

Nitrogen Oxides as a By-product of Ammonia/Hydrogen Combustion Regimes

Syed Mashruk^{a,*}, Marina Kovaleva^a, Cheng Tung Chong^b, Akihiro Hayakawa^c, Ekenechukwu C. Okafor^d, Agustin Valera-Medina^a

^a College of Physical Sciences and Engineering, Cardiff University, Cardiff

^b China-UK Low Carbon College, Shanghai Jiao Tong University, Shanghai, China

^c Institute of Fluid Science, Tohoku University, Sendai, Japan

^d FREA, National Institute of Advanced Industrial Science and Technology, Fukushima, Japan
 mashruks@cardiff.ac.uk

Alternative fuels are under scrutiny for mitigating carbon dioxide emissions. One of these alternatives is ammonia, which can be produced from waste sources, renewable energy and even nuclear power with potentially zero carbon emissions over most of its life cycle. The difficulties of pure ammonia combustion, partially due to its low flame speed and flammability, can be addressed by doping ammonia mixtures with hydrogen, which increases the reactivity of these blends and allows combustion features similar to those of some fossil fuels. However, NO_x emissions are still a problem when burning ammonia, with some circumstances where emissions are even worse than with fossil-based systems. This is a consequence of the considerable formation of N₂O, a greenhouse gas that is known to possess up to 300 times the Global Warming Potential (GWP) of carbon dioxide, making these regimes unsuitable for the purpose of fuel replacement to combat climate change. Therefore, this work shows bespoke results for unburned NH₃ and NO_x emissions, specifically NO, NO₂ and N₂O, at various conditions of operation whilst employing ammonia-hydrogen blends in a tangential swirl burner representative of industrial gas turbines. The results show a good compromise of NO_x emissions at the near 1.05 - 1.2 equivalence ratio, with further understanding behind the chemistry that precludes the formation/consumption of these unwanted emissions for full deployment of ammonia-based energy systems.

1. Introduction

Ammonia has recently received considerable attention as an alternative fuel for mobility and power generation based on its hydrogen content. Ammonia has been used in DeNO_xing applications for power generation (Lauri, 2015) and cleaning applications (Wang et al., 2015) for decades. However, the characteristics of ammonia also make it a feasible chemical for the storage and deployment of stranded energy (Elishav et al., 2020). The high hydrogen content of ammonia (Valera-Medina et al., 2021) combined with its zero carbon features and its mature, extensive infrastructure (Valera-Medina and Roldan, 2020) make it a relatively fast transitional fuel towards zero-carbon deployment agendas. Ammonia can also deliver energy at higher densities than hydrogen (Salmon and Bañares-Alcántara, 2021), creating a potential for low-cost scenarios for hydrogen transportation. Concurrently, life cycle assessments seem to demonstrate that ammonia-fueled systems have the possibility to decarbonize large power and transportation cycles (Dincer and Bicer, 2018), hence reducing greenhouse gases considerably (Razon and Valera-Medina, 2021). Unfortunately, ammonia toxicity and high NO_x emissions are some of the technical barriers that need to be surpassed before ammonia can be globally deployed as a fuel. Simultaneously, low flame stability and low flame speed of pure ammonia usually lead to doping strategies employing other molecules. The problem is that the impacts of these new blends on NO_x emissions are still not fully understood and very limited work exists on their production under turbulent combustion regimes.

Ammonia blending with molecules such as methane, hydrogen or other synthetic gases range from micro to large scale power production (De Vries et al., 2021). For gas turbines, considerable work has progressed since the resurrection of the concept in Japan (Hayakawa et al., 2015). Pure ammonia blends, which are difficult to stabilize using gas turbine combustors, have been successfully used in medium size gas turbine applications

(Okafor et al., 2020), whilst ammonia/hydrogen blends have provided results with potential for reduction of emissions, improved flame stability and enhanced operability ranges (Pugh et al., 2020). Complex injection and combustion strategies in combination with new cycles have also elucidated a vast innovation field that has recently been started for the mitigation of NO_x emissions in ammonia-based systems (Jiang et al., 2021) and power trains (Thomas and Northrop, 2021). These works have been accompanied by novel kinetic modelling (Stagni et al., 2020) and comparisons between models in complex 3D numerical rigs (Mikulčić et al., 2021). Further research has also assessed new methods and geometries that can be used for a wide range of applications with ammonia blends, going from micro-combustors (Cai et al., 2021) to large power systems (Mitsubishi Heavy Industries Group, 2021). The problem with these studies is that they have only assessed NO as the main problem in ammonia-blends. More research is needed to elucidate the impact of species such as N_2O , a well-known greenhouse gas with higher potential (~ 300 times) than CO_2 (Valera-Medina and Banares-Alcantara, 2021). Similarly, NO_2 can have a detrimental effect on health, and may promote smog and acid rain production in populated regions (US EPA, 2017). In these lines, turbulent combustion analyses still lack approaching this molecule.

Studies done under rich fuel conditions always show considerable reduction in NO as a consequence of lower temperatures and recombination of species, thus presenting a solution towards ammonia combustion with low NO concentrations (Mashruk et al., 2020) and high power outputs (Guteša Božo et al., 2021). Interestingly, a recent publication (Khateeb et al., 2020) denoted the potential of low NO formation at very lean fuel conditions (>0.5 equivalence ratio), posing the possibility of using Dry Low NOx gas turbine technologies with high dilution as a solution for the use of ammonia-blends. Unfortunately, some emissions such as NH_3 , NO_2 and N_2O species were not quantified in their work. Recently, further analyses clarified that the heat loss from ammonia combustors increases N_2O emissions (Okafor et al., 2021). However, limited explanations around these emissions exist in literature that approaches ammonia combustion blends, a recurrent problem potentially caused by some of the limitations of the measuring systems used for these analyses.

For that purpose, this work evaluates the production of NOx emissions (including NO, N_2O and NO_2) in a tangential swirl burner using high-ammonia/low-hydrogen blends. The study, first of its kind, approaches a high turbulence, medium power study with progressive increase in hydrogen content within ammonia blends. Results are complemented with spectroscopy analyses of the flames to provide further information about radical formation across the different profiles. Conclusions are drawn around equivalence ratio, blends and radical formation.

2. Methodology

The experiments employed a tangential swirl burner at atmospheric pressure and inlet temperature of 288 K, Figure 1. The burner was supplied with fully premixed mixtures of hydrogen and ammonia as shown in Table 1, using Bronkhorst mass flow controllers that enabled a precision of 0.5 % within a range of 15-95 % mass flow.

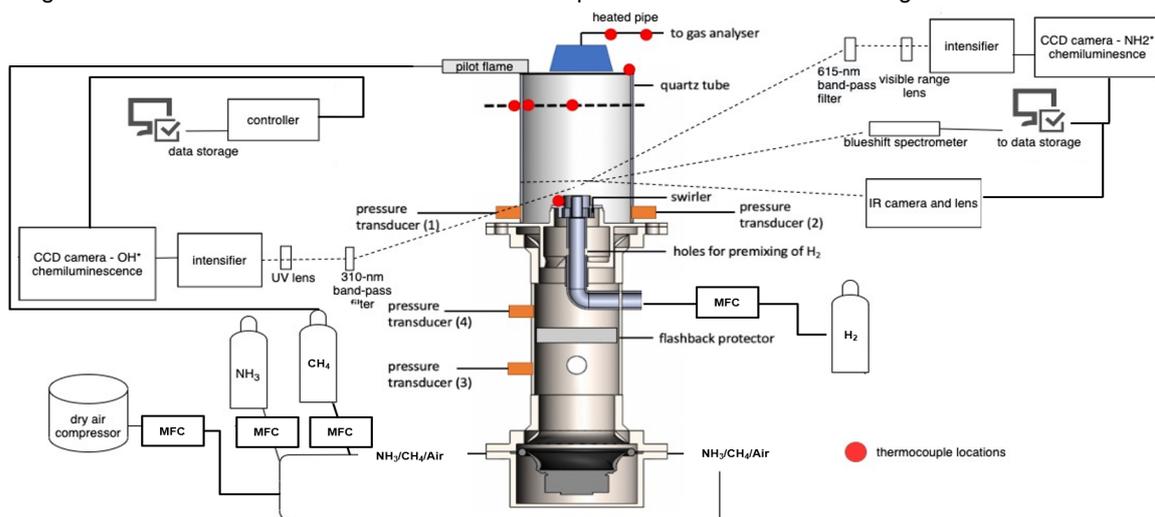


Figure 1: Tangential combustor with measuring techniques and control systems.

Nitrogen oxides (NO , NO_2 , N_2O), water content, oxygen percentage and ammonia concentration were measured using a bespoke Emerson CT5100 Quantum Cascade Laser analyser at a frequency of 1 Hz, a repeatability of ± 1 %, 0.999 linearity, and a sampling temperature of 190 °C. A heated line set at 160 °C was employed to avoid

condensation of water vapor. Emissions are presented with a 15 % oxygen correction. A simple Logitech C270 webcam was used to monitor the flame stability at a distance of 5 m. Finally, a Blue-Wave StellarNet CMOS spectrometer with a detector ranging from 200 to 1,100 nm was focused on the flame core to measure the emission spectral during the combustion process.

Table 1: Experimental and numerical boundary conditions.

Parameter	Value	Parameter	Value
Blends NH ₃ /H ₂ (vol %)	100 - 0, 90 - 10, 80 - 20, 70 - 30	Inlet Temperature	288 K
Power	8 kW	Inlet Pressure	0.11 MPa
Equivalence Ratios (Φ)	0.55 - 1.40	Swirl	1.05

3. Results

Results were obtained at various equivalence ratios and blends, Figures 2 and 3. Figure 2a shows NO emission trends, with peaks between 0.7 to 1.0 equivalence ratio. The trend, already explored by previous work (Honza et al., 2019), shows that the excess in oxygen, H/O radical pools, and higher temperatures lead to the production of fuel-NO. The trend is recurrent using all blends. NO drastically decreases for richer conditions >1.0 equivalence ratio (ϕ) and very lean conditions <0.7 ϕ . For the rich case, excess ammonia and reduced oxygen/hydrogen pools, in combination with lower temperatures, enable a lower production of NO. Furthermore, unburned ammonia interacts with NO at the post-combustion zone through $\text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O}$, an important reaction that contributes to the abatement of nitric oxide (Guteša Božo et al., 2021). As for the lean case, NO reduction corresponds to the reduction in temperature (Zhu et al., 2021). However, the effect might lead to the formation of other molecules if all ammonia is fully consumed, as later discussed.

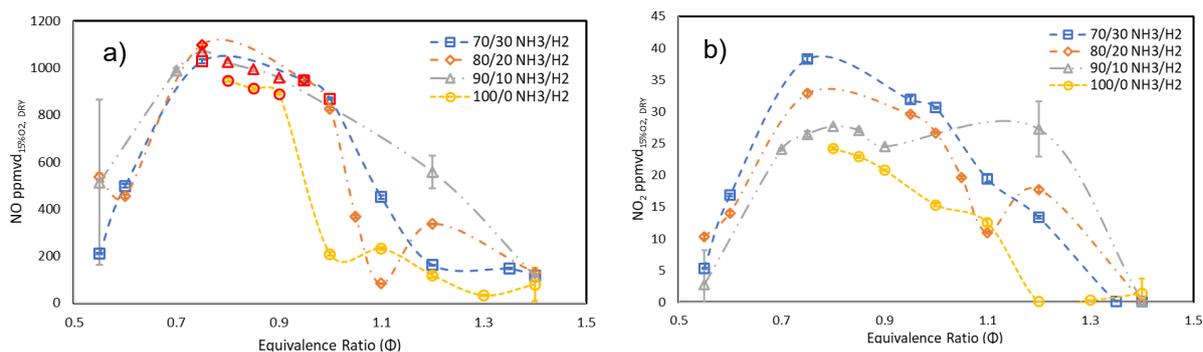


Figure 2: (a) NO emissions, and (b) NO₂ emissions for all blends and equivalence ratios. Red coloured symbols are out of the measurement range.

In terms of NO₂ emissions, these peak at lean conditions between 0.7 – 1.0 ϕ , following a similar trend to NO, but at far lower concentrations. Similarly, the higher ammonia blends show a faster decrease in NO₂ emissions at the lean end of the spectrum, and those with higher hydrogen content show less NO₂ being produced under rich fuel conditions, Figure 2b. The only exception is for pure ammonia flames, which show a fast decrease in NO₂ at high equivalence ratios, probably a consequence of further reactions with greater concentrations of unburned ammonia. It is believed that the effect observed in the ammonia/hydrogen blends is a consequence of higher temperatures of reaction caused by the hydrogen addition. This effect combines with the presence of greater pools of O⁺ free radicals under lean conditions, which keep reacting with NO available in the flow field. Meanwhile, under rich conditions, the slightly higher temperatures of reaction, with higher hydrogen and ammonia concentrations and reduced oxygen flow encourage NO₂ consumption.

The previous statement agrees well with the appearance of unburned NH₃ at high concentrations at both ends of the equivalence ratio spectrum, Figure 3a. Interestingly, the high concentration of ammonia under lean equivalence ratios shows that at these conditions, ammonia is neither completely combusted at the flame nor the production of the molecule is enhanced by the pools of free H⁺ radicals. As Figure 3a shows, it is likely that the phenomenon lays more on the incomplete combustion of the ammonia molecule at those lower temperatures. These results clarify the low production of NO at lean equivalence ratios, Figure 2a. As theorised, less ammonia combustion would also lead to less NO formation. It was also observed that when the concentration of ammonia in the blend decreases, the burning velocity of the mixture decreases. This is a

consequence of a decrease flame temperature and active radicals such as O, H, and OH which are necessary in promoting chain branching reactions that speed up the chemistry. The overall effect is higher unburned fuel emissions and hence a decrease in combustion efficiency at a constant residence time.

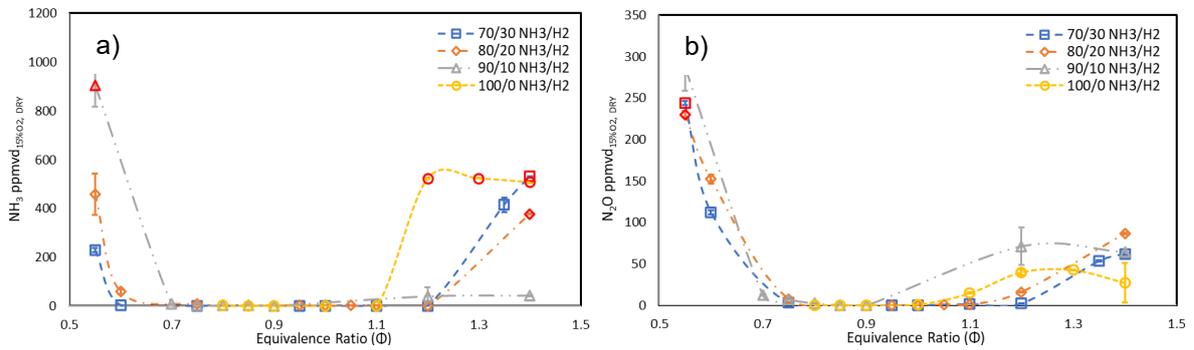


Figure 3: NH₃ emissions (a), and N₂O emissions (b) for all blends and equivalence ratios. Red coloured symbols are out of the measurement range.

Finally, N₂O formation is also addressed, Figure 3b. Surprisingly, the trend of this molecule is opposite to NO and NO₂, showing peaks of formation at both ends of the equivalence ratio range. The results are attributed to the lower temperatures of combustion at these conditions, as denoted elsewhere (Okafor et al., 2021). High hydrogen production, with an excess of ammonia and relatively higher temperatures to those under lean cases show much lower N₂O emissions. Also, lower ammonia/higher hydrogen fuel blends, corresponding to higher temperature blends, denote lower emissions, with 70/30 NH₃/H₂ (vol %) showing the best results up to 1.2 ϕ . Interestingly, the pure ammonia blend also shows low N₂O emissions at $\phi = 1.4$, likely a consequence of low combustion efficiency, Figure 3b. On the other hand, lean conditions show the worst case for N₂O production. It is theorised that the lower temperatures of combustion do not enable further reaction of recently formed N₂O, increasing its concentration that is not mitigated by any unburned ammonia nor further reactions at the post-flame region. Therefore, results show that in terms of overall NO_x and unburned ammonia emissions, the best operating condition lies at slightly rich equivalence ratios between 1.05 to 1.20 ϕ .

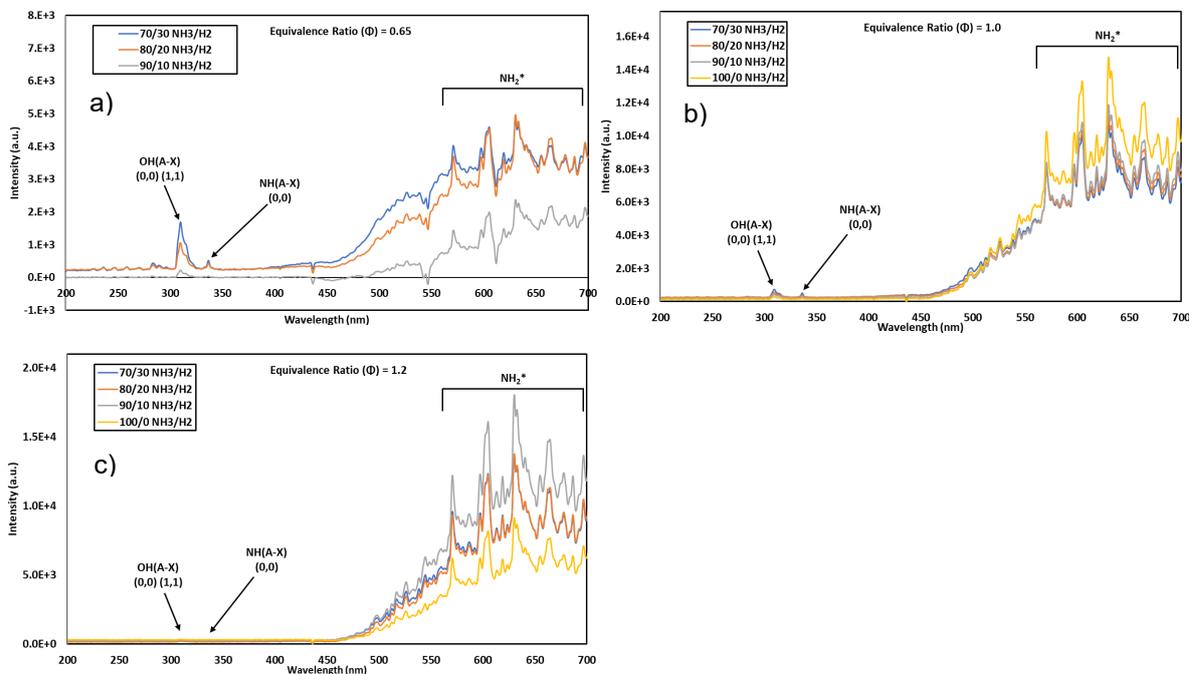


Figure 4: Spectroscopy analyses of various blends at $\Phi = 0.65$ (a); $\Phi = 1.0$ (b) and $\Phi = 1.2$ (c).

The results are complemented with spectroscopy analyses of various blends. For brevity, only three samples are discussed further, namely a very lean condition (a), a stoichiometric case (b) and a rich case (c), Figure 4.

Results show how under lean conditions the blends have a high production of OH with some NH radical production. An increase in hydrogen in the fuel blend leads to the formation of higher OH, as expected. Hydroxyl molecules are known to initiate most of the NH_x chains of reaction, hence their abundance under high oxygen concentration conditions would be anticipated. The high OH concentration enables the oxidation of NH_2 amidogens, leading to NH formation that under high temperature conditions lead to NO production via HNO formation, as depicted by previous work (Kobayashi et al., 2019). Another point of interest is that higher ammonia fuel blends have lower NH_2 production at the lean condition, a point that can be related to the lower reactivity of the blend, with lower combustion efficiency and more unburned ammonia, Figure 3a. Concurrently, the production of amidogen is considerably enhanced at stoichiometric condition due to higher reaction temperatures. Higher ammonia blends deliver more NH_2 , also an anticipated effect which is a consequence of splitting more NH_3 molecules.

Finally, the rich case shows that NH_2 formation slightly decreases compared to the stoichiometric case. The results denote the decrease in concentrations of OH radicals, as predicted, due to the reduced oxygen concentration in the reactant mixture. Interestingly, the 90/10 NH_3/H_2 (vol %) shows higher amidogen production, which is believed to be a consequence of the increased reactivity of the blend. If compared to pure ammonia, which is known to be poorly reacting under these conditions, Figures 3a and 3b, a slight addition of hydrogen seems to boost combustion. It was observed that an interesting behaviour exists between the 80/20 and 70/30 NH_3/H_2 (vol %) blends, which show almost the same spectroscopic trends. This is also evident under stoichiometric conditions, hence requiring further analyses and research to fully address the phenomena causing this similitude.

4. Conclusions

A series of experiments were conducted to determine the production of NO_x emissions using ammonia/hydrogen blends at various equivalence ratios. Results depict a sweet zone between 1.05 and 1.20 ϕ for the use of these blends. Very lean conditions generate large N_2O , whilst moderate lean to stoichiometric cases produce large NO concentrations. Finally, very rich fuel addition lead to high unburned ammonia but low NO_x . The work is complemented by spectroscopy analyses to discuss the production of NH_2 , NH and OH at different intensities. Some blends show similar trends between themselves, a pattern that requires further investigation. Simultaneously, some cases, especially those with high ammonia concentration, denote trends that relate to the efficiency of combustion (i.e. lean conditions), available reacting fuel (i.e. stoichiometric conditions) or blend reactivity (i.e. rich conditions), all showing the complex nature of these mixtures and the need for further investigation.

Acknowledgments

Cardiff University authors gratefully acknowledge the support from the ESPRC through the program SAFE-Pilot AGT (EP/T009314/1). Information on the data underpinning the results presented here, including how to access them, can be found in the Cardiff University data catalogue at <http://orca.cf.ac.uk/144277>.

References

- Cai T., Zhao D., Li X., Shi B., Li J., 2021, Mitigating NO_x emissions from an ammonia-fueled micro-power system with a perforated plate implemented, *Journal of Hazardous Materials*, 401, 123848.
- De Vries N., Okafor E. C., Gutesa-Bozo M., Xiao H., Valera-Medina A., 2021, Use of Ammonia for Heat, Power and Propulsion, Chapter In: A Valera-Medina, R Banares-Alcantara, *Techno-Economic Challenges of Green Ammonia as an Energy Vector*, Academic Press, Elsevier Inc, London, UK, 105–154.
- Dincer I., Bicer Y., 2018, Ammonia, Chapter In: I Dincer (Ed.), *Comprehensive Energy Systems*, 2, Elsevier Inc, London, UK, 1–39.
- Elishav O., Mosevitzky Lis B., Miller E.M., Arent D.J., Valera-Medina A., Grinberg Dana A., Shter G. E., Grader G.S., 2020, Progress and prospective of nitrogen-based alternative fuels, *Chemical Reviews*, 120(12), 5352–5436.
- Guteša Božo M., Mashruk S., Zitouni S., Valera-Medina A., 2021, Humidified ammonia/hydrogen RQL combustion in a trigeneration gas turbine cycle, *Energy Conversion and Management*, 227, 113625.
- Hayakawa A., Goto T., Mimoto R., Kudo T., Kobayashi H., 2015, NO formation/reduction mechanisms of ammonia/air premixed flames at various equivalence ratios and pressures, *Mechanical Engineering Journal*, 2(1), 14-00402-14-00402.
- Honzawa T., Kai R., Okada A., Valera-Medina A., Bowen P. J., Kurose R., 2019, Predictions of NO and CO emissions in ammonia/methane/air combustion by LES using a non-adiabatic flamelet generated manifold, *Energy*, 186, 115771.

- Jiang X., Zhang R., Chen J., Huang Z., 2021, Effect of hydrogen blending on the high temperature auto-ignition of ammonia at elevated pressure, 38th International Symposium on Combustion Poster Session, 12th-17th July, Abelaide, Australia.
- Khateeb A.A., Guiberti T.F., Zhu X., Younes M., Jamal A., Roberts W.L., 2020, Stability limits and NO emissions of technically-premixed ammonia-hydrogen-nitrogen-air swirl flames, *International Journal of Hydrogen Energy*, 45(41), 22008–22018.
- Kobayashi H., Hayakawa A., Somarathne K.D.K.A., Okafor E.C., 2019, Science and technology of ammonia combustion, *Proceedings of the Combustion Institute*, 37(1), 109–133.
- Lauri R., 2015, DeNOX Plants: A Prediction method of the overpressure generated by an ammonia vapor cloud explosion, *Chemical Engineering Transactions*, 43, 2065–2070.
- Mashruk S., Xiao H., Valera-Medina A., 2020, Rich-Quench-Lean model comparison for the clean use of humidified ammonia/hydrogen combustion systems, *International Journal of Hydrogen Energy*, 46(5), 4472–4484.
- Mikulčić H., Baleta J., Wang X., Wang J., Qi F., Wang F., 2021, Numerical simulation of ammonia/methane/air combustion using reduced chemical kinetics models, *International Journal of Hydrogen Energy*, 46(45), 23548–23563.
- Mitsubishi Heavy Industries Group, 2021, Mitsubishi Power Commences Development of World's First Ammonia-fired 40MW Class Gas Turbine System <
[https://power.mhi.com/news/20210301.html#:~:text=YOKOHAMA%2C%20JAPAN%20\(March%20%2C,%25%20ammonia%20\(NH3\).&text=As%20firing%20of%20ammonia%20produces,free%20power%20generation%20is%20achieved](https://power.mhi.com/news/20210301.html#:~:text=YOKOHAMA%2C%20JAPAN%20(March%20%2C,%25%20ammonia%20(NH3).&text=As%20firing%20of%20ammonia%20produces,free%20power%20generation%20is%20achieved)> accessed 12.09.2021.
- Okafor E.C., Somarathne K.D.K.A., Ratthan R., Hayakawa A., Kudo T., Kurata O., Iki N., Tsujimura T., Furutani H., Kobayashi H., 2020, Control of NOx and other emissions in micro gas turbine combustors fuelled with mixtures of methane and ammonia, *Combustion and Flame*, 211, 406–416.
- Okafor E.C., Tsukamoto M., Hayakawa A., Somarathne K.A., Kudo T., Tsujimura T., Kobayashi H., 2021, Influence of wall heat loss on the emission characteristics of premixed ammonia-air swirling flames interacting with the combustor wall, *Proceedings of the Combustion Institute*, 38(4), 5139–5146.
- Pugh, D., Valera-Medina, A., Bowen, P., Giles, A., Goktepe, B., Runyon, J., Morris, S., Hewlett, S., Marsh, R., 2020, Emissions performance of staged premixed and diffusion combustor concepts for an NH₃/Air flame with and without reactant humidification, *Journal of Engineering for Gas Turbines and Power*, 143(5), 051012-051019.
- Razon L.F., Valera-Medina A., 2021, A comparative environmental life cycle assessment of the combustion of ammonia/methane fuels in a tangential swirl burner, *Frontiers in Chemical Engineering*, 3, 631397.
- Salmon N., Bañares-Alcántara R., 2021, Green ammonia as a spatial energy vector: A review, *Sustainable Energy and Fuels*, 5, 2814-2839.
- Stagni A., Cavallotti C., Arunthanayothin S., Song Y., Herbinet O., Battin-Leclerc F., Faravelli T., 2020, An experimental, theoretical and kinetic-modeling study of the gas-phase oxidation of ammonia, *Reaction Chemistry and Engineering*, 5(4), 696–711.
- Thomas D., Northrop W., 2021, Ammonia-Hydrogen Combustion in Diffusion Flames, 38th International Symposium on Combustion Poster Session, 12th-17th July, Abelaide, Australia.
- US EPA, O., 2017, Basic Information about NO₂, *Environmental Science and Pollution Research*, 24(3), 2781–2789.
- Valera-Medina A., Amer-Hatem F., Azad A.K., Dedoussi I.C., de Joannon M., Fernandes R.X., Glarborg P., Hashemi H., He X., Mashruk S., McGowan J., Mounaim-Rouselle C., Ortiz-Prado A., Ortiz-Valera A., Rossetti I., Shu B., Yehia M., Xiao H., Costa M., 2021, Review on ammonia as a potential fuel: From synthesis to economics, *Energy and Fuels*, 35(9), 6964–7029.
- Valera-Medina A., Banares-Alcantara R., 2021, Techno-Economic Challenges of Green Ammonia as an Energy Vector, Academic Press, Elsevier Inc, London, UK.
- Valera-Medina A., Roldan A., 2020, Ammonia from steelworks, Chapter In: Inamuddin, R Boddula, A. M. Asiri (Ed.), *Sustainable Ammonia Production*, Springer International Publishing, Switzerland, 69–80.
- Wang J., Jin W., Guo H., Wang X., Liu J., 2015, Experimental Study on Ammonia Nitrogen Adsorption Performance of Zeolite Powder, *Chemical Engineering Transactions*, 46, 79–84.
- Zhu X., Khateeb A.A., Guiberti T.F., Roberts W.L., 2021, NO and OH* emission characteristics of very-lean to stoichiometric ammonia-hydrogen-air swirl flames, *Proceedings of the Combustion Institute*, 38(4), 5155–5162.