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Fuel Rich Ammonia-Hydrogen Injection for Humidified Gas Turbines

Guteša Božo M^{a*}, Viguera-Zuniga MO^b, Buffi M^c, Seljak T^d, Valera-Medina A^e

^aTermoinžinjering d.o.o, Research and Development Department, Dragice Pravice 52, Zrenjanin, Serbia, email: milanagutesha@gmail.com

^bUniversidad Veracruzana, Juan Pablo II, Costa Verde, 94294, Mexico, email: mviguera@uv.mx

^cUniversity of Florence, Viale Morgagni 40, 50134, Florence, Italy, email: marco.buffi@unifi.it

^dUniversity of Ljubljana, Kongresni trg 12, 1000 Ljubljana, Slovenia, email: tine.seljak@fs.uni-lj.si

^eCollege of Physical Sciences and Engineering, Cardiff University, Wales, UK, email: valeramedinaa1@cardiff.ac.uk

Abstract

The use of new fuels and operating strategies for gas turbine technologies plays a relevant component for carbon emissions reduction and the use of sustainable energy sources. Among non-carbon fuels, hydrogen-based fuels have been proposed as one of the main strategies for decarbonisation of the power sector. Ammonia is a good representative of these fuels as it is carbon-free and the second largest chemical commodity, having been produced worldwide for more than a century from various energy resources, i.e. fossil fuels, biomass or other renewable sources. However, the use of ammonia as a fuel in industrial gas turbines brings some practical challenges directly linked to the final efficiency of these systems, especially when the latter are compared to current Dry Low Nitrogen Oxides technologies. Thus, this work covers a series of analytical, numerical and experimental studies performed to determine the efficiency of using ammonia/hydrogen blends in combination with humidified methodologies to deliver competitive systems for the use of ammonia-hydrogen power generation. The study was conducted using CHEMKIN-PRO reaction networks employing novel reaction chemical kinetics, in combination with bespoke analytical codes to determine efficiencies of systems previously calibrated experimentally. Finally, experimental trials using steam injection were carried out to determine potential of these blends. The novel results demonstrate that the use of humidified ammonia-hydrogen injection provides similar efficiencies to both Dry Low Nitrogen Oxides and humidified methane-based technologies ~30%, with flames that are stable and low polluting under swirling conditions, thus opening the opportunity for further progression on the topic.

Keywords: ammonia power, hydrogen blends, humidified gas turbine, alternative fuels.

Nomenclature

b	Fuel mass flowrate relative to the air mass flowrate at the combustion chamber inlet [-]	T	temperature [K]
c_p	specific heat at constant pressure [kJ/kgK]	T_o	the inlet compressor temperature [K]
h_{CC1}	is enthalpy of steam at the combustion chamber inlet [kJ/kg]	T_2	the outlet compressor temperature [K]
h_{CC2}	is enthalpy of steam at the combustion chamber outlet [kJ/kg]	T_{3t}	combustion products temperature at the turbine inlet [K]
h_{fuel}	specific enthalpy of fuel at combustion chamber inlet [kJ/kg]	T_{4t}	combustion products temperature at the end of the expansion [K]

L_c	specific work of compression [kJ/kg]	η_{cc}	the efficiency of a combustion chamber [-]
L_{GT}	plant specific work [kJ/kg]	η_{GTP}	the efficiency of a plant [-]
LHV	the lower heating value [kJ/kg]	η_m	the mechanical efficiency [-]
L_T	overall specific work of the expansion of the combustion products and cooling air mixture [kJ/kg]	η_{pc}	is the polytropic efficiency of a compressor [-]
\dot{m}_{cp}	combustion products mass flow [kg/s]	η_{pT}	is the polytropic efficiency of a turbine [-]
\dot{m}_{fuel}	fuel mass flow at the combustion chamber inlet [kg/s]	Π_c	the compressor pressure ratio [-]
\dot{m}_1	air mass flow at the compressor inlet [kg/s]	M	is the cooling air distribution factor [-]
\dot{m}_2	air mass flow at the combustion chamber inlet [kg/s]	q_{sup}	is the amount of supplied heat [kJ/kg]
M	is the cooling air distribution factor [-]	α	is the ratio of the vapor mass flow and fuel mass flow at the combustion chamber inlet [-]
p	pressure [Pa]	z	air mass flow for sealing relative to air mass flow at the compressor inlet [-]
R	the universal gas constant [J/molK]	δ	average relative error [%]
r_{air}	cooling air mass flow specified to compressor inlet mass flow [-]		

1. Introduction

A hydrogen economy has been in the sight of government, industry and research communities for decades. However, techno-economic barriers have always accompanied the transition to a hydrogen economy from an economy based on fossil fuels. Storage and distribution of hydrogen are clear examples of the challenges that the concept phases, with expensive, hard to handle infrastructures that would be required to properly store and distribute the chemical in an efficient way, excluding the expenses that will be needed to ensure its safe use. Thus, other chemicals have been proposed to support the transition to a hydrogen economy, chemicals that contain great quantities of hydrogen and can serve as energy vectors of a wide variety of renewable and conventional energy sources. One of these chemicals, ammonia, has been presented in the last few years as a promising medium for energy storage and distribution of hydrogen at cost-effective, easier to handle conditions [1], with studies that document its thermochemical storage potential [2]. Recently, ammonia has been recognised as a major player in the combustion field due to its unique properties [3]. Therefore, ammonia has been analysed for its implementation in a great variety of power generation devices. For example, studies have been conducted to displace diesel with wind-powered produced ammonia. Results have demonstrated competitive patterns to enable fuel exchange [4]. Therefore, the path to replace fossils with “green” ammonia as a sustainable fuel in internal combustion engines keeps progressing [5]. Another possible use of ammonia for power generation is for fuelling fuel-cells [6]. Ammonia can be used directly or indirectly (i.e. cracking the molecule and producing hydrogen) to produce combined power and heat. However, large power outputs are still impossible using these systems. Thus, another technology needs to evolve to enable large power densities in combination with the long storage periods that ammonia is capable of providing.

In the international context economies such as Japan, Fig. 1 [7], have incurred in complex studies and demonstration projects to set the foundations for the creation of a hydrogen economy. Economies such as the USA invest in programs such as REFUEL which will enable energy generated from domestic, renewable resources to increase fuel diversity in the

transportation and power sectors through cost-effective and efficient methods [8]. In the UK, companies such as Siemens, with support from the UK government, are participating in demonstration programs to show the potential of green ammonia and its reconversion to electricity using internal combustion engines [9]. Simultaneously, Oxford University has analysed ammonia-based energy storage systems integrated with renewable electricity generation in Islandic regions, showing the economic feasibility of producing ammonia for combined storage and fertilizing applications with current technologies [10]. Finally, and with a global interest in the use of ammonia for power, the International Energy Agency (IEA) has recently become a promoter of ammonia for a carbon-free future [11]. The Renewable Energy Division [12] has recognised that ammonia can be used to tap into stranded energy produced from renewable sources (wind, solar, tidal, etc.), and then be used to redistribute hydrogen product of electrolyzers connected to these systems. Thus, the interest in the topic increases constantly. Nevertheless, there is still a gap in understanding the use of more powerful systems to efficiently extract the energy from ammonia, a barrier that has stopped industry pursuing the use of ammonia at large scale.

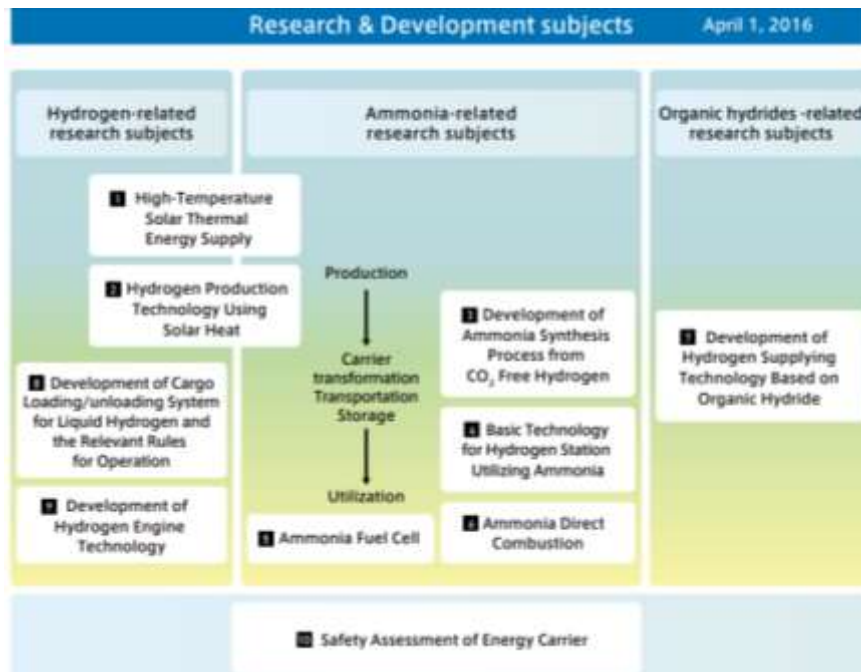


Fig. 1. Research and Development Subjects of Strategic Innovation Program (SIP), Japan [7].
Courtesy of the Japan Science and Technology Agency (JST)

Ammonia is a colourless gas with a sharp, penetrating odour, with very particular characteristics such as a boiling point of $-33.35\text{ }^{\circ}\text{C}$ and freezing point of $-77.7\text{ }^{\circ}\text{C}$. Further details of its chemical characteristics can be found elsewhere [13]. As a fuel, the combustion of ammonia is challenging due primarily to its low reactivity, but yields nitrogen gas and water, with a stoichiometric Air Fuel Ratio (AFR) of 6.06 by weight,



Ammonia is potentially hazardous to inhale. However, ammonia is readily detected by its odour, and being lighter than air it rapidly dilutes in a spill. Its ignition temperature is $650\text{ }^{\circ}\text{C}$. The energy content of ammonia is 5.2 kWh/kg (LHV) [14], making it feasible for energy distribution.

However, a viable energy system based on ammonia faces four primary barriers:

1. Carbon-free synthesis of ammonia,
2. Power generation from small to utility-scale size,
3. Public acceptance through safe regulations and appropriate community engagement,
4. Economic Viability for integration of technologies and green production of ammonia.

Out of these barriers, barrier (2) is the concern of this project. As previously depicted, current ammonia based systems are run in the range of 0.1-1.0MW power in general, consequence of the gap of knowledge behind the use of the chemical. Ammonia can potentially decarbonise large-scale power production with low NO_x emissions, having water as the main flue gas with easy handling of a hydrogen vector.

Therefore, the current analysis concentrates on the use of gas turbine engines to extract the energy from ammonia at large power outputs >5MW. Gas turbine technologies, being systems widely employed for large-scale power generation, are the obvious candidates for the production of energy at these power levels. Current technologies are based on the use of swirling flows that due to enhanced fluid dynamics produce coherent structures that can provide stabilisation and anchoring to the flame [15]. Although these technologies have been developed for the use of lean combustion conditions to mitigate NO_x production via Dry Low NO_x (DLN) technologies, employment of swirling flows in ammonia-fuelled systems has been an advantage to stabilise and anchor a fuel that presents low reactivity [16].

Initial ammonia gas turbine tests took place during the 1960's, a period in which the fuel was assessed for power and propulsion applications. Solar and Berkeley investigated through a 250 HP T-350 turbine the potential of the chemical for power generation [17]. Combustion tests were achieved with adequate combustion performance, although it was recognised that burning ammonia was much more complex and difficult than hydrogen due to the lower flame speed of ammonia [18]. Almost simultaneously, propulsion programs developed by NASA were evaluated using ammonia [19]. A Viking engine (XLR-10) used a mixture of ammonia and liquid oxygen which showed stable combustion patterns combined with easy handling fuelling [20]. Nevertheless, the program was discontinued due to lack of interest.

Currently, various groups around the globe are fundamentally assessing this technology by employing pure ammonia for laminar ammonia/air premixed flames [21]. Pure ammonia has been also analysed for turbulent ammonia/air premixed swirling flames [22]. Other groups are working with methane-ammonia blends developing mechanisms for simulation studies [23]. Ammonia/methane combustion has showed potential as a turbine fuel with moderate flame stability and high emissions, requiring lower swirl and different injection strategies [24]. Tian's mechanism proved, at the time, to be the most appropriate for further studies of ammonia/methane combustion [24]. However, this chemical path still includes a carbon source, i.e. methane, because other doping agents have been in the scope of researchers.

One of the promising solutions is to burn ammonia with hydrogen. Research has showed that efficient combustion can be achieved with relative high powers using hydrogen as doping agent [26]. Studies on premixed combustion of ammonia-hydrogen showed that some blends can produce flame velocities close to methane. However, other studies demonstrate that under lean conditions, hydrogen diffusivity is detrimental and under lean conditions tends to lead to boundary layer flashback [27]. Chemical kinetic mechanism studies have showed that the Mathieu mechanism yields one of the best agreements within experimental data ranges of

different ammonia/hydrogen concentrations, equivalence ratios, and pressures [28], although there are many studies going on that seek to improve these findings. Most of these studies have identified that the sweet spot of operation for low NO_x production is located in the rich combustion region between 1.05-1.31 equivalence ratios [3]. Thus, further work under these conditions is required.

Concurrently, humidified gas turbine cycles with the injection of steam into gas turbine combustion chambers are conceptualised to increase specific power output and efficiency [29]. Steam injection into gas turbine cycles has been done over decades, with studies focused on improving this technique [30]. Currently, humidified gas turbine cycles have been assessed for Combined Heat and Power (CHP) and Combined Cooling, Heat and Power (CCHP) applications [31]. The main aspects of using humidification techniques are to properly stabilise both the combustion regime (i.e. ignition, flame stability, etc.) and the impacts on other components of the cycle (i.e. compressor) [32]. However, once the technique is properly implemented, this is an effective way to improve a gas turbine's efficiency [33]. Steam injection can also be applied for optimization of CCHP systems that work under off-design conditions [34]. With increased electrical power outputs due to greater overall gas turbine plant efficiency, implementation of humidification in gas turbine cycles has a significant effect on the overall performance and emissions abatement compared to simple gas turbine cycles [35-36]. Moreover, one advantage of using steam injection is that more waste heat could be recovered from exhaust gases, waste heat that can be used to produce the required steam [37]. Furthermore, steam injection is 1.69 times more efficient in nitrogen oxide emission reduction than inlet air humidity increase. This is a consequence of flame temperature reduction, thus a decrease of thermal NO_x [38]. When hydrogen-based blends are employed, steam dilution inhibiting effects on the formation of the nitrogen oxides are more pronounced than many other techniques [39]. Further studies have investigated CO₂ recirculation with steam injection. Results have demonstrated improvements to the turbine efficiency on a specific fuel consumption basis by up to 5.5% [40]. Other authors have rated the increase of specific work of the expansion in the gas turbine at 2.95% for every 2% of steam to air ratio increase [41]. Therefore, presenting humidified injection is a well-known method to increase power that can be applied to highly hydrogenated fuel blends. However, no study exists on the effects and efficiency changes of ammonia fuelled systems.

However, there is no existing research to demonstrate the use of humidified conditions in the implementation of ammonia-based fuelled cycles. As previously shown, humidification can potentially increase efficiencies and power outputs. Implementation of steam injection in the ammonia combustion could deliver better overall economics from the use of ammonia. Combustion analyses of the implementation of humidified ammonia/hydrogen blends in gas turbine cycles are extremely scarce. As presented in this paper, the use of humidified conditions for ammonia/hydrogen flames shows potential for stable flames, low emissions and efficient humidified cycles.

Therefore, before exploring all the different alternatives for the use of ammonia blends for large power generation, barrier (4) also needs to be assessed in order to determine regimes that have the potential of providing competitive options for power generation that can not only reduce emissions and enable hydrogen utilisation for stable combustion, but also that are competitive to current fossil-based technologies which usually show efficiencies above 30%.

Therefore, this work explores the use of rich combustion of ammonia-hydrogen blends combined with humidified injection, thus employing previous research that shows good combustion regimes under rich conditions combined with higher power outputs with humidification techniques. A series of analytical, numerical and experimental trials have been conducted to demonstrate the feasibility of using these blends for low emission, stable combustion in combination with efficiency studies that show high efficiency profiles, thus tackling barriers (2) and (4) as above. The novel results inform on the type of blends that can be used to raise efficiency whilst minimizing emissions with ammonia-based blends, opening opportunities for further studies on stability, operability and techno-economic feasibility analyses of the concept. Moreover, this paper also denotes some of the technical challenges that might appear in the use of these blends, challenges related to the corrosive atmospheres created by diluted ammonia or nitrogen oxide emissions. These are points also addressed in this script. To the knowledge of the authors, there is no literature on this particular subject, with findings that can be applied for further progression on the use of ammonia-based gas turbines.

2. Materials and Methods

A numerical model based on chemical kinetics was evaluated to deliver results that would be employed in a calibrated analytical model of a Brayton Cycle. The latter was evaluated using air-methane lean conditions and compared to a humidified rich ammonia-hydrogen blend. Finally, results were complemented with experimental trials that demonstrated the feasibility of using humidified rich ammonia-hydrogen blends. Results denoted several technical aspects that require further studies to progress on the subject.

2.1. Chemical-kinetic numerical model

A 1D simulation was conducted using Chemical Reactor Network (CRN) modelling to determine the species and conditions of the chemical products during the combustion phase of the gas turbine cycle to include them in the cycle analyses. The used CRN was formed by two clusters, Fig. 2. The first cluster represents the swirling flame with a central recirculation zone (CRZ) whose recirculation was set at 20%. Recirculation strength was approximated from previous experimental campaigns using similar burners [42]. The second cluster uses a single Plug Flow Reactor for post-flame (secondary zone) processes along a 0.10 m duct. Simulations were conducted using CHEMKIN-PRO. An inlet temperature of 567K and 9.67 bar pressure, inlet conditions of a reference gas turbine employed for this study, were adopted for all performed calculations. For the study, a 70%NH₃-30%H₂ (vol%) blend was used at 1.20 equivalence ratio, as this condition showed the best emissions performance in previous campaigns [23]. The model was calibrated to previous experiments [27] in order to determine heat losses that mainly accounted to the primary combustion zone. Results were compared to a Dry Low NO_x (DLN) condition at 0.65 equivalence ratio using methane as fuel, condition that is widely used in industrial units to reduce NO_x, unburned hydrocarbons (UHC) and CO emissions.

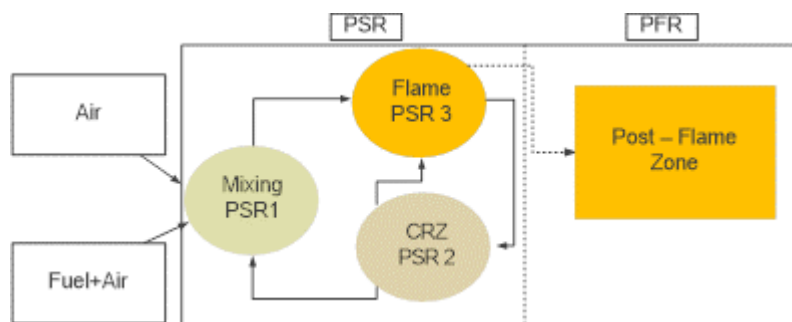


Fig. 2. Chemical Reactor Network for the numerical simulation of the combustion chamber

To study ammonia/hydrogen combustion in gas turbines, a detailed chemical-kinetics mechanism which can comprehensively validate the combustion properties under high pressure conditions was required. Mathieu's mechanism was built for shock-tube experiments of ammonia ignition delay time measurements under pressure conditions of up to 30 atm [43]. Therefore, the chemical kinetic model proposed in the present work was mostly based on recent work performed by Mathieu under high-pressure conditions. To improve mechanism performance on NO_x emissions and burning velocity prediction, several reactions were modified. The modifications of rate constants were performed based on contribution rate calculations and sensitivity analyses. To develop a kinetic mechanism which can comprehensively validate different combustion properties of NH₃/H₂ fuel blends, NO_x emission, laminar burning velocity and ignition delay times were all taken into consideration in this study. Further details of the model are given in [44]. It must be emphasized that although the model shows good correlations, it has been demonstrated that it still presents inaccuracies with experimental trials. Therefore, further studies are underway by several groups to improve ammonia-based chemical kinetic models [47]. This is a concept that is under continuous development and requires further attention.

2.2. Thermodynamic simulation model

An analytical, thermodynamic model was employed considering the processes of non-adiabatic expansion and cooling in the turbine as a whole. The basic assumption of the method is the continual distribution of the cooling air along the gas turbine, with the computation of the expansion process of the combustion gases and cooling air separately. This method was selected as the 'reference method' [45]. Verification of the thermodynamic model was based on the comparison of model predictions against the manufacturer's data for the reference gas turbine [46]. For the thermodynamic model, it was necessary to make some adjustments for correspondence to the actual gas turbine plant [46].

First adjustment was based on the introduction of steam injection, as done in the reference gas turbine plant. This step was not considered in the basic reference method. This adjustment to the thermodynamic model is marked as the simulation model S1. The second adjustment, model S2, was developed to enhance S1 model by considering the variation of the polytropic efficiency due to operational regime changes. The reference method only considers full load operation regimes with a constant value of the gas turbine polytropic efficiency. For verification purposes, it was necessary to analyse both design and off-design operation regimes. Finally, the third adjustment, model S3, considered the fuel enthalpy influence on the flow behaviour, heat transfer and energy transformation. The fuel enthalpy was not considered in

the basic reference model, therefore it was integrated into the simulation model for high accuracy purposes.

For the designed operation mode, the specific compression work relative to the compressor inlet air mass flowrate is treated as adiabatic and polytropic, and is calculated as a function of compressor pressure ratio, air temperature at the compressor inlet and specific heat by the following equation [45],

$$L_C = c_{p_{air}} \Big|_0^2 \cdot T_0 \cdot \left(\Pi_C^{(1/\eta_{pC}) \cdot (R_{air}/c_{p_{air}} \Big|_0^2)} - 1 \right) \quad (1)$$

In the case of polytropic compression, the impact of the compressor construction is included through the polytropic compression efficiency, η_{pC} . Unlike the isentropic efficiency, the compression polytropic efficiency is not a function of pressure ratio, therefore it is suitable for off-design operation analyses, which consider compression at variable pressure ratios.

The total temperature of the air at the compressor outlet T_{2t} is calculated as a function of air temperature at the compressor inlet T_0 , compressor pressure ratio, and thermodynamic irreversibilities during compression and working fluid characteristics by the equation [45],

$$T_{2t} = T_0 \cdot \Pi_C^{(1/\eta_{pC}) \cdot (R_{air}/c_{p_{air}} \Big|_0^2)} \quad (2)$$

Fuel mass flowrate relative to the air mass flowrate at the combustion chamber inlet b is determined from the combustion chamber energy balance equation in the following form [32],

$$b = \frac{\dot{m}_{fuel}}{\dot{m}_2} = \frac{c_{p_{cp}} \Big|_0^3 \cdot (T_{3t} - T_0) - c_{p_{air}} \Big|_0^2 \cdot (T_{2t} - T_0)}{\eta_{CC} \cdot LHV - c_{p_{cp}} \Big|_0^3 \cdot (T_{3t} - T_0)} \quad (3)$$

The supplied heat specified by the air mass flowrate at the compressor inlet is a function of the low heating value of the fuel and coefficient b ,

$$q_{sup} = b \cdot \frac{\dot{m}_2}{\dot{m}_1} \cdot LHV \quad (4)$$

Air for combustion and cooling air are simultaneously compressed in the compressor. It is assumed that the cooling air distribution along the gas turbine is continuous. In case of the non-adiabatic expansion it is necessary to determine the cooling air distribution in the gas turbine. The overall specific work of the expansion of the combustion products and cooling air mixture is expressed by the following equation:

$$L_T = c_{p_{cp-air}} \Big|_3^4 \cdot \frac{(1-z-r_{air}) \cdot (1+b) \cdot T_{3t} + r_{air} \cdot M \cdot T_{2t}}{(1-z-r_{air}) \cdot (1+b) + r_{air}} \cdot \left(1 - \Pi_T^{-\eta_{pT} \cdot R_{cp-air}/c_{p_{cp-air}} \Big|_3^4} \right) \quad (5)$$

The temperature at the end of the expansion is,

$$T_{4t} = T_0 + \frac{(1-z-r_{air}) \cdot (1+b) \cdot c_{p_{cp}} \Big|_0^3 \cdot (T_{3t} - T_0) - r_{air} \cdot c_{p_a} \Big|_0^2 \cdot (T_{2t} - T_0) - [(1-z-r_{air}) \cdot (1+b) + r_{air}] \cdot L_T}{[(1-z-r_{air}) \cdot (1+b) + r_{air}] \cdot c_{p_{cp-air}} \Big|_0^4} \quad (6)$$

Finally, the efficiency of the entire gas turbine plant is defined as,

$$\eta_{GTP} = \frac{(L_T - L_C) \cdot \eta_m}{q_{sup}} \quad (7)$$

Where η_{GTP} is efficiency of the entire gas turbine plant [-], η_m is mechanical efficiency [-].

In the reference gas turbine plant, steam is introduced into the combustion chamber. As previously stated, the basic mathematical model [45] does not consider steam injection, and so it is necessary to expand the thermodynamic model and include the impact of steam on the combustion process. Therefore, the first adjustment of the base thermodynamic model is the introduction of steam impacts through the ratio of steam and fuel mass flow rates at the combustion chamber inlet.

As mentioned, the enhanced version of the thermodynamic model considers the variation of the turbine polytropic efficiency due to operational regime changes. Variation of the polytropic efficiency due to operational regime changes is not analysed sufficiently to date. Drawing upon preliminary analyses and comparisons with reference data [46], it was concluded that the assumption of a constant polytropic efficiency regardless operating regime change needed to be replaced. Mass flowrates changes of combustion products through the gas turbine result in ‘off-design’ operation, and hence variation of the turbine polytropic efficiency. Therefore, the second adjustment of the base model was the introduction of the variable polytropic gas turbine efficiency. Polytropic efficiency variation as a function of mass flowrate of combustion products was determined using the following equation:

$$\eta_{pT} = k_1 \cdot \dot{m}_{cp}^2 + k_2 \cdot \dot{m}_{cp} - k_3 \quad (8)$$

This polytropic efficiency equation is defined as a function of the combustion products mass flowrate, consistent with the gas turbine plant reference data [46]. Equation (8) shows acceptable accuracy for the reference gas turbine using the following coefficient values $k_1 = -1.0372$, $k_2 = 32.179$ and $k_3 = -248.68$. It is recognized that application of this polytropic efficiency equation to different gas turbine types should be further analysed. However, for this study and for comparison with the reference gas turbine, the results provided good agreement, as presented in the following sub-section.

In order to better understand the influence of fuel enthalpy, this parameter was introduced into the thermodynamic model for simulation of the flow behaviour, heat transfer and energy transformation, i.e. third adjustment. After implementing the adjustments in the thermodynamic model, coefficient b is calculated using the following equation,

$$b = \frac{\dot{m}_{fuel}}{\dot{m}_2} = \frac{c_{p_{cp}} \Big|_0^3 \cdot (T_{3t} - T_0) - c_{p_{air}} \Big|_0^2 \cdot (T_{2t} - T_0)}{\eta_{CC} \cdot (LHV + h_{fuel}) - c_{p_{cp}} \Big|_0^3 \cdot (T_{3t} - T_0) \cdot (1 + \alpha) - \alpha \cdot (h_{CC2} - h_{CC1})} \quad (9)$$

The heat supplied, specified by air mass flowrate at the compressor inlet, is a function of the lower heating value of the fuel and coefficient b with introduction of fuel enthalpy and adjustment for steam injection,

$$q_{sup} = \frac{1}{\eta_{CC}} \cdot \left[(1 - z - r_{air}) \cdot (1 + b \cdot (1 + \alpha)) \cdot c_{p_{cp}} \Big|_0^3 \cdot (T_{3t} - T_0) - (1 - z - r_{air}) \cdot c_{p_{air}} \Big|_0^2 \cdot (T_{2t} - T_0) - \alpha \cdot b \cdot (1 - z - r_{air}) \cdot (h_{CC2} - h_{CC1}) \right] - b \cdot (1 - r_{air}) \cdot h_{fuel} \quad (10)$$

The overall specific work of the expansion of the combustion products and cooling air mixture, after adjustments, is expressed by the following equation,

$$L_T = c_{p_{cp-air}} \Big|_3^4 \cdot \frac{(1-z-r_{air}) \cdot (1+b \cdot (1+\alpha)) \cdot T_{3t} + r_{air} \cdot M \cdot T_{2t}}{(1-z-r_{air}) \cdot (1+b \cdot (1+\alpha)) + r_{air}} \cdot \left(1 - \Pi_T^{-\eta_{pT} \cdot R_{cp-air} (3-4) / c_{p_{cp-air}} \Big|_3^4} \right) \quad (11)$$

After implementation of the model adjustments, the temperature at the end of the expansion process is calculated by,

$$T_{4t} = T_0 + \frac{(1-z-r_{air}) \cdot (1+b \cdot (1+\alpha)) \cdot c_{p_{cp}} \Big|_0^3 \cdot (T_{3t} - T_0) - r_{air} \cdot c_{p_{air}} \Big|_0^2 \cdot (T_{2t} - T_0) - [(1-z-r_{air}) \cdot (1+b \cdot (1+\alpha)) + r_{air}] \cdot L_T}{[(1-z-r_{air}) \cdot (1+b \cdot (1+\alpha)) + r_{air}] \cdot c_{p_{cp-air}} \Big|_0^4} \quad (12)$$

2.3. Experimental studies

Experiments were performed at the Gas Turbine Research Centre (GTRC). The GTRC is a facility which consists of two major combustion rigs each designed for detailed investigation of combustion and emissions characteristics at representative gas turbine conditions. For the present project a High Pressure Optical Chamber (HPOC) was fitted with a generic premixed swirl burner, Fig. 3.

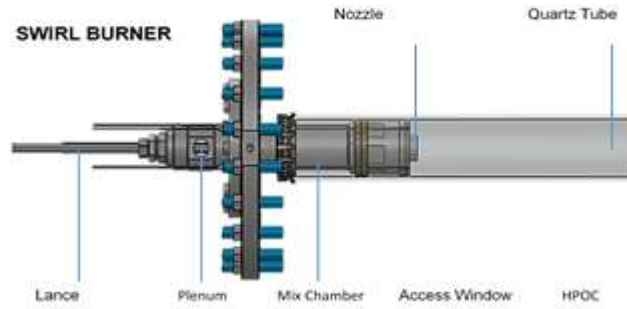


Fig. 3. Generic Swirl burner for detailed investigation of combustion and emission characteristics using representative gas turbine systems

The campaign was performed with a 70%NH₃-30%H₂ (%vol) blend at 1.2 equivalence ratio, condition that has previously demonstrated relatively low NO_x emissions and good stability [47]. Further tests were conducted at various steam flowrates, ranging from 0.0 to 1.0 g/s (0 to 72% Steam/Fuel ratio, mass). Test points were evaluated at a power output of 39.3kW under atmospheric pressure. High inlet temperatures of 400K and 500K, representative of industrial gas turbines, were employed. No bypass was used to avoid dilution of emissions.

An integrated Signal Instruments equipment comprising several analysers was used. The system is comprised of a heated vacuum chemiluminescence analyser (Signal 4000VM) to quantify NO_x concentrations, calibrated to 37.1 ppm NO and 1.9 ppm NO₂. Unfortunately, due to connection failures in the gas lines, NH₃ emissions were impossible to obtain. However, discussion on this emission is based on posterior works performed with this configuration. These can be found elsewhere [49]. Measured errors have been account to ~5%.

Finally, pools of chemicals were formed at the exit of the HPOC, consequence of condensation of the product gases. Samples of these chemicals were analysed to determine pH via a Seven Excellence pH multimeter with a ± 0.3 variance during the measurements.

3. Results

First sets of data are results using the chemical-kinetic numerical model for analysis of humidified ammonia-hydrogen blends combustion. The following sub-section refers to the thermodynamic model and its numerical predictions on a gas turbine cycle running on humidified ammonia/hydrogen blends previously resolved using the chemical-kinetic model. In addition to chemical-kinetic and thermodynamic model results, experimental results of humidified ammonia-hydrogen blends combustion are presented.

3.1. Chemical – kinetics numerical model

It was observed in the numerical results that the use of DLN technologies generates colder flames, Fig. 4, accompanied by vast amounts of hydrogen, which along the secondary zone is consumed due to the remaining hot oxygen, bringing down the hydrogen molecule in one order of magnitude at the discharge point, Fig. 5. Similarly, low NO are produced, characteristic pattern of burning methane under lean premixed conditions.

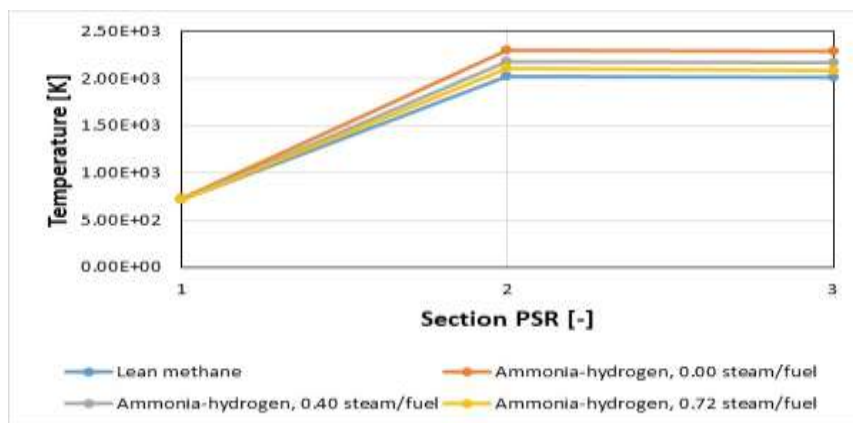


Fig. 4. Lean methane (0.65) flames are colder than rich ammonia-hydrogen flames due to excess air, thus mitigating more efficiently thermal NO_x.

On the other hand, Figs. 6 to 8 show the effect caused by the use of steam injection in various ammonia/hydrogen scenarios. Figure 6, with null steam injection, shows the complete combustion of NH₃ by the discharge point, with NO emissions close to 0.001 molar fraction. Interestingly, hydrogen concentration is relatively high compared to other cases. It must be emphasized that complete consumption of NH₃ might be related to inaccuracies of the reaction model, a problem that researchers are currently trying to solve [48] and which is out of the scope of this work.

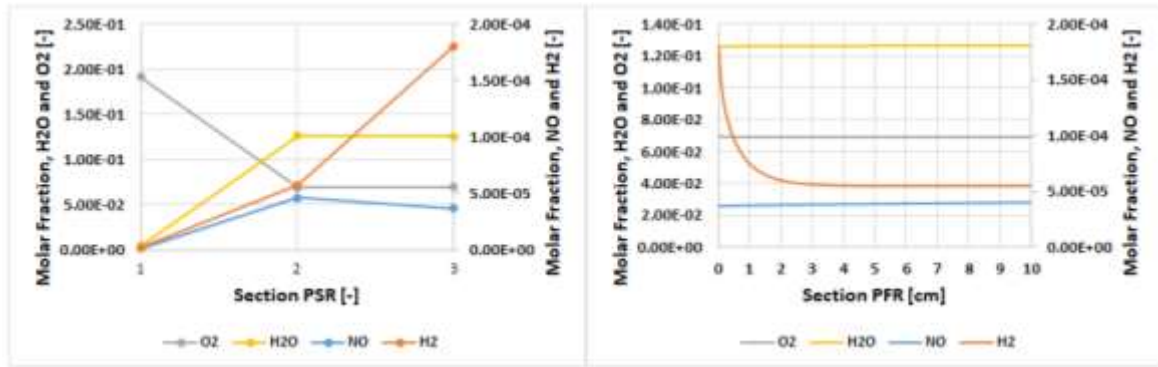


Fig. 5. Simulation using DLN (0.65 equivalence ratio-methane), pressurised, high temperature inlet conditions. Flame temperature $\sim 2015\text{K}$

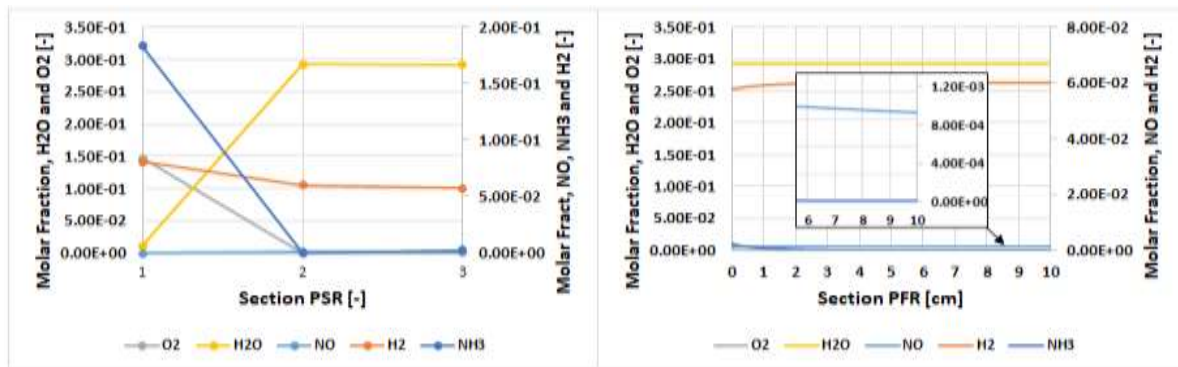


Fig. 6. Simulation using ammonia-hydrogen at 1.2 equivalence ratio, pressurised, high temperature inlet conditions. Flame temperatures $\sim 2300\text{K}$

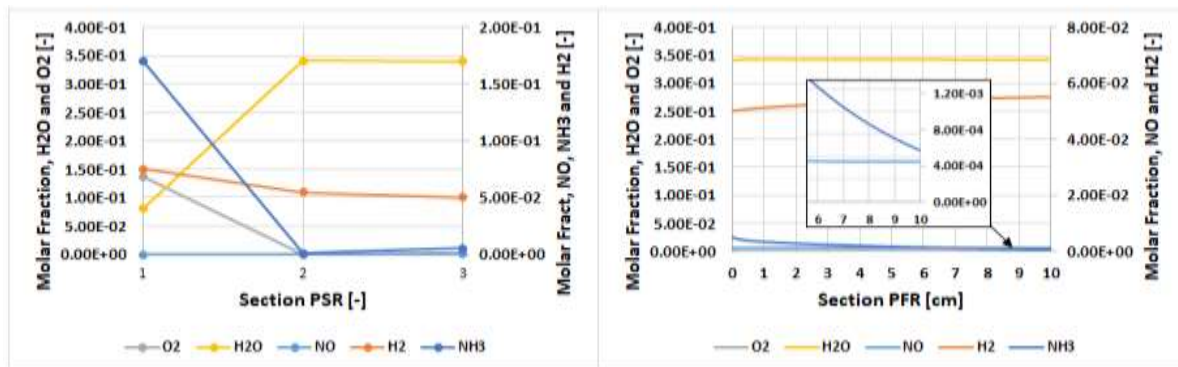


Fig. 7. Simulation using ammonia-hydrogen at 0.40 Steam/Fuel ratio (mass), 1.2 equivalence ratio, pressurised, high temperature inlet conditions. Flame temperature $\sim 2185\text{K}$

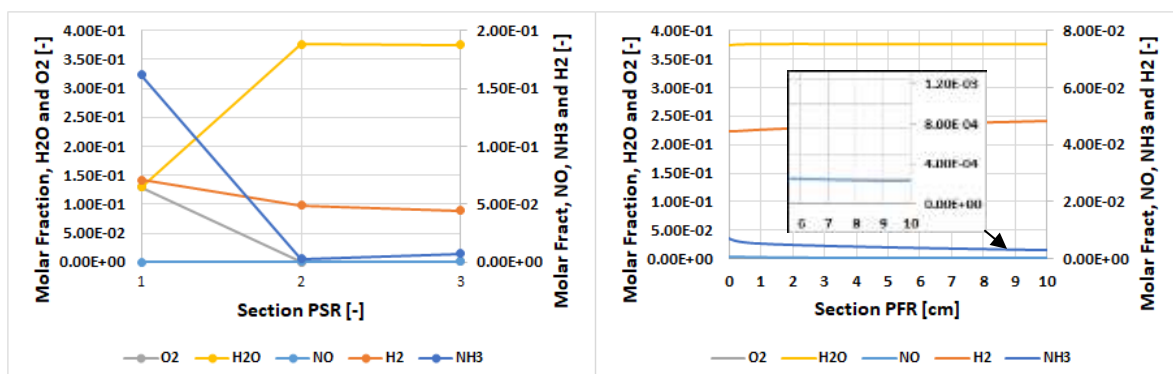


Fig. 8. Simulation using ammonia-hydrogen at 0.72 Steam/Fuel ratio (mass), 1.2 equivalence ratio, pressurised, high temperature inlet conditions. Flame temperature ~2105K

As steam is injected, Fig. 7 and 8, NH_3 is less consumed at the flame front, leaving traces of the chemical that are partially consumed in the secondary zone. Accompanying this effect is the reduced amount of hydrogen that is obtained for post-combustion. However, NO are considerably reduced compared to the case without water injection.

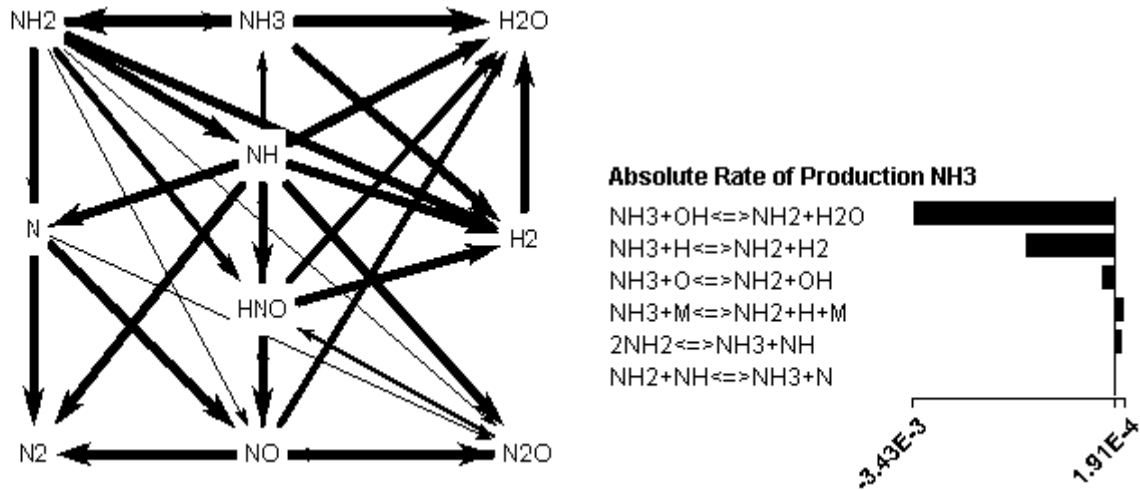


Fig. 9. Left) Reaction path and, right) Absolute Rate of Production of NH_3 , respectively. Ammonia-hydrogen with 0.40 Steam/Fuel ratio injection

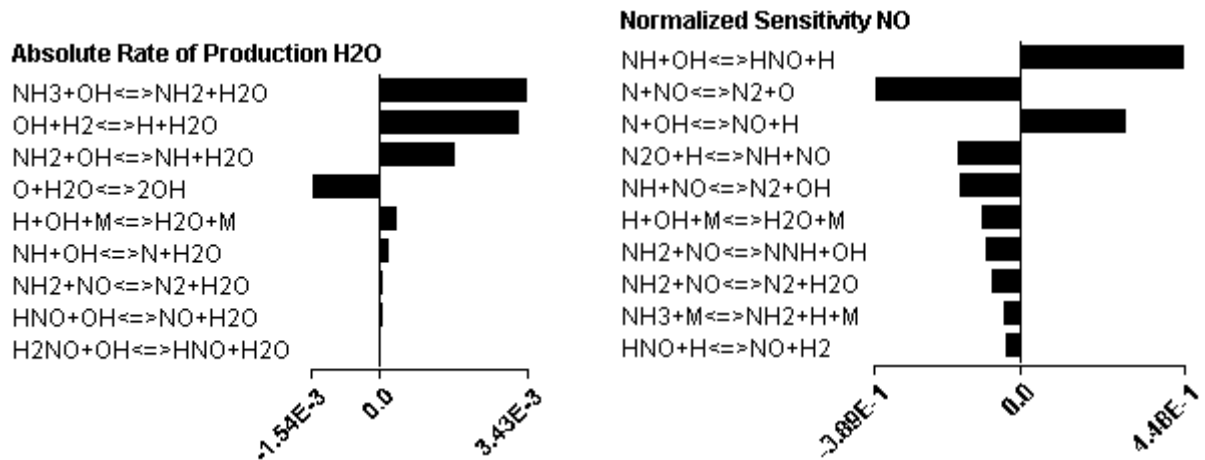


Fig. 10. Left) Absolute Rate of Production of H_2O and, right) Normalized Sensitivity of NO, respectively. Ammonia-hydrogen with 0.40 Steam/Fuel ratio injection

In order to understand the chemical reaction behind this effect, the case with ammonia-hydrogen at a steam/fuel ratio of 0.40 was analysed, Figs. 9 and 10. As can be observed from the reaction path, Fig. 9 (left), ammonia is essentially converted into water and NH_2 , which due to the production of OH radicals will eventually lead to NO through the reaction path $\text{NH} \rightarrow \text{HNO}$. However, there will be also an excess of O and H radicals in the combustion process as a consequence of the split of water molecules, all which have negative impact in the production of NO. Moreover, extra production of OH from water will also lead to more NH_2 , Figs. 9(right) and 10(left), with its impact on the reduction of nitrogen oxides. If the impact of all these radicals, i.e. O, H and NH_2 , is gathered to assess NO reduction, Fig. 10 (right), the

resultant effect will be greater than the impact from reactions such as $\text{NH} + \text{OH}$ or $\text{N} + \text{OH}$ which lead to NO formation. Finally, combustion temperatures will also be affected due to steam injection, thus reducing thermal NO_x as well as the splitting of NH_3 and consequently the production of NO via fuel bound production, augmenting the remnants of ammonia while mitigating emissions. In order to compare the case without steam addition, please refer to recent work performed by the authors [47].

3.2. Thermodynamic Model Testing and Verification

The thermodynamic model was used for analyses of the main parameters of the gas turbine plant running at various operating conditions (for the design regime with 100% load and for off-design regimes from 90% to 10% load). Analyses of the model sensitivity were done for the following parameters: supplied heat, power, heat rate, gas turbine plant efficiency and temperature of the combustion products at the gas turbine outlet.

Validation of the thermodynamic model was performed using the same input parameters employed during the test campaign of the reference gas turbine plant [46]. An aeroderivative humidified single – shaft gas turbine delivering 3,900 kW_e was analysed. Measurements were obtained with natural gas (i.e. LHV = 47.497 MJ/kg at 15°C and $\alpha = 0.4 \text{ kg/kg}_{\text{fuel}}$) [46]. In addition to the reference gas turbine plant data, the following values were also quantified: compressor pressure drop, combustion chamber pressure drop, polytropic efficiencies of the compressor and turbine, the combustion efficiency and mechanical efficiency. Ambient temperature and pressure were adopted for all calculations performed.

For testing and verification of the thermodynamic model, three simulations were undertaken, S1, S2 and S3 as above. The main parameters of the gas turbine plant that were calculated through all three simulations are compared to manufacturer's gas turbine data (M) [46]. The variation of the main parameters is presented as a function of gas turbine plant operating regimes, Fig. 11 – 15.

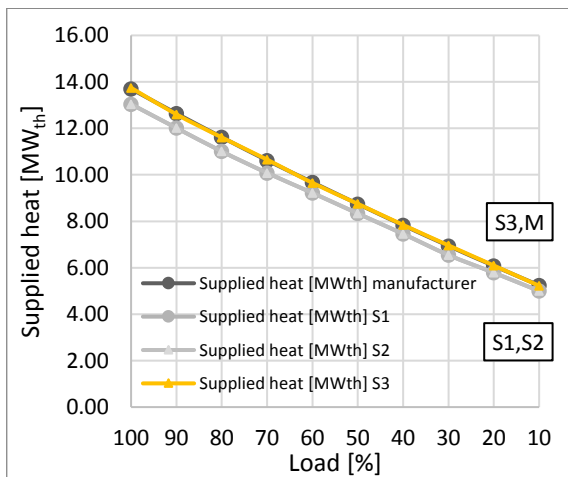


Fig 11. Supplied heat [MW_{th}] values as a function of the operation load with natural gas combustion

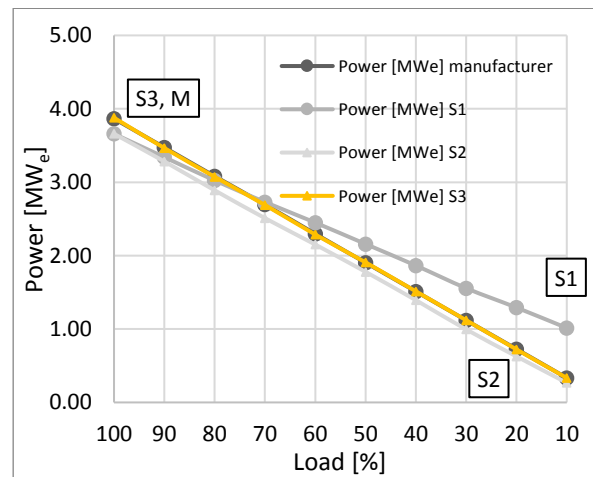


Fig. 12. Generated power [kW_e] values as a function of the operation load with natural gas combustion

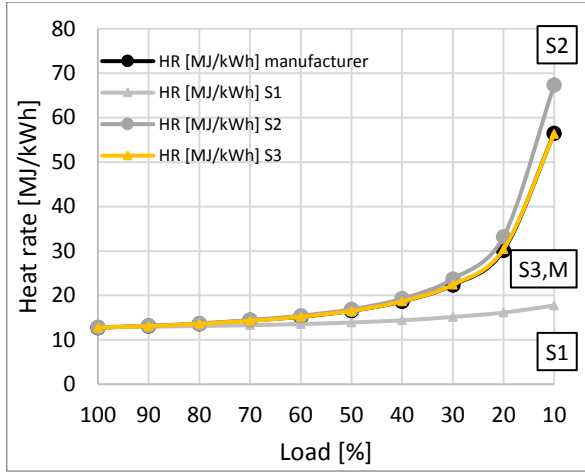


Fig. 13. Heat rate [MJ/kWh] values as a function of the operation load with natural gas combustion

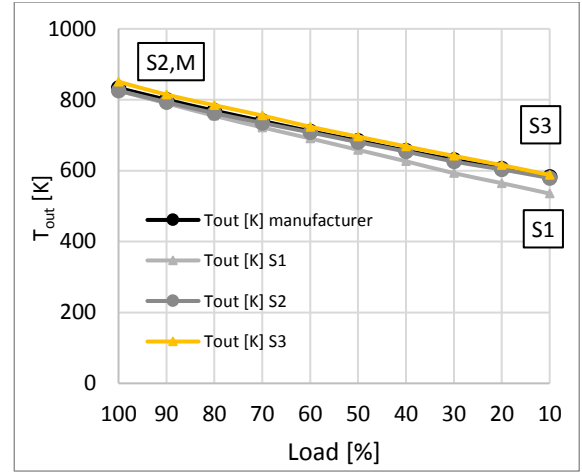


Fig. 14. T_{out} [K] values as a function of the operation load with natural gas combustion

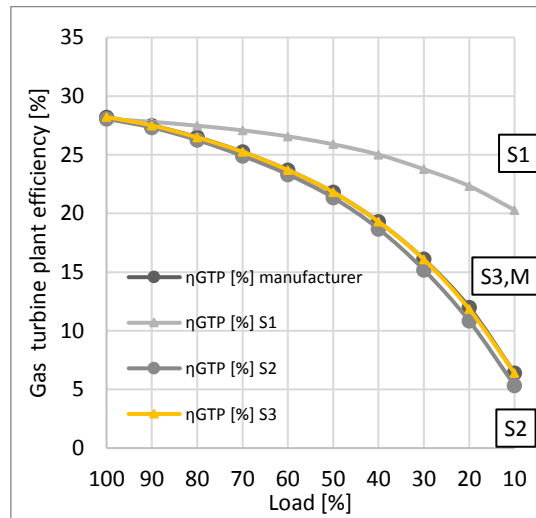


Fig. 15. Gas turbine plant efficiency [%] values as a function of the operation load with natural gas combustion

Comparative analyses show that the basic mathematical method [45] is not good at predicting the gas turbine performance under off-design regimes, especially for predicting the gas turbine efficiency and heat rate with value of δ (average relative error) equal to 20.84% and 42.52%, respectively. A comparison of the results obtained using S2 and S1 shows significant improvement of the model accuracy after adding polytropic efficiency variations with operating regime changes. Notwithstanding the achieved improvement, the accuracy level is still unacceptable. Finally, by comparing the results obtained from the S3 with those of S2, it can be concluded that the introduction of fuel enthalpy in the combustion chamber energy balance provides simulation results with significantly less errors compared to the experimental values [46]. The level of accuracy of the results of the S3 is acceptable, with very low δ values for all analysed operating regimes, i.e. supplied heat 0.26%, generated power 0.27%, heat rate 0.22%, gas turbine outlet temperature 1.74% and gas turbine plant efficiency of 0.18%. Thus, the curves of these parameters approximately match those of the reference data [46], as shown

in Figures 11 - 15. Therefore, the modified thermodynamic model provided the confidence to be used for the off-designed conditions of the current study.

3.3. Cycle analyses

The modified thermodynamic model was then used to compare the efficiency of the humidified ammonia/hydrogen cycle with the efficiency of both a DLN cycle operating with methane at 0.65 equivalence ratio and a humidified methane-fuelled cycle at full load. The first step of the cycle analysis was to define the power output at which the analysis needed to be performed. Fuel flowrate was restricted due to the calibration limit; therefore 0.367 kg/s of a 70-30% (vol%) ammonia-hydrogen blend was used as inlet parameter. The amount of steam injected into the combustion chamber was determined based on the reference gas turbine plant at a ratio of 0.4 kg/kg_{fuel}. Thus, the introduced amount of steam was 0.147 kg/s for the ammonia/hydrogen cycle. To keep rich combustion conditions at 1.2 equivalence ratio, air was supplied at 2.260 kg/s. For the DLN cycle, the analysis was performed with a total fuel mass flowrate of 0.207 kg/s and an air flowrate of 5.480 kg/s, ensuring dry low NO_x conditions at 0.65 equivalence ratio. These conditions allowed comparison between blends at 10.4MW heat. Finally, a 100% load using methane and premixed combustion was simulated, as this case used humidified conditions and the calibration of the thermodynamic mathematical model. Supplied heat was set at 14.4MW, with 0.288 kg/s fuel, 0.115 kg/s steam and 14.99 kg/s air.

Results from the cycle based on the DLN methane-fuelled combustor predict efficiencies of ~19.35%, i.e. with a system designed to run at higher fuel flowrates and power, having air in the combustion primary zone accounting ~37% of the total available air flowrate, thus producing turbine inlet temperatures of 1275K.

In parallel, initial analyses demonstrated that the use of dry ammonia-hydrogen delivered efficiencies ~9.77%. This was caused by high dilution of the combustion products, as only 15% of air was used for the combustion process, while the remaining 85% was employed for the secondary, dilution zone. Similarly, the turbine inlet temperature for the humidified ammonia/hydrogen cycle produced combustion products of only 880K as a consequence of the excessive dilution that occurs at the secondary combustion zone, similar to the dry case, phenomenon needed to keep rich combustion conditions. However, specific heats of the humidified fuel blend combined with the combustion products of the process are significantly higher than those for the reference gas turbine plant at the simulated temperatures. Therefore, the simulation of the ammonia/hydrogen cycle with steam injection predicts overall efficiencies of ~28.59% for 10.4MW supplied heat. These values are similar to those obtained in the simulations of the humidified cycle at full load using methane with efficiencies of ~28.20%.

The rationale behind these results lies on the calibration of the polytropic efficiency, equation (8) and Fig. 16. Overall efficiency values of the gas turbine plant are a function of both the compression and expansion works. In the case of off-design regimes, the expansion work significantly depends on the polytropic efficiency of the gas turbine. Specifically to this case, the thermodynamic model considers variations of the polytropic efficiency as a function of the combustion products' mass flowrate that are delivered to the gas turbine. Therefore, polytropic efficiency values are highly sensitive to mass flowrate changes. Thus, the polytropic efficiency for humidified ammonia-hydrogen combustion is ~65%, significantly higher than for the case using dry ammonia-hydrogen combustion (i.e. ~45%), a consequence of the change in combustion products' mass flowrate, Fig. 16. Consequently, the increase of the polytropic

efficiency increases the turbine useful work, raising the overall efficiency of the cycle. However, it must be emphasized that the mass flowrates employed for both the humidified and dry ammonia-hydrogen cycles are lower than the mass flowrate of the reference plant at 10%, leading to unresolved uncertainties consequence of the extrapolation of the polytropic efficiency of the gas turbine for these conditions. Therefore, further research is needed on new cycles designed to burn humidified ammonia blends that employ smaller compressors to ensure less post-combustion dilution – turbines that can only be theorised at the moment.

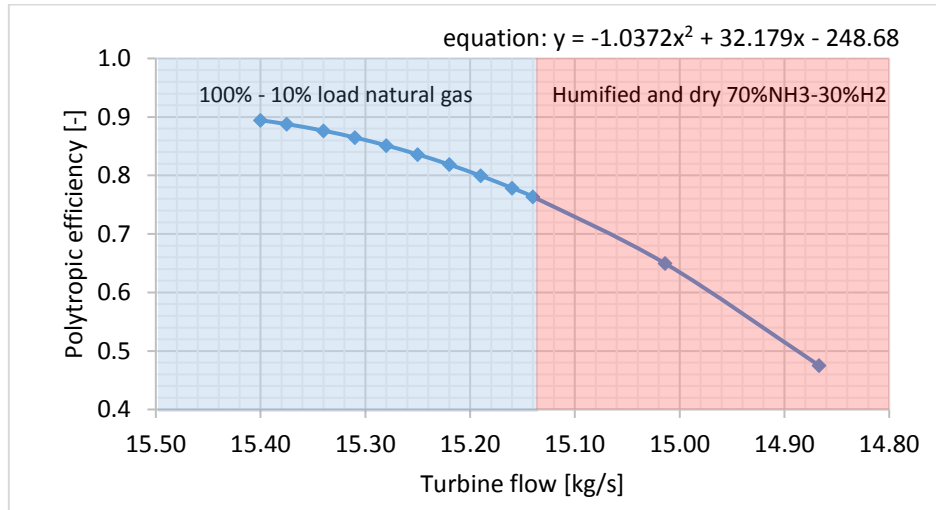


Fig. 16. Polytropic efficiency equation that will be used in equation (8) - variation of gas turbine polytropic efficiency as a function of gas turbine mass flow rate.

3.4. Experiments

Experimental results demonstrated that combustion using a highly humidified 70%NH₃-30%H₂ blend were feasible, generating a flame that showed relatively high stability (qualitatively measured based on the fluctuation of the base and core of the flame). Once stable combustion was achieved, steam injection followed. Injection was performed in steps of 0.2g/s in order to verify impacts on the flame while ensuring combustion feasibility, avoiding blowoff. It was observed that steam injection affected the flame at values above 0.6g/s, with a flame that showed greater fluctuation at the base, a phenomenon directly linked to the increased likelihood of blowoff. In order to observe the resistance of the flame to humidity, injection was increased and the flame was still visible up to 1.0g/s – i.e. 0.72 steam/fuel ratio (mass) – point at which the flame became so unstable that was eventually lost. Interestingly, these type of flames are highly resistant to humidified conditions.

NO_x emissions were measured, as presented in Fig. 17. It is clear that emissions decrease with the increase of steam to levels as low as <10ppm. The increase of inlet temperature augments the production of nitrogen oxides, as expected, due to the increased reactivity of the fuel blend.

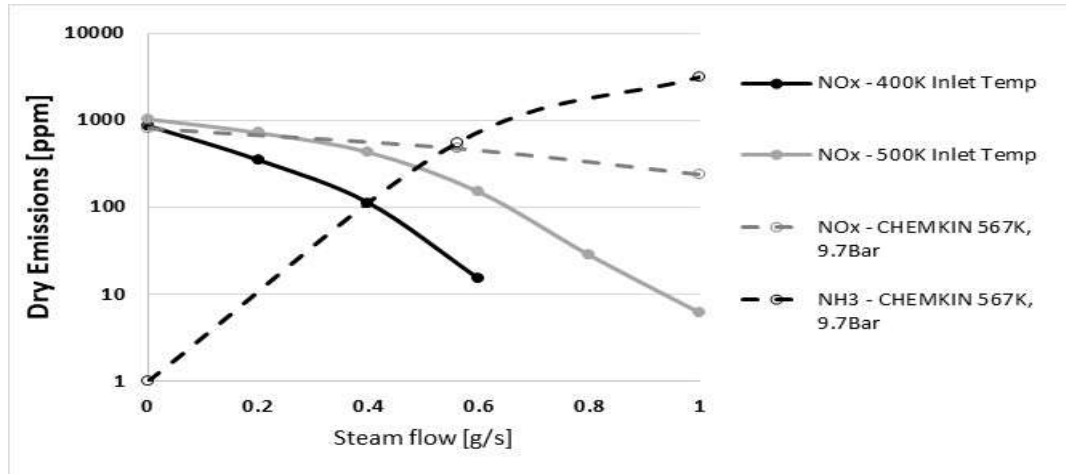


Fig. 17. NO_x emissions at different steam injection ratios (experimental and numerical). NH₃ emissions included (numerical results) for comparison purposes.

Results obtained from the chemical-kinetic studies, Fig. 6-8, have been also added to Fig. 17. It is clear that as the temperature increases, NO_x emissions increase. However, the results also show that an increase in pressure can decrease NO_x emissions. The latest assertion has been numerically and experimentally validated elsewhere [44, 49].

Ammonia emissions from the chemical-kinetic studies were also added to Fig. 17. It is evident that the increase of steam in the blend will increase unburned ammonia. Although no NH₃ measurements were possible during this campaign, further works using this combustor were posteriorly performed by Pugh et al [49]. Their results show that at higher steam fractions unburned ammonia increases in up to two orders of magnitude, thus being in agreement with the present calculations. It is believed that lower combustion temperatures contribute to this phenomenon [49]. Moreover, Pugh's results and those obtained through this work suggest a point of balance between steam injection, unburned ammonia concentration and inlet temperature values. The region at which both NO_x and NH₃ seem to be more efficiently reduced appears to be located between 28 and 40% steam/fuel injection (mass) for high inlet temperatures.

As part of the emissions reduction process, it has been suggested that for NH₃ and NO_x emissions their relatively low values are also linked to their recombination and posterior reaction with steam in the post-combustion chamber. Supporting this statement, large pools of condensate were recovered from the HPOC rig, which after analyses showed alkaline characteristics with ~8.5pH. Thus, it is believed that this alkalinity is caused by the remaining, unburned ammonia, which in practice will need to be minimized to increase efficiency of combustion and to reduce the pH of the final condensates, a topic that requires further research for implementation of these humidified conditions in the combustion of ammonia-hydrogen blends.

4. Conclusions

A numerical, analytical and experimental analysis was carried out to determine the efficiency and potential of using ammonia-hydrogen blends under humidified conditions to achieve regimes that can potentially compete with current Brayton cycles fuelled with fossil fuels. After

employing a modified thermodynamic model, a new reaction chemical mechanism and bespoke experiments, it was found that:

- The use of steam up to 0.72 Steam/Fuel ratio (mass) is feasible. However, combustion performance is low and unstable, leading eventually to blowoff.
- The use of steam up to 0.40 Steam/Fuel ratio (mass) provides efficiencies similar to those obtained using humidified natural gas cycles (~28.59% v ~28.20%). Although these values are based on extrapolated calculations, it is clear that there is opportunity for efficient energy production using humidified ammonia-hydrogen blends, with the requirement of novel cycles that can enable lower post-combustion products dilution.
- Simultaneously, flames under humidified ammonia-hydrogen conditions present relatively good stability, with low fluctuation at the base and core of the flame, thus being feasible for further research that includes more complex analyses on flame stability and operability.
- Nitric oxides can be mitigated by using steam injection via reduction of temperatures (i.e. lower thermal nitric oxide and reduced reaction of ammonia) and the formation of radicals that have a negative sensitivity to the production of the contaminant. However, large steam injection has disadvantageous effects, as lower combustion efficiencies are expected with higher unburned ammonia, a consequence of the reduced temperatures that lead to remnants of unburned fuel in the post-combustion zone. Consequently, condensates appear with high pH. Thus, a region of balance between 0.28 and 0.40 steam/fuel ratio seems to be the most feasible to control both emissions. Further research is needed to assess different steam injection strategies to minimise even further these unwanted emissions.
- All obtained results demonstrate the potential to efficiently use ammonia gas turbines for power generation via humidified, hydrogenated blends under rich conditions. Results denote a range of humidified conditions that need to be targeted for further works, raising the need of more accurate reaction mechanisms for humidified conditions at representative industrial conditions (i.e. high pressure and high temperature inlet conditions).

5. Acknowledgements

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