Ammonia/Hydrogen Blends for Zero-Carbon Energy

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ABSTRACT

The use of ammonia for fuelling applications has recently received considerable interest from industry and academic institutions. However, the difficulty to employ pure ammonia has led to the use of doping agents capable of decreasing ignition energy whilst increasing flame speed and stability of such ammonia-blends. Therefore, ammonia/hydrogen blends have received some attention towards the development of new technologies focused on gas turbine combustion systems. Therefore, this manuscript approaches current developments in Europe, whilst exploring a reduced mechanism, namely Okafor's mechanism, comparing its performance and accuracy against obtained experiments to assess the impact of ammonia/hydrogen blends in species such as NH2 and NO. CFD models running on RANS Complex Chemistry and CHEMKIN-PRO flow reactors were employed for the study. The results are expanded to various inlet pressure and temperature conditions, hence showing the contribution of these parameters to the behaviour of NH2 and NO. The results are of great interest to reaction kinetic developers as well as combustor designers working with ammonia blends.

1. Introduction

Ammonia as an energy vector has recently gained vast attention across scientific and industrial communities [1]. The role of the molecule in the decarbonisation of storage technologies comes as a supplement to the use of hydrogen for recovery of stranded renewable sources [2]. However, the implementation of ammonia technologies capable of using this vector is constraint by the improvement of their efficiency in order to reach power outputs and cost benefits similar to those of current fossil fuels [3]. Current works on this field have demonstrated that ammonia can be used as energy storage medium at relatively high efficiencies [4], whilst the implementation of the technology in hybrid systems can provide economic benefits that will be competitive in the near future [5]. Ammonia from these facilities has the potential of being used as a fertilizer, or in terms of energy storage, as a medium to transport efficiently these renewables to be employed as main or backup fuelling source.

Progress has been done on the analysis of pure ammonia as fuelling source [6]. However, since ammonia flame speed is only a few cm/s (6-8 cm/s compared to hydrogen that is 100 cm/s) [7], other doping agents can also be employed to boost the energy density of such ammonia blends whilst increasing reactivity, thus enabling the increase in flowrates and power outputs to higher levels.

Combinations with methane have been attempted in recent years [8]. Simultaneously, the use of hydrogen has also been attempted in power devices fuelled with ammonia [9,10]. Initial attempts were performed using internal combustion engines (ICE) [11]. Further trials, conducted in support to the U.S. Army, were conceived to deliver data to inform the use of the chemical as backup power for the army forces. Results showed that the doping of ammonia blends up to 28% could provide flame speeds similar to those of some hydrocarbons [12]. However, it was observed in those trials that quenching distances of the flame were considerably higher than for other conventional sources. Concurrently, ammonia/hydrogen blends were analysed using fundamental rigs [13,14] and swirling flows in further works [9]. The results initially demonstrated that the use of high hydrogen concentrations were detrimental to flame stability, a consequence of the high diffusivity of the hydrogen molecule and increased reactivity of the flame. Further tests enabled the study of ammonia/hydrogen blends at concentrations of 60/40, 70/30, 80/20 and 90/10 % (vol) [10]. The results demonstrated that the 80/20 and 70/30 blends were the most stable. Since higher power outputs under much higher flowrates were conceived for the technology, the higher hydrogen content 70/30 blend was employed for additional trials. Experimental campaigns denoted the production of lower NOx emissions at high equivalence ratios close to 1.20. The blend was also assessed at higher pressures, showing that the NOx emissions are dependent on the surrounding pressure [15]. The phenomenon is linked to the reduced reaction consequence of the thinner reaction zone product of the decrease of reactivity. This effect was posteriorly mitigated by increasing reactant inlet temperatures, thus raising the reactivity of ammonia to reduce unburned fuel. The reaction, known to produce large quantities of NH2, NH, OH, O and H radical pools, is still not fully understood, as the production of these radicals can produce different paths for the production of NOx emissions and heat profiles. Therefore, further work has been attempted with the support of numerical modelling [16]. However, models show a variety of trends when hydrogen is employed under industrial conditions (i.e. high pressure and temperature), a problem that limits the ability of using CFD models to design new combustors fuelled with ammonia/hydrogen.

Concurrently, available models for ammonia studies include a great variety of elements such as carbon, hydrogen, helium, oxygen, etc. There are many chemical kinetic models for combustion of ammonia, ammonia/hydrocarbon or ammonia/methane mixture fuels, e.g. Glarborg mechanism [16], Okafor's mechanism [8], Mathieu's mechanism [17], Tian's

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mechanism [18], Konnov's mechanism [19], Lindstedt et al. [20], Miller et al. [21], Li's et al [22], etc. As previously raised, for CFD modelling, reduced kinetic models are required to make computations affordable, therefore several reduced/skeletal mechanisms have been developed employing different reduction methods as summarized by Li et al. [22] over the years. Ammonia mechanisms are not the exception. Most of these reduced models use different detailed kinetic mechanism as a starting point, thus providing different results based on their independent development path. This causes conflict between users, as the results tend to vary and provide different combustion results.

Therefore, more studies are required for the use of these blends at industrial representative conditions. Thus, the present study assesses the combustion process of ammonia/hydrogen blends using a widely employed model, namely Okafor's [8], under elevated condition regimes (i.e. high temperature, elevated pressure). Apart from determining the performance of the mechanism, results were expanded to determine the reactivity of various reactions that have been currently conceptualized as major contributors for stability, NO formation and combustion enhancement. Therefore, the results inform modelers of the potential (or detrimental) of these conditions. Further works on these models are recommended on the analysed grounds, with suggestions for follow up considerations.

2. Method

The software Star-CCM+ v19.3 was employed to conduct CFD analyses using Okafor's reduced reaction mechanisms. The analysis was conducted using RANS k-w SST modelling that is known to provide good average results for tangential swirling flows [23,24]. For the resolution of combustion, Complex Chemistry was employed in combination with the Turbulent Flame Speed Closure model. The model employs Zimont's Turbulent Flame Speed approach, which includes wall effects for quenching the flame near these regions with unburnt thermal diffusivities estimated using a power law. Simultaneously, clustering methods were employed to reduce the computational expense of Complex Chemistry calculations [25].

Initial analyses were performed to compare the hydrodynamics within the system, with special emphasis on velocity profiles, coherent structures and flame features (i.e. angle, diameter, etc.). Previous experiments [4] were employed for combustion comparison and calibration. For CFD resolution, a numerical mesh consisting of 3.4 million cells was used for the calculations, Fig. 1. The mesh represents only one-third of the entire section of the burner. Periodicity was established in all the side frontiers of the mesh in order to simulate the entire flow. The mesh was improved using Local Mesh Refinement in the downstream zone of the burner, just passed the nozzle. Preliminary characterization was conducted for a mesh independency analysis. Meshes with ~1.5, 3.4 and 7.5 million cells were also compared, with the intermediate cell providing

similar results to the finest case and 2/3s of the computation time for resolution. Residual values ranged from 10^{-4} to 10^{-9}.

Further analyses were performed using CHEMKIN-PRO for each condition, Table 1 and Fig. 2. A PREMIX reactor [26] and the equilibrium tool [27] were used to calculate the laminar flame speed (S_L) and adiabatic flame temperature (AFT), respectively. An adaptive grid of 1000 points was employed with mixture-averaged transport properties and trace series approximation. The objective was to better understand the discrepancy between models and address the most sensitive reactions to the production of important species such as NH2 and NO.
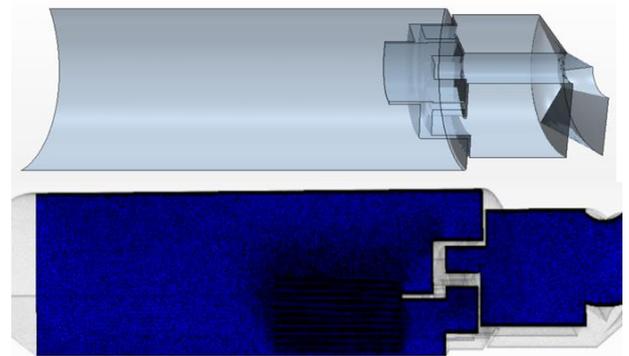
Fig. 1. Burner geometry and mesh.

Table 1. Boundary conditions.

Parameter	Value	Parameter	Value
Quartz Temperature	870 (T1), 890 (T2), 910 (T3) K	Blend	70-30 NH$_3$-H$_2$ (vol%)
Burner section	Symmetry (120°)	Mechanism	Okafor et al
Swirler walls	Adiabatic	Method	Segregated Flow
Inlet Velocity	2.5 m/s	Ignition Temperature	3000 K
Inlet Temperature	310, 410, 499 K	Turbulence	10%
Pressure	0.11 (P1), 0.14 (P2), 0.17 (P3) MPa	Walls	No-slip
Outlet Pressure	0.10, 0.13, 0.16 MPa	Swirl	1.50
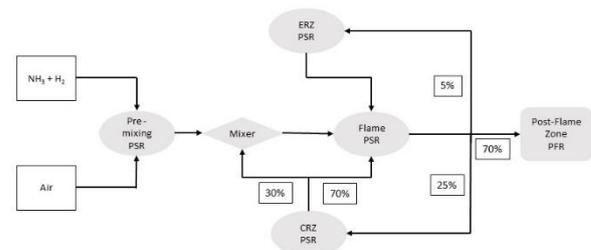
Fig. 2. Chemical reaction network.

3. Results and Discussion

Once the isothermal profiles were validated, Fig. 3, the combustion patterns were also compared with previous experiments, showing good correlation between the numerical and experimental cases, Fig. 4. However, it is emphasized that further experiments are required for a clearer validation, work that is ongoing.
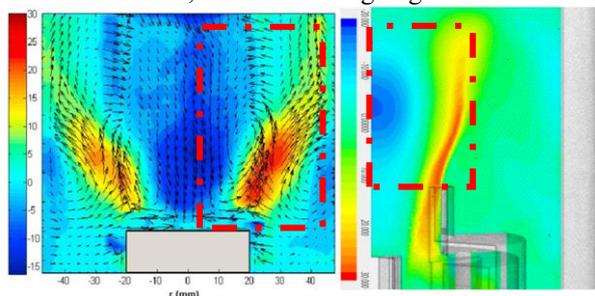

Fig. 3. Isothermal validation.
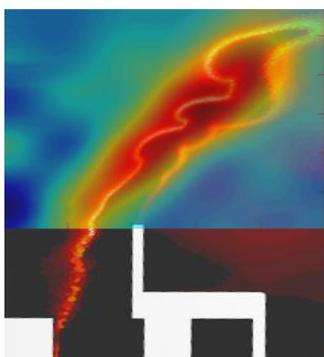
Fig. 4. Comparison with previous experiments.

Once resolved, the combustion results were initially analysed at atmospheric pressure. The highest chemical heat release denotes clear NH2 production peaks. Similarly, N2 shows correlated peaks with minor delay located withing the central recirculation zone, consequence of the reaction of NH2 with nitric oxide (NO) to produce the nitrogen molecule, a trend that repeats with H2O due to the reaction NH2+NO → N2+H2O. Similarly, NO and N2O show clear, positive trends with the production rates of amidogen, with all peaks slightly displaced within the central recirculation zone. This is an expected behaviour consequence of the high reactivity of NH2 and the high temperatures in this region, leading to the production of species such as O, OH and NH that impact on the production of nitrogen oxides via HNO, molecule well-known to spur the production of nitrogen oxides.

However, contrary to what was expected, NO2 is mostly consumed within these peaks, probably due to the high concentration of NH2 and high temperatures, leading to decomposition and recombination of nitrous oxides. On that line, molecules such as O and NH show peaks correlated to the highest point of production of NH2, as would be expected due to the increased reactivity of oxygen and the formation of OH that interacts with ammonia for the decomposition of the latter to form NH2. However, other radicals such as NNH and N2H3 also denote an increase in production with NH2. Whilst NNH

is known to be a molecule that is of great importance in the consumption of N and NO [28], its production under these conditions is two orders of magnitude lower than the production of NO, thus slightly contributing to the consumption of nitric oxides in this region. Moreover, N2H3, molecule that also shows opposite correlations, has received less attention. It must be emphasized that the latter shows a negative correlation to the production peaks of amidogen, thus acting as a specie whose consumption greatly impacts the formation of NH2. Due to the high reactivity of NH2, the correlation with residence time and vorticity, which are orders of magnitude greater than amidogen's chemical reaction rate, are not clear.

Further analyses were conducted at higher pressure and higher inlet temperature. Results denote how at different inlet temperatures and pressures a critical change in NH2 reactivity and chemical heat release occurs, Figs. 5 and 6. Furthermore, the size of the flame has also contracted at higher pressure with a thinner, more active reaction layer for the production of NH2. Interestingly, NH2 shows not only more production but also higher consumption ratios at higher environmental conditions, thus leading to higher NO emissions in the flame zone. This has been demonstrated experimentally elsewhere [4].
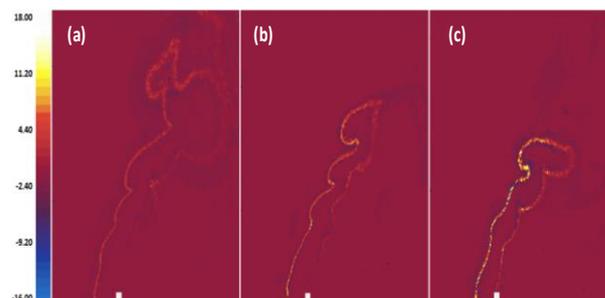

**Fig. 5.** Production rate of NH2. (a) T1/P1, (b) T2/P2, and (c) T3/P3 conditions. Units [kg/m3s].
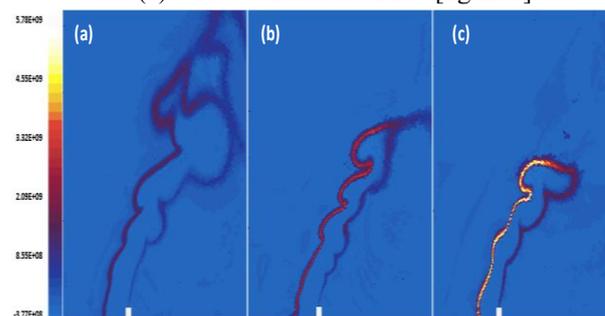
Fig. 6. Chemistry Heat Release rate. (a) T1/P1, (b) T2/P2, and (c) T3/P3. Units [J/m3s].

The higher increase in NO emissions is in accord with the high peaks of NH2 specific to the locations where amidogen reacts with pools of OH, O and H, thus delivering high NH concentrations that interact with OH to form HNO, precluding the production of NO. However, different to those cases at lower temperature and pressure, unburned ammonia and larger unconsumed pools of NH2 located in colder recirculation zones keep acting further downstream the flame zone in post-flame regions,

mitigating the overall production of NO emissions further.
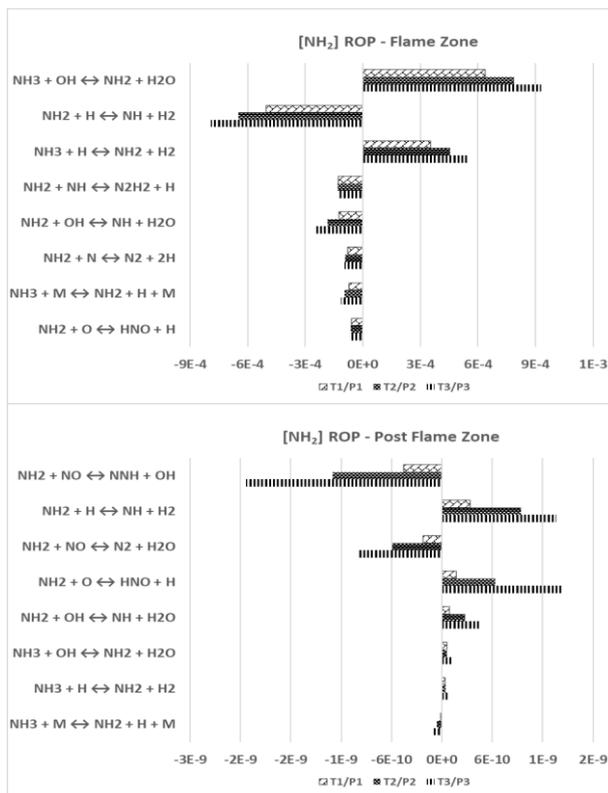
**Fig. 7.** Production of NH2 at the top) flame and bottom) Post flame zones.
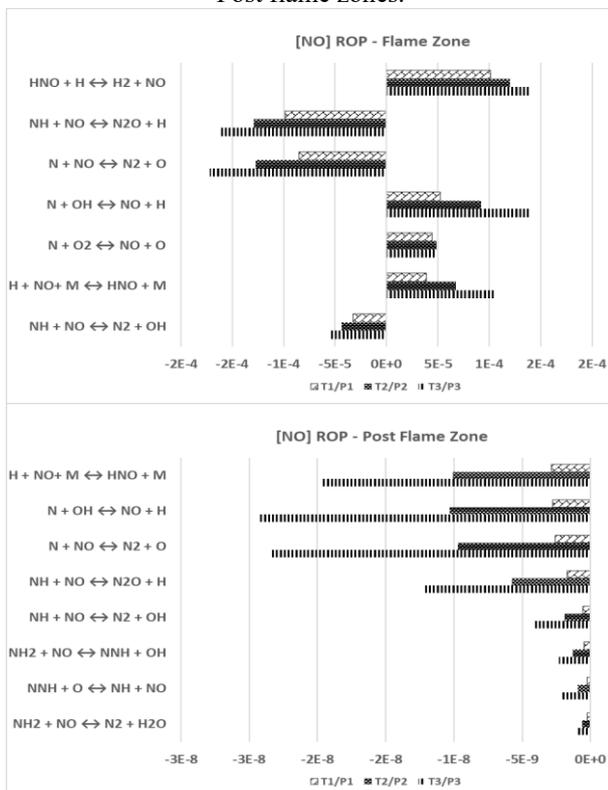
Fig. 8. Production of NO at the top) flame and bottom) Post flame zones.

The effect, discussed next, shows how the increase in pressure accompanied by higher inlet temperatures will promote NO at the flame but will also ensure that unreacted NHx can recombine with surrounding NOx molecules to mitigate emissions.

At the flame zone, NH3 reacts with H and OH radicals to produce NH2, which in turn reacts with H and OH radicals to produce NH. The major source of NO in the flame zone is from HNO, by reacting with H radicals and third bodies. HNO is mainly produced directly from NH2, or via NH radicals. The absolute rate of production increases with increasing temperature and pressure, due to higher kinetic energy.

At the post flame zone, NH2 produced from unburned NH3, consumes NO through the chain carrying reaction NH2+NO$\leftrightarrow$NNH+OH and the chain terminating reaction NH2+NO$\leftrightarrow$N2+H2O. Some of the NH radicals convert back to NH2 by reacting with H2 and H2O. As the temperature and pressure increases, substantial amount of HNO convert to NH2 by reacting with increasingly available H radicals. Vast amount of NO produced in the flame zone burn away at the high temperature post flame zone through various NO reburn mechanisms, as shown in Fig. 8 (bottom).

4. Concluding Remarks

A numerical analysis using RANS Complex Chemistry and CHEMKIN-PRO was validated and used to detail the reaction patters of various ammonia/hydrogen flames at various conditions. The results denote the impact of pressure and inlet temperature on the reactivity of the molecules, leading to an increase in NH2 production with shortened flames. Furthermore, NH2 radicals produced in the post-combustion zone considerably increase at more representative industrial conditions (i.e. higher pressure, high inlet temperature), thus showing that NO can be mitigated from the source. The statement justifies the use of ammonia/hydrogen in gas turbines for cleaner power generation. However, it was observed that further experiments are still required to validate the reaction mechanism employed at these higher atmospheric conditions, work that is encouraged amongst chemical mechanism developers.

References

[1] David WIF. Ammonia: zero-carbon fertilizer, fuel and energy storage. 2020.
[2] International Energy Agency. The Future of Hydrogen - Executive Report. 2019.
[3] Zamfirescu C, Dincer I. Using ammonia as a sustainable fuel. J Power Sources 2008. https://doi.org/10.1016/j.jpowsour.2008.02.097.
[4] Valera-Medina A, Gutesa M, Xiao H, Pugh D, Giles A, Goktepe B, et al. Premixed ammonia/hydrogen swirl combustion under rich fuel conditions for gas turbines operation. Int J Hydrogen Energy 2019;44:8615–26.

https://doi.org/10.1016/j.ijhydene.2019.02.041.

[5] Ezzat MF, Dincer I. Comparative assessments of two integrated systems with/without fuel cells utilizing liquefied ammonia as a fuel for vehicular applications. Int J Hydrogen Energy 2017.

[6] Kobayashi H, Hayakawa A, Somarathne KDKA, Okafor EC. Science and technology of ammonia combustion. Proc Combust Inst 2019;37:109–33.

[7] Valera-Medina A, Xiao H, Owen-Jones M, David WIF, Bowen PJ. Ammonia for power. Prog Energy Combust Sci 2018;69:63–102. https://doi.org/10.1016/j.pecs.2018.07.001.

[8] Okafor EC, Naito Y, Colson S, Ichikawa A, Kudo T, Hayakawa A, et al. Experimental and numerical study of the laminar burning velocity of CH4–NH3–air premixed flames. Combust Flame 2018;187:185–98. https://doi.org/10.1016/j.combustflame.2017.09.002.

[9] Valera-Medina A, Pugh DG, Marsh P, Bulat G, Bowen P. Preliminary study on lean premixed combustion of ammonia-hydrogen for swirling gas turbine combustors. Int J Hydrogen Energy 2017. https://doi.org/10.1016/j.ijhydene.2017.08.028.

[10] Valera-Medina A, Gutesa M, Xiao H, Pugh D, Giles A, Goktepe B, et al. Premixed ammonia / hydrogen swirl combustion under fuel-rich conditions for gas turbines operation. Proc Combust Inst 2018;under revi:8615–26. https://doi.org/10.1016/j.ijhydene.2019.02.041.

[11] Cornelius W, Huellmantel LW, Mitchell HR. Ammonia as an engine fuel. SAE Technical Paper; 1965.

[23] Pratt DT. Performance of ammonia-fired gas-turbine combustors. DTIC Document; 1967.

[12] Ichikawa A, Hayakawa A, Kitagawa Y, Kunkuma Amila Somarathne KD, Kudo T, Kobayashi H. Laminar burning velocity and Markstein length of ammonia/hydrogen/air premixed flames at elevated pressures. Int J Hydrogen Energy 2015;40:9570–8. https://doi.org/10.1016/j.ijhydene.2015.04.024.

[13] Lee JH, Kim JH, Park JH, Kwon OC. Studies on properties of laminar premixed hydrogen-added ammonia/air flames for hydrogen production. Int J Hydrogen Energy 2010;35:1054–64. https://doi.org/10.1016/j.ijhydene.2009.11.071.

[14] Pugh DG, Bowen PJ, Marsh R, Crayford AP, Runyon J, Morris S, et al. Dissociative influence of H2O vapour/spray on lean blowoff and NOx reduction for heavily carbonaceous syngas swirling flames. Combust Flame 2017;177. https://doi.org/10.1016/j.combustflame.2016.11.010.

[15] Vigueras-Zuniga M, Tejeda-del-Cueto M, Vasquez-Santacruz J, Herrera-May A, Valera-Medina A. Numerical Predictions of a Swirl Combustor Using Complex Chemistry Fueled with Ammonia/Hydrogen Blends. Energies 2020;13:288. https://doi.org/doi.org/10.3390/en13020288.

[16] Glarborg P, Miller JA, Ruscic B, Klippenstein SJ. Modeling nitrogen chemistry in combustion. Prog Energy Combust Sci 2018;67:31–68. https://doi.org/10.1016/j.pecs.2018.01.002.

[17] Mathieu O, Petersen EL. Experimental and modeling study on the high-temperature oxidation of Ammonia and related NOx chemistry. Combust Flame 2015;162:554–70. https://doi.org/10.1016/j.combustflame.2014.08.022.

[18] Tian Z, Li Y, Zhang L, Glarborg P, Qi F. An experimental and kinetic modeling study of premixed NH3/CH4/O2/Ar flames at low pressure. Combust Flame 2009;156:1413–26. https://doi.org/10.1016/j.combustflame.2009.03.005.

[19] Konnov AA. Implementation of the NCN pathway of prompt-NO formation in the detailed reaction mechanism. Combust Flame 2009. https://doi.org/10.1016/j.combustflame.2009.03.016.

[20] Lindstedt RP, Lockwood FC, Selim MA. Detailed Kinetic Modelling of Chemistry and Temperature Effects on Ammonia Oxidation. Combust Sci Technol 1994;99:253–76. https://doi.org/10.1080/00102209408935436.

[21] Miller JA, Bowman CT. Mechanism and modeling of nitrogen chemistry in combustion. Prog Energy Combust Sci 1989;15:287–338. https://doi.org/10.1016/0360-1285(89)90017-8.

[22] Li R, Konnov AA, He G, Qin F, Zhang D. Chemical mechanism development and reduction for combustion of NH3/H2/CH4 mixtures. Fuel 2019. https://doi.org/10.1016/j.fuel.2019.116059.

[23] Eriksson P. The Zimont TFC model applied to premixed bluff body stabilized combustion using four different rans turbulence models. Proc. ASME Turbo Expo, 2007. https://doi.org/10.1115/GT2007-27480.

[24] Baej H, Valera-Medina A, Bowen P, Syred N, O'Doherty T, Marsh R. Impacts on blowoff by a variety of CRZs using various gases for gas turbines. Energy Procedia, 2014. https://doi.org/10.1016/j.egypro.2014.12.301.

[25] Siemens. Complex Chemistry. Star-CCM+ Doc 2019. https://documentation.thesteveportal.plm.automation.siemens.coml (accessed September 24, 2019).

[26] Kee RJ, Grcar JF, Smooke MD, Miller JA, Meeks E. PREMIX: a Fortran program for modeling steady laminar one-dimensional premixed flames. Sandia Natl Lab Rep 1985.

[27] Gordon S, McBride BJ. Computer program for calculation of complex chemical equilibrium compositions rocket performance incident and reflected shocks, and Chapman-Jouguet detonations. Comput Progr Calc Complex Chem Equilib Compos Rocket Perform Incid Reflected Shock ChapmanJouguet Detonations 1971.

[28] Klippenstein SJ, Harding LB, Glarborg P, Miller JA. The role of NNH in NO formation and control. Combust Flame 2011;158:774–89. https://doi.org/10.1016/j.combustflame.2010.12.013.