CHEMICAL ENGINEERING TRANSACTIONS

VOL. 98, 2023

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Sauro Pierucci, Carlo Pirola

ISBN 978-88-95608-97-6; **ISSN** 2283-9216

DOI: 10.3303/CET2398004

Numerical study of MILD Combustion of Ammonia/hydrogen Mixtures

Luis F. Cardona*, Pedro N. Alvarado

Instituto Tecnológico Metropolitano, Facultad de Ingenierías, Departamento de Investigación, Grupo de Investigación en Materiales Avanzados y Energía MATyER, Carrera 31 # 54 - 10, Medellín, Colombia, 050013
luiscardona@itm.edu.co

The combustion of ammonia (NH_3) has sparked a renewed interest in the scientific community because it is a carbon-free fuel that does not contribute to global warming. Nevertheless, some of its disadvantages include the fact that (i) it has lower laminar flame speeds when compared to hydrocarbons, and (ii) that it is prone to the formation of nitride oxides (NOx) through the fuel route. As an alternative to address the first issue, it has been proposed to mix ammonia with hydrogen, but at the expense of even higher NOx emissions. Such emissions, however, can be reduced by operating at restrictive equivalence ratios near stoichiometry, which reduces oxygen availability in the reactions for NOx formation. This is a drawback because lean combustion, a technique that has been proven to reduce emissions for most fuels, is usually avoided in NH_3 combustion. Therefore, with the goal of reducing NOx, this paper presents a numerical study using perfectly stirred reactors to investigate the potential use of both lean equivalence ratios and hydrogen enrichment in the MILD combustion of NH_3. Some features of the MILD regime, such as low temperature increases due to reaction and the possibility of sustaining reactions under low oxygen concentrations, could be beneficial to ammonia combustion. Simulations were carried out in open-source software Cantera. According to the results, reaction can be sustained at lean equivalence ratios like 0.6 with a 50% hydrogen enrichment, and emissions of less than 100 ppm NO at 15% O_2 on a dry basis can be obtained. In conclusion, MILD is a promising strategy for the clean burning of ammonia.

1. Introduction

Since carbon dioxide (CO_2) released by the combustion of fossil fuels is the major contributor to global warming, many countries have committed themselves to reduce emissions in recent years. Several engineers and scientists have set out to devise strategies to lower CO_2 emissions, as well as to develop of more efficient and environmentally friendly combustion systems. In the energy sector, some of these key strategies include energy conservation, the replacement of carbon-rich fuels with low carbon content and high hydrogen content or carbon–free fuels, the use of renewable energy sources, and the capture and storage of CO_2. Energy conservation, for instance, can be achieved by using new combustion technologies that improve the energy consumption efficiency. This combined with the use of carbon-free fuels could further help mitigate CO_2 emissions and thus move closer to the goal of zero carbon emissions (Astbury, 2008).
Ammonia (NH_3) is a chemical substance that is widely used in industrial applications as a refrigerant (Vuppaladadiyam et al., 2022) and as a raw material for fertiliser production (Faria, 2021). It has also been explored as a potential energy carrier and due to its carbon-free composition, it is regarded as an environmentally friendly fuel that does not release CO_2 when burned (Kobayashi et al., 2019). Its combustion properties and features, however, do not compare favourably to those of the most popular and polluting hydrocarbon fuels (Elbaz et al., 2022). On the one hand, its laminar flame speed (S_L) and heating values are lower. For example, its S_L is about seven times slower under stoichiometric conditions and its lower heating value is less than half that of methane (Chiong et al., 2021). On the other hand, NH_3 combustion tends to produce NOx through the fuel route rather than the Zeldovich route typical of hydrocarbons, which is associated with high temperatures. This is a disadvantage because proven techniques that generate dilution and lower temperature levels, such as lean combustion, are not expected to yield the same results as in the case of most hydrocarbons (Bradley, 2016).

Paper Received: 25 October 2022; Revised: 24 January 2023; Accepted: 5 April 2023
Please cite this article as: Cardona L.F., Alvarado P.N., 2023, Numerical Study of Mild Combustion of Ammonia-hydrogen Mixtures, Chemical Engineering Transactions, 98, 21-26 DOI:10.3303/CET2398004

Due to this, conventional NH_3 combustion technologies produce NO emissions that exceed the limits imposed by governments for stationary combustion equipment, for example, 70 ppm at 16% O_2 for gas turbines in Japan (Ministry of the Environment, Government of Japan, 1998).
There are, nonetheless, ways to mitigate NOx emissions in NH_3 combustion. One alternative is to use an equivalence ratio (φ) near unity (stoichiometric conditions) to avoid supplying excess oxygen to the reaction. According to the results of various studies on the matter, NOx formation is reduced as equivalence ratios move to the rich side (φ>1). Yet, a particular problem in rich combustion is the emission of unburned fuel, known as "slip ammonia" in the specialised literature. This phenomenon, however, may serve as the basis for NOx abatement techniques such as staged combustion, in which fuel-rich combustion is followed by fuel-lean combustion (Somarathne et al., 2021).
To address the combustion issues arising from using pure NH_3, it has been suggested to mix it with other fuels. For example, there are studies in which ammonia was mixed with methane (Somarathne et al., 2021), hydrogen (Yang et al., 2022), and even low-molecular-weight alcohols such as methanol (Ariemma et al., 2022). Among the several alternatives available, hydrogen (H_2), in addition to also being carbon-free, is a key option that could be produced using renewable energies (Panchenko et al., 2022). Additionally, it improves the reactivity of ammonia and can help overcome some of its disadvantages. For instance, the laminar flame speed of NH_3/H_2/air mixtures has been found to be higher than that of NH_3/air mixtures. However, NOx emissions rise as the H_2 enrichment ratio increases (da Rocha et al., 2019). Also, higher stability limits have been reported for H_2-enriched ammonia flames (Khateeb et al., 2020).
In the Moderate or Intense Low-oxygen Dilution (MILD) combustion regime, the reactive mixture is above the self-ignition temperature (T_{si}) while achieving a temperature rise due to reaction (ΔT) that is lower than the T_{si} itself (Cavaliere & De Joannon, 2004). In practical burners, this is accomplished by internal or external flue gas recirculation, which results in dilution, decreased oxygen concentration, and no visible flame front, thus becoming a flameless combustion (Perpignan et al., 2018). In the specialised literature, the MILD combustion of pure NH_3 has been numerically investigated under conditions similar to those found in gas turbine operation (Rocha et al., 2021).
This study presents a numerical study of the MILD combustion of NH_3/H_2/air mixtures using a perfectly stirred reactor model. Its main objective is to analyse how NOx emissions from reactive mixtures behave when they are highly diluted by flue gases at lean equivalence ratios under the MILD combustion regime. In turn, it seeks to determine whether there is an operating point without trade-offs, in which NOx emissions are low enough to theoretically comply with the regulations, and improved laminar flame speeds are obtained.

2. Methodology

The reactor network that was numerically analysed in this paper is shown in Figure 1. As observed, premixed fuel and oxidiser at 300 K and 101.325 kPa are fed into a mixer before reacting. Then, the mixer takes a portion of recirculated gases from the exhaust of an adiabatic Perfectly Stirred Reactor (PSR). In this study, NH_3/H_2/air mixtures were used. Air was approximated as a mixture of 21% O_2 and 79% N_2 by volume. Moreover, equivalence ratios ranged from 0.6 to 1 and the fuel composition varied from 100% NH_3 to up to 50%NH_3/50%H_2 by volume. Although several reaction mechanisms for ammonia combustion have been reported in the literature (Elbaz et al., 2022), Stagni-Mech was chosen for all the simulations because of its simplicity, as it only comprises 31 species and 203 reactions (Stagni et al., 2020). The residence time was 1 s assuming complete oxidation, and the combustor volume was $2.5x10^{-4}$ m^3 to mimic experimental conditions (Luan et al., 2020). Simulations were carried out using the opensource software Cantera (version 2.6.0) (Goodwin et al., 2022).

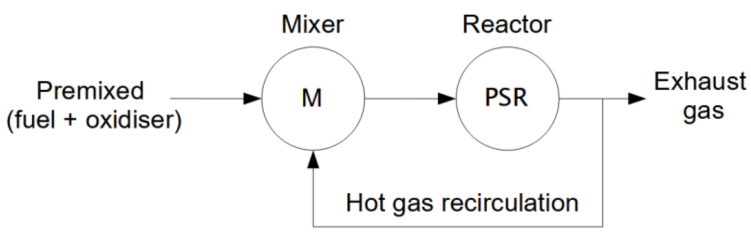


Figure 1: Reactor network used in this study.

For all the compositions considered in this study, the simulations were performed with a recirculation factor (kV) ranging from 0 to 2. Here, kV is defined as the ratio of recirculated gases as shown in Eq(1).

$$kV = \frac{\dot{m}_{rec}}{\dot{m}_{fuel} + \dot{m}_{air}} \quad (1)$$

Table 1 presents the criteria employed in this study, which were adapted from prior research (Luan et al., 2020) to classify combustion. Under this classification, MILD combustion is further divided into two categories that are separated by a critical recirculation ratio (kV_{cr}) which is obtained as the intersection between the T_{si} line and the $\Delta T = T_{si}$ line in the MILD combustion map.

Table 1: Combustion regimes. Adapted from the study by Luan et al. (2020).

Acronym	Combustion regime	Conditions
UMC	Unconditional MILD combustion	$T_{inlet} > T_{si}$, $\Delta T < T_{si}$ and $kV \geq kV_{cr}$
CMC	Conditional MILD combustion	$T_{inlet} > T_{si}$, $\Delta T < T_{si}$ and $kV < kV_{cr}$
HTC	High-temperature combustion	$T_{inlet} > T_{si}$ and $\Delta T \geq T_{si}$
FC	Feedback combustion	$T_{inlet} < T_{si}$ and $\Delta T < T_{si}$
UC	Unsteady combustion	$T_{extinction} < T_{inlet} < T_{si}$ and $\Delta T < T_{si}$
NR	No reaction	$T_{inlet} < T_{extinction}$

Figure 2 shows the algorithm used in this study. As can be seen, T_{inlet} is increased until ignition occurs when reactor ΔT due to reaction is above a constant C1 (250°C). When mixtures are significantly diluted, this straightforward condition may not hold true because it is possible that ΔT will go below C1; however, this was not the case in the simulations conducted here. A similar stepping procedure was followed to estimate $T_{extinction}$ and inlet temperature at which $\Delta T = T_{si}$.

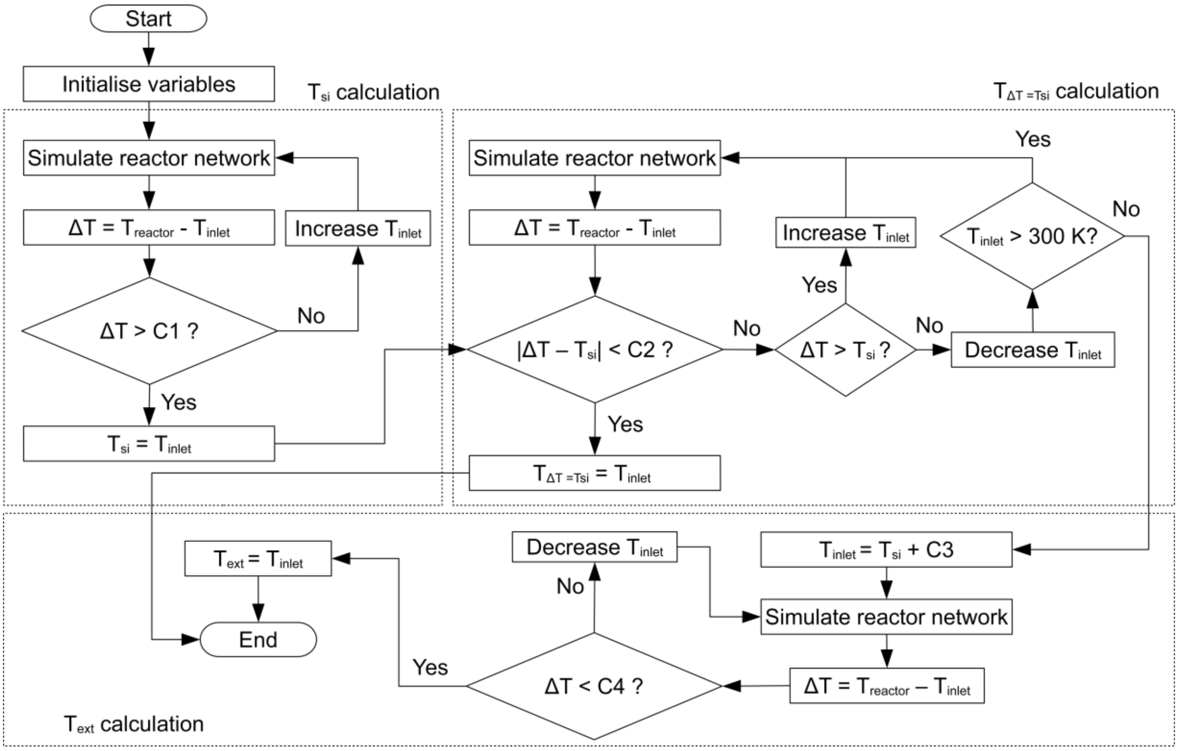


Figure 2. Algorithm used for temperature calculation.

3. Results

To validate the mechanism used for the H_2-enriched mixtures, 1D laminar flame simulations were carried out using Cantera, and the results were compared with those of two other experiments reported by Pfahl et al. (2000) and Ichikawa et al. (2015). As observed in Figure 3, the obtained results are in reasonable agreement with those of the two experiments on the lean side of combustion for NH_3/H_2 mixtures. Hence, the simulation framework proposed in this study is considered acceptable.

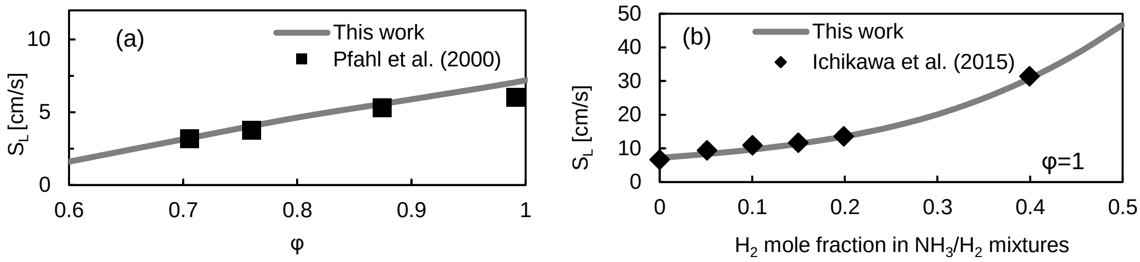


Figure 3: Laminar flame speed for pure NH_3 (a) and H_2-enriched NH_3 combustion (b).

Figure 4 presents the MILD combustion map obtained for the NH_3 case under stoichiometric conditions. In this case, the critical recirculation ratio (kV_{cr}), which is defined as the point where the Tsi and ΔT=Tsi lines intersect, was 0.52. This point separates the UMC region from the CMC region. Although both regions satisfy the original MILD combustion criteria, UMC is only achieved for O_2 mole fractions of about 10.5% and below. This region is preferable because NOx production is discouraged for two reasons: (i), there is less O_2 available for reaction, and NO formation due to fuel composition is expected to be lower; and (ii) as kV increases above kV_{cr}, ΔT decreases and the thermal production of NO is also reduced. Tsi, which, in this case, happens to remain almost unchanged near 795°C for all the kV evaluated in the UMC region, also contributed to this.

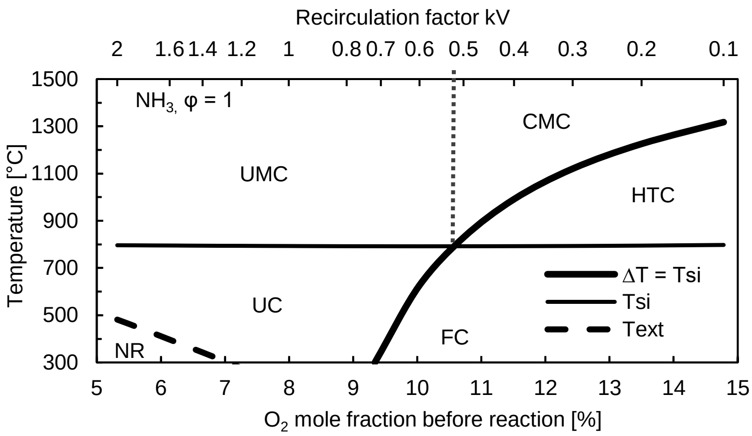
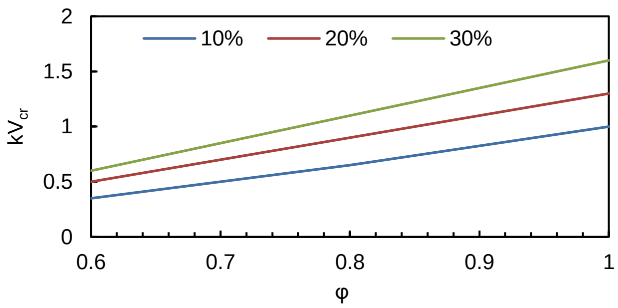


Figure 4: MILD combustion map obtained for the stoichiometric NH_3/air mixture.

Figure 5 shows the variation of kV_{cr} with respect to the equivalence ratio for three different dilution levels (10, 20, and 30% H_2). As observed, kV_{cr} diminishes with leaner equivalence ratios φ, which means that the need for exhaust gas recirculation decreases as excess air is introduced into the system. Nonetheless, the minimum kV required to achieve UMC increases with the addition of hydrogen, although this effect is less pronounced at leaner equivalence ratios. A higher kV_{cr} is undesirable because it will entail more exhaust gas recirculation for MILD combustion.



.

Figure 5: Critical recirculation ratio (kV_{cr}) obtained for the NH_3/H_2 mixtures.

Figure 6 presents the NO emissions from the UMC-MILD combustion of NH_3/H_2 mixtures at φ = 1 and φ = 0.6. In the stoichiometric case, only 100% NH_3 can establish a UMC regime with a kV between 1 and 2 (as it is also shown in the Figure 4). As explained before, when H_2 is added, kV_{cr} increases, and UMC is achieved with 1 < kV < 2 operating at φ = 1. Figures 6a and 6b, show that enrichment with H_2 reduces NO emissions and that a NO concentration below 100 ppm can be obtained with or without adding excess air to the reaction. For instance, about 80 ppm at 15% O_2 are obtained at φ = 0.6 with 40% H_2 enrichment, which is close to the limit of 70 ppm at 16% O_2 for gas turbines in Japan, showing potential for making this process feasible in such market. Such low NO emissions may be associated with a decrease in the amount of nitrogen in the fuel mixture and a lower effect of the fuel-NO mechanism. However, since the φ = 1 case may result in ammonia slip, the φ = 0.6 scenario would be preferable. Furthermore, the NO emissions from fuels containing between 30% and 50% H_2 were not found to be significantly different. Hence, adding more than 30% H_2 to the fuel does not considerably contribute to the abatement of the pollutant emissions investigated in this paper. In contrast, a higher amount of H_2 will require a higher kV (more recirculation).

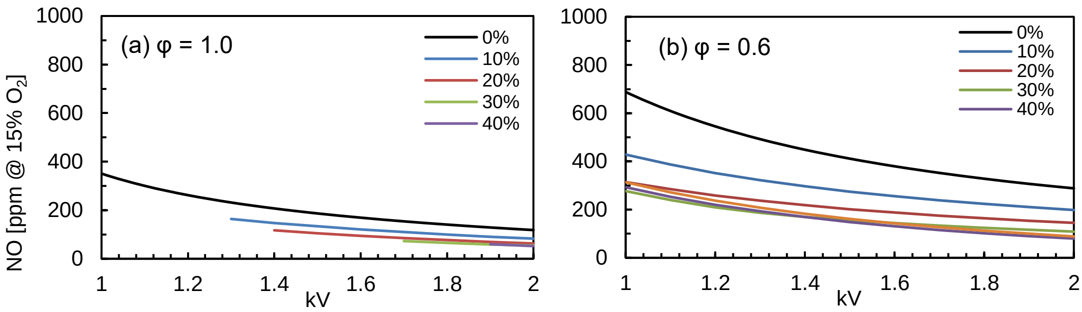


Figure 6: NO emissions from the UMC-MILD combustion of NH_3/H_2 mixtures at (a) φ = 1 and (b) φ = 0.6.

4. Conclusions

This paper presented a numerical study of the MILD combustion of NH_3/H_2/air mixtures. The main conclusions derived from such study are (i) a MILD combustion regime can be achieved with the lean equivalence ratios (from φ = 0.6 up to φ = 1) and fuel compositions (from 100% NH_3 up to 50% H_2/50% NH_3) used in this study. Also, the NO emissions of NH_3 mixed with H_2 were found to be lower than those of 100% NH_3 at same equivalence ratio. However, under the tested conditions, NO emissions did not differ significantly when between 30 and 50% of H_2 were added to the fuel, (ii) NO emissions lower than 100 ppm at 15% O_2 on a dry basis can be obtained from the MILD combustion of NH_3 and NH_3/H_2 mixtures. However, in all the studied scenarios, this requires recirculation ratios (kV) close to 2 and (iii) adding H_2 to NH_3 increases the amount of mass that must be recirculated into the system to achieve an unconditional MILD combustion regime (UMC). Despite being a drawback, this effect is less pronounced at leaner equivalence ratios.

Nomenclature

kV – Recirculation ratio, -
kV_{cr} – Critical recirculation ratio, -
$\dot{m}_{air}$– Air mass flow, kg/s
$\dot{m}_{fuel}$ – Fuel mass flow, kg/s
$\dot{m}_{rec}$– Recirculated mass flow, kg/s
T_{inlet} – Inlet temperature, °C
T_{si} – Self ignition temperature, °C
$T_{extinction}$ – Extinction temperature, °C
φ – Equivalence ratio, -

Acknowledgments

The authors' editor was ITM Translation Agency (traducciones@itm.edu.co).

References

Ariemma G. B., Sorrentino G., Sabia P., Ragucci R., de Joannon M., 2022, MILD Combustion of Methanol, Ethanol and 1-Butanol binary blends with Ammonia, Proceedings of the Combustion Institute.

Astbury G. R., 2008, A review of the properties and hazards of some alternative fuels, Process Safety and Environmental Protection, 86, 397–414.

Bradley D., 2016, 2—Fundamentals of Lean Combustion, Chapter In: D. Dunn-Rankin & P. Therkelsen (Eds.), Lean Combustion (Second Edition), Academic Press, Boston, USA, 21–61.

Cavaliere, A., & De Joannon, M. (2004). Mild combustion. Progress in Energy and Combustion Science, 30(4), 329–366. https://doi.org/10.1016/j.pecs.2004.02.003

Chiong M. C., Chong C. T., Ng J.H., Mashruk S., Chong W. W. F., Samiran N. A., Mong, G. R., Valera-Medina A., 2021, Advancements of combustion technologies in the ammonia-fuelled engines, Energy Conversion and Management, 244, 114460.

da Rocha R. C., Costa M., Bai X.-S., 2019. Chemical kinetic modelling of ammonia/hydrogen/air ignition, premixed flame propagation and NO emission, Fuel, 246, 24–33.

Elbaz A. M., Wang S., Guiberti T. F., Roberts, W. L., 2022, Review on the recent advances on ammonia combustion from the fundamentals to the applications, Fuel Communications, 10, 100053.

Faria J. A., 2021. Renaissance of ammonia synthesis for sustainable production of energy and fertilizers, Current Opinion in Green and Sustainable Chemistry, 29, 100466.

Goodwin D. G., Speth R. L., Moffat H. K., Weber B. W., 2022, Cantera: An object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes, <www.cantera.org> accessed 12.12.2022.

Ichikawa A., Hayakawa A., Kitagawa Y., Somarathne K. D. K. A., Kudo T., Kobayashi, H., 2015, Laminar burning velocity and Markstein length of ammonia/hydrogen/air premixed flames at elevated pressures, International Journal of Hydrogen Energy, 40(30), 9570–9578.

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.

Luan C., Xu S., Shi B., Tu Y., Liu H., Li P., Liu, Z., 2020, Re-Recognition of the MILD Combustion Regime by Initial Conditions of Tin and XO2 for Methane in a Nonadiabatic Well-Stirred Reactor, Energy & Fuels, 34(2), 2391–2404.

Mashruk S., Vigueras-Zuniga M. O., Tejeda-del-Cueto M. E., Xiao H., Yu C., Maas U., Valera-Medina, A., 2022, Combustion features of CH4/NH3/H2 ternary blends, International Journal of Hydrogen Energy, 47(70), 30315–30327.

Ministry of the Environment, Government of Japan, 1998, Regulatory measures against air pollutants emitted from factories and business sites and the outline of regulations- Emission Standards for soot, dust, and NOx. <www.env.go.jp/en/air/aq/air/air4_table.html> accesed 12.12.2022

Panchenko V. A., Daus Yu. V., Kovalev A. A., Yudaev I. V., Litti Yu. V., 2022. Prospects for the production of green hydrogen: Review of countries with high potential, International Journal of Hydrogen Energy. In press <doi.org/10.1016/j.ijhydene.2022.10.084> accessed 12.12.2022

Perpignan A. A. V., Gangoli Rao A., Roekaerts D. J. E. M., 2018, Flameless combustion and its potential towards gas turbines. Progress in Energy and Combustion Science, 69, 28–62.

Pfahl U. J., Ross M. C., Shepherd J. E., Pasamehmetoglu K. O., Unal, C., 2000, Flammability limits, ignition energy, and flame speeds in H2–CH4–NH3–N2O–O2–N2 mixtures, Combustion and Flame, 123(1), 140–158.

Rocha R. C., Costa M., Bai X.-S., 2021, Combustion and Emission Characteristics of Ammonia under Conditions Relevant to Modern Gas Turbines, Combustion Science and Technology, 193(14), 2514–2533.

Somarathne K. D. K. A., Okafor E. C., Sugawara D., Hayakawa A., Kobayashi, H., 2021. Effects of OH concentration and temperature on NO emission characteristics of turbulent non-premixed CH4/NH3/air flames in a two-stage gas turbine like combustor at high pressure, Proceedings of the Combustion Institute, 38(4), 5163–5170.

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 & Engineering, 5(4), 696–711.

Vuppaladadiyam A. K., Antunes E., Vuppaladadiyam S. S. V., Baig Z. T., Subiantoro A., Lei G., Leu S.-Y., Sarmah A. K., Duan H., 2022, Progress in the development and use of refrigerants and unintended environmental consequences, Science of The Total Environment, 823, 153670.

Yang W., Ranga Dinesh K. K. J., Luo K. H., Thevenin D., 2022, Direct numerical simulation of turbulent premixed ammonia and ammonia-hydrogen combustion under engine-relevant conditions, International Journal of Hydrogen Energy, 47(20), 11083–11100.