂. Kovaleva et al. [110] proposed an advanced kinetic reaction mechanism for the combustion of NH₃/CH₄ blends. Experimental measurements specifically obtained for validation purposes were employed. The researchers reported that the refined model exhibits a good performance in predicting the levels of NO and N₂O under lean conditions compared to the core mechanism [15]. Likewise, Glarborg et al. [21] established a kinetic model for NH₃ pyrolysis to describe the implications of pyrolysis reactions on the combustion characteristics of NH₃. The newly developed model relied on Glarborg et al.'s [21] baseline mechanism, which was formulated to refine and validate their mechanism against shock tube measurements of NH₃ and major species (NH₂ and NH) in NH₃ pyrolysis. The research group reported that the enhanced model demonstrates a satisfactory performance with observations obtained under diluted conditions ($\leq 0.5\%$ NH₃). However, at higher concentrations of NH₃ ($\approx 8\%$), the model underestimates NH₃ consumption.

It is worth noting that each kinetic model has been developed and validated for specific conditions of interest, aligning with the objectives of the respective studies. However, some models exhibit better performance in estimating certain combustion characteristics compared to others. Therefore, further research is required to develop a comprehensive kinetic mechanism capable of predicting combustion characteristics under various blending conditions. To provide an overview of the progress in this field, Table 1 presents a summary of the published kinetic reaction mechanisms for NH₃ over the past 53 years. Meanwhile, Table 2 showcases the newly published kinetic models, highlighting their range of validity, operating conditions (pressure, temperature, and equivalence ratio), and the types of flames used for validation.

In summary, the optimization of NH₃ combustion characteristics has

Table 2

Newly reported kinetic reaction mechanisms in terms of operating conditions and flame type used for validation.

NO	The mechanism name as per the first author	Refs.	Range of applicability/ Validation				Validation method	Combustion parameter	Mixing ratio
			Pressure	Temperature	ϕ	Flame type			
1	(Gotama et al. 2022)	[15]	0.1–0.5 (MPa)	298 (K)	0.8–1.8	NH ₃ /H ₂ /air	CVCC	LBV	60/40% (vol% of NH ₃ /H ₂)
2	(Marshall et al. 2023)	[137]	0.1 (MPa)	1000–2500 (K)	–	NH ₃ /Air NH ₃ Pyrolysis N ₂ O/H ₂	ST-IDT, FR, JSR	IDT and speciation	–
3	(Zhou et al. 2023)	[138]	0.1 (MPa)	298–423 (K)	0.7–1.4	NH ₃ /air NH ₃ /H ₂ /air NH ₃ /CO/air NH ₃ /CH ₄ /air	CVCC	LBV	30–70% (vol% of H ₂) 50–90% (vol% of CO) 50–100% (vol% of CH ₄)
4	(Manna et al. 2022)	[139]	0.14 (MPa)	900–1350 (K)	0.8	NH ₃ /Air NH ₃ /NO	JSR	LBV IDT speciation	0–800 of NO (ppm)
5	(Stagni et al. 2022)	[140]	0.105- 4.43 (MPa)	900–1200 (K)	0.2–0.35	NH ₃ /Air NH ₃ Pyrolysis	JSR, FR, RCM	IDT and speciation	–
6	(Zhang et al. 2023)	[141]	0.004–10.13 (MPa)	298–2000 (K)	0.13–2	CO/NH ₃ /air CO/H ₂ /NH ₃ CH ₃ OH/NH ₃ CH ₄ /NH ₃	ST, JSR, FR, BSF	LBV IDT	50–60% (vol% of CO) 5–100% (vol% of CH ₃ OH) 10–20% (vol% of CH ₄)
7	(Tang et al. 2022)	[142]	0.1 (MPa)	700–1200 (K)	0.1–1	NH ₃ / O ₂ /Ar	JSR	IDT and speciation	–
8	(Sun et al. 2022)	[136]	0.1 (MPa)	600 - 1200 (K)	–	NH ₃ /NO/NO ₂ /O ₂ CH ₄ /NH ₃ /NO/NO ₂ /O ₂	FR	Speciation	0 – 0.006 ppm (CH ₄) 0.001 ppm (NH ₃) 0.0008–0.001 ppm (NO) 0–0.0005 ppm (NO ₂) 0.06 ppm (O ₂)
9	(Shrestha et al. 2022)	[143]	3–5 (bar)	298 (K)	0.8–1.3	NH ₃ -DEE	ST, JSR, FR, BSF, RCM, CVCC	LBV IDT Speciation	10–40% (vol% of DEE)
10	(Singh et al. 2022)	[144]	1–74 (atm)	298–1240 (K)	0.5–1.67	NH ₃ /air NH ₃ /H ₂ /air	HF, JF, OPSF, RCM	LBV IDT	0–80% (vol% of NH ₃) 0–66.7% (vol% of H ₂)
11	(Dagaut 2022)	[56]	1 (atm)	1100 - 1450 (K)	0.1–2	NH ₃ /air NH ₃ /NO/air	JSR	IDT LBV	500–1000 ppm (NH ₃) 0–1000 ppm (NO)
12	(Wang et al. 2022)	[145]	1–5 (atm)	298 (K)	0.6–1.6	NH ₃ /CH ₄ /air NH ₃ /H ₂ /air	HF	LBV	0–1% (vol% of NH ₃)
13	(Zhou et al. 2021)	[47]	1 (atm)	298–423 (K)	0.7–1.4	NH ₃ /syngas/air NH ₃ /bio-syngas/air	CVCC	LBV	10–90% (vol% of H ₂) 0–100% (vol% of Bio-Syngas)
14	(Shrestha et al. 2021)	[23]	1–10 (bar)	298–473 (K)	0.6–1.8	NH ₃ /air NH ₃ /H ₂ /air	CVCC	LBV	21–30% (vol% of O ₂) 0–100% (vol% of H ₂)
15	(Mei et al. 2021)	[44]	1–10 (bar)	298 (K)	0.7–1.4	NH ₃ /air NH ₃ /H ₂ /air	CVCC	LBV	cracking ratio (γ) 10–80%
16	(Han et al. 2021)	[133]	1 (atm)	298 (K)	0.4–2	NH ₃ +N ₂ O+air	HF	LBV	15–100% (vol% of N ₂ O)
17	(Zhang et al. 2021)	[26]	1 (atm)	800–1280 (K)	0.25–1	NH ₃ /air NH ₃ /H ₂ /air	JSR	Speciation	0–70% (vol% of H ₂)
18	(Dai et al. 2021)	[146]	10–70 (bar)	610–1180 (K)	0.5–2	NH ₃ /DME	RCM	IDT	0–100% (vol% of DME)
19	(Bertolino et al. 2021)	[131]	0–100 (bar)	0–3000 (K)	0– ∞	NH ₃ /air	RCM, PRF, JSR, PPF	IDT LBV Speciation	–
20	(Xu et al. 2023)	[147]	10–15 (bar)	600–1000	1–2	n-heptane/NH ₃	ST, RCM, HF, CVCC, JSR	IDT LBV Speciation	20–40% (vol% of NH ₃)
21	(Glarborg 2022)	[27]	1 (atm)	580–1350 (K)	–	NH ₃ /NO ₂ /O ₂	BR, FR	IDT Speciation	285–500 ppm (NO ₂) 0–2% (vol% of O ₂)
22	(Mei et al. 2021)	[132]	1 (atm)	298 (K)	1.1–1.9	NH ₃ /NO/N ₂	OPSF	LBV	NH ₃ /(50%NO/50%N ₂) (%vol)

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Table 2 (continued)

23	(Stagni et al. 2020)	[25]	1 (atm)	500–2000 (K)	0.01–0.375	NH ₃ /Air NH ₃ pyrolysis NH ₃ /SYN/A (5 vol% H ₂ +95 vol% CO)/air NH ₃ /SYN/B (50 vol% H ₂ +50 vol% CO)/air	JSR, FR HF	Speciation LBV	2–4% (vol% of O ₂) 20–60% (vol% of SYN)
24	(Han et al. 2019)	[42]	1 (atm)	298 (K)	0.6–1.6				
25	(Mei et al. 2020)	[61]	1–10 (atm)	298 (K)	0.7–1.5	NH ₃ /Syngas/air	CVCC	LBV	$\beta = 10\% - 90\%$ $\alpha = 10\% - 95\%$
26	(Mei et al. 2019)	[43]	1–5 (atm)	298 (K)	0.6–1.5	NH ₃ /O ₂ /N ₂	CVCC IDT LBV		25%–45% (vol% of O ₂)
27	(Han et al. 2019)	[42]	1 (atm)	413 (K)	0.6–1.8	NH ₃ /air, NH ₃ /H ₂ /air, NH ₃ /CO/air NH ₃ /CH ₄ /air	HF	Speciation LBV	0%–100% (vol% of H ₂) 0%–100% (vol% of CO) 0%–100% (vol% of CH ₄)
28	(Thomas et al. 2022)	[148]	1 (atm)	298 (K)	–	NH ₃ /H ₂ /air	CFDF	Speciation	0%–15% (vol% of H ₂)
29	(Arunthanayothin et al. 2021)	[106]	1 (atm)	600–2000 (K)	0.5–2	NH ₃ /CH ₄ /air	JSR, FR	IDT Speciation	10,000 ppm (CH ₄) 500 ppm (NH ₃)
30	(Li et al. 2019)	[130]	0.1–5 (MPa)	1000–2000 (K)	0.5–2	NH ₃ /H ₂ /CH ₄ /air	ST, CVCC	IDT LBV	Various mixing ratio involved

* ST: Shock Tube; FR: Flow reactor; JSR: Jet Stirred reactor; RCM: Rapid compression machine; BSF: Burner-Stabilized Flames; HF: Heat Flux; JF: Jet flame; OPSF: Outward Propagating Spherical Flame; RCM: Rapid Compression Machine; PRF: Plug flow reactor; PFP: Freely propagating flame; BR: Batch Reactor; CFDF: Counterflow Diffusion Flame; β : H₂ contents in syngas; α : syngas contents in fuel mixtures.

been a subject of significant research. By analyzing experimental data and updating rate constants, researchers aim to enhance the accuracy of kinetic models and improve predictions of flame speed, NOx formation, and ignition delay time. However, further work is needed to develop a comprehensive mechanism capable of accurately estimating combustion characteristics under a wide range of blending conditions.

Comparison between mechanisms

Numerous mechanisms of NH₃ have been established or improved upon by using existing mechanisms as baseline references. Kinetic optimization offers a valuable approach for validating and refining theoretical mechanisms of chemical reactions. In this context, experimental data plays a crucial role as it provides a basis for comparison with numerical predictions. By comparing experimental data with predicted results, the accuracy of the tested kinetic mechanism can be enhanced, thereby enabling a more comprehensive description of the underlying chemistry. Ultimately, this iterative process contributes to the development of robust theoretical frameworks, which in turn facilitate a deeper comprehension of chemical reactivity and enable more accurate predictions.

Comprehensive studies have been conducted using multi-combustion systems measurements to enhance the prediction performance of kinetic reaction mechanisms for NH₃ as a standalone fuel or when blended with other fuel agents. These studies have incorporated a wide range of experimental data points, as outlined in Tables 1 and 2. Notably, the improved mechanisms have taken into account factors such as equivalence ratio, pressure, and temperature of the mixture, aiming to extend the operability limits of the kinetic model. This iterative process has played a pivotal role in refining the kinetic model by accurately predicting key combustion characteristics of NH₃. These characteristics include laminar burning velocity, ignition delay time, and the formation/decomposition of nitrogen oxides (NOx). The San Diego kinetic model [58], for instance, has further improved its prediction capabilities by incorporating additional reaction steps based on the measurements reported by [118,149], such as NH₂+N ⇌ N₂+H+H and N₂H+O₂ ⇌ N₂+HO₂. These additional steps aid in more accurate

calculations of flame speed. Moreover, the model has included reactions including NH₂+O₂ ⇌ HNO+OH, NH₂+O₂ ⇌ H₂NO+O, H₂NO+O ⇌ HNO+OH, and H₂NO+O₂ ⇌ HNO+HO₂ to enhance the estimation of ignition delay time.

Recently, the laminar flame speed of NH₃, both as a pure fuel and when blended with H₂, has been extensively studied by [16,32]. The focus of these studies was to identify the key reactions that govern fuel reactivity under atmospheric conditions. This was achieved through sensitivity analyses and reaction path flux analyses. According to investigations by Alnasif et al. [32], who examined 36 reaction mechanisms from the literature, Table 3, the kinetic model developed by Duynslaeger et al. [19] demonstrated the best performance in predicting laminar flame speed measurements for a 70/30 vol% of NH₃/H₂ mixture under atmospheric conditions. The Duynslaeger model [19] demonstrated a high level of accuracy in reproducing laminar flame measurements under lean conditions, with an average percentage error ranging from 2.0% to 6.0%, Fig. 4. It is worth noting that the design conditions of the Duynslaeger kinetic mechanism did not match the experimental setup of Alnasif's study in terms of pressure and equivalence ratio conditions. The kinetic model of Duynslaeger was developed based on experimental measurements conducted on eight ammonia/hydrogen flames. These experiments aimed to analyze flame structures at low pressures (60–120 mbar) and over a range of equivalence ratios (0.9 < ϕ < 1.1), with hydrogen content in the fuel ranging from 5% to 12.5%. The Duynslaeger mechanism improved upon the Konnov mechanism, which tended to overestimate NH₂ mole fraction profiles and underestimate N₂O mole fraction profiles. The improvement involved incorporating N₂Hx species, which are relevant to the formation and consumption of nitrogen oxides in practical combustors. In the improved model of Duynslaeger, rate constants were updated, and for four reactions (NH + NO ⇌ N₂O + H, N₂O + H ⇌ N₂ + OH, NH₂ + H ⇌ NH + H₂, and NH₂ + NH₂ ⇌ N₂H₂ + H₂) were modified based on the kinetic analysis of the primary reactions involving these chemical species. Alnasif's sensitivity analysis for lean conditions revealed the significant role of the reactions NH₂ + NH₂ ⇌ N₂H₂ + H₂ and NH₂ + H ⇌ NH + H₂ in promoting and retarding the laminar flame speed of NH₃/H₂ flames, respectively. Both reactions were considered, and their kinetic

Table 3

Chemical kinetic mechanisms investigated [32].

No.	Kinetic mechanisms	No. of Reactions	No. of species	No.	Kinetic mechanisms	No. of Reactions	No. of species
1	(Bertolino et al., 2021)	264	38	19	(U. Mechanism, 2018)	41	20
2	(Mei et al., 2021a)	264	38	20	(Klippenstein et al., 2018b)	211	33
3	(Han et al., 2021)	298	36	21	(Nakamura et al., 2017)	232	33
4	(Mei et al., 2021b)	257	40	22	(Zhang et al., 2017)	251	44
5	(Gotama et al., 2022)	119	26	23	(Lamoureux et al., 2016)	934	123
6	(Shrestha et al., 2021)	1099	125	24	(Xiao et al., 2016)	276	55
7	(Wang et al., 2021)	444	91	25	(Song et al., 2016)	204	32
8	(Zhang et al., 2021)	263	38	26	(Nozari and Karabeyoglu, 2015)	91	21
9	(Arunthanayothin et al., 2021)	2444	157	27	(Mathieu and Petersen, 2015)	278	54
10	(Stagni et al., 2020)	203	31	28	(Duynslaeger et al., 2012)	80	19
11	(Han et al., 2019b)	177	35	29	(Klippenstein et al., 2011)	202	31
12	(De Persis et al., 2020)	647	103	30	(Zhang et al., 2011)	701	88
13	(Mei et al., 2019)	265	38	31	(Lamoureux et al., 2010)	883	119
14	(Li et al., 2019)	957	128	32	(Konnov, 2009)	1207	127
15	(Okafor et al., 2019)	356	59	33	(Mendiara and Glarborg, 2009)	779	79
16	(Glarborg et al., 2018)	231	39	34	(Tian et al., 2009)	703	84
17	(Shrestha et al., 2018)	1081	124	35	(Dagaut et al., 2008)	250	41
18	(Otomo et al., 2018)	213	32	36	(Gregory P. Smith et al., 2000)	325	53

rates were improved in the study by Duynslaeger et al. [19], which may explain the accurate performance in predicting laminar flame speed under lean conditions, as observed in Alnasif's study. It was also reported that most kinetic mechanisms had poor performance in the prediction of the laminar flame speed at the leanest conditions, especially when the equivalence ratio ~ 0.6 . Similarly, high equivalence ratios ($1.2 < \phi < 1.4$) denoted large discrepancies that require further mechanism developments, Fig. 5.

Rocha et al. [16], also evaluate the performance of ten kinetic reaction mechanisms in predicting the laminar flame speed of NH_3/Air mixtures under specific conditions. Mathieu and Petersen [10], Okafor et al. [20], and Otomo et al. [8] demonstrated good performance across

a wide range of equivalence ratios, displaying similar trends in flame speed sensitivity coefficients and key reactions ($\text{H}+\text{O}_2=\text{H}+\text{OH}$, $\text{H}+\text{NO} (+\text{M}) \rightleftharpoons \text{HNO} (+\text{M})$, $\text{NH}_2+\text{NO} \rightleftharpoons \text{NNH}+\text{OH}$) that significantly influence NH_3 flame propagation. However, most models overestimated flame speed under rich conditions, Fig. 6. Regarding NH_3/H_2 blends, sensitivity analysis revealed a different chemistry scenario compared to pure NH_3 fuel. The relative importance of nitrogen sub-mechanisms decreased gradually, while the significance of H_2/O_2 reactions increased. Additionally, reactions between nitrogen-containing radicals and OH, such as $\text{NH}_2 + \text{NO} \rightleftharpoons \text{NNH} + \text{OH}$, became more influential for all tested mechanisms. Glarborg et al. [21], Konnov [17], and Dagaut et al. [9] overestimated flame speed at stoichiometry, while

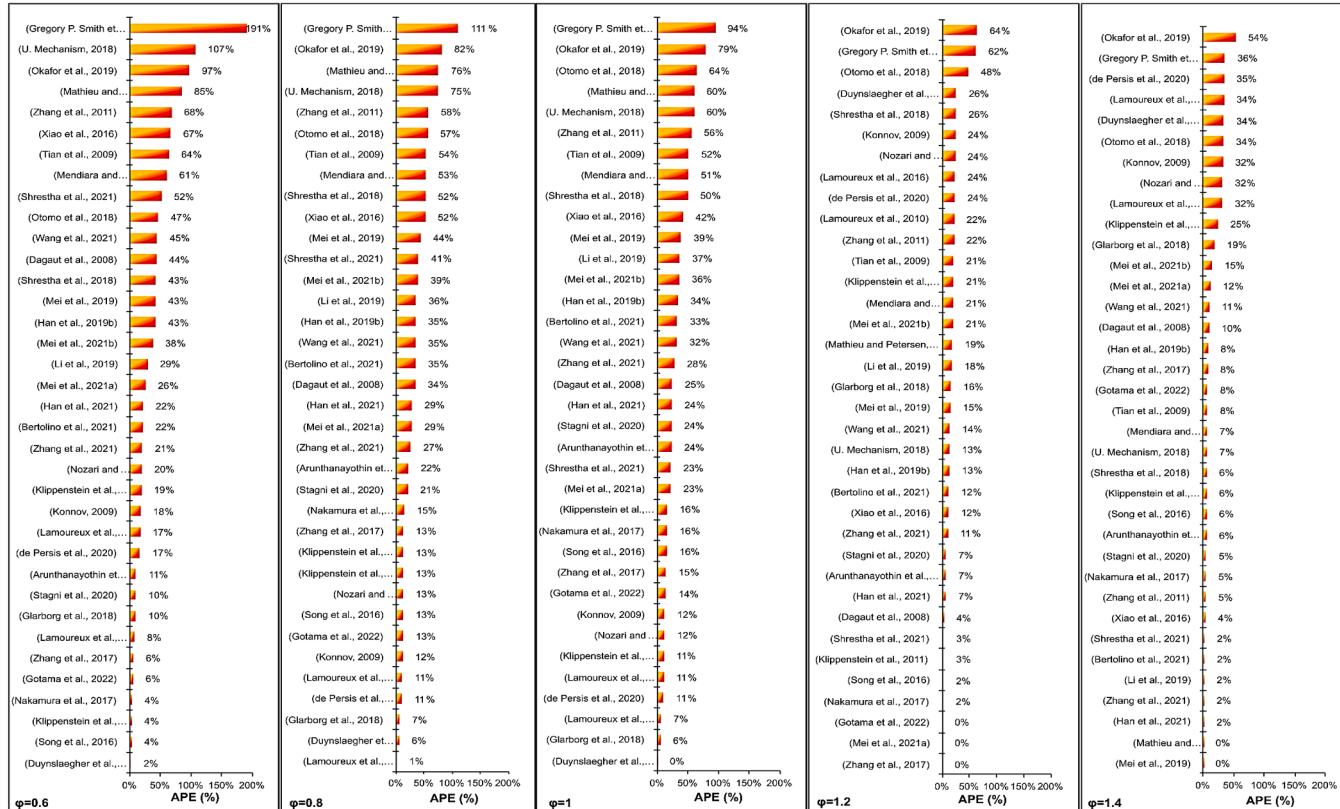


Fig. 4. The Absolute Percentage Error (APE) analysis in terms of equivalence ratios predicted for 36 kinetic reaction mechanisms. Reproduced from Ref. [32] with permission from Elsevier.

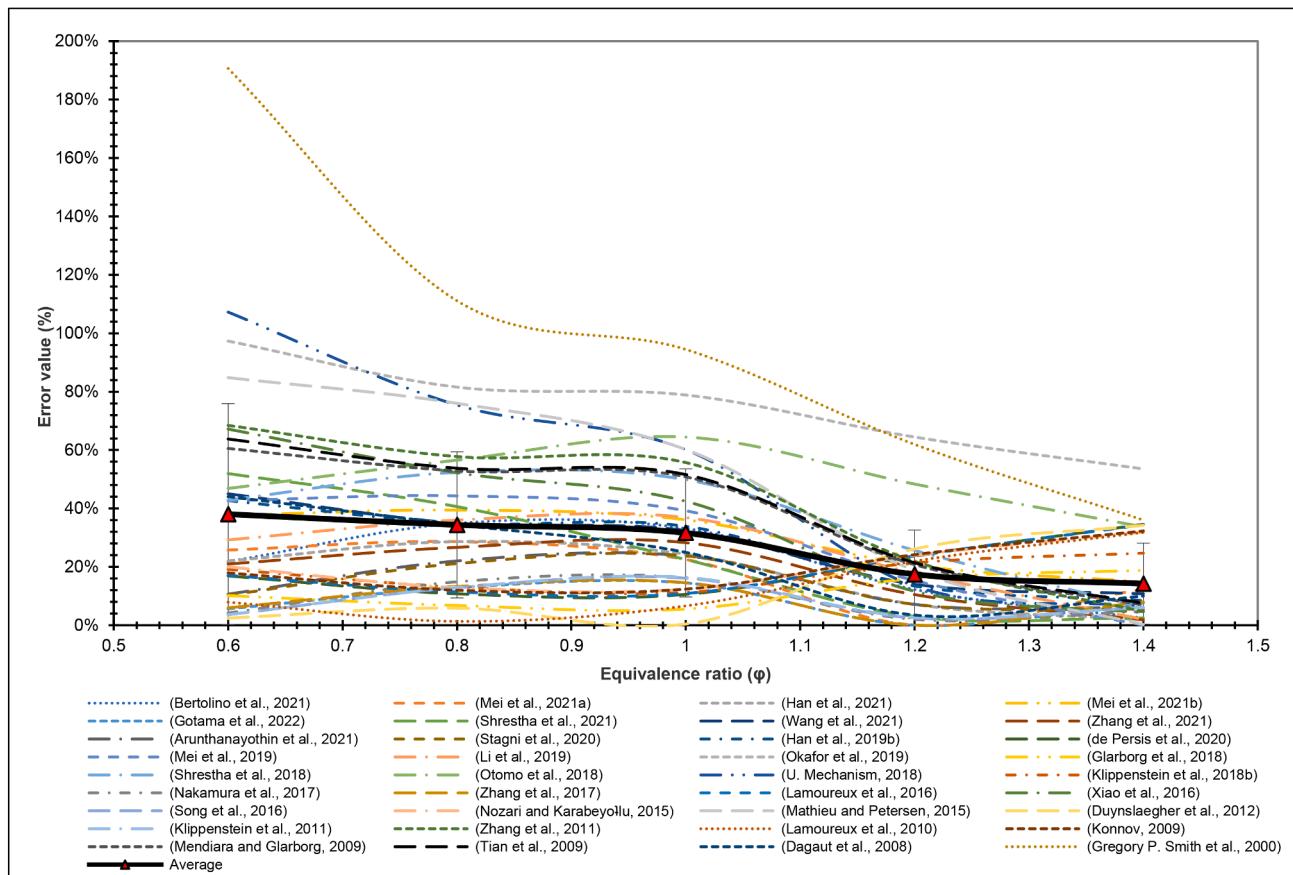


Fig. 5. The trend line of prediction error related to the experimental data on the laminar flame speed of 70/30 (%vol) NH₃/ H₂ blend estimated by kinetic mechanisms investigated as a function of the equivalence ratio. Symbols denote the average prediction error of 36 kinetic model. Reproduced from Ref. [32] with permission from Elsevier.

Duynslaeger et al. [19] overestimated at low H₂ content and underestimated at high H₂ content. On the other hand, Klippenstein et al. [11] and Song et al. [14] accurately predicted combustion characteristics, Fig. 7

In another study conducted by Alnasif et al. [22] the aim was to identify the most accurate kinetic model for predicting experimental measurements of NO mole fractions at binary flames of NH₃/H₂ (70/30%vol). A total of 67 kinetic reaction mechanisms were evaluated in this investigation, Fig. 8. The experimental data used were reported by Hayakawa et al. [150], who conducted their experiments under atmospheric conditions and various equivalence ratios (ranging from 0.57 to 1.4) using a stabilized stagnation flow combustion configuration. This setup was specifically designed to avoid flame instability issues and ensure higher measurement accuracy. The findings of Alnasif's investigations revealed that both the kinetic models proposed by Glarborg [27] and Nakamura et al. [28] demonstrated proper estimation capabilities and accurately reproduced the experimental measurements within the reported uncertainty range. Glarborg [27] developed the mechanism based on previously published model [21], utilizing them as a baseline, and further optimized the model by incorporating experimental data obtained from batch reactors (operating at temperatures between 580 K and 690 K) and flow reactors (operating at temperatures between 850 K and 1350 K) for NH₃/NO₂ flames. In addition, novel results from flow reactor experiments investigating the influence of O₂ addition were integrated into the model. The improved model by Glarborg [27] highlighted the significance of key reactions such as NH₃ + NO₂ \rightleftharpoons NH₂ + HONO, NH₂ + NO₂ \rightleftharpoons H₂NO + NO, and NH₂ + NO₂ \rightleftharpoons N₂O + H₂O in NH₃ combustion and N₂O formation. Notably, the NH₂ + NO₂ reaction initiates a sequence of reactions that promote NO

formation: NH₂ + NO₂ \rightleftharpoons H₂NO + NO; H₂NO + O₂ \rightleftharpoons HNO + HO₂; HNO + O₂ \rightleftharpoons NO + HO₂. Another chain-branching sequence involving NO occurs under conditions where O₂ is absent: H₂NO + NO₂ \rightleftharpoons HNO + HONO; HNO + NO₂ \rightleftharpoons NO + HONO; HONO(+M) \rightleftharpoons NO + OH(+M). By constraining the rate constants of reactions involving NH₃ and NH₂ with NO₂, as well as subsequent steps involving H₂NO and HNO intermediates, the model's accuracy in predicting NO formation can be significantly improved. Notably, NO serves as one of the chain carriers in

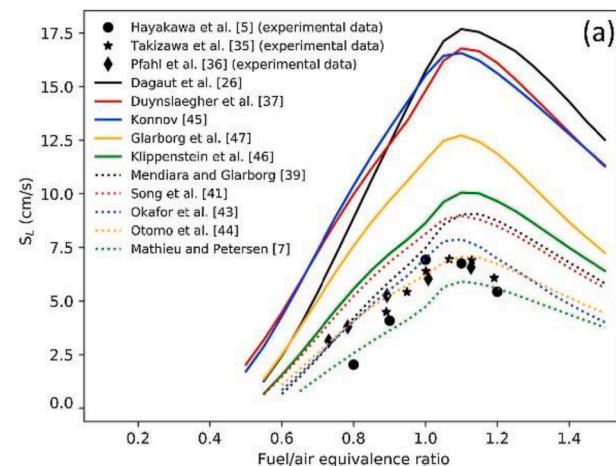


Fig. 6. Laminar flame speeds for NH₃/air mixtures as a function of the equivalence ratio at 1 bar and 298 K. Reproduced from Ref. [16] with permission from Elsevier.

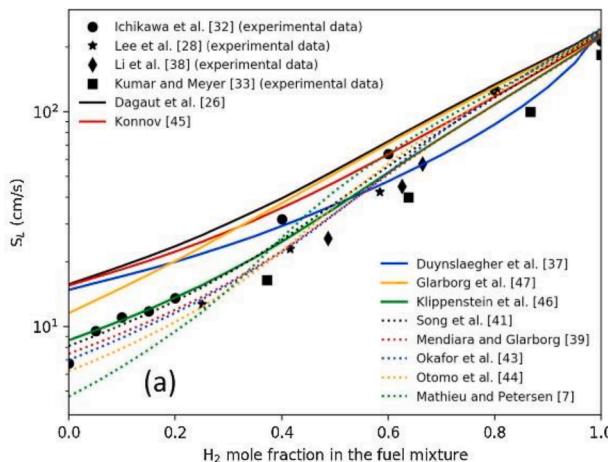


Fig. 7. Laminar flame speeds for NH₃/H₂ at stoichiometric conditions and for various mole fraction of H₂ in the fuel. Reproduced from Ref. [16] with permission from Elsevier.

the subsequent steps, and the accurate representation of its formation and consumption processes directly affects the overall predictions.

Overall, the investigations conducted have made significant contributions to the field by identifying appropriate kinetic models for predicting combustion characteristics based on experimental measurements. The findings have provided valuable insights into the key reactions and pathways involved in the chemistry of NH₃ as a pure fuel or when blended with other fuel agents. As a result, understanding these intricate processes leads to a deeper comprehension of NH₃ combustion.

Future trends and proposed optimization for NH₃ kinetic mechanisms

It has been clearly mentioned that several investigations have done to analyze and study the chemical kinetic performance of NH₃ oxidation mechanisms as a pure fuel or blended with other fuels as a binary blend of NH₃ mixtures with different mixing ratios for the optimization of combustion characteristics parameters of NH₃ flames (i.e. LBV, NO_x, and IDTs). Although many reaction mechanisms have been established and improved considering particular conditions of interest aiming to understand the chemical kinetics of NH₃ at the gas phase, the majority of the proposed mechanisms are not capturing the reaction kinetic of numerous species experimentally obtained. Also, the possibility of applying an efficient kinetic mechanism with good performance in predicting all combustion parameters such as LBV, NO_x, and IDTs accurately and for a wide range of operation conditions, equivalence ratios, and mixing ratios of fuel is still challenging. Therefore, further investigations are needed to reveal the causes behind the discrepancies in these predictions. Furthermore, the interaction/coupling of species and kinetics needs to be studied carefully, especially for the blended fuels of NH₃ (i.e., NH₃-H₂ and NH₃-CH₄), investigating its effects on the above-mentioned combustion parameters, especially NO_x formation. Similarly, most of the previously mentioned mechanisms update the rate constants as a way of optimization for prediction improvement, hence the process might increase uncertainties and affecting negatively the performance of the kinetic mechanisms. For example, Burcat et al. [151] mentioned the enthalpy of formation of the N₂H₃ radicals is 53.8 ± 17 kcal/mole, points that affected negatively on the influence of N₂H₃ species in the decomposition of ammonia as a diluted blend. Further, the heat of formation uncertainty for NH and NH₂ radicals is proposed to be ± 0.5 kcal/mole, which causes an additional uncertainty that is lower than the scattering of the experimental magnitudes of the rate constants [115,117]. Thus, it is important to take these issues into consideration while establishing a model capable of modeling parameters accurately

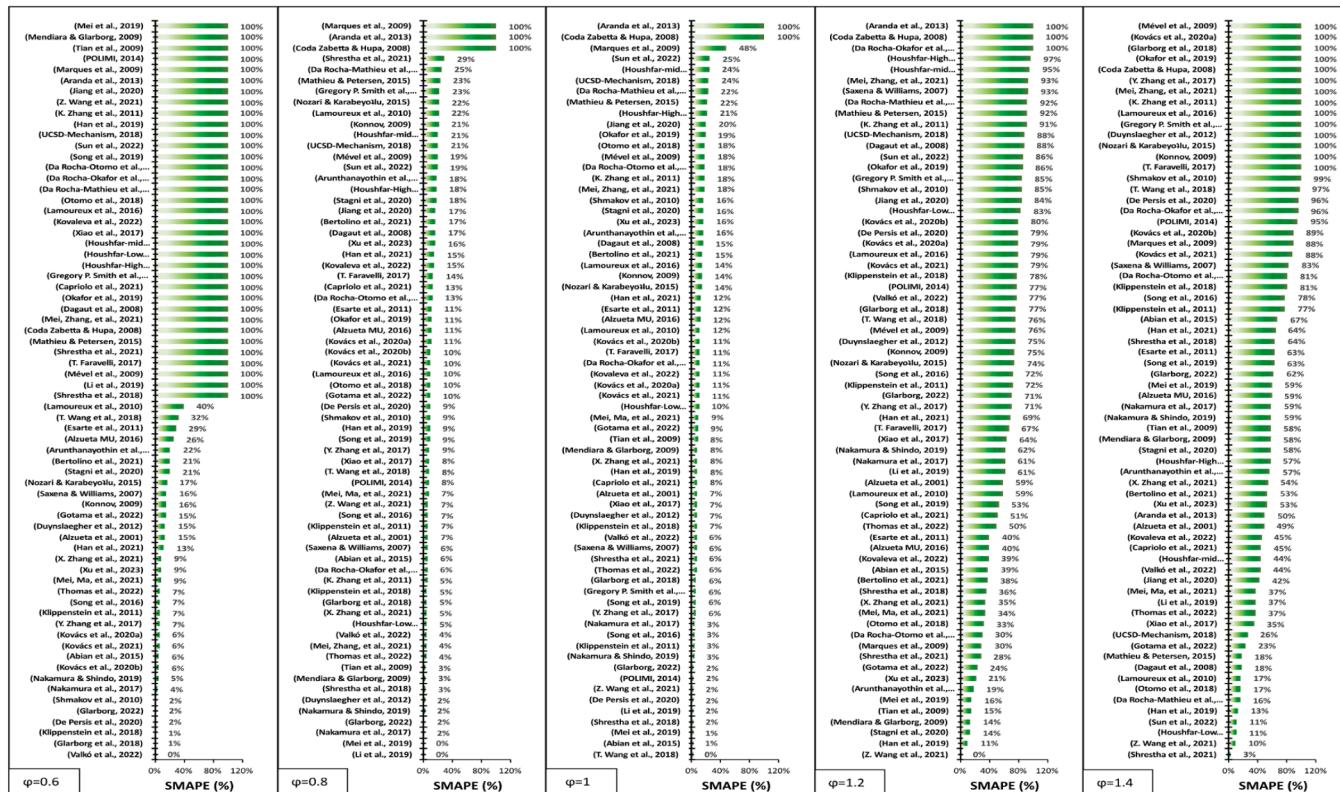


Fig. 8. A preliminary investigation by the symmetric mean absolute percentage error (SMAPE) for predicting of the NO mole fraction based on experimental measurements from [150] and numerical data from Chemkin-Pro-software. Reproduced from Ref. [22] with the permission from MDPI.

and with a low level of discrepancy. Furthermore, the majority of the reaction mechanisms have been developed considering atmospheric conditions. However, more studies need to be focused on improving the kinetic mechanism of NH₃ and its mixtures under pressurized conditions similar to large application systems such as gas turbine. Finally, improving the kinetic mechanisms for formation/consumption of NO and N₂O has been accomplished at some extent, with most mechanisms optimised better prediction of the previously mentioned species. However, the nitrogen dioxide (NO₂) chemistry is still poor and requires further improvement. The NO₂ is as important as NO and N₂O due to its harmful effects, especially at high concentrations, on the environment and human beings.

All these points and the previous literature also denote that the methods for comparison between mechanisms provide a variation of results where mechanisms are (or not) good for certain conditions under specific conditions but not for others, making final conclusions around their accuracy difficult to obtain. Therefore, a standardized methodology for validating and comparing mechanisms is critically required and needs to be properly addressed across the scientific community, hence providing homogeneous approaches for the definition of “best mechanisms” for distinct combustion parameters.

Conclusions

A comprehensive review of recent trends in the chemical kinetics of ammonia was presented in this article. Numerous experimental data in the field of ammonia-based fuel combustion, carried out in several combustion systems, were highlighted to validate the evaluation of kinetic reaction mechanisms of NH₃. There is still a need for a better understanding of the nitrogen reaction paths, making the development of a few reaction mechanisms capable of capturing most operating conditions critical. Also, the rate coefficients of the kinetic reactions that govern the reaction's performance need to be studied carefully and updated to capture the experimental measurements more accurately. Fundamental properties such as Laminar Burning Velocity, Ignition delay time, NOx mole fractions, etc., will still require vast research, especially at very lean conditions, to fully address the impacts of using ammonia and various doping agents, as their properties tend to change on the basis of the ammonia content and combustion conditions. However, the improvement of the kinetic mechanisms in the last 10 years in terms of including new routes and updating modeling parameters has achieved a big leap in the estimation of the combustion characteristics, hence improving predictions of experimental measurements and decreasing the discrepancy among the measurements.

Declaration of Competing 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.

Data availability

Data will be made available on request.

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