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On the use of ammonia as a fuel – A perspective

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Abstract

Ammonia has long been considered as a candidate vector for power generation, and has specifically gained significant interest recently. Though it is not free of drawbacks, ammonia has been identified as a promising potential alternative fuel for future power generation. Current studies and a growing body of works in this direction drive us closer to a viable solution of ammonia as an important transition into a cleaner future of the energy sector. In this perspective, we explore the use of ammonia as a fuel in combustion applications (with and without additives) and in fuel cells. The objective of this work is to show the prospects and challenges of ammonia as a fuel, and suggest significant topics that could benefit from additional studies.

Keywords: Ammonia, Combustion, Gas turbines, Fuel cells, Emissions, Future research, Alternative fuel

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1. Introduction: ammonia as a fuel

Chemical fuels are a promising approach for long-term energy storage: fluid fuels are reliable, relatively easily transported, can possess relatively high gravimetric and volumetric energy densities, and the required infrastructure is already in place on a global scale. To combat the current energy and climate change crisis, sustainable fuels for energy storage [1,2] should be synthesized from excess power ("power-to-X"). As technologies for hydrogen production from seawater advance [3,4], chemical storage of the produced hydrogen will be required for many applications due to the extremely low volumetric energy density of pure hydrogen and the potential safety and infrastructure cost issues associated with its distribution on a global scale. Ammonia could serve as an energy vector for renewable hydrogen [5] in a future nitrogen economy, in which abundant nitrogen is the main hydrogen carrier [6]. Ammonia may densify hydrogen at relatively low costs [7].

The advantages of ammonia as a fuel include a relatively high power-to-fuel-to-power (PFP) efficiency [6], a large-scale distribution infrastructure that is already in place [8,9] a high-octane rating of 110–130 [10], and a narrow flammability range, making it relatively safe in terms of explosion risks. On the other hand, ammonia is toxic, emits significant levels of pollutants upon combustion (NO_x and NH_3 residuals), and has an overall relatively low reactivity as a fuel [11]. Numerous studies were conducted in ongoing efforts to address the key challenges of low reactivity and pollutant reduction in ammonia systems.

Interest in fuel applications of ammonia has gathered significant momentum in recent years. For example, searching for the phrase "ammonia" in past issues of the journal *Fuel* (ISSN 0016–2361) over the past dozen years (considering only studies that focus on ammonia as a fuel) results in a clear trend of increased interest and a growing body of works in the recent few years compared to the preceding decade (Figure 1). Surely, there are interesting and "burning" questions to be addressed; the present perspective attempts to highlight some of them and suggest significant topics that could benefit from additional studies.

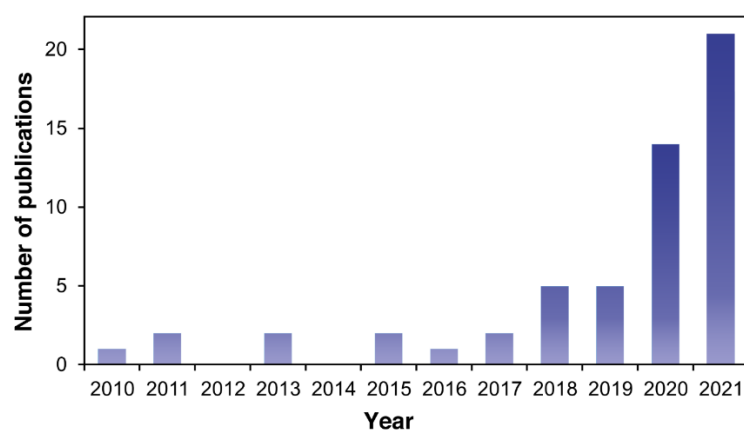


Figure 1. The number of publications per year that report novel research studies on ammonia as a fuel that have been published in the journal *Fuel* (ISSN 0016–2361) since 2010. The data were gathered by searching for the keyword "ammonia" and considering only research papers that directly study ammonia as a fuel application (i.e., not including other published works on SCR, SNCR, DeNO_x , or NH_3 production methods such as biomass gasification; review papers were not considered here).

2. Combustion theory

Ammonia gas-phase kinetics has been the subject of numerous studies. The overall goal of these studies is the development of detailed kinetic models accurately representing the chemistry of intermediate species at the molecular level. These models are then useful for the development of efficient and clean technologies. Accurate computational predictions can be nowadays performed with reasonable CPU time by coupling CFD codes and detailed kinetic models as long as the number of species remains reasonable.

The development of high-quality predictive detailed kinetic models relies on two pillars: the use of the most reliable thermodynamic properties and kinetic parameters and the benchmarking of the model against the updated experimental datasets obtained over a wide range of conditions (e.g., temperature, pressure, composition, residence time, equivalence ratio, and reactor hydrodynamics). Thermodynamic properties and kinetic rate coefficients can be obtained using experiments or can be calculated using ab initio quantum-chemical calculations. Quantum-chemical calculations can also be used to explore potential energy surfaces and find new reaction pathways that are missing in detailed kinetic models. The variety of literature datasets available and the process of carefully selecting data from different sources result in a plethora of literature models, even for a simple fuel like ammonia, each with different parameters. This results in a chaotic state in the field that hampers advancement, and calls for a data-centric approach [12].

2.1. Comparison of the H/N/O sub-system in literature chemical kinetic models

Several detailed kinetic models were released in the last few years which show a growing interest in gas-phase ammonia kinetics [13-19]. Some models only include the chemistry of neat ammonia oxidation [14-19], whereas others also consider the chemistry of some carbon-containing species like methane [13,16,17]. Literature H/N/O models generally have comparable sizes in terms of the number of species, as can be seen in Figure 2. All of these models (except for the reduced model by Jiang et al. [15]) consider the same 29 species (H, N, O, H₂, N₂, O₂, OH, NO, NH, HO₂, H₂O, H₂O₂, N₂O, NO₂, HNO, HNO₂, HONO, HONO₂, N₂H₂, H₂NN, NH₂OH, HNOH, NH₃, N₂H₄, NO₃, NNH, NH₂, H₂NO, and N₂H₃). The difference relies on three species: HON, HNO₃ and O₃. The model of [19] does not consider these three species, that of [14] considers HON, but not HNO₃ and O₃, those of [13,17,18] consider HON and HNO₃, but not O₃, and that of [16] considers HON and O₃, but not HNO₃.

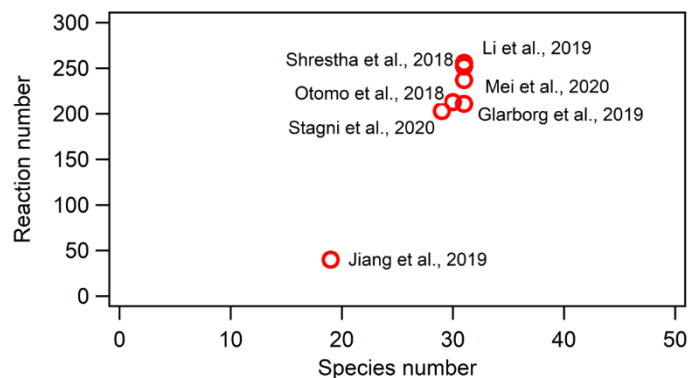


Figure 2. Structure of recently published detailed kinetic models. Only H/N/O containing species and associated reactions are considered. Electronically excited species such as OH* were not considered in this comparison.

The structure of these models mainly differs from each other in the number of reactions they involve (203 for [19] versus 256 for [17], other models lying in between). The chemical pathways considered in these models are basically the same. For example, all these models include the unimolecular initiation of ammonia (yielding NH_2+H), the bimolecular initiation ($\text{NH}_3+\text{O}_2=\text{NH}_2+\text{HO}_2$) and H-atom abstraction reactions ($\text{NH}_3+\text{R}=\text{NH}_2+\text{RH}$, where R represents a radical). The models consider H-atom abstractions by H, O, OH, HO_2 and many open shell nitrogen-containing species such as N, NH, etc. Literature studies highlighted the complexity of the sequence of reactions consuming ammonia and forming products [5,13,19]. The first step in continuous operation is the formation of NH_2 by H-atom abstraction. The fate of the NH_2 radical depends on the conditions and various subsequent pathways are possible, illustrating the complex chemistry of this simple system. For example, according to the rate of production performed at an intermediate temperature of 1050 K by [19], NH_2 mainly reacts with NO and NO_2 forming mainly N_2 and NO, respectively, but also with HO_2 and NO_2 to H_2NO yielding NO via HNO. Minor pathways also contribute to the formation of N_2 from NH_2 (via NNH and N_2O) and to that of NO from H_2NO (via HONO). The scheme is even more complex at higher temperatures with new routes via the intermediate NH which is a source for both N_2 and NO. Actually, the branching between different possible pathways is highly sensitive to the temperature as shown in Figure 3. Figure 3A displays the rate coefficients for the reactions of NH_2 with NO leading to NNH+H, $\text{N}_2+\text{H}_2\text{O}$, and $\text{N}_2\text{O}+\text{H}_2$ over the temperature range 300–3000 K. The kinetic coefficients of the first two pathways show little evolution with the temperature, whereas the $\text{N}_2\text{O}+\text{H}_2$ route is of the same order of magnitude only at very high temperatures (~ 2000 K). The kinetic coefficient of the $\text{N}_2+\text{H}_2\text{O}$ route is larger than that of NNH+H (about one order of magnitude) up to ~ 600 K. The three kinetic coefficients intersect at around 2000 K, and the reaction coefficient ranking reverses. Similarly, Figure 3B shows the kinetic coefficients for the reactions of NH_2 with NO_2 leading to $\text{H}_2\text{NO}+\text{NO}$, $\text{HNNO}+\text{OH}$, and $\text{N}_2\text{O}+\text{H}_2\text{O}$. The $\text{H}_2\text{NO}+\text{NO}$ pathway is the most favorable over the whole temperature range. The $\text{N}_2\text{O}+\text{H}_2\text{O}$ pathway is less important up to 1700 K where its kinetic coefficient intersects with that of the $\text{N}_2\text{O}+\text{H}_2\text{O}$ route.

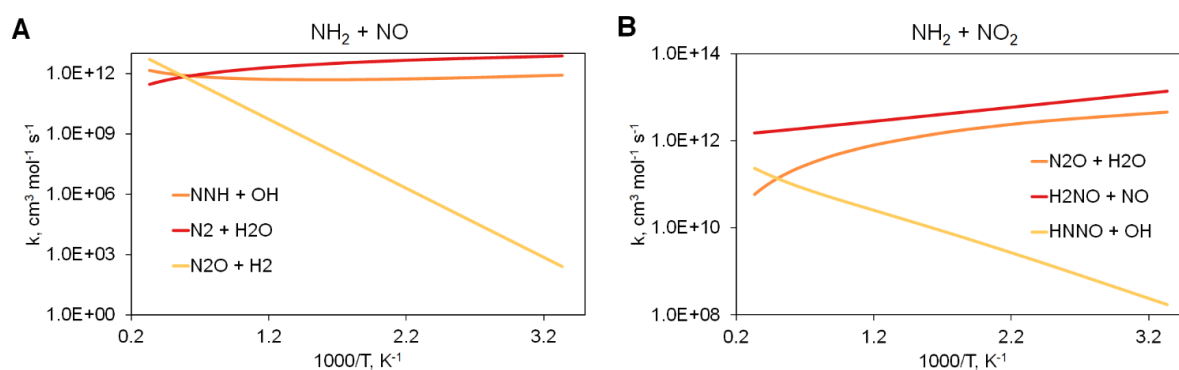


Figure 3. Rate coefficient comparisons of (A) $\text{NH}_2 + \text{NO}$ and (B) $\text{NH}_2 + \text{NO}_2$. The following sources were used: $\text{NH}_2 + \text{NO} \rightleftharpoons \text{NNH} + \text{OH}$ from [20], $\text{NH}_2 + \text{NO} \rightleftharpoons \text{N}_2 + \text{H}_2\text{O}$ from [20], $\text{NH}_2 + \text{NO} \rightleftharpoons \text{N}_2\text{O} + \text{H}_2$ from [21], $\text{NH}_2 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O} + \text{H}_2\text{O}$ from [22], $\text{NH}_2 + \text{NO}_2 \rightleftharpoons \text{H}_2\text{NO} + \text{NO}$ from [22], $\text{NH}_2 + \text{NO}_2 \rightleftharpoons \text{HNNO} + \text{OH}$ from [22].

A specificity of the oxidation of ammonia is the De NO_x process occurring as long as ammonia is not fully consumed, similarly to the principle of the NO_x selective catalytic reduction process used in various post treatment units [23]. The main reaction responsible for this phenomenon in the gas phase is that of NH_2+NO yielding N_2 and water. This phenomenon was well observed by [19] in their flow reactor study with the mole fraction of N_2 increasing simultaneously with the consumption of ammonia and the mole fraction of NO only increasing once the full consumption

of ammonia was reached (Figure 4A). The sensitivity analysis performed by the authors highlighted a set of eight reactions having an antagonistic effect on the mole fractions of the two species NO and N₂, the NH₂+NO to N₂+H₂O being one of them (Figure 4B). It is obvious that a better understanding of this specific chemistry and the refinement of kinetic parameters will be valuable for the prediction of the behavior of ammonia oxidation in terms of emissions and the optimization of practical applications like gas turbines or internal combustion engines.

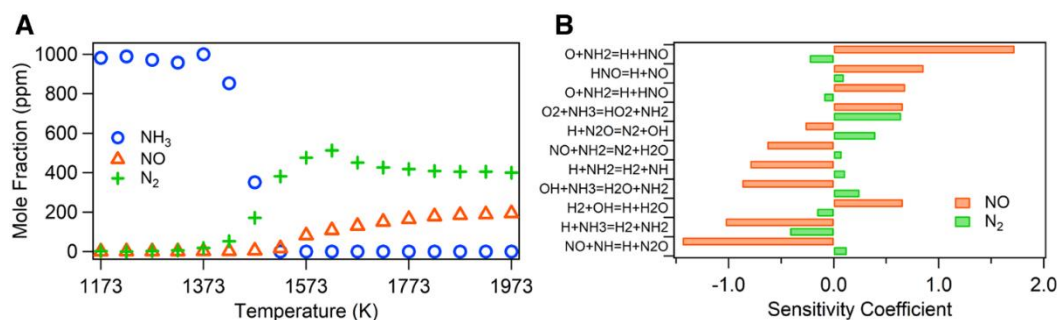


Figure 4. Ammonia oxidation study in a flow reactor. (A) Mole fraction of NH₃ (fuel), NO and N₂ as a function of temperature. (B) Sensitivity analysis to NO and N₂ mole fractions at 1523 K (graphs redrawn from [19]).

2.2. Kinetic parameters: towards a unified kinetic model?

One problem with the development of detailed kinetic models is the lack of consensus on kinetic parameters. This problem is not insoluble, but it takes time and effort to find a general agreement on the best set of kinetic parameters to be used and the release of a quasi-unified model. This quest is still far from conclusion for ammonia. The sensitivity analyses displayed in Figure 5 (extracted from reference [24]) illustrate the discrepancies in kinetic parameters used in the different models. The sensitivity analysis bar charts computed using two literature models [16,19] look different, with even an antagonistic effect for one of the reactions.

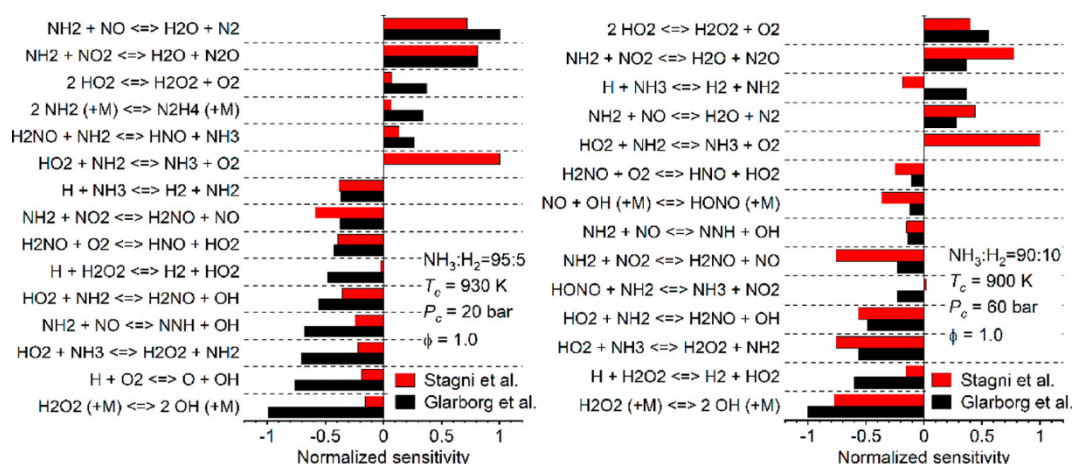


Figure 5. Normalized sensitive analysis on the ignition delay times of NH₃/H₂ (RCM conditions) using two literature models [16,19] (figure excerpted from [24], with permission of ACS. Further permissions related to the material excerpted should be directed to the ACS).

Elishav et al. have recently reviewed the kinetic parameter data available in literature for some reactions of the HNO system [5]. Several lessons can be learned from this comprehensive review: a limited number of reactions have been the subject of several experimental studies (for example, the apparent unimolecular initiation of ammonia: NH₃ + M = NH₂ + H + M, and ammonia H-atom

abstractions by H, OH and O), whereas the literature is clearly lacking experimental data for some other reactions; when experimental data are available, this is usually only for a limited range of conditions (temperature, pressure for third body reactions), and the different sets of data are not always consistent; the use of mathematically fitted kinetic constants outside their domain of validity is clearly not recommended as the extrapolation can cause problems of divergence. The temperature dependence is usually not well caught by the fit as it is performed over a limited range of temperatures and against experimental data having relatively high uncertainties, for reactions for which no literature experimental data are available (which are the majority), quantum calculations have been performed by different authors, but they are not necessarily consistent.

The variability of calculated kinetic parameters can be illustrated by the graph in Figure 6 drawn for the reaction $\text{NH}_2 + \text{OH} = \text{NH} + \text{H}_2\text{O}$. Measurements and computations of kinetic rate coefficient values are spread over more than three decades (even more for some other reactions involved in the HNO system, see reference [5]) and they do not exhibit the same temperature dependence at all. These discrepancies could be due to the use of different calculation methods (e.g., energy calculations at different levels of theory, entropy and heat capacity corrections), which highlights that there is no general agreement on the way calculations should be done for nitrogen-containing compounds.

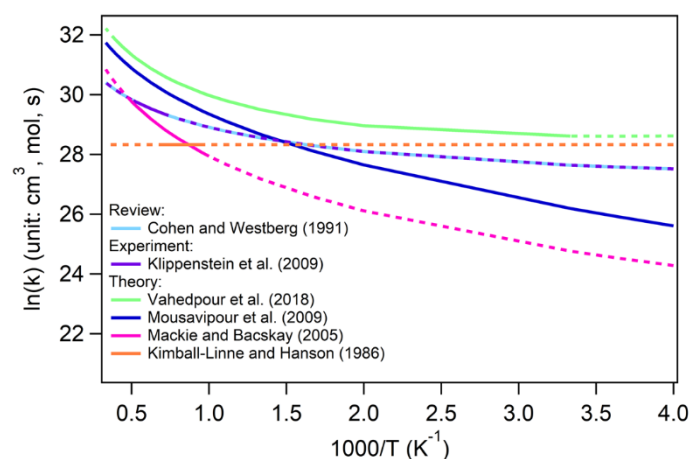


Figure 6. Comparison of kinetic constants for the reaction $\text{NH}_2 + \text{OH} = \text{NH} + \text{H}_2\text{O}$ [25-30]. Dashed lines are for extrapolation outside the validity temperature range (adapted from Figure 25 in [5]).

Due to the structure of ammonia, species included in the H/N/O system are small molecules and radicals with a limited number of degrees of freedom. Further, unimolecular reactions, having pressure-dependence phenomenological rate coefficients, are common in this system. An example is the unimolecular initiation of ammonia: $\text{NH}_3 = \text{NH}_2 + \text{H}$. As it can be seen in Figure 7, the kinetic rate coefficient value of this reaction at 1500 K over the usual range of pressures is still in the fall-off region and far from the high-pressure limit (kinetic parameters from [30]). Consequently, accurate predictions require that kinetic parameters accurately account for pressure-dependent rates and branching ratios. Different formalisms can be considered in models to account for the pressure-dependence effect. Some models [13,17,18] consider kinetic parameters based on those recommended by Baulch et al. [31] for this reaction. The Lindemann-Troe formalism is used ($\text{NH}_3 (+\text{M}) = \text{NH}_2 + \text{H} (+\text{M})$); it involves in the last calculation step a third body efficiency factor depending on the nature of the collider (values in models developed by [13,17,18] come from Griffiths and Barnard for the reaction $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$, see page 175 in [32]). Another formalism

found in models is the pressure logarithm ("PLOG") expression for interpolating kinetic rate coefficients from values at different pressures (formalism used in [33] for example). This formalism assumes a specific collider and is dependent on the energy transfer model used in the master equation. Detailed kinetic models of ammonia oxidation would definitely benefit from further works in this area with more experimental pressure and temperature dependent studies (considering different bath gasses) combined with recent and future developments around master equation models [33].

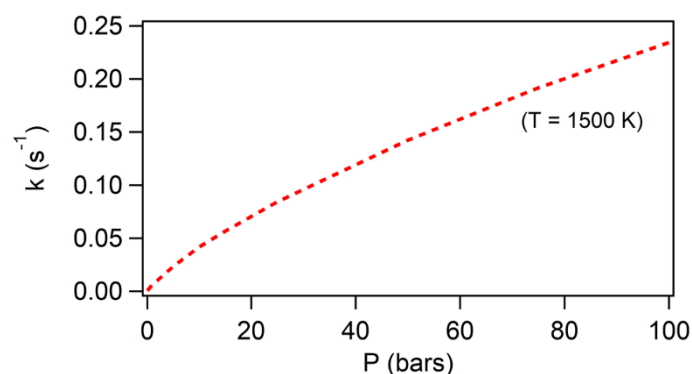


Figure 7. Evolution of the kinetic constant of the reaction $\text{NH}_3 = \text{NH}_2 + \text{H}$ at 1500 K as a function of the pressure (according to kinetic parameters from [33]).

Even if recent detailed kinetic models perform better in predicting literature experimental data (this point is discussed further), there are clear ways of improvement of the chemistry involved therein. Refining kinetic parameters will likely benefit from new experimental data acquisition through dedicated measurements, but also from theoretical accurate calculations. For this last point, the literature shows that there is a variety of methods used by different authors and that there is no general agreement on methods to be used for the specific HNO system. A better consideration of kinetic rate coefficients including pressure-dependence effects is also a necessary task to converge towards a more accurate chemistry.

2.3. Validation of detailed chemical kinetic models

As stated earlier in the introduction of this part, the validation of a detailed chemical kinetic model relies on the comparison of predictions with experimental data obtained over a wide range of conditions. There are two categories of experimental targets that can be used for model validation: global reactivity indicators such as fuel conversion, ignition delay time, extinction strain rate, or laminar flame speed; and more specific data such as time-resolved concentration profiles of intermediates (so called "speciation"). Valera-Medina et al. proposed an overview of the evaluation of some ammonia oxidation literature models in their recent review [24]. This informative overview highlights that models for ammonia oxidation have mainly been tested against ignition delay times (e.g., [34-38]) and laminar burning velocities (e.g., [39-45]), i.e., mostly against global reactivity indicators. This is due to the fact that there are still very little data providing speciation in flames (e.g., [46,47]) or at the outlet of flow and jet-stirred reactors (e.g., [19,48]). They also highlighted from their model benchmark that recent models overall performed better than older ones, in agreement with the improved accumulation of benchmarking data. The work by Stagni et al. can be used to illustrate these points [19]. Indeed, the quantification of NO and N_2 , the two main reaction products from ammonia oxidation, led to revisiting the specific chemistry responsible for the formation of these two species as the initial model version was not

able to reproduce the branching ratio correctly. In general, speciation data of intermediates are rarely reported in studies, while they are most useful for constrained benchmarking. Davidson and coworkers investigated the pyrolysis of ammonia behind reflected shock waves [49] and performed quantitative time-history measurements of NH and NH₂ radicals using laser absorption. Maclean and Wagner investigated the structure of ammonia-oxygen flames using mass spectrometry for the detection of NO, H₂O, N₂, NH₃, H₂, and N₂O as well as spectroscopic diagnostics for the detection of OH, NH, NH₂, and NO species [50]. N₂O was detected in several studies about ammonia oxidation in open flow reactors [51-53] mainly using infrared spectroscopy. Last but not least, the comparison of laminar burning velocities obtained under the same conditions but by different authors shows that there is still variability in experimental data (Figure 8), and some authors reported uncertainties up to +/- 1 cm s⁻¹ on their measurements which is significant compared to the absolute values of recorded flame speeds (in the range 2–8 cm s⁻¹). Despite its simple structure, ammonia is a fuel that is difficult to handle due to potential adsorption phenomenon and subsequent catalytic effect at walls (as reported by several authors – e.g., [19,54,55] – and discussed in the appendix of [16]).

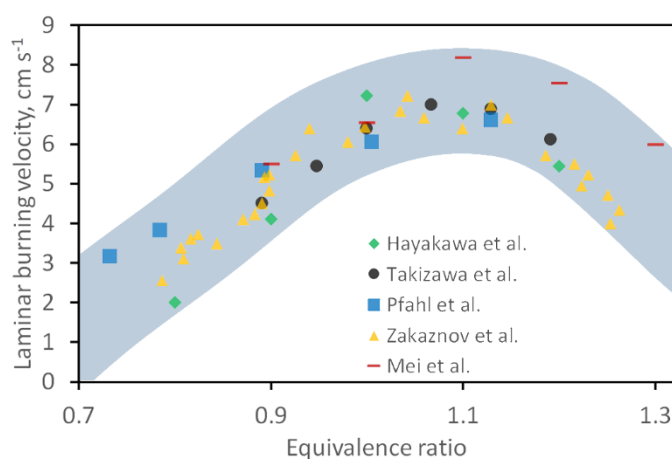


Figure 8. Laminar burning velocities of an ammonia-air mixture at 1 bar and 298 K and equivalence ratio of 1.1 [18,39,41,42,44]. The gray area is the envelope including all data.

Even if more experimental data become available for benchmarking models, collection of additional accurate measurements is still encouraged. Attention should be paid to data of intermediate species necessary to better understand the complex chemistry of the H/N/O system and to refine detailed kinetic models with better constraints. Global indicators must not be put aside as there are still large uncertainties in ignition delay times and laminar burning velocities measured by different groups.

2.4. Coupling with CFD codes

The development of efficient practical combustion systems (like gas turbines or internal combustion engines) requires strong CFD analyses [56]. This type of calculation provides valuable information about flow field and composition (flame structure for the case of burners), enabling a better understanding of the coupled effect of hydrodynamics and kinetics on reactivity and emissions. As discussed earlier, the H/N/O system in ammonia oxidation detailed kinetic models contains about 30 species which are compatible for the coupling with CFD codes. Nevertheless, ammonia systems are often coupled to hydrocarbon (e.g., methane) oxidation, and the number of

species is often more than 100, making the coupling with CFD codes very challenging in terms of computational resources and time. Thus, some authors proposed several model versions for neat ammonia and for ammonia-hydrocarbon blends (e.g., [19,57]). Another strategy is to reduce a detailed kinetic model, keeping only the species and reactions relevant under the conditions of the simulations. For example, this is the strategy adopted by Xiao et al. for investigating ammonia combustion in a lean premixed swirl burner [58], and by Li et al. for their study considering $\text{NH}_2/\text{H}_2/\text{CH}_4$ mixtures [17]. Most of literature studies focus on emissions, and particularly on NO_x . As an example, the numerical flame structure predictions performed by Li et al. highlighted high NO formation in high temperature regions near the stoichiometric zone, while NO_2 was dominant in the lean flame zone.

Xiao et al. used OpenFOAM [59] to run 3D simulations of ammonia in a lean premixed swirl burner [58]. They used a reduced mechanism accounting for ammonia oxidation chemistry based on the detailed kinetic model from Konnov [60]. Simulations highlighted high level of NO_x emissions and the authors suggested to investigate new stratified injection techniques. Mikulčić et al. performed the numerical simulation of ammonia/methane/air combustion [61] using three literature chemical kinetic models [15,17,62] with two goals: benchmarking the numerical data calculated using the three models and comparing them with literature experimental data obtained in a generic swirl burner [63]. According to the model benchmark, the San Diego mechanism [62] behaves differently from the two other models “in all aspects”. The San Diego mechanism provides the best performance compared to experimental data. The authors also state that further improvement of detailed models is needed as none of the three was able to reproduce CO emissions under lean conditions.

Recently Viguera-Zúñiga et al. used chemiluminescence to characterize concentrations of radicals such as OH^* , CH^* , NH^* , and NH_2^* across ammonia/methane flames [64]. Comparisons show a good agreement with CFD numerical calculations. This study highlighted complex evolution of species in flames and differences in trend for NH_2^* compared to other radicals. Ilbas et al. performed the numerical study of a swirl gas turbine combustor for turbulent air and oxy-combustion of ammonia/kerosene fuel mixtures (with up to 30% of ammonia) [65]. In contrast to previous cited studies, global steps were used for describing the consumption of kerosene (assumed to have a global formula of $\text{C}_{12}\text{H}_{23}$) and the formation of NO through three different mechanisms (thermal, prompt and fuel NO_x mechanisms). The numerical data obtained showed that the formation of NO_x in the flame zone is enhanced when ammonia is added in the fuel mixture due to fuel-bound nitrogen. After peaking in the flame front (800–1400 ppm according to the percentage of ammonia in the mixture), NO concentration dropped almost to zero and then increased slowly in the secondary and dilution regions.

CFD numerical simulations were also applied to other configurations. For example, Frankl et al. [66] performed a study of the use of ammonia and hydrogen in a high-pressure-dual-fuel combustion process combining engine experiments (with one diagnostic based on OH-chemiluminescence) and CFD numerical calculations (with ammonia chemistry coming from the GRI 3.0 model [67]). A good qualitative resemblance between models and chemiluminescence experiments was obtained. Another example is the numerical investigation on ammonia co-firing in a pulverized coal combustion facility by Zhang et al. [68]. A set of 12 global reactions was considered to represent the chemistry of fuels. Their simulations highlighted changes in the flame shape and in emissions (NO_x) when increasing the ammonia co-firing ratio.

In summary, these studies show the potential and the benefit of running simulations coupling kinetics and CFD codes for the development of advanced technologies using ammonia as fuel or as a co-fuel through a better understanding of the inductive effect of hydrodynamics and kinetics. An important point is that the results are very sensitive to the chemistry used for running simulations. Thus, the reliability of the chemistry included in the detailed kinetic model used for the coupling is a key point. In line with the previous comment, experimental data are needed to validate the numerical calculation methodology. In this area, flow field and radical chemiluminescence measurements are two diagnostics which can provide useful information.

2.5. Perspective summary

Despite the simple structure of ammonia, its oxidation chemistry is still far from being fully understood and it still deserves a lot of attention. The development of accurate and detailed kinetic models will require the generation of new sets of accurate experimental data assessing global reactivity (laminar flame speeds, ignition delay times) and the specific chemistry of intermediates involved in ammonia oxidation chemistry (speciation data). Despite the difficulties of performing oxidation experiments of ammonia (e.g., adsorption phenomena and potential catalytic effects at walls), obtaining additional experimental data in different reactor types with different sampling methods and analytical tools by different groups under similar conditions is desired. Detailed chemical kinetic model performances will also benefit from additional high-level kinetic parameter calculations and benchmarking. The variety of methods used for the calculation of kinetic parameters and the discrepancies of the data sets obtained by different authors should be addressed before being able to move towards a unified model.

3. Combustion with additives

Ammonia combustion has many associated challenges that can be categorized into a relatively low reactivity compared to conventional fuels and its nitrogenous emissions (NO_x and NH_3 residuals). The relatively low reactivity results in a low laminar burning velocity (the laminar burning velocity of a NH_3 /air flame is about 20% of the respective value in a CH_4 /air system [11]), a long ignition delay time, a low volumetric heat release rate, and flame instability. Ammonia combustion generates significant amounts of NO_x , particularly via the fuel-NO pathway, and unburnt ammonia levels remain relatively high. A dual-fuel strategy, where ammonia is blended with other fuels to various extents, was suggested to overcome some of these challenges [69-71]. Among the possible ammonia combustion promoters are hydrogen [70,72-80], syngas [18], methane [17,70,81-88], alkanes [89,90], dimethyl ether [91,92], diethyl ether [198], alcohols [93,199], kerosene or diesel [94,97], coal [68,98,200] and biofuels/biomass [199,200].

Enhancing ammonia with hydrogen is advantageous for simultaneously achieving a carbon-free combustion process in addition to flame stabilization. The laminar burning velocity of a NH_3/H_2 /air flame increases super-linearly with addition of H_2 (Figure 9A), eventually reaching the CH_4 /air flame value at a 2:3 H_2/NH_3 volumetric ratio [71]. Note, however, that one should not necessarily approach such a high H_2 ratio, as lower H_2 concentrations may be practically required to achieve steady operation, e.g., in an internal combustion engine [99]. Higher additive to ammonia ratios result in increased flame speeds (Figure 9A, B), but may also increase the emitted NO_x levels (Figure 9C). Zhang et al. [70] have shown that while a 10% addition of H_2 increases the

laminar burning velocity, it has negligible effect on NO_x levels. The same cannot be said for CH_4 as an additive, nor for the higher level of H_2 additive tested which result in higher NO_x emissions (Figure 9B, C). It is still left to be shown that the small increase in laminar burning velocity of 23% (7.8 to 9.6 cm s^{-1}) due the presence of 10% H_2 is enough to stabilize the flame and address the relatively low reactivity of ammonia. Alternatively, a higher ratio of an ammonia combustion promoter could also be used while employing the rich-to-lean combustion approach [74], where the first combustion stage is done at fuel-rich conditions to mitigate NO_x formation, followed by a lean-fuel combustion conditions phase for the oxidation of the remaining reactants. Additional works are required to show the usefulness of this approach to ammonia combustion with additives.

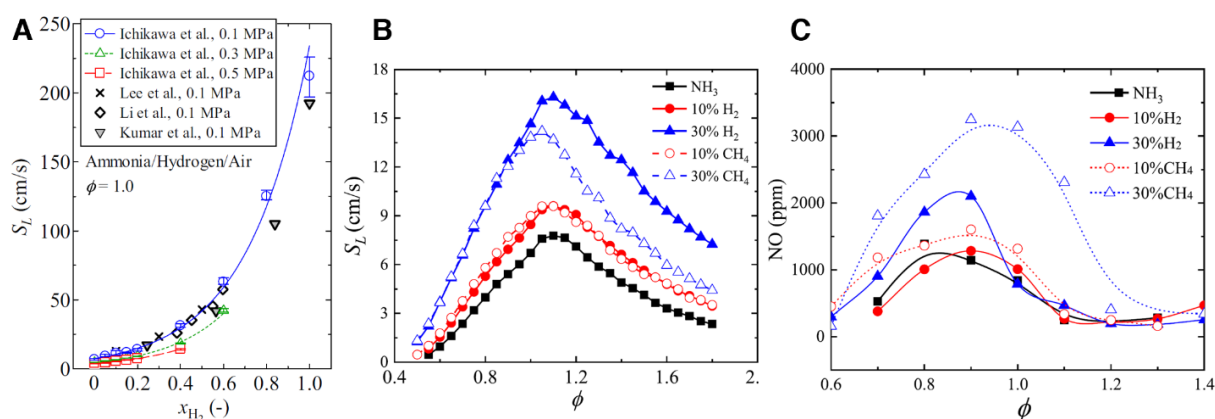


Figure 9. (A) Laminar burning velocity vs. the volumetric hydrogen fraction in the binary NH_3/H_2 fuel mixture. Values were obtained from Ichikawa et al. [69], Lee et al. [197], Li et al. [43], and Kumar et al. [72]. The initial mixture temperature was 298 K. (B) Laminar burning velocity for a 1D flame vs. the equivalence ratio for NH_3/H_2 and NH_3/CH_4 for 1D flames. (C) NO emission vs. the equivalence ratio for NH_3/H_2 and NH_3/CH_4 swirl flames. Subfigure A is reprinted from Proceedings of the Combustion Institute 37, 109–133, H. Kobayashi, A. Hayakawa, K. Somaratne, W.C. Okafor, "Science and technology of ammonia combustion", Copyright (2019), with permission from Elsevier. [71] Subfigures B and C are reprinted from International Journal of Hydrogen Energy, M. Zhang, Z. An, L. Wang, X. Wei, B. Jianayihan, J. Wang, Z. Huang, H. Tan, "The regulation effect of methane and hydrogen on the emission characteristics of ammonia/air combustion in a model combustor", Copyright (2021), with permission from Elsevier [70].

Using CH_4 rather than H_2 is less effective in stabilizing the NH_3 flame for the same molar additive ratio, and it was found to significantly increase the NO_x levels, especially at relatively high ratios (Figure 9C). Of the carbon-based additives, the least explored option is using biofuels or introducing relatively small amounts of ammonia into a biofuel flame. Using biofuels together with ammonia may be beneficial for both fuels, adding a reducer to the partially oxidized biofuel on one hand and stabilizing the ammonia flame on the other hand, overall achieving a net zero carbon footprint fuel. Additional research is therefore required to characterize NH_3 combustion in representative biofuels.

While ample literature chemical kinetic models exist for NH_3 [34,100], NH_3/H_2 [101,102], and NH_3/CH_4 combustion, [17,103,104] some of the models deviate from each other [56,72,78], highlighting the need for a data-centric approach. New models in this field should specifically better describe rich flame conditions.

While plasma-assisted combustion of ammonia does not strictly classify as an additive, a brief discussion in this context is nevertheless beneficial. This approach could reduce the ignition delay time and decrease the flammability limit of ammonia/air flames [105] while simultaneously

reducing NO_x emissions [106]. The current literature is missing validated chemical kinetic models of plasma-assisted combustion in general, and particularly for ammonia [105,107]. This is a novel field in which many discoveries are yet to be made, and a potential combination of plasma-assisted combustion in the presence of ammonia combustion promoters could get the field closer to more practical ammonia utilization as a fuel.

Ammonia could also be used indirectly in an aqueous solution as an ammonium cation, balanced by an anion, e.g., nitrate or hydroxide. In the case of aqueous ammonium nitrate, the oxidation potential of the nitrate is stronger than the reduction potential of an equimolar amount of ammonium, and another reducer should be introduced into the system as a separate stream of ammonia or another solute, e.g., urea. The low-carbon three-component aqueous urea ammonium nitrate (UAN) monofuel was extensively studied [108-112] and was shown to be safe to handle [113]. It endothermically dissociates into NH₃, HNO₃, and HNCO (isocyanic acid) upon decomposition [109,110]. This gas-phase mixture further undergoes exothermic reactions, [110] and has the potential to emit lower NO_x levels than CH₄ combustion on an energy basis (e.g., NO_x mass per MJ) [6].

The topics of rich-to-lean combustion approach for ammonia with additives (particularly H₂), combustion of ammonia with biofuels, and plasma-assisted combustion of ammonia require additional attention and further works in these directions could facilitate significant advancement in the field.

4. Combustion applications

In terms of final applications of ammonia as a fuel in the energy and transport sectors, key parameters appear to be efficiency and emissions (especially NO_x and unburned NH₃ emissions). These vary also depending on the final conversion technology which is chosen. In this perspective we take into consideration mainly gas turbines, internal combustion engines and fuel cells. These have different technology readiness levels (TRL), as shown in Figure 10.

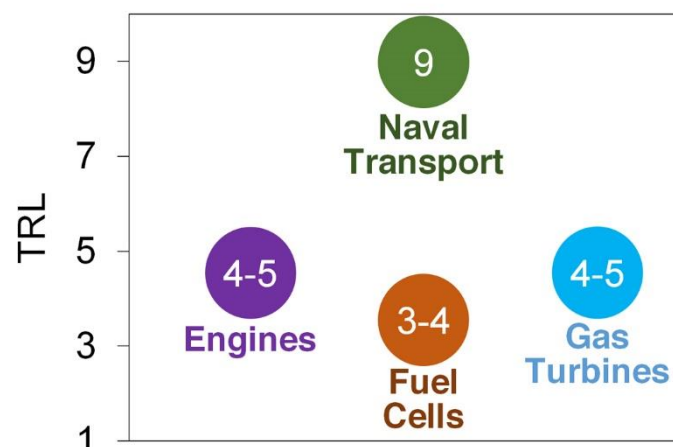


Figure 10. TRL of main technologies to be used in transportation and power industry with ammonia as a fuel [114].

The importance of ammonia as a fuel for naval transportation can be seen in Figure 10, which is mainly due to the technologies developed by Mann Energy Solutions [115] and in particular the dual fuel naval engine designed to be fueled with "green" ammonia. On the other hand, according

to [116], alkaline fuel cells and solid oxide fuel cells (SOFCs) running on ammonia have a TRL between 3 and 4. Moreover, proton exchange membrane fuel cells (PEMFCs) cannot be used with ammonia due to their acidic environment. A list of electrolytes and electrodes used in ammonia-fed SOFCs is given in Table 4.

For combustion applications we have to take into consideration the following barriers for implementation [92,117]:

- Low burning velocities and flame speeds
- High ignition delay time and high autoignition temperature
- Blending or cracking into hydrogen is required
- Low energy density per unit of mass (22.5 kJ kg⁻¹)
- Low radiation intensity, high NO_x emissions, low cetane number (practically equal to 0), narrow flammability range (16–25% by volume in air), high heat of vaporization, and a power output in SI engines lower than 20%.

On the other hand, as reported in Kobayashi et al. [71], NH₃ has a higher volumetric and gravimetric H₂ density compared to many relevant hydrogen carrier molecules (NH₃BH₃, decaline, AlH₃, MgH₂, N₂H₄•H₂O, HCOOH, LiAlH₄, LiH, Mg(BH₄)₂, LiBH₄, Al(BH₄)₃, LiBH₄). Ammonia's fuel properties were reported in the work of Kenanoğlu and Baltacıoğlu [118] and are given in Table 1.

Table 1. Ammonia characteristics as a fuel, compared with liquid and gaseous hydrogen [118].

Parameter	Gaseous hydrogen	Liquid Hydrogen	Gaseous ammonia
Storage pressure (bar)	240	1	10
Storage Temperature (°C)	25	-253	25
Density (kg/m ³)	17.5	71.1	60.3
Auto-ignition Temperature (°C)	571	571	651
Laminar Flame Speed (m/s)	3.51	3.51	0.15
HHV (MJ/kg)	142	142	22.5
Octane Rating (RON)	130	130	110-130

Combustion process efficiency is influenced by the equivalence ratio among other parameters. For example, according to Verkamp et al. [119], efficiency can also be influenced by the “efficiency parameter”, calculated as:

$$EP = (BIP^{1.81}/BIT^{3.2v}) \times 10^4 \quad (\text{Eq. (1)})$$

Where EP is the Efficiency Parameter, BIP is the Burner Inlet Pressure, BIT is the Burner Inlet Temperature, and v is the combustion velocity.

Average combustion efficiencies detected in experimental tests using ammonia as a fuel are presented in Figure 11. One interesting series of experiments has been performed at the National Institute of Advanced Industrial Science and Technology (AIST) and the Institute of Fluid Science, Tohoku University [120]. These tests have been performed mainly on a 50 kW class micro gas turbine using a prototypal swirl combustor operating in a diffusion combustion regime, due to its flame stability. The combustor has a central injector for kerosene and ammonia gas is supplied from 12 orifices positioned outside the kerosene injector. Ammonia is fed into the gas turbine at a pressure of 0.5 MPa, while the combustor operated at an almost constant inlet temperature of

500 °C. The combustor operates with a lower flow of air, since the laminar burning velocity of ammonia is lower than that of natural gas, which is the fuel on which the micro gas turbine was designed to operate. The overall efficiency of the micro gas turbine has been measured to be 25%, when operating with 17 kg hr⁻¹ of ammonia gas. It has also to be considered that 12 kW are necessary to evaporate the ammonia and to feed it into the 50 kW gas turbine, which is not an irrelevant amount of power.

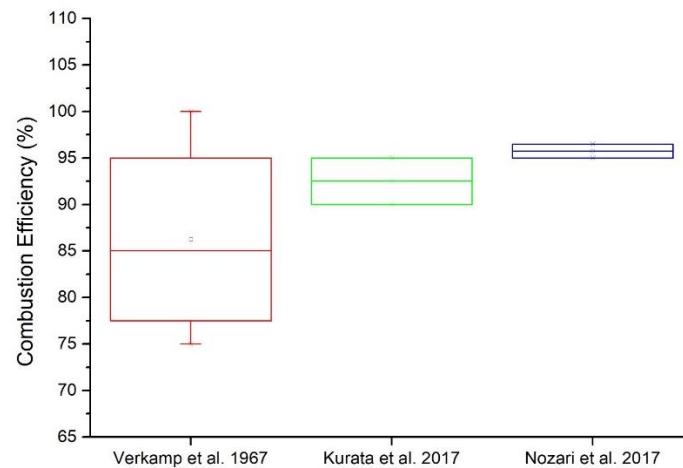


Figure 11. Experimental ammonia combustion efficiency, taken from [119-121]. The variation in combustion efficiency reported by Verkamp et al. [119] is mainly due to the efficiency parameter; The variability identified in Kurata et al. [120] is mainly due to the different load at which the gas turbine is operated; The variability identified in Nozari et al. [121] is mainly due to different equivalence ratios ranging from 0.9 to 1.3.

Other sets of experiments were performed by General Motors Applied Research Department in 1967 [119]. The interesting aspect in this case is the use of additives together with ammonia (e.g., hydrazine, acetylene, carbon monoxide, and nitrogen oxides). In this case ammonia has been tested in a T63-A-3 gas turbine burner at engine air-flow conditions. The conditions at the inlet of the burner for air were 272 °C, 6.6 bar, and 1.4 kg s⁻¹ of flow. The most promising performances have been obtained with hydrogen-enriched ammonia and gaseous ammonia, as reported in Figure 11.

In the experiments performed by the Koç University and the Istanbul Technical University [121] ammonia combustion tests were performed at ambient pressure. The burner is fed with a premixed jet through a small pipe of steel. The NH₃/H₂ fuel consists of 60–90% vol. NH₃ and a stoichiometric ratio of 0.9–1.5 is used. The mixture inlet velocity ranges between 4 and 18 m s⁻¹, implying that the Reynolds number is between 4500 and 25,000. The power capacity of the burner was about 30 kW.

4.1. Gas turbines

Increasing the combustion efficiency of ammonia in gas turbines is challenging. Interestingly, in the experiments of Kurata et al. [122] NH₃ is pre-vaporized before feeding it into the turbine. In fact, in the case of a thermal machine with 25% electrical efficiency the requirements to vaporize ammonia would be about 6% of its Higher heating value (HHV). This implies that ammonia preheating and vaporization should be thermally integrated with the entire plant.

Different electrical efficiencies are proposed in Figure 12 for gas turbines fed with neat ammonia or with additives. In the study of Kenanoğlu and Baltacıoğlu [118], a 1 kW gas turbine is fed with NH_3 enriched with water electrolysis products. In the study of Valera-Medina et al. [124], a mathematical model for design of gas turbines is coupled with the results of the ammonia combustion model, to understand what would be the efficiency of the operated gas turbine. Experiments are performed at the Cardiff University's Gas Turbine Research centre (GTRC), a premixed lean burner is fed with a mixture of 70% in volume of NH_3 and 30% in volume of H_2 . Different equivalence ratios are tested and they are comprised between 1 and 1.4. A similar approach is used in the publication of Guteša Božo et al. [123], which reported a ~65% polytropic efficiency for humidified ammonia-hydrogen combustion, significantly higher than the value for dry ammonia-hydrogen combustion of ~45%. The difference can be explained with the change in the mass flow rate of the combustion products. The promising use of humidified ammonia mixtures in RQL combustors is highlighted also in reference [24]. Additional combustion applications include Combined Cycle Gas Turbine (CCGT), where co-firing of ammonia in this setting was already demonstrated (e.g., at Mizushima Power Station in Japan).

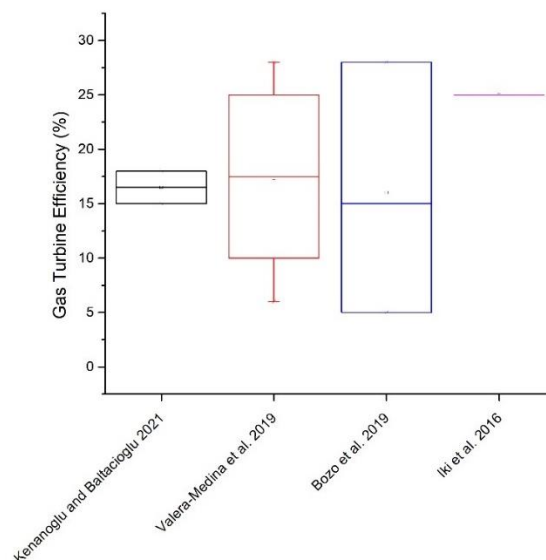


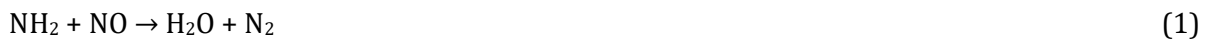
Figure 12. Gas Turbine Combustion efficiency. Variability of efficiency in Kenanoğlu and Baltacıoğlu [118] depends on rotating speed; Variability of efficiency in Valera-Medina et al. [124], Božo et al. [123] and Kurata et al. [120] depends on the variation in the load; in Iki et al. [122] only a single efficiency data is reported.

In the works of the National Institute of Advanced Industrial Science and Technology (AIST, Japan) [120,122] the same conditions, which have been discussed when describing Figure 11, were adopted.

One of the most important aspects to take into consideration when dealing with the use of ammonia fuel (neat or blended) in gas turbines is emissions, particularly NO_x . These will be probably higher than in other fuels because of the fuel NO_x mechanism [16,56,101,124,126,128,133-135], whereas in hydrocarbon flames NO_x are mainly produced by the thermal mechanism [16,136]. For this reason, many researchers have focused their attention on this aspect, measuring the influence of different combustion parameters on NO_x production (e.g., using different fuel blends and equivalence ratios, see [63,120,125-130]). Khateeb et al. [131] reported that in the case of premixed flames low NO_x emissions are encountered for lean equivalence ratios (in the range of 0.8 to 0.9). This is also confirmed by other studies

[125,126,128,131-133]. On the other hand, it was not possible to achieve emissions lower than 500 ppm due to flame stability problems with lean ammonia-air and ammonia-methane-air mixtures [126,128,133]. Due to the fact that ammonia-hydrogen mixtures are more reactive, leaner mixtures can preserve stability and achieve lower NO_x emissions, arriving at a threshold of 100 ppm with a mixture of 50% ammonia and 50% hydrogen and an equivalence ratio of 0.4 [125].

Given that NO_x emissions in ammonia combustion stem from the fuel nitrogen mechanism, flames which are close to stoichiometric conditions would generate many OH radicals, which are responsible for NO formation [16,69,101,124,126,133,134,137]. For the same reason when the equivalence ratio increases and the mixture becomes rich, NH₂ radicals will prevail and promote the following reaction:



The above-mentioned reaction is responsible for consuming NO, explaining the good performance of rich mixtures in terms of NO_x emissions [16,124]. The summary of NO_x emissions trends in different experimental and modeling tests is provided in Figure 13.

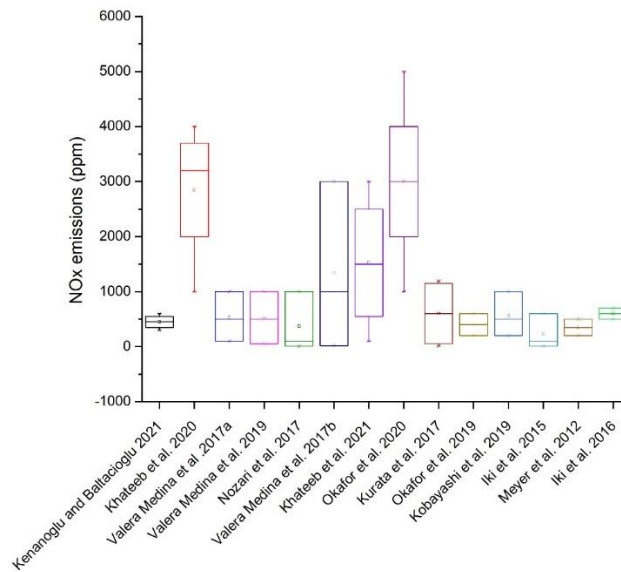


Figure 13. Gas turbine NO_x emission range when fueled with NH₃. The variation reported in Kenanoğlu and Baltacıoğlu [118] is due to different rotating speeds; the variation reported in Khateeb et al. [131] is due to the changing of the equivalence ratio (concentration is referred to dry gasses with 6% of oxygen in volume); the variation presented in Valera-Medina et al. [63] is also due to changing equivalence ratio; the variation presented in Valera-Medina et al. [124] is due to changing equivalence ratio (NO_x concentrations are measured on dry gasses with 15% O₂); the variation presented in Nozari et al. [121] is also due to changing equivalence ratio; the variation presented in Valera-Medina et al. [125] are due to changing equivalence ratio; the variation presented in Khateeb et al. [138] are due to changing equivalence ratio (concentration is referred to dry gasses with 6% of oxygen in volume); the variation reported in Okafor et al. [126] is dependent on equivalence ratio; the variability reported in Kurata et al. [120] is dependent on power production; the variability displayed in Okafor et al. [129] is dependent on the equivalence ratio (concentration is referred to dry gasses with 6% of oxygen in volume); the variability reported in Kobayashi et al. [71] is dependent on equivalence ratio; the variability reported in Iki et al. [139] is dependent on the ratio between kerosene and ammonia which are fed in the combustor; the variation reported in Meyer et al. [140] is due to the change in the equivalence ratio; the variation reported in Iki et al. [122] is due to the efficiency of the NO_x removal equipment (NO_x concentration is measured at 15% O₂).

The combustor inlet temperature is of paramount importance for emission control in micro-GTs fueled with ammonia. Kurata et al. 2017 [120] have shown how this temperature is a function of both power load and rotating speed. In particular, the combustor inlet temperature, when fueled with ammonia, follows Eq. (2),

$$BIT = 9.7 \times W + 0.016 \times (N_0 - N) + T_0 + 132 \tag{2}$$

where W , N_0 , N , and T_0 are the electric power (kW), rated rotating speed (rpm), rotating speed (rpm), and atmospheric temperature ($^{\circ}\text{C}$), respectively, indicating that the BIT is a function of the electric power as well as rotating speed.

A short summary of selected combustors and plant layouts tested with ammonia is given in Figure 14.

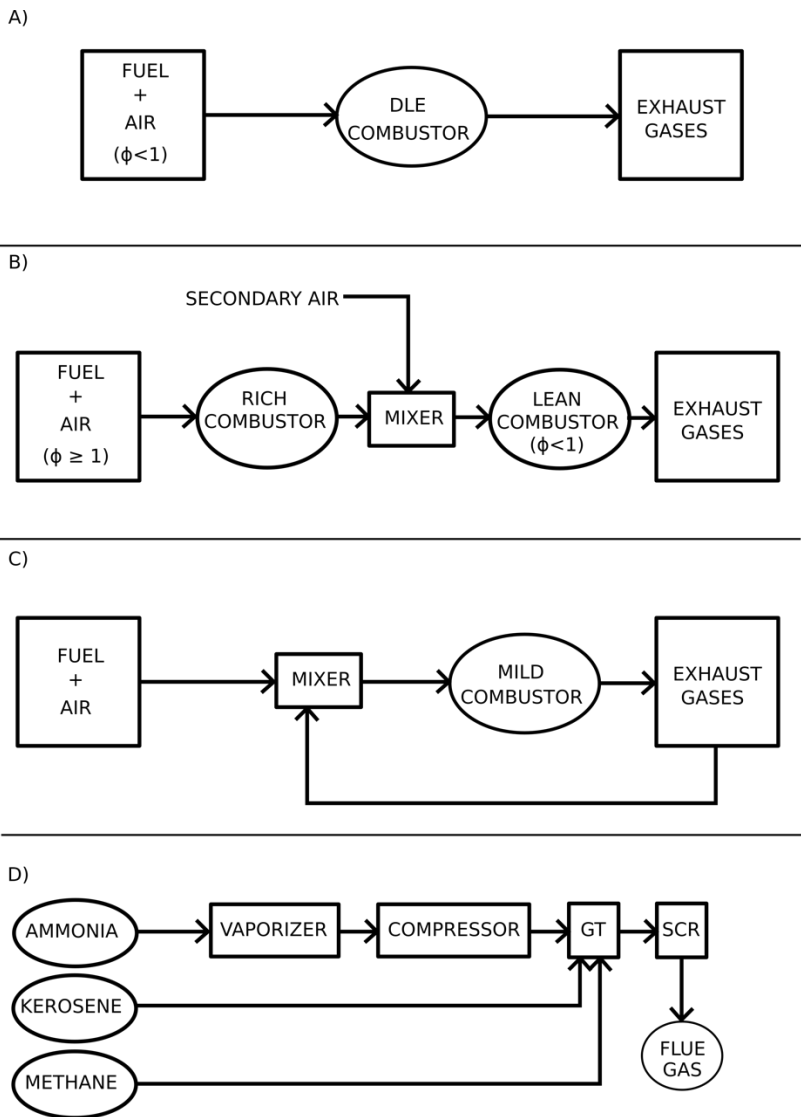


Figure 14. Combustors used in ammonia fueled GTs. (A) lean-burn dry-low emissions (DLE) combustor; (B) rich-burn, quick-quench and lean-burn (RQL) combustor; (C) moderate or intense low-oxygen dilution (MILD) combustor; (D) Ammonia based microgas turbine layout. Adapted from Figures 1-3 from reference [117].

The following conclusions can be drawn from the comparison in Figure 14:

- The Lean Burn Dry-low (DLE) emissions combustor does not perform well when fed with ammonia because lean ammonia/air mixtures have low flame speed and very high NO_x emissions. The only advantage of this combustor is reducing emissions of unburned ammonia;
- The rich-burn, quick-quench and lean-burn (RQL) and the moderate or intense low-oxygen dilution (MILD) combustors show promising performance.
- The RQL combustor assures a stable flame in fuel rich conditions. It is based on a two-stage combustor where in the first stage hydrogen is produced and then combusted in a second stage combustor working at MILD conditions, to reduce NO_x emissions;
- The MILD combustor is disadvantageous since it requires relatively high rates of dilution to maintain MILD conditions, which is a challenging in terms of design and operation.

4.2. Internal combustion engines

4.2.1. Challenges in the use of ammonia in engines

Main experimental studies on the use of ammonia in internal combustion engines are listed in [114]. The state of the art is well described in Cardoso et al. [114], in which the use of ammonia in internal combustion engines is described as feasible for mixtures of NH_3 and fossil fuels, while pure ammonia combustion in engines has not yet been proven a reliable process, due to some unresolved challenges, as described in Section 4. These challenges make the use of ammonia in internal combustion engines particularly difficult for low load and high-speed regimes. A 100% ammonia engine has not been achieved yet for road transportation, due in part to the relatively high NO_x emissions and flame instability. To lower the emissions, it is very probable that modifications of the combustion system will be required to enhance the combustion kinetics and dynamics [114]. Key aspects of research for combustion system modifications are: introducing improved injection design; introducing modifications which allow the engine to operate at higher temperatures and pressures with respect to conventional values.

To circumvent the challenges associated with ammonia in combustion, especially in the ignition phase, both Avery in 1988 [141] and Dimitriou and Javaid in 2020 [142] have suggested to operate the engine at high compression ratios comprised between 35:1 and 100:1. On the other hand, spark ignition (SI) engines can operate with ammonia more easily because ignition is given by the spark plug and in this case NH_3 high octane number can reduce the risk of knocking [77,143].

The current research on ammonia in internal combustion engines is focused on using it as an additive in a mixture. The major players in the use of ammonia have been divided by the Ammonia Energy Association [144] into spark ignition engines vs. compression ignition engines of ammonia mixed with hydrocarbon fuels or with hydrogen

Bigas International, an Italian company, adapts engines to be used with ammonia, as implemented in the Toyota GT86-R Marangoni sports car. Other tests have been performed by South Korean Institute for Energy Research (KIER) [145], China (e.g., Xiamen University [146]), University of Orleans [147], Sturman Industries in the US [114], Iowa state university [148], the Canadian company Hydrofuel Inc. [149], Caterpillar and Toyota [114], and the Hydrogen Fuel center in the

US [114]. In the maritime sector the pioneer is MAN industries which plans to deliver relevant solutions by 2024 [150].

Gross and Kong (2013) [92] used mixtures of DME and ammonia in a CI engine and observed that the high load engine performance was lower compared to pure diesel. Also, Niki et al. 2016 [151] have shown that mixing ammonia with diesel generally resulted in a decrease of cylinder compression and cylinder maximum pressure together with ignition time. Mixing ammonia with methanol or ethanol was found to increase its solubility in gasoline mixtures [152]. Diesel can be substituted with kerosene to improve ammonia ignition and decrease carbon monoxide emissions [95]. In general, the advantages of using ammonia as a fuel in ICEs have shown that with fuel blending high torque and power output can be achieved, while there is a risk of obtaining high NO_x emissions at high temperatures and high unburned NH₃ emissions at low temperatures [97], [142,153]. This problem can be addressed by either using an SCR system or changing injection modalities [151,154]. Examples of ammonia use in ICEs are given in Tables 2-3.

Mixing ammonia with hydrogen can facilitate better engine cyclic stability and lower NO_x emissions [155]. Here, the injection strategy should be considered. Frigo et al. 2012 [156] have introduced electro-injectors for the injection of hydrogen and ammonia to the intake manifold. The benefit of such an injection system is usually to have accurate injector control and enhanced fuel economy.

The partial dissociation of ammonia can bring benefits to engine performance and decrease emissions in exhaust combustion gasses [91]. The partial dissociation can also mitigate the corrosiveness of ammonia on the component of the engine fabricated in brass copper and nickel. Even though the addition of hydrogen improves ammonia combustion performances, the drawback can be identified in the NO_x emissions which can increase with the addition of hydrogen, in that case an efficient SCR system is required [157]. Hydrogen can also exert a negative effect on the metals of the engines making them brittle and more fragile [158].

Dealing with the combustion of 100% ammonia, a relevant patent has been filed by Toyota, using plasma jet igniters and a spark plug to avoid the use of H₂ as fuel promotor and facilitate the ignition of ammonia [159]. No current literature study reports stable combustion of pure ammonia in ICEs due to flame instabilities, and a minimum threshold of 5% H₂ injection was found to be required for smooth engine operation [80]. The following subsections deal with Spark Ignition (SI) Engines, Compression Ignition (CI) Engines, and Homogeneous Charge Compression Ignition (HCCI) engines.

4.2.2. Spark-Ignition engines

Main tests performed on SI engines with ammonia are reported in Table 2. Yapicioglu and Dincer [160] have performed combustion tests in stationary engines for CHP substituting part of gasoline with ammonia, which proved to be quite successful and the power of the engine was not reduced in an important way. Grannel et al. [161] used blends of 70%/30% NH₃: gasoline on an energy basis for the regular operation of a car engine while an idle 100% gasoline was required. This is because idle cycles usually had a lower pressure and the addition of NH₃ influences ignition timing which also influences the final pressure. Haputhanthri et al. [162] used ethanol and methanol to emulsify ammonia and enhance its solubility. The obtained well performing blends contained

about 17.35% in volume of ammonia. The torque of the engine increased with the use of ammonia and so did the power output, particularly at high rpm values. Mørch et al. [80] used ammonia and hydrogen mixtures, usually containing about 10% of hydrogen. This enhanced once again engine performances in terms of efficiency and power. The obtained values were significantly higher than those obtained with gasoline. On the other hand, there was a need of an SCR to limit NO_x emissions. Westlye et al. 2013 further increased the hydrogen ratio to 20%; in this case, an SCR was tested and it was demonstrated that this could reduce the NO_x emissions to the levels required by legislation. Li et al. 2014 [43] identified a synergy between ammonia and hydrogen in the combustion environment: ammonia significantly reduces the combustion temperature, while hydrogen increases the burning velocity. Koike and Suzuoki [163] have shown the necessity to operate the engine with retarded spark timing and high hydrogen ratio to overcome ammonia inefficient combustion behavior. Lhuillier et al. [77] used small quantities of hydrogen (~20%) as an ignition promoter with very positive effects during the first stages of combustion. Wang et al. [164] noted that mixing ammonia with hydrogen granted better performances at high compression ratio, compared to mixing ammonia with hydrocarbons. Higher knock resistance was obtained.

Table 2. SI engine tests.

Source	Author and Year	Fuel blend composition
[161]	Grannel et al. 2008	70% NH ₃ /30% gasoline
[162]	Haputhanthri et al. 2015	Gasoline + 30 vol% ethanol or methanol + 17.35 vol% NH ₃
[80]	Mørch et al. 2011	NH ₃ + 5-100 vol% H ₂
[165]	Westlye et al. 2013	80 vol% NH ₃ /20 vol% H ₂
[43]	Li et al. 2014	40-66.7% NH ₃ + H ₂
[163]	Koike and Suzuoki 2019	40% NH ₃ /60% H ₂
[77]	Lhuillier et al. 2020	NH ₃ /0-60% H ₂
[164]	Wang et al. 2021	NH ₃ /40-60% H ₂

4.2.3. Compression ignition engines

Main experimental tests of NH₃ use in CI engines are shown in Table 3. The same ratio used by Yapicioglu and Dincer [160] has been also tested by the Korean Institute of Energy Research (KIER) [166]. Reiter and Kong [167] reached a very high percentage of ammonia mixed to diesel, up to 95%. On the other hand, the same authors, in another set of tests [97] determined that the more ammonia was mixed with diesel the more the NO_x emissions grew. Gross and Kong [92] confirmed the increase in NO_x emissions with the increase in ammonia blending ratio and also added that engine performance generally decreased with the use of ammonia. Isayev et al. [168] demonstrated the high stability of Diethyl Ether (DEE) and ammonia mixtures. Gill et al. [169] demonstrated that at high loads the use of ammonia improved brake thermal efficiency and combustion stability. Pochet et al. [170] demonstrated how the use of EGR could decrease significantly the emissions of NO_x. It is also important to note that to increase engine efficiency in [170], it was required to increase compression ratio and intake pressure.

Table 3. CI engine tests.

Source	Author and Year	Fuel blend composition
[167]	Reiter and Kong 2010	95% NH ₃ /5% diesel
[97]	Reiter and Kong 2011	60% NH ₃ /40% diesel; 40% NH ₃ /60% diesel
[92]	Gross and Kong 2013	20% NH ₃ /80% Dimethyl Ether (DME); 40% NH ₃ /60% DME
[171]	Tay et al. 2017	NH ₃ (via fumigation)/100% diesel; NH ₃ (via fumigation)/50% diesel + 50% kerosene
[168]	Isayev et al. 2020	95-80% NH ₃ /5-20% DEE
[169]	Gill et al. 2012	2012 1-2% NH ₃ + 75% H ₂ + 23-24% N ₂
[170]	Pochet et al. 2017	70 vol% NH ₃ + H ₂ (for stable combustion)

4.2.4. Homogeneous charge compression ignition engines

Finally, the analysis of engine behavior when fed with ammonia terminates with the evaluation of the use of ammonia in homogeneous charge compression ignition (HCCI) engines. Few examples are available on real tests [91,172], and modeling studies [173]. In particular from the results of the test performed at the HCCI test bench of UCLouvain, [172] it can be inferred that:

- with a compression ratio of 15:1, ammonia can balance hydrogen high reactivity and allow to use high equivalence ratios [170];
- Van Blarigan managed to feed a free piston HCCI engine using 40:1 compression ratio without pre-heating ammonia [8];
- in [35] ammonia equivalence ratio of 0.5 have been successfully operated in a Rapid Compression Machine;
- about 1800 K of combustion temperature is required when using only ammonia [170]. Such conditions can be met by fueling the engine with 50 or 90% vol ammonia and a IMEP of 4.5 and 5.0 bar.

Such conditions can be met by fueling the engine with 50 or 90% vol ammonia and a IMEP of 4.5 and 5.0 bar.

5. Fuel cells applications

As reported in Jeerh et al. [174], the use of ammonia in fuel cells can be either direct or indirect, where in the latter ammonia is first cracked into hydrogen and nitrogen and then H₂ is fed into the fuel cell. Here we only consider the direct case since indirect approaches are practically hydrogen-driven fuel cells, and are out of the scope of this work.

In Table 4 we propose an interesting comparison between the performance of ammonia when used in fuel cells and that of ammonia used in gas turbines. Gas turbines are the system of choice for large-scale ammonia utilization as fuel for power generation, while power generation at small scales (below 10 MW) can be better performed using solid oxide fuel cells (SOFCs). Ammonia SOFCs are tested in pilots by IHI corporation in Japan [175] (capacity of 1 kW electric), while gas turbines fueled with ammonia are tested in pilots in the UK [176].

Table 4. Comparison of ammonia to power solutions [116].

Technology	Advantages	Disadvantages
Alkaline FCs Operation range: 20°C to almost 100°C [183] [184-185] Electrical Efficiency: 60-65% (LHV) (Pure Oxygen) [184-185] Electrolyte: NaOH/KOH [186] TRL: 1-3	Can operate at room temperature [183] Fast start-up High electrical efficiency [184-185]	Pure oxygen feed required [183] Low life time (target 1 year) [184] Large temperature swing between ammonia decomposition and fuel cell
SOFCs Operation range: 770-775°C [187,188] or 500-1000°C [183-184] Electrical efficiency: >50%(LHV) [187-189] Electrolyte: e.g., YSZ [182] TRL: 4	Operation with air [183-188] Fast hot start-up (130 s) [187] High efficiency (> 50%(LHV) in commercial application) [188] Near ambient pressure operation [190]	High operation temperature (700–775 °C) [187-188] Minimum load of 7% required [188] Brittle ceramic components [186] Slow cold start-up [186] Not commercial (demonstration stage) [191]
Gas turbine Operation range: 900-1100°C [190] Electrical Efficiency: 25-30% (LHV) [192,193] TRL: 4-6	Operation with (oxygen-enriched) air [194] Conventional combustion equipment [116] Demonstration stage with near-term use-case [197-199]	Minimum load of 10% required to suppress NO _x emissions [196] Slow start-up (hours range) Low electrical efficiency High pressure operation (> 5 bar) [190] Low laminar burning velocity [41,42,44] Increased NO _x formation [134] High ignition temperature required Slow burning speed (5 times smaller than methane) [195] Low flame stability Increased oxygen content required Not commercial

SOFC fuel cells can be of two types [177,178], in both types ammonia is cracked at the anode:

- SOFC-O: oxygen anion conducting electrolyte-based solid oxide fuel cells;
- SOFC-H: proton conducting electrolyte-based solid oxide fuel cells (also indicated as PCFC).

In SOFC-O, the anode is responsible for two reactions: ammonia cracking and hydrogen oxidation [179]. Since water, oxygen anions, and nitrogen are all present at the anode side at elevated temperatures, NO_x formation pathways become possible. Using further catalysis to abate NO_x at the SOFC-O anode to obtain N₂ would dilute the hydrogen flow and decrease the reversible potential of the cell [177].

In summary, given the challenges of SOFC-O, SOFC-H probably represents a better choice for ammonia utilization in a fuel cell. In fact, since ammonia is oxidized at the anode of SOFC-H, water

is produced at the cathode site mediated by protons passing through the electrolytes, and NO_x formation is avoided [177]. Furthermore, hydrogen is not being diluted by nitrogen, and a higher theoretical efficiency could be achieved [180]. The work of [177] shows the materials most commonly used in the electrolyte and electrode in ammonia-fed SOFCs.

Alkaline fuel cells have been tested in the lab, for example by the group of Prof. Dincer at the Clean Energy Research Laboratory in Ontario, Canada. The proposed system is based on the development of a molten alkaline electrolyte fuel cell which can be directly fed with ammonia. Here, a molten salt electrolyte was used at intermediate temperatures between 220 and 320 °C [181]. Specifically, salts of sodium and potassium hydroxide are used as electrolytes with a mole ratio of 1:1. Ammonia is fed into the fuel cell at a pressure of 1 bar and a mass flow of 0.2 mg s⁻¹. Humidified air is fed at the cathode. Comparing alkaline fuel cells to SOFCs, it can be seen that alkaline fuel cells can be more promising for the use in the automotive sector (due to their lower working temperature), when the barriers of slow kinetics of reaction and high NO_x emissions will be effectively solved, see [182] which reports on.

6. Concluding remarks

Ammonia is an important energy vector, and it is foreseen that it will play an important role in the future energy economy. While there remain many challenges before large scale deployment of ammonia as a significant energy vector, various works of safe utilization of ammonia as a fuel already underway could significantly advance its feasibility. In this perspective, we explored the prospects and challenges of ammonia as a fuel, and suggest significant topics that could benefit from future studies.

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