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RE	Restricted to a group specified by the consortium (including the Commission Services)	
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Reference benchmark

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Objective: This deliverable aims at offering an assessment of existing concepts and reference technologies that are a reference for the assessment of the HiPowAR plant concept.

Background: It appears useful to identify potential synergies between the HiPowAR concept and existing experiences on similar working conditions, as well as to develop a benchmark framework to represent the status of competing technologies.

Results: The deliverable investigates two main topics. First, past research and development experiences related to fluid expansion in presence of nitrogen and steam mixtures are studied, showing that the field has not been covered in the conditions expected for the HiPowAR plant operation (90% H₂O, 10% N₂). Then, the main technologies for power generation that can constitute a benchmark or comparison reference for the HiPowAR assessment are identified and described, categorizing mature and highly efficient technologies and systems using ammonia as a fuel. The latter appear to have promising features for zero-emissions electric generation, but they are in general at an early development stage. A set of tables is developed to summarise quantitatively the main techno-economic features of the listed technologies.

Deviations/delays: n.a.

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Introduction

This deliverable provides the results of the activities included in Task 5.1 of the HiPowAR project. The task is developed within WP5, which is devoted to the modelling, simulation, and optimization of the HIPOWAR system layout, as a starting point.

The goal is to obtain a comprehensive benchmark framework that will constitute a comparison reference in support to the development of the new HiPowAR plant concept, aiming to successfully optimize its layout and performance with respect to state-of-the-art competitive solutions.

In particular, the analysis focuses on two elements:

- a) assessing existing power plant concepts and experiences related to power generation with high pressure gas expansion with conditions comparable to the steam and nitrogen expansion envisaged by the HiPowAR project;
- b) building a benchmark framework for competitive solutions, both for stationary and mobile applications, in terms of power, efficiency and costs.

Concepts and experiences related to operating conditions comparable to HiPowAR

This section looks into power plant concepts and experiences related to power generation with high pressure gas expansion that feature conditions comparable to those of the steam and nitrogen expansion envisaged in the HiPowAR plant, in order to identify potential issues and synergies.

High-pressure gas expansion – the case of gas and steam turbines

The foreseen expansion conditions in the HiPowAR plant are rather peculiar, at the same time showing similarities and differences with respect to both gas turbines and steam turbines.

The predicted high temperature at turbine inlet ($> 850\text{ °C}$) is similar to that achieved in conventional gas turbine systems, even “safe” when compared to today’s BAT (where the Turbine Inlet Temperature or TIT of the expanding gas is in the range $1400\text{-}1500\text{ °C}$, sustained adopting air cooled blades, with maximum metal temperatures in the range $900\text{-}950\text{ °C}$). Nevertheless, the turbine inlet pressure in the HiPowAR concept is higher, since the expected range is starting around 50 bar, while conventional gas turbines operate at a maximum pressure of around 35-40 bar (for aero-derivative types). Moreover, since one of the main advantages of the HiPowAR system is the possibility to achieve a very high pressure with negligible pumping work, the optimal expansion inlet pressure may further increase in a scale-up and long-term perspective. The limit could be either the sealing technology or the mechanical resistance of the membrane material. At the same time, the expander isentropic efficiency would significantly drop when operating with very large expansion ratios, hence the maximum pressure may be also dictated by electric efficiency maximization.

Regarding the working fluid, conventional gas turbines expand a mixture of exhaust gases typical of natural gas combustion with high air excess, thus not too far from air composition with addition of water and CO_2 (e.g. in volumetric fractions 74-76% N_2 , 12-15% O_2 , 6-8% H_2O , 3-4% CO_2), whereas the HiPowAR system features a mixture of only N_2 and H_2O after the oxidation reactor having quite different proportions. Indeed, based on preliminary simulations of the HiPowAR plant scheme developed using the Aspen® Plus software (Task 5.2), it has been found that the fluid expanded in the turbine is a mixture of $\text{H}_2\text{O}\text{-N}_2$ with molar fractions 90%-10%, respectively. Therefore, the only common parameter with conventional gas turbines is the expansion inlet temperature, as the low N_2 content in HiPowAR expansion does not justify a parallelism with air.

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Considering the large steam fraction in the expanded fluid predicted for the HiPowAR system, the comparison with a steam turbine seems more fair. Moreover, the expansion inlet pressure envisaged for the HiPowAR plant (> 50 bar) is not uncommon at the inlet of the intermediate-pressure turbine of a modern steam cycle with 3 pressure levels, typically found in combined cycle; moreover, the maximum inlet pressures at the high pressure level of a steam plant can also be much higher (150-180 bar or supercritical above 220 bar). Nevertheless, steam turbines are not operated at a temperature larger than 600-620 °C, which are the BAT values both for ultra-super-critical (USC) steam cycles and for the steam section of combined cycles. Therefore, the most similar expansion conditions to those of the HiPowAR system are found, in terms of pressure, at the intermediate pressure after reheat of a modern combined cycle with 3-pressure level Heat Recovery Steam Generator (HRSG); although the typical temperatures are in that case lower (max 600-620°C). In steam cycles, the temperature limit is imposed by the mechanical and chemical material resistance, combined with the need for an inexpensive material given the large amounts required in the steam generator and in the turbine components (super-heating and re-heating heat exchangers, piping, HP turbine blades, IP turbine blades, etc.).

As mentioned, a feature of the HiPowAR scheme is the expansion of a high pressure mixture of steam and nitrogen, i.e., a non-ideal mixture comprising steam plus a non-condensable gas (N_2). As discussed, the N_2 fraction is rather low: from preliminary Aspen simulations, even when varying the reactor cooling, it does not surpass a level of 15%vol. Literature studies have not focused on nitrogen expansion.

Expanding the investigation to non-condensable fluid management, CO_2 is found as a studied element due to its presence in geothermal plants. Indeed, in direct geothermal plants, CO_2 usually expands through the turbine together with steam and is then separated to be reinjected in the geothermal well. In the HiPowAR plant, N_2 must be separated from water at expander outlet and possibly recompressed to ambient pressure for release, with a similarity to the situation of geothermal plants. Indeed, given that preliminary simulations (Task 5.2) are predicting significant efficiency advantages when operating with sub-atmospheric expansion, in the final plant design it is sought the implementation of a N_2 compressor, able to eject in the atmosphere the N_2 flow, which will be saturated with H_2O , following the separation via condensation.

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Injection of water or steam at expander inlet – the case of STIG cycle

Despite temperature is the only common parameter when comparing the HiPowAR expansion with conventional gas turbines operating conditions, it is interesting also to consider the case of Steam Injected Gas Turbines (STIG cycles, also found as Cheng cycle from the name of its first inventor), a variant of the gas cycle which envisages steam injection ahead of the turbine expansion.

In this type of gas turbines, steam injection can be applied either in the combustion chamber or at compressor discharge, as a modification to the conventional Brayton cycle allowing for power and efficiency augmentation and NO_x reduction (due to enhanced control of max combustion temperatures). Steam can be generated by recovering heat from the gas turbine exhaust gases, at a pressure level sufficient for injection in the high pressure air flow (thus requiring a pressure 25-40% higher). Gas turbines are generally designed to allow a steam injection up to 5% of the compressor intake airflow [1]. This design allows a sufficient steam injection to meet the NO_x abatement requirement, while further steam injection would increase operational costs, including a significant cost for demineralized water consumption, and is therefore generally not implemented. At any rate, the STIG configuration assumes to increase the steam injection up to higher fractions, reaching up to 15-20% of the inlet air mass flow rate in specific aeroderivative gas turbines (the increase of flow rate is limited by the necessity of a parallel increase of pressure ratio at turbine inlet, exploiting part of the compressor surge margin, which is sufficient only in some GT models). Assuming that air is essentially a mixture of N₂ and O₂ with molar fractions 79% and 21%, respectively, and considering to burn pure methane with usual fuel to air ratios, the composition of the expanding gas in presence of a 5% steam injection is a mixture composed by N₂, O₂, H₂O and CO₂ with molar fractions 70%, 12%, 14% and 4%, respectively. Adding 20% steam injection the mixture would become nearly 60% N₂, 10% O₂, 27% H₂O and 3% CO₂ respectively. Even in this technological application, it can be concluded that despite the conditions are closer to those expected in the HiPowAR plant due to increased steam amount, the mixtures entering the expander are still too different in the two cases to offer much insight by direct comparison. However, the operation of STIG cycles demonstrates the feasibility of expanders running at very high temperature with a significant, though not major, presence of steam.



Benchmark framework

In this section, a framework is built that includes existing and upcoming technologies for power generation that can represent a benchmark against which the HiPowAR system performance can be evaluated. The analysis looks at both stationary and mobile applications and considers rated power, efficiency, specific costs, and operating cost.

The technologies are selected according to the following criteria:

- high maturity;
- simplicity and compactness;
- flexibility;
- high efficiency;
- low CO₂ emissions;
- use of ammonia as fuel.

Two main categories are identified, which correspond to short-term or long-term comparisons:

1. mature and high-efficiency plants;
2. ammonia-fed plants.

First, the technologies are briefly described and compared. The comparison focuses on technical and economic parameters, such as capacity range and modularity, maximum temperature, electric efficiency, CO₂ emissions, specific investment costs (€/kW) or CAPEX, and maturity level (TRL).

Finally, the main features of the identified benchmark technologies are summarized in a table for easy comparison.

The maturity level of the technologies is expressed in terms of TRL, considering the classification proposed by the EU Horizon 2020 guidelines [2]:

- TRL 1: basic principles observed;
- TRL 2: technology concept formulated;
- TRL 3: experimental proof of concept;
- TRL 4: technology validated in lab;
- TRL 5: technology validated in relevant environment (industrially relevant environment in the case of key enabling technologies);
- TRL 6: technology demonstrated in relevant environment (industrially relevant environment in the case of key enabling technologies);
- TRL 7: system prototype demonstration in operational environment;
- TRL 8: system complete and qualified;

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- TRL 9: actual system proven in operational environment (competitive manufacturing in the case of key enabling technologies; or in space).

MATURE AND HIGH-EFFICIENCY TECHNOLOGIES

Internal combustion engines

Internal Combustion Engines (ICEs) are a very well-known technology, with a variety of both stationary and mobile applications: from combined heat and power units to emergency generators, from road vehicle propulsion to maritime transport. ICEs are a relevant term of comparison for multiple reasons: the technology has a very high TRL, a good flexibility in terms of partial load operation (although at the price of efficiency), and is the major competitor for mobile uses. Moreover, they can also run on ammonia.

The technology is very mature and units are commercially available from a number of manufacturers in a wide variety of nominal power ratings, from few kW (or even below) to many tens of MW. Historically developed for use with liquid fuels (gasoline, Diesel), their evolution involved the adoption of other oil-derived liquid fuels (like LPG), natural gas in either compressed or liquid form (CNG or LNG, respectively), biofuels (either pure or blended with fossil ones), and even NH_3 (which is discussed later).

ICEs offer flexibility for partial load operation, but their design and manufacture do not offer much modularity. Indeed, the optimized design requires significant modification depending on the power output, except for the possibility to change the number of cylinders in a given range of capacity, leading to different models and characteristics. Some optimization elements are: number and size of cylinders, nominal rotational speed, maximum torque, etc. The final application also strongly affects the design: mobile units for road vehicles require pairing with gearbox and variable speed, whereas stationary devices for power generation operates at constant rotational speed with an electrical generator.

The design differences at varying capacity explain the variation in nominal efficiency (ratio of electric output and fuel LHV input): small-scale stationary units feature net electrical efficiency values in the range 27-30%, whereas large-scale units reach up to 45%.

Looking at devices for stationary applications and power generation, the capital cost of this technology is highly sensitive to the nominal capacity, with values as low as 900-1000 €/kW_{el,nom} for capacity above 100 kW_{el,nom}, then increasing at smaller capacities (1500 €/kW_{el,nom}), up until a further steep ramp for capacities below 10 kW_{el,nom} (2000 €/kW_{el,nom}). Very small units also exists, e.g., 1-5 kW_{el,nom}, with costs ramping to 3000-5000 €/kW_{el,nom}.

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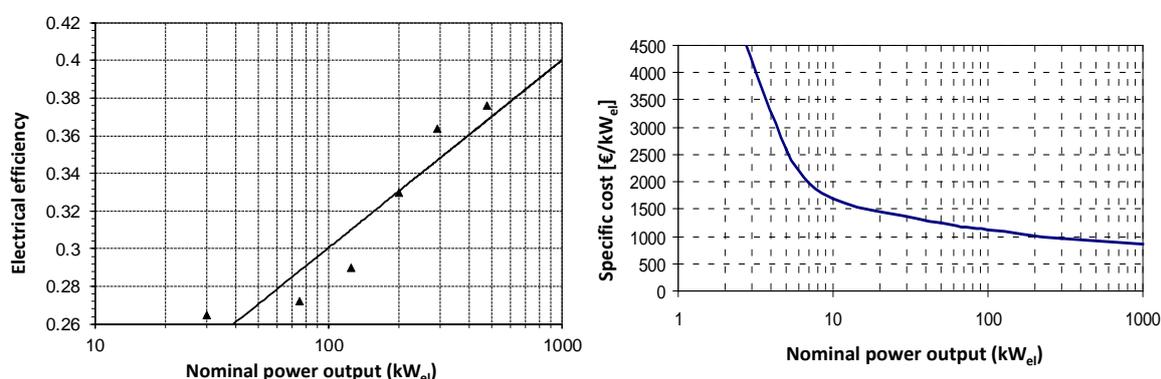


Figure 1. ICE efficiency (left) and capital cost (right) as functions of the nominal electric power output [3].

It shall be evidenced that the design of ICE for stationary power is significantly different from that used for mobile applications, especially due to the lower rotational speed (e.g. 1500 RPM instead of 5000-6000 RPM in automobiles) and more robust design adopted to meet the much longer lifetime required in power generation (40-80.000 h vs. the 5000 h of a car engine), which brings about a higher specific cost (€/kW).

Emissions of pollutants (unburnt fuel, particulate, NO_x) depend strongly on operational conditions (nominal vs. part load) and on the type of flue gas treatment equipment (which may include three-way catalytic converters, exhaust gas recirculation, selective catalytic reduction, particle matter filtering depending on the type of engine and fuel), whereas CO₂ emissions depend upon the adopted fuel and the system efficiency. The CO₂ emissions are about 590-660 g_{CO2}/kWh_{el} when using diesel as a fuel (considering 0.835 g/l and 2.56 kg_{CO2}/l) or 460-520 g_{CO2}/kWh_{el} when using low-emission fuels like LNG/LPG. The use of biofuels allows to offset the CO₂ emissions since the global effect of using a biomass-derived feed is nearly neutral.

Gas turbines

Gas turbines are continuous-flow engines that exploit the Joule-Brayton cycle: air is first compressed in a compressor and then sent into a combustor for temperature increase (lean combustion), after which the expansion of exhaust gases in a turbine from high temperature and high pressure generates mechanical power. In most designs, the two machines (compressor and turbine) share the same shaft, so that the work provided by the turbine drives the compressor and the residual is available for the user.

Gas turbines are a well-known technology, broadly applied in different fields. In power generation applications, an electrical generator is mounted onto the shaft to convert

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mechanical power into electric power. In mechanical-drive gas turbines, the shaft drives a separated mechanical load, typically a second compressor used to increase the pressure of a fluid (e.g., natural gas recompression for transport via pipeline, gas compression in oil&gas applications). Mobile applications are widely diffused: turbo-fans and turbo-props are used on most types of aircrafts (essentially a mechanical-drive configuration where the mechanical load is given by a fan or a propeller that moves air) and helicopters; naval implementations are possible in alternative to ICEs and successfully applied in fast ferries and in military applications. Installations on road vehicles instead have been only very limited, so that they cannot be considered a regular application.

Although the thermodynamic cycle has been known since the 19th century, gas turbines became available in the first half of the 20th century due to the need for machines capable of high isentropic efficiencies and materials able to withstand reasonably high expander inlet temperature. The technological development is still ongoing, with a trend of performance increase mainly related to temperature increase. Today's best available technology (BAT) reaches up to 1500 °C at turbine inlet, with appropriate ceramic coating and air-cooled blades on the first expansion stage rows.

In a way similar to ICEs, gas turbines are available in a variety of nominal capacities (from few kW to 600 MW) with little or no modularity and a specifically optimized design, considerably influenced by the plant size.

The main fuel adopted in stationary applications is natural gas, thanks to its 'clean' features such as absence of particulate and residues that would impact the expander operation. Aircraft engines use kerosene-based liquid fuels for ease and safety of storage. Moving towards low-carbon fuels, biomethane and biofuels can be used. In recent years, the manufacturers' attention focused on hydrogen-ready devices, which required the development of profoundly revised combustion systems. Some of the most recent configurations involve a multi-stage combustion chamber in order to balance the spike in temperature and in NO_x formation during the initial step of reaction [4]. Both pure-hydrogen and variable-fraction NG-H₂ mixtures are studied, with a short-term view in favour of the second, given the frequently discussed possibility to start injecting small hydrogen quantities in NG grids soon [5,6]. The introduction of hydrogen-ready combustors has focused mostly on large-scale gas turbines of the latest generation (H class) for use in combined cycles (see next section), such as the GT36 by Ansaldo Energia (based on former Alstom technology), introduced in 2020 [7] and currently being installed in a combined cycle facility in Venezia (Italy); the unit features a 450 MW power output (50 Hz version, rated at 41% efficiency in simple cycle). Other gas turbines models designed for 100% H₂ have also been proposed by Baker Hughes and General Electric.

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The performance is strongly favoured by the size, thanks to lower flow losses and improved mechanical design. Considering typical gas turbines that use axial turbomachines, a distinction can be made between small-scale devices (1-30 MW) featuring nominal efficiencies in the range 25-35% and large-scale units (hundreds of MW) reaching up to 44% [8].

In case of hydrogen firing, CO₂ emissions are totally absent. With natural gas feeding, emissions are in the range of 470-520 g_{CO2}/kWh_{el} for large-scale devices (40-44% efficiency) and rise to 620-690 g_{CO2}/kWh_{el} for small-scale units featuring 30-33% nominal efficiency.

Excluding the case of small-scale units below 10 MW_{el}, that are more costly and have a quite limited offer of models (including special cases of turbines employing a radial design [10]), capital cost for gas turbines ranges from 400-500 €/kW_{el} at 30-50 MW_{el} capacity and then decreases at growing capacity, dropping to 300 €/kW_{el} for devices above 80 MW_{el}, and further down to 150-200 €/kW_{el} in the case of units above 400 MW_{el} [8].

For very low power ratings (below 500 kW_{el}), a different layout is proposed which employs a recuperated cycle architecture, featuring low pressure ratios and using radial turbomachines (centrifugal compressors and radial inflow expanders); these devices are referred to as micro gas turbines. In these machines, hydrogen fuelling seems to be able to offer improved performance over natural gas or syngas operation [9], although, just like in larger gas turbines, this option requires the development of appropriate combustors that can tackle the risk of increasing temperature and NO_x formation. Although the HiPowAR test rig size (10-30 kW_{el}) falls within the capacity range of micro gas turbines, these are not deeply investigated since they typically operate with too low pressure ratios (e.g. 4-6) and their adoption is of little interest for the final goal of the project, which is the evaluation of the concept scale-up.

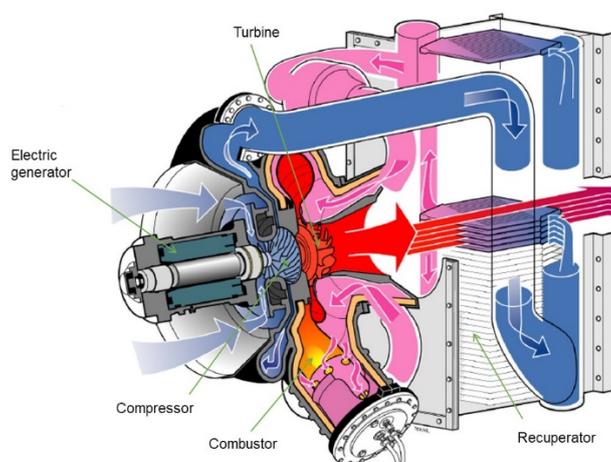


Figure 2. Representation of a micro gas turbine, with labels evidencing the main elements (image courtesy of Turbec).

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Combined cycles

The state-of-the-art power generation technology for high-efficiency electricity generation is the combined cycle. It comprises a gas turbine and a bottoming Rankine cycle, linked through the heat recovery steam generator (HRSG), where the gas turbine exhaust gas flow is used as a heat source to evaporate and overheat the water acting as working fluid in the steam cycle.

Combined cycles offer today's highest efficiency values for power generation, with recent designs passing 64% nominal LHV-to-electricity conversion efficiency [8]. These plants were originally featuring rather slow start-up and ramp-up due to the large inertia involved with the HRSG, but today's advancements and a design oriented to flexibility allows hot start-up in less than 30 minutes. Also, when equipped with a bypass valve on the exhaust line, they can exploit the gas turbine in simple-cycle configuration for low output operation or fast start-up, while the bottoming cycle is shut off and/or is heated up.

Typical capacities range from tens of MW to 1.5 GW. The performance is favoured by larger size thanks to more efficient gas turbines and steam turbines as well as improved integration. Plants with an overall net power output below 100 MW may still feature electrical efficiencies in the range 45-50%, but 55% or higher is the common value when passing 200 MW and 62-64% for large plants rated at 500+ MW. Modularity is not a point of strength, since the design of gas turbines is not modular and bottoming steam turbines and heat exchangers are also designed on purpose. However, a certain degree of design flexibility is provided in the case of large-scale plants by the possibility of system configurations with a variable number of gas turbines and/or steam turbines (e.g. it is quite frequent to have a 2+1 configurations with two gas turbines and a single steam section).

Fuel flexibility follows the same considerations discussed for gas turbines, since the combustion device is identical. Post-firing downstream the GT, aimed at increasing the temperature of the exhaust gases before entering the HRSG section, is possible but uncommon. The possibility to run on hydrogen can be considered an already reached or nearly reached objective, since most manufacturers are implementing the newly designed combustors in demo plants and in commercial systems that aim at withstanding variable-fraction NG-H₂ mixtures with a very limited effect on efficiency and on emissions. See for instance some recent installations in Australia, Italy or in Malaysia [11]. Pure hydrogen feeding fully avoids CO₂ emissions, whereas the use of NG-H₂ mixtures falls in between the two extremes.

Specific CO₂ emissions from NG-fed combined cycles depend upon the system efficiency, from 420 g_{CO2}/kWh_{el} in case of 50% efficiency (assumed as a reasonable average for small-size plants) to 320-350 g_{CO2}/kWh_{el} when efficiency reaches 60-64% (today's best performance, assumed as a reasonable average for capacities above 500 MW_{el}).

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The capital cost of NG-fuelled combined cycle systems averages at 600 €/kW_{el} for the common range 400-1000 MW_{el} nominal capacity, with an increase to 800-1000 €/kW_{el} below 200 MW_{el} and a decrease to 500 €/kW_{el} for systems above 1 GW_{el} [8]. Official data regarding systems equipped with hydrogen-ready combustors are not available, but the cost increment is expected to be marginal and will be reabsorbed in perspective, as soon as such type of components will become ordinary.

Combined cycles with CO₂ capture

Combined cycles, just like most large-scale combustion-based power generation plants, are suitable for the installation of CO₂ capture systems. Different capture technologies exist, which are typically categorized into pre-combustion, post-combustion, and oxy-combustion methods.

Pre-combustion capture refers to removing the CO₂ from the fuel before the combustion is completed and it is relevant for plants involving fuel pre-treatment, such as coal gasification, that generates a syngas (H₂+CO+CO₂) from which the CO₂ can be separated after water gas shift, so that only H₂ is sent to the combustor. However, this has little interest for NG-based plants, unless for the case of converting natural gas to hydrogen in steam reformers with CO₂ capture (producing the so-called “blue hydrogen” or low-carbon hydrogen) before feeding the power plant.

Post-combustion solutions allow conceptually a rather easy retrofit of existing power stations. They include three main techniques: scrubbing reactors where water and amines are injected into the flue gas flow in order to remove the CO₂ via absorption, selective membranes that are only permeable to CO₂, adsorption on solid sorbents. Of these, the most mature and commercially ready option is the use of amine scrubbing. Nevertheless, it entails a significant drop in power output and efficiency of the power plant, mainly due to the significant consumption of steam required for the regeneration of amines in addition to the electrical consumption for CO₂ compression and liquefaction.

The oxy-combustion solution involves the separation of O₂ from air, so that the combustion is carried out with pure oxygen and the flue gases contain only CO₂ and water, which can be easily separated via condensation. However, the process of air separation (through cryogenic Air Separation Units or ASU) is highly energy-intensive.

The installation of CO₂ capture affects the efficiency since all such systems introduce additional processes having a significant energy consumption, that reduces the net power output and/or increases the fuel input. The effect is a decrease of net electrical efficiency in the range of 8-10 percentage points.

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Two parameters are used to describe the performance of CO₂ capture systems and capture-equipped plants:

- the CO₂ capture efficiency: it indicates the capability of the system to remove CO₂ and is equal to the fraction of generated CO₂ that is removed from the flue gases over the total amount generated; it can be as high as 99%, although the impact on costs becomes more and more significant at growing values, so that 90% or max 95% values are usually considered as optimal;
- the avoided CO₂ fraction: it evaluates the difference between the actual emissions of the new plant and the emissions of the same plant without the capture system, dividing such difference by the total amount emitted in the no-capture case.

The second parameter combines the effects of the actual CO₂ removal amount and of the plant performance decrement; it is typically smaller than CO₂ capture efficiency since the new system features an increased consumption.

The effect on costs is also relevant, with a breakeven capture cost of about 60 to 90 €/t_{CO2} [12], which corresponds to a 35 €/MWh_{el} increase on the LCOE (considering the implementation of a 95%-efficient capture system on a GTCC featuring 64% efficiency that reduces to 54% due to CO₂ capture). Capital costs involve roughly a doubling from regular GTCCs (+80-110%).

Just like the combined cycle plants they attach to, CO₂ capture systems do not offer much modularity, since CO₂ capture technologies rely on chemical reactors or processing plants (scrubbing, air separation, ...) which are designed and sized on purpose. An exception are membrane technologies, which are however uncommon.

As of today, CO₂ capture technologies are mostly implemented in small-scale pilot plants, either on small-capacity plants or on a portion of large-scale plants. However, the attention and the study are mostly focused on large-scale applications, which may have a potential impact on global CO₂ emission reduction strategies, which allow to exploit economies of scale both for the capture system and for the CO₂ transport&storage phase.

Proton Exchange Membrane Fuel Cells (PEMFCs)

Electrochemical devices for power generation are inherently different from most conventional technologies since they operate a direct energy conversion process (chemical to electrical) instead of the traditional multi-step process of power cycles (chemical to thermal to mechanical to electrical). Among these, low-temperature fuel cells feature good performance combined with flexibility thanks to the limited heat integration and small thermal inertias. In particular, proton exchange membrane fuel cells exploit a solid electrolyte and a non-complex system configuration that favours the operation under variable power output.

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This technology is highly modular, since it is based on single cells connected in series into stack that are then combined into modules at a size where balance-of-plant integration is optimal. Capacities can range from kW to MW per module, and plants can increase the rated power output by repeating modules.

PEMFCs feature good performance: today's stationary systems operate with 42-45% nominal efficiency and the development target is above 50% with scale-up of both system and manufacturing capacity (a level already shown in some demonstration projects [16]), whereas devices for mobile applications may already go above 50% thanks to a simpler balance-of-plant. Moreover, part-load operation features a slight efficiency increase thanks to reduced ohmic and polarization losses (the increasing trend stops at very low loads, when the balance-of-plant consumption becomes relevant due to the underutilization of the equipment). Combined heat and power applications are also possible, given the exothermic nature of the overall electrochemical reaction, e.g., for residential applications, given that the stack temperature is in the range 60-90 °C (operating temperature is limited below 100-120 °C due to the properties of Nafion® and similar sulfonated polymers, which are the most commonly used membrane material). High-temperature fuel cells (HT-PEMFCs) have been proposed and investigated [13] as an alternative, which involves different materials for the electrolyte, capable to withstand 150-200 °C.

The reacting fuel within the cell is hydrogen and a high purity is required due to the low tolerance of the catalytic materials which are most frequently employed (Platinum and Platinum group metals) to impurities. Operation with other fuels (e.g., NG, biogas, DME) is possible, but requires a reformer and adequate pre-treatment for purification in order to avoid any impurities entering the cells, such as carbon monoxide (a typical residue of hydrogen production from reforming of hydrocarbons). The use of methanol has also been widely studied, developing direct-methanol fuel cells (DMFCs) with significant progress.

Today's costs are not very competitive, mostly due to small plant scale and limited manufacturing rate. Perspectives involving system scale-up, catalyst load reduction, and manufacturing scale up are promising. For example, the EU-H2020 GRASSHOPPER project [14] is targeting a CAPEX of 1500 €/kW_{el} for a 25 MW_{el}/year manufacturing capacity, considering flexible devices able to undergo frequent ramps to offer ancillary grid services [15], as shown in Figure 3. This is a strong reduction from the previous EU-FP7 DEMCOPEM-2MW project target of 4000 €/kW_{el} [16] and it is in line with the multi-annual workplan targets set by both the Fuel Cell and Hydrogen Joint Undertaking (FCHJU) and the US Department of Energy (US-DOE).



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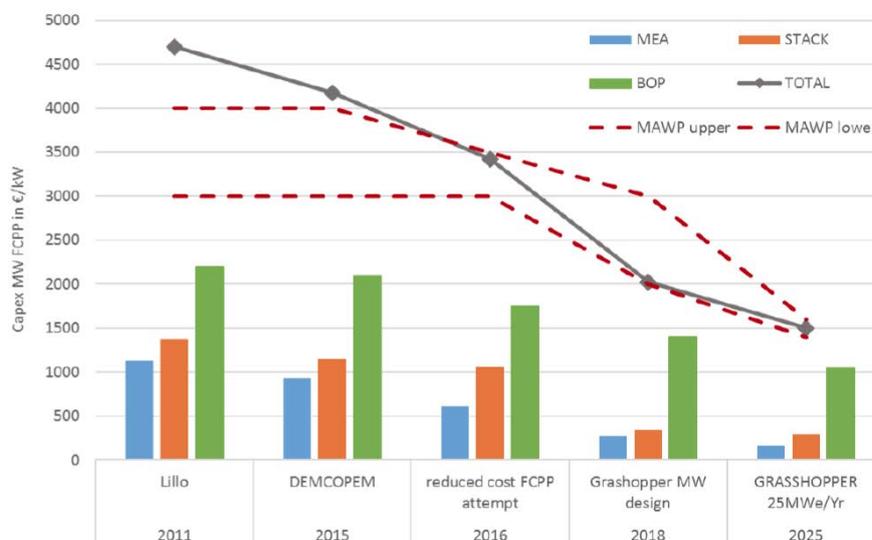


Figure 3. CAPEX evolution in multi-MW fuel cell power plants, from past and current projects and recent forecasts [15].

Solid Oxide Fuel Cells (SOFCs)

Solid oxide fuel cells are electrochemical devices that perform the direct chemical-electric energy conversion process at high temperature. The main difference of SOFCs from most other types of fuel cells (AFCs, PEMFCs, DMFCs) is the high operating temperature (> 800 °C). This is the main factor determining both advantages and drawbacks of such systems. Like all fuel cells, they benefit of large modularity (cells are combined into stacks, which are then assembled into modules that share a common balance-of-plant). Current largest installations feature capacities in the order of hundreds of kW to tens of MW_{el} per plants.

The main advantage of SOFC systems over conventional power plants and other fuel cell systems is the high electric efficiency, which can pass 60% (e.g., Bloom Energy – one of the leading manufactures - declares 67% at peak efficiency), and the low emission of pollutants (NO_x, particulate, ...). In principle, a larger operating temperature should reduce the maximum voltage achievable by a fuel cell, due to a lower Gibbs free energy for the H₂ oxidation reaction. Nevertheless, the high operating temperature also significantly reduces the electrochemical losses within the cell. Therefore, despite the maximum voltage decreases, this is more easily approached by the cell and the actual operating voltage increases. Another advantage of SOFCs is that expensive catalyst materials (such as platinum-group metals used in PEMFCs) are not required, since the high operating temperature is sufficient to accelerate the electrochemical reactions in presence of Ni or other inexpensive catalysts.

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The reacting element on the active surface is always hydrogen, which combines with oxygen transferred through the solid electrolyte; but SOFCs can exploit internal steam reforming, which is favoured by the high temperature, to convert inlet hydrocarbons to hydrogen. Hence, they can smoothly process a variety of fuels such as H₂, CO, CH₄, NH₃, etc. For comparison, low-temperature fuel cells are stricter in terms of compatible fuels, since PEMFCs are poisoned even by very small quantities of CO or NH₃ and Alkaline Fuel Cells (AFCs) can be negatively affected by the presence of CO₂ in air.

The drawbacks of SOFCs are also related to the high operating temperature, which imposes the need for heat-resistant ceramic materials, for which expensive manufacturing processes are required. Moreover, the high temperature causes significant materials degradation over time, which has been the main obstacle for the commercialization of SOFCs [17,18], although recent generations have reached a stack lifetime in the range of more than 20.000 h. Nowadays, R&D is working on limiting the operating temperature of SOFCs, aiming to operate in the range 500-700 °C, which requires the development of new electrolyte and electrodes materials.

Today's investment cost of SOFC systems is rather high (>5000 €/kW), whereas prospective figures are in the range 500-3500 €/kW_{el} [19], the lower value being an optimistic target for a medium-/long-term perspective, which is a reasonable comparison case for the HiPowAR project.

CO₂ emissions from SOFC systems depend on the fuel. When operated on natural gas, given the similar range of efficiency to GTCCs, CO₂ emissions are also expected to be similar.

The field of high temperature fuel cells also includes Molten Carbonate Fuel Cells (MCFC), which share similarities with SOFC in terms of high temperature operation (nearly 650°C), fuel flexibility, low emissions, but also issues with material and manufacturing costs as well as lifetime limitation. Although this type of fuel cells has reached remarkable large-scale demonstration (with max size of existing power plants approaching 70 MW), their specific cost is still high (>3000-4000 €/kW) and their typical efficiency from natural gas is limited to 47-48%, making them less attractive for power generation. Moreover, their commercial development is nowadays sustained by practically a single company (Fuel Cell Energy, USA). However, they may offer distinctive advantages when applied to CO₂ capture, especially if coupled to industrial processes, a factor which has raised further interest in their application by companies like Exxon Mobil [130].

Hybrid cycles (GT/GTCC+SOFC+CCS)

A broad field of study is the development of hybrid cycles that can combine multiple technologies to gain the best advantages of each. The scientific literature is rich of examples

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of technology integration, such as combination of gas turbines, steam cycles, or combined cycles with high-temperature fuel cells (SOFCs or MCFCs) aiming to optimize heat recovery at different temperature levels to increase the overall efficiency [20,21].

System simulations under different integration options show promising performance, above 60% and in some cases above 70%. However, little practical implementation has been developed so far. Cost assumptions uncertainty can be pretty strong due to the limited commercial development of the key plant components, including the high-temperature fuel cells in general as well as optimized heat exchangers or dedicated turbomachinery.

Allam cycle

In recent years, an innovative thermodynamic cycle has been proposed by Allam et al. [22] for power generation with very high efficiency and zero GHG emissions. The Allam cycle, or NET Power cycle (from the name of the company developing the concept), adopts oxy-combustion of natural gas, occurring at high pressure (200-400 bar) and with the injection of CO₂ as moderator, which is preheated to nearly 700 °C via a regenerative heat exchanger. At the expander outlet, water is removed via condensation, then a fraction of the CO₂ is extracted to avoid inventory build-up and the rest is recycled to the combustor through an intercooled compressor. The extracted CO₂ stream is purified and compressed to be sent to permanent storage [23,24]. The turbine inlet temperature is above 1100 °C and the expansion pressure ratio is limited between 6 and 12. The system scheme is presented in Figure 4.

The additional complexity with respect to a traditional gas turbine cycle is evident (although the compressor-turbine design can be quite compact, the cycle requires a multi-flow heat exchanger as well as an air separation unit) as are the advantages: a high electrical efficiency with 100% CO₂ capture. Based on literature analyses and simulations, optimized cycle operation of a 420 MW_{el} system attains 55% electrical efficiency with turbine inlet conditions of 280-300 bar and 1150 °C. Part-load simulations predict a modest efficiency reduction with respect to that of conventional combined cycles. The efficiency loss remains below 5% in a wide range of thermal power input (65-100%), whereas the reduction grows to 20% at 40% load.

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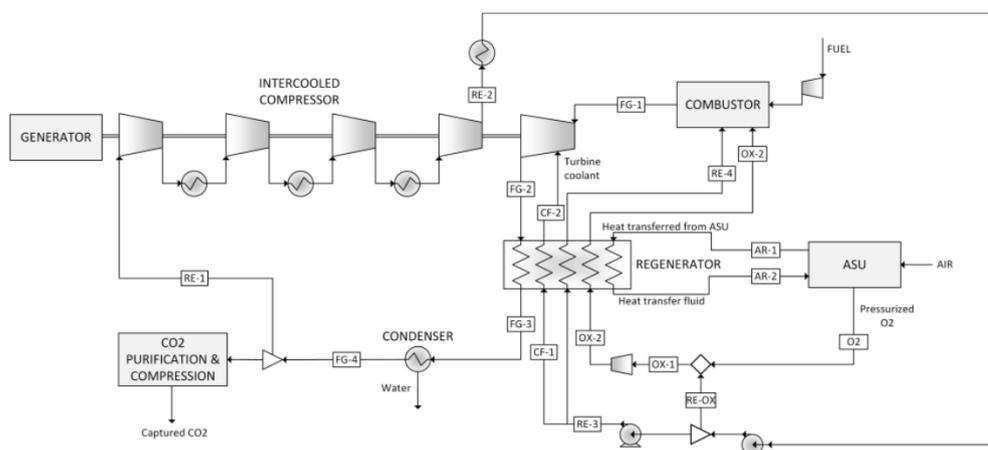


Figure 4. Scheme of the NET /Allam power cycle [23].

Currently, a prototype has been built in Texas, USA, with a nominal power output of 25 MW_{el} and construction is ongoing for a 300 MW_{el} plant to be completed in 2022. Most plant components are not commercial units (e.g., the turbine is designed on purpose by Toshiba). Capital costs are undisclosed.

Interestingly for the purpose of a comparison with the HiPowAR concept, the gas turbine expands an unconventional fluid mixture which is composed by an inert (CO₂, e.g. 90% or more) and steam, the latter coming from the oxidation of hydrogen contained in methane and natural gas hydrocarbons. At any rate, the expanded mixture in HiPowAR is still quite different, being composed by a majority of steam and a minority of inert Nitrogen.

AMMONIA-FED TECHNOLOGIES

NH₃-based technologies for electricity generation have up to now featured little practical application and are therefore relatively immature in general. Currently, the only commercially available option is the alkaline fuel cell, coupled with NH₃ cracker. However, this type of technological option is expected to significantly improve and possibly diffuse more widely in the future.

The interest in using NH₃ as fuel is due to the intrinsic avoidance of carbon-related emissions, such as CO₂, CO, and unburnt hydrocarbons. Nevertheless, NO_x emission must still be addressed, considering that a large amount of NO_x may be directly produced by fuel-bound nitrogen. It shall also be considered that NO_x, in addition to being directly harmful for health and impacting the environment through the mechanism of acid rain, can have a greenhouse effect up to 300 times more impactful than CO₂ [25]; so that this type of emission shall be

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strictly controlled. Moreover, direct NH_3 emission into the environment must be controlled and avoided due to toxicity of NH_3 . Therefore, a technology relying on NH_3 combustion must successfully address the containment of emissions of NO_x and NH_3 .

The research on NH_3 -based technologies such as GTs, ICEs, and FCs is currently active. As an example, the Japanese government included all these technologies in a Strategic Innovation Promotion Program (SIP) named 'Energy Carriers', started in 2014 [26]. This research has produced encouraging and unprecedented results for several NH_3 -based technologies in the last few years. In Europe, a large consortium belonging to the Campfire project has been developing advanced technologies for ammonia production and utilization [27]. The project, funded by the German Federal Ministry for Education and Outreach, is particularly focused on the decarbonisation of maritime transportation. Nevertheless, the technologies which are studied and developed go far beyond the specific maritime application.

Gas turbines

Gas turbines will likely keep a major role in the field of power generation. This is due to their relatively low cost and high flexibility, which is a highly desirable characteristic with large renewables penetration. Moreover, gas turbines can be more efficient compared to other flexible and conventional technologies such as reciprocating engines, when working in combined cycle. For the above reasons, NH_3 -fueled gas turbines may be considered as an enabling technology to reach a scenario in which NH_3 is one of the main energy vectors.

The companies interested in development of NH_3 -based gas turbines are mainly those involved in the SIP project, such as IHI Corporation and Toyota Energy Solutions (Japan) [28,29].

Space Propulsion Group Inc. (US, CA) also declared its interests in NH_3 as a gas turbine fuel, and is one of the few companies on the way for the development of commercial systems [30,31]. They installed a testing facility for conducting a thorough experimental campaign, as shown in Figure 5. The facility includes supply lines for NH_3 , H_2 , N_2 to simulate NH_3 cracking, and a J-79 turbojet engine.

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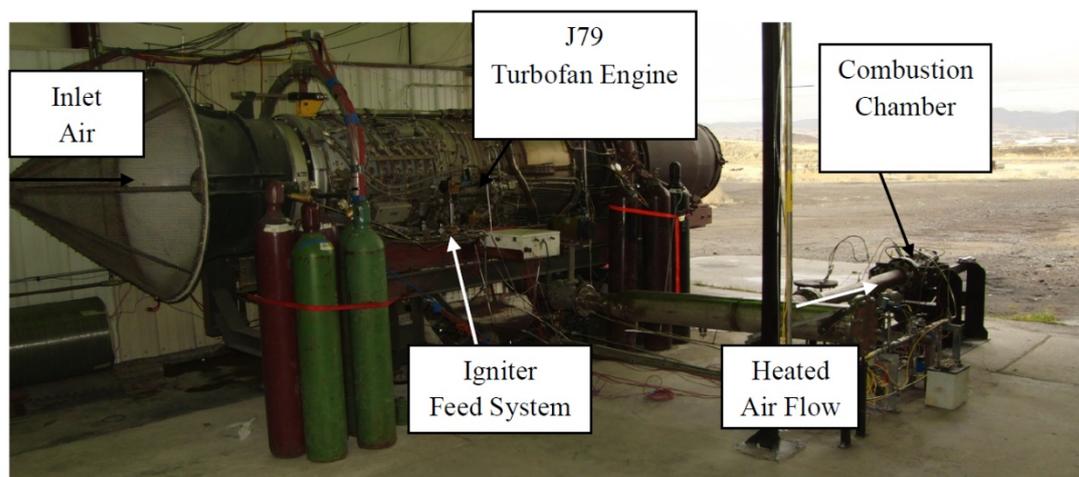


Figure 5. NH_3 -fed gas turbine test rig implemented by SPG Group (USA) [30].

In the report published in 2012 [30], they claimed to have achieved successful NH_3 -air combustion under realistic turbine operation. In addition, they have also developed methods for NH_3 and air injection into the combustion chamber and performed computer simulations for the reactions occurring within the chamber. Nevertheless, no further details on the experimental results and on the precise methods used are available.

Early work

The interest in NH_3 -fueled gas turbines dates back to the 1960s [32–35]. Despite some encouraging theoretical and experimental results, it was pointed out that specific combustor design is mandatory in order to use pure NH_3 vapour as a fuel. The reasons for this were attributed to the poor combustion characteristics of NH_3 : low flame speed, narrow flammability range, high ignition energy and large quenching distance.

In the studies conducted by Solar (a division of the former International Harvester Company, US) [33,36], two different combustor design strategies were used in order to burn NH_3 successfully. One design strategy is based on the increase of residence time, obtained by significantly increasing the combustor volume compared to the size which fitted hydrocarbons combustion. The second strategy was the integration of a NH_3 oxidation catalyst within the combustor. Using NH_3 instead of a hydrocarbon led to a power increase of 10%-20% at similar turbine inlet temperature.

Verkamp et al. [34] found that dissociating 28% of NH_3 into H_2 and N_2 before injection improved the combustion properties of the fuel mixture to a range comparable to that of hydrocarbons, achieving a stable combustion. This is due to the high reactivity of H_2 compared to NH_3 (and conventional hydrocarbons).

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Note that, in this early stage of development, also direct liquid NH_3 injection in the combustion chamber was attempted. Nevertheless, this solution was discarded as even more problematic than injection in the vapour phase [33,34,36].

The early interest in NH_3 as a gas turbine fuel rapidly dropped, due to unclear and somewhat limited advantages with respect to the already consolidated use of hydrocarbons. Also, the need to redesign combustion equipment was evident and inevitably costly, at a time of modest environmental concerns about CO_2 emissions. Then, it restarted during the 1990s and have been increasing until our days. To the best of the authors knowledge, the most wide and active research on NH_3 gas turbines is that conducted within the Japanese SIP research program.

50-kW class gas turbine system within SIP program

NH_3 gas turbines have been included in the already mentioned SIP program 'Energy Carriers', a strategic innovation program involving Japanese industries, universities, research institutes and government [26]. As a result, a great amount of papers have been published since 2014 by the Japanese research group, led for the activities regarding NH_3 -combustion technologies by Prof. Hideaki Kobayashi. The interests of the research community towards NH_3 gas turbines have been surging since 2014, probably stimulated by the encouraging results achieved within the SIP program.

The Japanese research group set up a gas turbine test rig facility in order to demonstrate electricity generation by using NH_3 as fuel. The rig employed a recuperative micro gas turbine, which was originally designed to burn kerosene, but a modification to the swirling diffusion combustor allowed injection of both kerosene and NH_3 [37,38]. The microturbine works with a compression ratio of 3.5 and a rated rotating speed of 80,000 RPM. Note that several characteristics support the stability of NH_3 combustion: the diffusion flame (instead of premixed reactants), the high temperature at combustor inlet allowed by regeneration and the presence of swirling flows. The swirling flows increase combustion stability and efficiency due to increased residence time and efficient mixing [39–41].

Successful operation using only NH_3 as fuel was obtained for the range 18.4-44.4 kW and for rotational speed in the range 70,000-80,000 RPM [38]. The start-up procedure was based on kerosene, as NH_3 ignition at ambient temperature was not successful.

Concerning NO_x and NH_3 emission in the system, it is believed that a mechanism of Selective Non-Catalytic Reduction (SNCR) of NO_x occurs in the relatively low-temperature secondary combustion zone. SNCR is a well known process adopted for NO_x reduction in some types of conventional power plants (e.g. waste-to-energy plants), consisting in the injection of small quantities of ammonia or urea in the exhaust gases of a conventional combustion process for the purpose of stimulating the reduction of nitrogen oxides to molecular nitrogen, thanks to

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the reaction with ammonia (with a reaction scheme: $4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$). SNCR is active in the temperature range 850-1150°C, although above 1000°C is increasingly contrasted by NO formation ($4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$). Hence, this mechanism should also be active in the temperature range envisioned by the HiPowAR project. Emissions of both NH_3 and NO_x were shown to be highly dependent on the inlet combustor temperature. A larger temperature determines higher NO_x emissions and lower NH_3 slip (because of faster combustion kinetics).

However, the additional use of a Selective Catalytic Reduction (SCR) unit downstream the combustion process was also experimented and showed to effectively decrease the NO_x to very low levels with no NH_3 slip (NH_3 is injected upstream the SCR to make it work; the process follows the same route of SNCR but is carried out at lower temperature, nearly 350°C, in presence of a suitable catalyst consisting in metal oxides of V,W,Mo on a basis of TiO_2). Nevertheless, it is also mentioned that the SCR unit is rather large [42].

In their work, they also demonstrated successful NH_3 - CH_4 -air combustion in the whole range of fuel composition. It was shown that NO_x emissions are dramatically increased by the presence of NH_3 , compared to CH_4 alone. Nevertheless, the NO_x emission as a function of NH_3 concentration in the fuel has a maximum, then it decreases up to 100% NH_3 . This is explained by considering the formation of NH_3 -rich regions where SNCR occurs.

Finally, thermal efficiency for the cases CH_4 -air, NH_3 -air and NH_3 - CH_4 -air were shown. The maximum thermal efficiency for CH_4 -air mixture was about 23%. Combustion efficiencies have been defined considering CH_4 -air mixture having 100% combustion efficiency. NH_3 -air mixture achieved a combustion efficiency in the range 89%-96%, while NH_3 - CH_4 -air achieved 93%-100% (considering a fuel mixture with an overall LHV supplied equally by CH_4 and NH_3).

The efforts from Kurata and co-workers demonstrated the possibility to achieve hydrocarbon-like efficiency for a gas turbine cycle using pure NH_3 as fuel or a blend of NH_3 - CH_4 . After that, a significant amount of papers from the same research group (more than 20 published works since 2014) and from other groups have been published.

Despite combustion of pure NH_3 was demonstrated, recent studies usually consider blends with a combustion promoter, usually CH_4 or H_2 . The NH_3 - CH_4 fuel mixture, usually with relatively low NH_3 content, has been considered for a minimum modification of existing gas turbine systems and possible retrofitting [43–45]. Nevertheless, the HiPowAR project considers a scenario in which NH_3 is used as the main fuel for electricity generation, hence we now focus on pure NH_3 and NH_3 - H_2 blends.

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The former director of SIP 'Energy Carriers' recently reported that also a 300 kW gas turbine system has been successfully operated with 100% NH₃ and a 2 MW system has been operated co-firing NH₃ and CH₄ [29]. Unfortunately, further information are not available.

Recent work on NH₃ and NH₃-H₂ combustion

The works published recently have been focusing on some specific topics: combustion properties of NH₃ and NH₃-H₂ blends [25,39,53–62,40,63–69,46–52], assessment of existing chemical-kinetics models [39,40,46,48,50,52–55], development of more accurate and efficient chemical-kinetics models [50,54,57,62], and development of strategies for NO_x reduction [42,52,74,61,63,68–73]. The development of reliable chemical-kinetics mechanisms for NH₃-based fuel mixtures is of major importance, as it is the basis for running 3D CFD simulations of the combustion process, like is currently done for the combustion of methane and other hydrocarbons. Once this is achieved, the combustor design, including the amount of H₂ blending and the NO_x reduction strategy will be easily optimized. Unfortunately, the available chemical models are not applicable for a wide range of operating conditions, and there is a general lack of detailed chemical mechanism studies [46,48,52,53].

The experimental campaign described in the previous section reported low NO_x emission by using a SCR unit. Nevertheless, it was also explained that such an equipment is rather large [42] and thus rather expensive. For this reason, it is necessary to design the combustor in order to minimize NO_x (and NH₃) emissions and try to reduce as much as possible the requirement of a SCR system. The first strategy is to use a premixed combustion instead of the diffusion combustion initially used in the SIP experimental campaign (adopted due to its intrinsic simplicity and stability). Premixed combustion is known to reduce NO_x production in conventional hydrocarbon-based combustors, but it has been proven valid also for NH₃ combustion [56,72]. The reason for this has been attributed to homogeneity of local Equivalence Ratio (ER), which is known to heavily affect NO_x production in NH₃ combustors. Therefore, the majority of the available works in the literature refer to premixed combustion. Moreover, the SIP Japanese group demonstrated stable combustion of pure NH₃ in a premixed combustor by using a swirling flow [40].

Regarding NO_x performance, similar trends have been reported for pure NH₃ and NH₃-H₂ (and NH₃-CH₄) fuel mixtures. The maximum NO_x production is achieved at slightly lean condition (ER ≈ 0.8-1.0), while working under slightly rich conditions significantly limits NO_x emission (ER ≈ 1.05-1.30) [40,47,71,74,49,50,52,57,59,61,63,66]. This is explained by a larger availability of NH_i radicals in rich conditions (NH₂, NH, N), which promote NO reduction. Nevertheless, a second combustion stage with supplementary air injection is necessary to complete the combustion, achieving an overall lean operation. This idea represents the Rich-Quench-Lean

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(RQL) combustion, which is one of the most promising strategy for NO_x reduction in NH₃ gas turbine combustors [52,68–70,74].

Another strategy is adopting a rather lean single-stage combustion, which has been proved to also produce a low amount of NO_x [63]. Nevertheless, in this case some H₂ should be present in the fuel mixture, as pure NH₃ suffer from lean flame blowout. Other strategies which proved to be effective in reducing NO_x emissions are: pressure increase [39,49,52,56,59,66,71], inclined fuel injection to increase swirling flows and mixing [72], post-flame fuel injection [60], and water vapour injection [61].

NH₃-H₂ fuel mixtures are interesting for several reasons. In general, NH₃ and H₂ have opposite and complementary combustion properties. Considering stoichiometric mixtures with air, the laminar burning velocity of NH₃ is ≈ 7 cm/s, that of H₂ is ≈ 350 cm/s (larger than the 35 cm/s featured by CH₄) [63]. The laminar burning velocity is a measure of flame stability in premixed conditions [42]. Moreover, NH₃ shows very narrow flammability limits in air, while H₂ range of flammability is rather wide. Finally, the adiabatic combustion temperature of H₂ is significantly larger than that of NH₃, which ensures faster kinetics, but is responsible for a larger production of NO_x in a pure H₂ flame. As a result, an increased amount of H₂ in the NH₃-H₂ fuel mixture would increase NO_x production due to thermal NO_x [47,63]. Nevertheless, a small amount of H₂ in the fuel (e.g., 10% vol.) may be sufficient to stabilize the combustion at very low Equivalence Ratios (ER) in a single stage combustion, not otherwise possible, reaching a very low NO_x production [63].

Regarding combustion stability, premixed H₂ flames suffer from flashback problems due to very high reactivity, for which an upper limit in the ER exists. On the other hand, NH₃ suffer from lean blowout due to very low reactivity, hence the ER must be above a certain threshold. It has been experimentally demonstrated that mixing NH₃ and H₂ in the right proportion allows achieving a stability range wider than both H₂ and NH₃ alone. In the conditions analysed by Khateeb et al [63], the widest possible stability range is achieved when $x_{H_2} \approx 10\%$ -30% (vol.), depending on Reynolds number.

In light of these considerations, cracking an optimized amount of NH₃ and producing some hydrogen prior to the combustion process is a promising strategy for NH₃ utilization in gas turbines, adding simultaneously a degree of freedom to the system design.

Regarding the costs, if NH₃ exits the tank in which it is delivered in the liquid state (ammonia can be stored as a liquid at ambient temperature when pressurized), a heat exchanger is required for its vaporization by using the heat available in the exhaust gases. In this case, the cost of the system increases for large sizes. Nevertheless, it should also be possible to draw vaporized NH₃ from the tank.

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The cost of cracking a fraction of NH_3 to produce H_2 is related to the design of the cracking reactor (which is a non-commercial unit). The cracking reaction is endothermic, hence some heat must be provided to the reactor. The heat could be available from exhaust gases or from burning part of the NH_3 . In the former case, a heat exchanger is required, which would increase the costs. The heat required for cracking (and the size of the required heat exchanger), the amount of catalyst needed, and the size of the cracker are related to the fraction of NH_3 to be cracked. According to literature studies, it is predicted that cracking 15%-35% of the NH_3 would result in a good compromise between combustion properties, flame stability and NO_x emission: above 28%, the resulting mixture shows similar combustion properties to CH_4 , whereas a 15% fraction would favour low NO_x and easier cracking. For comparison, this would result in a fuel mixture of 20%-45% H_2 by volume and complementary NH_3 (N_2 produced by cracking is not considered as it is generally low compared to N_2 in the air flow). Nevertheless, it is difficult to predict the relative cost of cracking this amount of NH_3 , considering that crackers are not commercial, and they can be designed in several ways.

Summary

To summarize, NH_3 utilization in gas turbines is a promising key technology in a future where NH_3 is one of the main energy vectors. Despite the poor combustion properties of NH_3 , its utilization as a fuel in gas turbine combustors has been proved experimentally in conditions comparable to real world applications, achieving hydrocarbon-like efficiencies. There are several methods to enhance NH_3 combustion stability. The most effective are: cracking a part of NH_3 to produce H_2 , generating swirling flows inside the combustor, increase the combustor inlet temperature, and working under a suitable equivalence ratio (ER, in order to avoid lean blowout, rich blowout and flashback risks).

It is possible to achieve efficient combustion with very low NH_3 slip and NO_x emission by using SCR technology. Nevertheless, the required equipment is large and potentially expensive, hence strategies for NO_x emission reduction are under development. The driver for NO_x production is the local ER. The mixture must be either slightly rich (ER \approx 1.05-1.35) with a second stage to complete combustion, or very lean (ER $<$ \approx 0.7). In the latter case, a little percentage of H_2 in the fuel mixture would avoid lean blowout. Fuel and air injection strategies, pressure increase, water vapour injection, and other strategies can also contribute to NO_x reduction. In the future, it would be useful to evaluate if mechanisms valid for NO_x reduction in conventional combustors are valid also for the HiPowAR membrane reactor (in which gaseous O_2 is not directly available). For instance, the rather large pressure envisioned for the HiPowAR membrane reactor could limit NO_x emissions if they follow the same trend valid for conventional combustors.

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It is believed that efficient chemical-kinetics models capable of predicting species concentrations with good accuracy for a wide range of operating conditions are fundamental for the development of NH₃ gas turbines. Once those models are available and the combustor is optimized, we don't see any reason why this technology would underperform, in terms of efficiency and NO_x emissions, compared to conventional CH₄ gas turbines. On the other hand, depending on the need of heat exchangers either for NH₃ vaporization or for supplying heat to the cracker, the cost and size of the system may increase compared to conventional gas turbines.

Internal combustion engines

The main advantages of Internal Combustion Engines (ICEs) over other technologies is their compactness, cost and flexibility. Moreover, the direct production of mechanical energy is an important advantage in the transportation sector compared to batteries and fuel cells (which need an inverter and an electric motor). Therefore, ICEs will probably play a role in the future, especially in the transportation sector and cogeneration applications.

MAN Energy Solutions (DE), which is one of the major producers of ICEs for maritime transportation, has recently declared its interests towards NH₃ as a fuel [75]. They plan to deliver the first engine in 2024, with a long-term target efficiency of 50% [76]. MAN has joined forces with Maersk (DK) and other partners for the realization of the project. Similar activities on ammonia fed ICEs have also been performed by Wartsila, another manufacturer of ICEs for large marine applications.

Toyota also showed some interest in NH₃ as fuel for ICEs in the automotive sector [77,78]. They found that NH₃ can be successfully burnt in ICEs, especially at high load, when blended with H₂, or in specific spark ignition systems. Moreover, Toyota presented the Marangoni-Toyota GT86 at Geneva Motor Show, which is a sport car powered by an ammonia-gasoline hybrid system.

The company Hydrofuel (Canada) recently started a project for developing NH₃-based ICEs for powering trucks [79]. Two approaches are followed, one is the dual fuel operation with diesel, the other one is using only NH₃ assisted by O₂ and H₂ enrichment.

Early work

The first important application of liquid NH₃ for ICEs dates back to 1943 in Belgium. After the interruption of public transports due to a diesel fuel shortage, around 100 buses were equipped for the use of NH₃ as fuel [80]. The results from this first experience were encouraging, as no loss of power neither corrosion occurred. Coal gas was used as an ignition promoter, but it was

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concluded that other promoters could also be viable, especially H₂. After the end of World War II the diesel shortage ceased, together with interests in NH₃ as an ICE fuel.

The interests raised again during the 1960s [32,81–88], due to the Energy Depot Project conducted by the US for military applications [89]. The goal of the project was the investigation of a concept where NH₃ fuel was produced by water and air, using the energy supplied by a mobile nuclear reactor [81]. These studies concluded that utilization of NH₃ as a fuel for IC engines was possible, without significant performance penalizations. Nevertheless, it was clarified that NH₃ combustion must be supported by some of the following design modifications:

- higher Compression Ratio (CR), Gray et al [82] found that a CR of 35:1 was necessary to use neat NH₃ as a fuel in a Compression Ignition (CI) engine;
- spark Ignition (SI), with relatively large spark energy;
- blending with a more reactive fuel as H₂, possibly derived by NH₃ cracking; it was found that H₂ concentration in the fuel of 3-5% by weight could be sufficient, corresponding to about 15%-25% NH₃ dissociation.

Recent developments

The research performed in the 1960s concluded that spark ignition systems were required to successfully burn NH₃ to avoid rather large compression ratios. This idea is supported by the high octane number of NH₃ (RON \approx 110), which makes it hard to auto-ignite. On the other hand, the high octane number is an advantage in spark ignition engines, as it provides knocking resistance allowing for larger compression ratios and efficiencies. As an example, Morch et al [90] shows that a NH₃-H₂ mixture of 90%-10% (vol.) could reach 37% efficiency at a compression ratio CR=11.64. The knock-limited compression ratio for gasoline was 7.12, with a maximum efficiency of about 30%.

Due to the high octane number of NH₃, which implies a low cetane number, burning pure NH₃ relying only on compression ignition has been mostly unsuccessful. Note that cracking NH₃ would not solve the problem, since H₂ has an octane number larger than 130. Nevertheless, the research on compression ignition engines has been carried on by introducing the concepts of pilot injection and dual fuel operation (mostly with diesel). This solution would still rely on hydrocarbons, differently from the scope of HiPowAR plant which aims at a full decarbonization. Regarding spark ignition engines, a lot of research has been developed regarding dual fuel operation with gasoline, which however does not represent a long-term solution to CO₂ reduction. The concept which directly compares to HiPowAR plant is a spark ignition engine operating either on pure NH₃ or a mixture of NH₃-H₂ attainable by NH₃ cracking. Therefore, these cases will be considered hereafter.

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Even with spark ignition (SI), operation with neat NH_3 has been hardly considered, as cracking a very low quantity of NH_3 seems to be sufficient to significantly improve the combustion and cyclic stability of SI engines even at part load. Nevertheless, specific ignition systems have been proposed to burn pure NH_3 , such as a plasma jet ignition plug, or a plurality of spark plugs [78]. The goal of the innovative ignition system was to achieve a more homogeneous and fast combustion by generating more than one ignition point. Moreover, Koike et al. stabilized the combustion of pure NH_3 at high loads [77]. On the other hand, the same authors developed an auto-thermal-converter to decompose part of NH_3 fuel, as it was recognized to help the combustion stability. Morch et al [90] found that it was possible to run the engine on pure NH_3 , but with a strong tendency to cut out. With addition of 5% (vol.) of H_2 in the fuel the engine run smoothly. This corresponds to cracking only 4% of the NH_3 fuel. Also Lhuillier et al stabilized pure NH_3 combustion, but a small amount of H_2 was necessary in most cases to ensure ignitability and stability [91]. In another work [92], they showed that pure NH_3 can be stabilized in a modern SI engine by increasing the load via intake pressure (supercharging), which had to be ≥ 1 bar. When the combustion was stabilized, the indicated efficiency (about 36%) was almost equal to that of CH_4 operation, and operation with slight H_2 enrichment. Nevertheless, combustion efficiency was lower.

The amount of H_2 in the fuel mixture should be minimized in general. There are trivial reasons for this, such as the minimization of both cracker size and energy required for cracking. Other reasons are the higher NO_x production [92–95] and lower efficiency and power at high H_2 content [90,91,95]. NO_x production is increased by thermal NO_x due to higher combustion temperature, while thermal efficiency and power may be penalized by high wall heat loss and air dilution with H_2 compared to NH_3 . Nevertheless, it is well understood that a higher amount of H_2 would increase combustion efficiency and the engine cyclic stability [91,92,95–97]. The COV(IMEP) (Coefficient of Variation of Indicated Mean Effective Pressure) indicates the variability of the work performed per cycle, this value should not overcome 10% (modern engines rarely overcome 5% [97]). Frigo and Gentili [96] investigated the minimum amount of H_2 to operate with $\text{COV(IMEP)} < 10\%$. They found that 7%-11% H_2 to NH_3 energy ratio was sufficient at 100% and 50% load respectively. This corresponds to cracking 6%-10% of the NH_3 fuel. Morch et al [90] found that a NH_3 - H_2 mixture of 90%-10% (vol.) was optimal regarding efficiency and power output. Note that this mixture can be generated by cracking 7% of NH_3 , but cracking only 4% of the NH_3 was sufficient to make the engine run smoothly. Note that the worse efficiency and power were recorded with fuels containing a large H_2 fraction due to wall heat losses and dilution effect of H_2 . The latter concept is also stressed by Lhuillier et al [95] by stating that H_2 content should be minimized to decrease the volumetric efficiency penalty due to a larger volume of the cracked gas (due to larger number of moles). They also achieved



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stable combustion by using fuel mixtures with 5%-15% (vol.) of H₂ provided that spark ignition timing is correctly advanced (larger advance for low H₂ content mixtures due to NH₃ slow combustion). They finally suggest that a fuel mixture with 10% (vol.) of H₂ might be a good compromise between stability, combustion efficiency, emissions and indicated efficiency. Another study from Lhuillier et al confirms that the best performance is achieved for slightly H₂ enriched mixture with H₂ < 20% (vol.), with highest efficiency values close to 39% [91].

Considering the results reported in the literature, it is predicted that cracking 5%-15% of NH₃ would provide sufficient cyclic stability and combustion efficiency, while limiting indicated efficiency penalization, NO_x emission and cracking apparatus size. This amount of dissociation would generate mixtures with 7%-20% H₂ by volume and complementary NH₃ (N₂ generated by cracking is not considered as generally low compared to N₂ from air).

Modern ICEs can be adapted to operate with NH₃ without significant changes in the system layout [98]. The major changes are the NH₃ fuel tank and supply line, which would result in larger space requirements due to relatively low NH₃ volumetric energy density. In case NH₃ is partially decomposed to H₂, a cracking reactor is required. Nevertheless, the H₂ requirement in the fuel is low, hence it is predicted that the presence of the cracker will not alter significantly neither the space requirements or the economics of the system. Minor changes to the spark system and the CR may be required.

It is suggested to work in lean conditions to keep comparable values for NH₃ and NO_x emissions and achieve high electric efficiency and low unburned emission [90–92,95]. In general, NO_x emissions are comparable to that achieved when using conventional fuels [99–102]. With ICEs it is more difficult to design the system to achieve low NO_x emissions compared to gas turbines, as concepts such as staged combustion are not applicable. Several authors suggested that the emission problem should be tackled by aftertreatment units as it is done in conventional ICEs.

Fuel cells

In principle, all kind of fuel cells can be used with NH₃ fuel provided that suitable cracking and purification technologies are used. In practice, a concentration of NH₃ of 1 ppm can significantly reduce the performance in a PEM fuel cell in a relatively short period of time [103], which set a significant constraint in the system design. On the other hand, Alkaline Fuel Cells (AFCs) can tolerate low NH₃ concentrations [104]. Therefore, complete NH₃ cracking is required, but further purification systems are not required. Moreover, a AFC-based system is currently the only commercial option for electricity generation using NH₃. The possibility of producing electricity by directly introducing NH₃ in molten alkaline hydroxide fuel cells have recently been

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confirmed by several studies. Nevertheless, the highest power density achieved is 40 mW/cm^2 [105], which is at least one order of magnitude lower than that reported by more mature technologies. Solid Oxide Fuel Cells (SOFCs) are by far the most suitable technology for NH_3 utilization, due to high efficiency and possibility of NH_3 internal decomposition (due to high temperature). SOFCs based on O^{2-} -exchanging electrolyte (O-SOFC) are more mature than those based on H^+ exchange (H-SOFC). Nevertheless, the latter may have a significant future breakthrough potential due to high conductivity of H^+ even at relatively low temperatures. Peak power densities reported are 1190 mW/cm^2 [106] and 390 mW/cm^2 [107] for O-SOFC and H-SOFC with direct NH_3 fuel, respectively.

Considering the above, the main fuel cell technologies to be considered for NH_3 electricity generation is the AFC due to its current commercial stage, and O-SOFC due to its breakthrough potential, relatively high maturity and similarities with HiPowAR plant.

Currently, the only commercial system for electricity generation using NH_3 is a AFC system manufactured by GENCELL (Israel) [108]. To the best knowledge of the authors, only another company is involved in the delivery of such systems, which is AFC Energy (UK). Nevertheless, this company only produces the AFC stack up to a rated power larger than $400 \text{ kW}_{\text{el}}$ [109], while the BoP is delegated to third parties. AFC Energy also offers a AFC stack with improved membrane technology allowing for higher power density, which can be interesting for space-constrained applications [110].

Solid Oxide Fuel Cells have also been included in the Japanese SIP program 'Energy Carriers'. As a result, about 20 papers have been published by the Japanese research group in the last 6 years, led for the program regarding NH_3 fuel cell technology by Dr. Koichi Eguchi. The Japanese companies interested in the development of NH_3 -based SOFCs are mainly those involved within the SIP consortium: Noritake Co. Limited and IHI Corporation [29,111,112].

AFC system

AFC systems have been studied mainly for off-grid applications, such as powering base transceiver stations for telecommunication applications [108,113]. Figure 6 shows a possible layout for the system, where complete NH_3 decomposition occurs (at $T > 300 \text{ }^\circ\text{C}$). Further purification units are not required since the AFC can tolerate small NH_3 concentrations. The heat for the endothermic cracking reaction is supplied by the exhaust gases, but catalytically burning part of the NH_3 inside the cracker can add a degree of freedom to the system design. Unfortunately, NH_3 crackers for energy conversion purposes are not commercial devices, hence it is difficult to evaluate the state-of-the-art system layout. For instance, from the information released by GENCELL about their system during the Ammonia Energy Conference 2020 [114],

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it seems that in the current version at least part of the generated electric energy is used to heat the cracker, which is not the thermodynamic optimum.

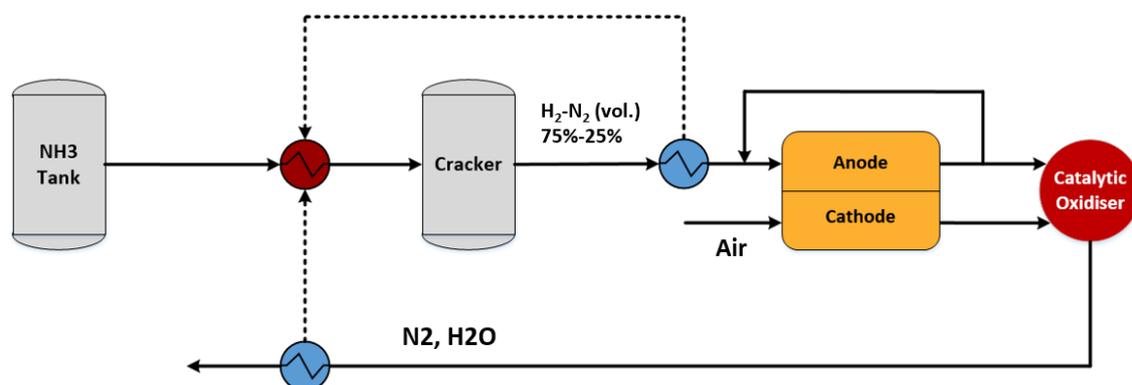


Figure 6. System layout for cracker + fuel cell plants (authors' drawing).

From data given at the conference, it is also inferred that such system may currently approach an efficiency of 40%. This figure is realistic also in comparison with data from the Alkammonia project [113]. Moreover, it is predicted that the development of cracking technology and optimization of the system layout and operating conditions may improve the system efficiency up to 50%. Despite the scarcity of published works regarding AFC systems, one work that support these efficiency values has been found [115].

The 50% efficiency is considered as a maximum efficiency for the AFC system. The HiPowAR plant could probably overcome this value in a long-term perspective, depending in particular on the maximum temperature achievable by the system. Regarding costs, it is difficult to make predictions since cost data for neither of the systems are available.

SOFC system

Initial interests towards NH₃-based Solid Oxide Fuel Cells were driven by simultaneous production of electricity and NO within the anode compartment [116,117]. NO production was desirable as it is was required for HNO₃ synthesis. Nowadays, NO production should obviously be minimized. To this end, H-SOFC seems a more logic option, as O atoms are not present at all within the anode compartment. Nevertheless, experiments have proved that NO production in the anode is negligible in O-SOFCs [118,119], since the mechanism of NO formation are governed by the presence of very high temperatures, as well as of an oxygen excess, which are not found at the anode.

Nowadays, there is high interest from researchers towards SOFCs directly powered with ammonia, due to the encouraging results achieved. The technology is still confined at a

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laboratory scale, with the highest power output reported being 1 kW [112]. Most of the last published papers are experimental works, aimed at assessing the influence of operating parameters, performance durability over time, performance under stress conditions and materials degradation due to ammonia fuelling [112,120–123]. Some works addressing cell-level and system-level modelling have also been published [124,125].

The conclusions drawn by different research groups working on ammonia-based SOFCs share some common aspects.

One established result is the path followed by chemical and electrochemical reactions when operating with direct NH_3 . The first step is ammonia decomposition, while electricity production only occurs via the usual hydrogen electro-oxidation (overall reactions reported):



This conclusion may seem trivial, but it implicitly entails that direct electro-oxidation of ammonia does not happen, which is an important result. Therefore, reaction (1) needs to proceed fast at the cell inlet, in order to avoid NH_3 acting as a fuel diluent, lowering the OCV and the cell performance. Moreover, NH_3 decomposition should occur as fast as possible to lower the surface exposed to NH_3 , which would otherwise lead to extended and fast cell degradation.

Commercially available SOFCs already show a good performance when operated with NH_3 . This confirms the excellent fuel flexibility of SOFCs, which can process several types of fuel due to high operating temperature. In the open literature, SOFCs operated with ammonia are analysed at temperatures varying in the range 550–850 °C. The operating temperature of a SOFC is of great importance for its performance and chemical and mechanical stability. Possibly, the temperature relevance is even enhanced when the SOFC is directly operated with NH_3 as it significantly increase NH_3 internal decomposition.

The percentage of NH_3 conversion is a key parameter for smooth operation. The first parameter controlling NH_3 conversion is temperature. A higher temperature boosts the kinetics of reaction (1), and pushes the thermodynamic limit of NH_3 conversion towards higher values due to its endothermic nature (up to 100%). Nevertheless, it is widely recognized that too high temperatures would lead to unacceptable materials degradation, thus it is important to find alternative routes to enhance NH_3 conversion. A long-term solution would be finding catalysts tailored for NH_3 decomposition, which is already driving some research work [126]. However, nickel (Ni) already used in commercial SOFCs, which already catalyses hydrogen electro-oxidation, seems to be a valid catalyst also for NH_3 decomposition [127].

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One remarkable and established result, proven by several authors, is that operating an SOFC directly with NH_3 , or with an equivalent amount of hydrogen and nitrogen does not alter significantly the cell performance. Direct use of NH_3 yields only a slightly worse performance, attributed to lower local temperatures throughout the cell, due to the endothermic nature of its decomposition. Nevertheless, this may be counter-balanced by less cooling power required by the air compressor, as suggested by several authors.

Matters such as degradation mechanisms and their influence on the cell performance are still open and need further clarifications. Operating SOFCs with NH_3 instead of conventional fuels introduces new materials degradation mechanisms. The most important is the formation of nickel nitride (Ni_3N), described in reaction (3), a reaction which holds increasing importance below 700°C . Despite this degradation mechanism seems to be common, also cases in which nickel nitride was not detected have been reported [128] (100 hours durability test at 750°C , ammonia conversion 100%).



How nickel nitride formation affects the cell performance seems still to be an open question, depending on the time scale, the electrodes morphology modification, the effects on the interconnects [121], the catalyst types and the thermal cycling [122].

Solid Oxide Fuel Cell technology is probably the most important competitor to the HiPowAR system, due to similarities such as the high efficiency target and presence of a O_2 membrane. Moreover, NH_3 -based Solid Oxide Fuel Cells are relatively more mature, since standard materials developed for H_2 fuel works very well also with direct NH_3 utilization. The SOFC-based system is generally simpler than the final HiPowAR scheme, due to the absence of turbine, off-gas compressor and condenser. Finally, under realistic simulation assumptions for the HiPowAR plant, the SOFC system can achieve better efficiencies up to 60%. However, note that the efficiency of a SOFC system is largely related to the cells operating voltage. The higher the voltage, the higher the system efficiency. Nevertheless, operating at very high voltage would significantly decrease the power density of the stack, hence a larger membrane area is required to achieve large efficiencies (at same power output). Therefore, a high efficiency SOFC system would likely show a relatively large investment cost. Cinti et al [129] calculated the efficiency of a NH_3 -based SOFC system, showing that direct NH_3 can be more efficient on a system-level compared to a H_2 - N_2 mixture, due to less air required for stack cooling (internal NH_3 cracking is endothermic). The results show efficiencies in the range 35%-67% for NH_3 fuel. Nevertheless, a cell voltage up to about 0.95 V was used for the highest efficiency case, which is generally not used in practical systems (cell voltage values were derived as they are not directly shown in the paper). Considering results with U_f (fuel utilization factor) being either 0.7 or 0.8 and cell voltage in the range 0.7-0.85 V, the calculated efficiency lies in the range 45%-60%. One

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disadvantage of the SOFC system is the need for very high temperature heat exchangers, which typically require expensive materials and a careful design. On the opposite, these are not required in the proposed HiPowAR plant scheme. Moreover, decay and durability issues of the HiPowAR oxygen membranes could be less severe than those typical of SOFC electrochemical cells.

The preliminary computed efficiency for the HiPowAR system under realistic conditions is about 50%, which is comparable to that obtained for a SOFC system. An increase in reactor pressure over 100 bar (which would require improved sealing and further tests on membranes' behaviour) or a turbine inlet temperature larger than 1100 °C may increase the ultimate efficiency of the HiPowAR plant approaching that of SOFCs. The maximum system temperature is the main parameter for efficiency increase, and it may be achieved by turbine blade coating and blade cooling, as well as checking performance of membrane materials at such temperature. Moreover, one inherent advantage of the HiPowAR plant is the net production of liquid water, which can be critical in the coming decades (water will be needed for agriculture, H₂ production, etc.). Part of the water produced may be used for turbine blade cooling in a final implementation. A more complete comparison between the SOFC technology and HiPowAR plant would have to include NH₃ and NO_x emissions and systems investment cost, which is not possible at this stage of the project. Nevertheless, it can already be inferred that a NH₃-based SOFC system will likely have a cost very similar to conventional SOFC systems, although differences in the overall process would exist (as an example, in conventional NG-fed systems a pre-reformer is usually present, whereas if no pre-treatment is required for NH₃, the system layout could be simplified; nevertheless, pre-cracking part of the NH₃ is known to hinder nickel nitride formation within the cell).



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SUMMARY

This section summarizes the findings discussed in the previous section in order to provide a comparison of the main techno-economic features of the investigated technologies. Table 1 and Table 2 constitute a benchmark framework for the most important technologies which are in competition with the HiPowAR project concept.

Table 1. Summary of techno-economic parameters for mature technologies.

Technology	Fuel	Capacity range	Max T [°C]	Electric efficiency (today BAT)	Electric efficiency (perspective 5-10y)	CO ₂ emissions [g/kWh _{el}] ⁽¹⁾	CAPEX [€/kW _{nom}]	Maturity (TRL)
Small-scale GT	NG H ₂	2-20 MW	1300	30-33%	33-36%	650-700	400-500	9
								7-8
Large-scale GT	NG H ₂	50-600 MW	1500	41-43%	43-45%	470-520	200-300	9
								7-8
PEMFC	H ₂	kW to MW (modular)	80	42-45%	50%	0	1500-2000	7-8
GTCC	NG H ₂	500-1000 MW	1500	60-63%	63-66%	320-350	600	9
								8
GTCC+CCS	NG	400-800 MW	1500	50-53%	55-60%	30-60	1000-1300	8
Allam cycle	NG	20-500 MW	1150	54%	58%	0	n.a.	6-7
SOFC	NG	kW to MW (modular)	850	52-55%	60%	320-350	500 ⁽²⁾ -	7-8
	H ₂		850	55-57%	65%	0	3500	7-8
Hybrid cycle GTCC-SOFC + CCS	NG	Multi MW	1500 / 850	n.a.	70-73%	250-270	n.a.	5-6
ICE	Diesel	few kW - 50 MW	>2000	40-42% ⁽³⁾	42-44% ⁽³⁾	590-660	1000 (>100 kW)	9
	LPG, LNG					460-520		9
HiPowAR target	NH ₃	Pilot: 10-15 kW Scale-up: 100 MW	900	n.a.	50%	0	n.a.	4

(1) when NG or H₂ are possible as fuels, values refer to NG fuelling since they are zero in case of hydrogen.

(2) long term target

(3) referring to a 1-2 MW range

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Table 2. Summary of techno-economic parameters for ammonia-based technologies.

Technology	Fuel	Capacity range	Max T [°C]	Electric efficiency (BAT today)	Electric efficiency (perspective 5-10y)	CO ₂ emissions [g/kWh _{el}]	CAPEX [€/MW _{nom}]	Maturity (TRL)
ICE	NH ₃ (+ auxiliary fuel)	kW to multi-MW.	1800	n.a. ⁽¹⁾	42-44% ⁽²⁾	depend on auxiliary fuel ⁽⁴⁾	1000 (>100 kW)	4
GT	NH ₃ (+ auxiliary fuel)	multi-MW to hundred MW	n.a. ⁽¹⁾	n.a. ⁽¹⁾	43-45% ⁽²⁾	depend on auxiliary fuel ⁽⁴⁾	As HC-based	4
SOFC	NH ₃	kW to MW (modular)	550-850	n.a. ⁽¹⁾	60-65% ⁽²⁾	0	500 ⁽³⁾ -3500	4
Cracking + AFC	NH ₃	kW to MW (modular)	300-500	≈ 40%	≈ 45%	0	n.a. ⁽¹⁾	7
HIPOWAR target	NH ₃	Pilot: 10-15 kW(?) Scale-up: 100 MW	900	n.a. ⁽¹⁾	50%	0	n.a. ⁽¹⁾	4

(1) not yet established.

(2) efficiency perspectives are expected to be equal to those of the case of HC fuels (see Table 1). Values for ICE refer to a 1-2 MW range. Values for GT refer to large scale aeroderivative or heavy duty machines operating in simple cycle.

(3) long term target.

(4) CO₂ emissions are zero if the auxiliary fuel is hydrogen (NH₃+H₂ mix).

Conclusions

Several R&D projects are pursuing the use of ammonia as a clean, de-carbonized fuel for both stationary power generation and mobility uses, building a framework in which the HiPowAR project can successfully take place. Mature competitive technologies in the field of power generation either rely on using hydrogen (e.g. in low temperature fuel cells) or on using hydrocarbons, with the burden of CO₂ capture, when they aim at the same zero-CO₂ target addressed by the HiPowAR concept, as reported in the deliverable and in the summary given in Table 1.

When looking to competitive technologies based on the use of ammonia, which are summarized in Table 2, Internal Combustion Engines (ICE) emerges as a quite competitive option in terms of versatility of application and availability on a wide range of sizes; while gas turbines (GT) become particularly attractive for large scale stationary power at the ten to hundred MW scale. However, they both have to deal with the evolution of combustion technology required to achieve low NO_x and NH₃ emissions in ammonia applications.

Among the findings of this analysis, it is found that Solid Oxide Fuel Cell technology is probably the most important competitor to the HiPowAR system, due to similarities such as the high efficiency target and presence of a O₂ membrane. Moreover, NH₃-based Solid Oxide Fuel Cells are relatively more mature, since standard materials developed for H₂ fuel are reported to work well also with direct NH₃ utilization. The SOFC-based system is generally simpler than the final HiPowAR scheme, due to the absence of turbine, off-gas compressor and condenser., and may achieve pretty high efficiencies (up to 60%). However, decay and durability issues of the HiPowAR oxygen membranes could be less severe than those typical of SOFC electrochemical cells. Moreover, the efficiency of a SOFC system is largely related to the cells operating voltage (the higher the voltage, the higher the system efficiency), where operating at very high voltage requires a lower current density and a larger cell active area (at same power output). Therefore, a high efficiency SOFC system would likely show a relatively large investment cost, with potential advantage for the HiPowAR concept which partly relies on lower cost components (in particular the turbine and the electro-mechanical equipment), although in parallel to the oxygen transport membrane, whose costs are still to be optimized and investigated by the project.

References

- [1] A. Poulikkas, An overview of current and future sustainable gas turbine technologies, *Renewable and Sustainable Energy Reviews*. 9 (2005) 409–443. doi:10.1016/j.rser.2004.05.009.
- [2] European Commission, Horizon 2020. Work Programme 2018-2020. 19-General Annexes, 2019.
- [3] E. Macchi, S. Campanari, P. Silva, *La microgenerazione a gas naturale*, Polipress, 2005.
- [4] M.R. Bothien, A. Ciani, J.P. Wood, G. Fruechtel, Sequential Combustion in Gas Turbines: The Key Technology for Burning High Hydrogen Contents With Low Emissions, in: *Proceedings of ASME Turbo Expo 2019*, 2019: pp. GT2019-90798.
- [5] SNAM e l'idrogeno. La sperimentazione a Contursi Terme, (2019). https://www.snam.it/it/hydrogen_challenge/snam_idrogeno/ (accessed June 10, 2020).
- [6] G. Guandalini, P. Colbertaldo, S. Campanari, Dynamic modeling of natural gas quality within transport pipelines in presence of hydrogen injections, *Applied Energy*. 185 (2017) 1712–1723. doi:10.1016/j.apenergy.2016.03.006.
- [7] Ansaldo Energia, Presentation of the first GT36 Gas Turbine produced in Genoa, (2020). <https://www.ansaldoenergia.com/Pages/Edison-Ansaldo-Energia-Porto-Marghera.aspx> (accessed January 15, 2021).
- [8] Gas Turbine World, 2019 GTW Handbook, vol. 34, 2019.
- [9] M.C. Cameretti, A. Cappiello, R. De Robbio, Comparison between Hydrogen and Syngas Fuels in an Integrated Micro Gas Turbine / Solar Field with Storage, (2020).
- [10] OPRA Turbines, Don't let it go to waste, (2019). <https://www.opraturbines.com/waste-no-more/> (accessed February 2, 2021).
- [11] J. Burke, GE's 9HA.02 turbines running commercially for the first time, (n.d.). https://www.diesलगasturbine.com/news/GE-s-9HA.02-turbines-running-commercially-for-the-first-time/8010557.article?utm_source=newsletter&utm_medium=Diesel-Gas-Turbine-Worldwide-News-Diesel-Gas-Turbine-Worldwide-News-25th-February-2021&utm_term=DGTWW (accessed February 3, 2021).
- [12] European Technology Platform for Zero Emission Fossil Fuel Power Plants (ZEP), *The Costs of CO2 Capture, Transport and Storage*, 2011.
- [13] A. Chandan, M. Hattenberger, A. El-Kharouf, S. Du, A. Dhir, V. Self, B.G. Pollet, A. Ingram, W. Bujalski, High temperature (HT) polymer electrolyte membrane fuel cells (PEMFC)-A review, *Journal of Power Sources*. 231 (2013) 264–278. doi:10.1016/j.jpowsour.2012.11.126.
- [14] Grasshopper Project - Grid Assisting Modular Hydrogen PEM Power Plant, (n.d.). <http://www.grasshopperproject.eu/>.
- [15] E. Crespi, G. Guandalini, J. Coolegem, M. Martín, S. Gößling, P. Beckhaus, J. Petkovšek, S. Buche, S. Campanari, GRASSHOPPER project: grid assisting modular hydrogen PEM power plant, in: *Proc. of EFCF 2019*, 2-5 July 2019, Lucerne (CH), 2019: pp. 94–103.
- [16] S. Campanari, G. Guandalini, J. Coolegem, J. ten Have, P. Hayes, A.H. Pichel, Modeling, Development, and Testing of a 2 MW Polymeric Electrolyte Membrane Fuel Cell Plant Fueled With Hydrogen From a Chlor-Alkali Industry, *Journal of Electrochemical Energy Conversion and Storage*. 16 (2019) 1–9. doi:10.1115/1.4042923.
- [17] J. Li, T. Lv, X. Dong, J. Yu, B. Yu, P. Li, X. Yao, Y. Zhao, Y. Li, Linear discharge model, power losses and overall efficiency of the solid oxide fuel cell with thin film samarium doped ceria electrolyte.

DELIVERABLE REPORT

- Part II: Power losses and overall efficiency, *International Journal of Hydrogen Energy*. 42 (2017) 17522–17527. doi:10.1016/j.ijhydene.2017.02.106.
- [18] T. Matsui, M. Inaba, A. Mineshige, Z. Ogumi, Electrochemical properties of ceria-based oxides for use in intermediate-temperature SOFCs, *Solid State Ionics*. 176 (2005) 647–654. doi:10.1016/j.ssi.2004.10.011.
- [19] L. Mastropasqua, A. Pegorin, S. Campanari, Low fuel utilisation solid oxide fuel cell system for CO₂-free hydrogen production in oil refineries, *Journal of Power Sources*. 448 (2020) 227461. doi:10.1016/j.jpowsour.2019.227461.
- [20] L. Mastropasqua, M. Spinelli, A. Paganoni, S. Campanari, Preliminary design of a MW-class demo system for CO₂ capture with MCFC in a university campus cogeneration plant, in: *Energy Procedia*, Elsevier B.V., 2017: pp. 453–460. doi:10.1016/j.egypro.2017.08.213.
- [21] S. Campanari, L. Mastropasqua, M. Gazzani, P. Chiesa, M.C. Romano, Predicting the ultimate potential of natural gas SOFC power cycles with CO₂ capture - Part B: Applications, *Journal of Power Sources*. 325 (2016) 194–208. doi:10.1016/j.jpowsour.2016.05.134.
- [22] R.J. Allam, M. Palmer, G.W.J. Brown, System and method for high efficiency power generation using a carbon dioxide circulating working fluid, US 8596075 B2, 2013.
- [23] R. Scaccabarozzi, M. Gatti, E. Martelli, Thermodynamic Optimization and Part-load Analysis of the NET Power Cycle, *Energy Procedia*. 114 (2017) 551–560. doi:10.1016/j.egypro.2017.03.1197.
- [24] S.A. Zaryab, R. Scaccabarozzi, E. Martelli, Advanced part-load control strategies for the Allam cycle, *Applied Thermal Engineering*. 168 (2020) 114822. doi:10.1016/j.applthermaleng.2019.114822.
- [25] M.O. Viguera-Zuniga, M.E. Tejada-Del-Cueto, J.A. Vasquez-Santacruz, A.L. Herrera-May, A. Valera-Medina, Numerical predictions of a swirl combustor using complex chemistry fueled with ammonia/hydrogen blends, *Energies*. 13 (2020). doi:10.3390/en13020288.
- [26] Cross-ministerial Strategic Innovation Promotion Program (SIP), *Energy Carriers*, 2015.
- [27] Campfire Project, (n.d.). <https://wir-campfire.de/en/project-en/> (accessed October 9, 2020).
- [28] T. Ito, Utilization of the hydrogen energy carrier in large scale power plant, in: *2019 MIT Energy Initiative Spring Symposium*, 2009.
- [29] B. Shiozawa, CO₂-Free Ammonia as CO₂-Free Fuel and Hydrogen Carrier - Achievements of SIP "Energy Carriers," 2019.
- [30] A. Karabeyoglu, B. Evans, J. Stevens, B. Cantwell, D. Micheletti, Development of ammonia based fuels for environmentally friendly power generation, *10th Annual International Energy Conversion Engineering Conference, IECEC 2012*. (2012) 1–27. doi:10.2514/6.2012-4055.
- [31] B. Evans, Using Local Green Energy and Ammonia to Power Gas Turbine Generators, in: *10th NH₃ Fuel Conference*, 24 Sept 2013, 2013.
- [32] H.K. Newhall, E.S. Starkman, Theoretical performance of ammonia as a gas turbine fuel, in: *SAE National Powerplant and Transportation Meetings*, 1966. doi:10.4271/660768.
- [33] D. Faehn, M.G. Bull, J.R. Shekleton, Experimental investigation of ammonia as a gas turbine engine fuel, in: *SAE - Combined Powerplant and Transportation Meeting*, 1966: p. 660769. doi:10.4271/660769.
- [34] F.J. Verkamp, M.C. Hardin, J.R. Williams, Ammonia combustion properties and performance in gas-turbine burners, *Symposium (International) on Combustion*. 11 (1967) 985–992. doi:10.1016/S0082-0784(67)80225-X.
- [35] D.T. Pratt, Performance of ammonia-fired gas-turbine combustors, 1967.

DELIVERABLE REPORT

- [36] M.G. Bull, Development of an Ammonia-Burning Gas Turbine Engine, 1968.
- [37] N. Iki, O. Kurata, T. Matsunuma, T. Inoue, M. Suzuki, T. Tsujimura, H. Furutani, Micro gas turbine firing kerosene and ammonia, in: Proceedings of ASME Turbo Expo 2015, GT2015-43689, 2017.
- [38] O. Kurata, N. Iki, T. Matsunuma, T. Inoue, T. Tsujimura, H. Furutani, H. Kobayashi, A. Hayakawa, Performances and emission characteristics of NH₃-air and NH₃-CH₄-air combustion gas-turbine power generations, Proceedings of the Combustion Institute. (2016) 3351–3359. doi:10.1016/j.proci.2016.07.088.
- [39] A. Valera-Medina, D.G. Pugh, P. Marsh, G. Bulat, P. Bowen, Preliminary study on lean premixed combustion of ammonia-hydrogen for swirling gas turbine combustors, International Journal of Hydrogen Energy. 42 (2017) 24495–24503. doi:10.1016/j.ijhydene.2017.08.028.
- [40] A. Hayakawa, Y. Arakawa, R. Mimoto, K.D.K.A. Somarathne, T. Kudo, H. Kobayashi, Experimental investigation of stabilization and emission characteristics of ammonia/air premixed flames in a swirl combustor, International Journal of Hydrogen Energy. 42 (2017) 14010–14018. doi:10.1016/j.ijhydene.2017.01.046.
- [41] A.A. Desoky, A.S.K. Halaf, F.M. El-Mahallawy, Combustion process in a gas turbine combustor when using H₂, NH₃ and LPG fuels, International Journal of Hydrogen Energy. 15 (1990) 203–211.
- [42] O. Kurata, N. Iki, T. Matsunuma, T. Inoue, T. Tsujimura, H. Furutani, A. Hayakawa, H. Kobayashi, SUCCESS OF AMMONIA-FIRED, REGENERATOR-HEATED, DIFFUSION COMBUSTION GAS TURBINE POWER GENERATION AND PROSPECT OF LOW NO_x COMBUSTION WITH HIGH COMBUSTION EFFICIENCY, in: Proceedings of the ASME 2017 Power Conference Joint With ICOPE-17, POWER-ICOPE2017-3277, 2017.
- [43] A.A. Khateeb, T.F. Guiberti, X. Zhu, M. Younes, A. Jamal, W.L. Roberts, Stability limits and exhaust NO performances of ammonia-methane-air swirl flames, Experimental Thermal and Fluid Science. 114 (2020) 110058. doi:10.1016/j.expthermflusci.2020.110058.
- [44] E.C. Okafor, H. Yamashita, A. Hayakawa, K.D.K.A. Somarathne, T. Kudo, T. Tsujimura, M. Uchida, S. Ito, H. Kobayashi, Flame stability and emissions characteristics of liquid ammonia spray co-fired with methane in a single stage swirl combustor, Fuel. 287 (2021) 119433. doi:10.1016/j.fuel.2020.119433.
- [45] A. Valera-Medina, R. Marsh, J. Runyon, D. Pugh, P. Beasley, T. Hughes, P. Bowen, Ammonia-methane combustion in tangential swirl burners for gas turbine power generation, Applied Energy. 185 (2017) 1362–1371. doi:10.1016/j.apenergy.2016.02.073.
- [46] P. Kumar, T.R. Meyer, Experimental and modeling study of chemical-kinetics mechanisms for H₂-NH₃-air mixtures in laminar premixed jet flames, Fuel. 108 (2013) 166–176. doi:10.1016/j.fuel.2012.06.103.
- [47] J. Li, H. Huang, N. Kobayashi, Z. He, Y. Nagai, Study on using hydrogen and ammonia as fuels: Combustion characteristics and NO_x formation, International Journal of Energy Research. 38 (2014) 1214–1223. doi:10.1002/er.
- [48] A. Ichikawa, A. Hayakawa, Y. Kitagawa, K.D. Kunkuma Amila Somarathne, T. Kudo, H. Kobayashi, Laminar burning velocity and Markstein length of ammonia/hydrogen/air premixed flames at elevated pressures, International Journal of Hydrogen Energy. 40 (2015) 9570–9578. doi:10.1016/j.ijhydene.2015.04.024.
- [49] A. HAYAKAWA, T. GOTO, R. MIMOTO, T. KUDO, H. KOBAYASHI, NO formation/reduction mechanisms of ammonia/air premixed flames at various equivalence ratios and pressures,

DELIVERABLE REPORT

- Mechanical Engineering Journal. 2 (2015) 14-00402-14-00402. doi:10.1299/mej.14-00402.
- [50] H. Nozari, A. Karabeyoglu, Numerical study of combustion characteristics of ammonia as a renewable fuel and establishment of reduced reaction mechanisms, *Fuel*. 159 (2015) 223–233. doi:10.1016/j.fuel.2015.06.075.
- [51] A. Valera-Medina, S. Morris, J. Runyon, D.G. Pugh, R. Marsh, P. Beasley, T. Hughes, Ammonia, Methane and Hydrogen for Gas Turbines, *Energy Procedia*. 75 (2015) 118–123. doi:10.1016/j.egypro.2015.07.205.
- [52] K.D.K.A. Somarathne, S. Hatakeyama, A. Hayakawa, H. Kobayashi, Numerical study of a low emission gas turbine like combustor for turbulent ammonia/air premixed swirl flames with a secondary air injection at high pressure, *International Journal of Hydrogen Energy*. 42 (2017) 27388–27399. doi:10.1016/j.ijhydene.2017.09.089.
- [53] H. Xiao, A. Valera-Medina, Chemical Kinetic Mechanism Study on Premixed Combustion of Ammonia/Hydrogen Fuels for Gas Turbine Use, *Journal of Engineering for Gas Turbines and Power*. 139 (2017). doi:10.1115/1.4035911.
- [54] H. Xiao, A. Valera-Medina, P.J. Bowen, Modeling Combustion of Ammonia/Hydrogen Fuel Blends under Gas Turbine Conditions, *Energy and Fuels*. 31 (2017) 8631–8642. doi:10.1021/acs.energyfuels.7b00709.
- [55] A. Goldmann, F. Dinkelacker, Approximation of laminar flame characteristics on premixed ammonia/hydrogen/nitrogen/air mixtures at elevated temperatures and pressures, *Fuel*. 224 (2018) 366–378. doi:10.1016/j.fuel.2018.03.030.
- [56] K.D.K.A. Somarathne, S. Colson, A. Hayakawa, H. Kobayashi, Modelling of ammonia/air non-premixed turbulent swirling flames in a gas turbine-like combustor at various pressures, *Combustion Theory and Modelling*. 22 (2018) 973–997. doi:10.1080/13647830.2018.1468035.
- [57] A. Valera-Medina, M. Gutesa, H. Xiao, D. Pugh, A. Giles, B. Goktepe, R. Marsh, P. Bowen, Premixed ammonia/hydrogen swirl combustion under rich fuel conditions for gas turbines operation, *International Journal of Hydrogen Energy*. 44 (2019) 8615–8626. doi:10.1016/j.ijhydene.2019.02.041.
- [58] R. Ichimura, K. Hadi, N. Hashimoto, A. Hayakawa, H. Kobayashi, O. Fujita, Extinction limits of an ammonia/air flame propagating in a turbulent field, *Fuel*. 246 (2019) 178–186. doi:10.1016/j.fuel.2019.02.110.
- [59] Y. Wang, L. Liang, X. Lin, T. Su, X. Wang, H. Xiao, Emissions of nitrogen-based fuel combustion in swirl burner, *Energy Procedia*. 158 (2019) 1706–1711. doi:10.1016/j.egypro.2019.01.397.
- [60] N.A. Hussein, A. Valera-Medina, A.S. Alsaegh, Ammonia- hydrogen combustion in a swirl burner with reduction of NO_x emissions, *Energy Procedia*. 158 (2019) 2305–2310. doi:10.1016/j.egypro.2019.01.265.
- [61] M. Guteša Božo, M.O. Viguera-Zuniga, M. Buffi, T. Seljak, A. Valera-Medina, Fuel rich ammonia-hydrogen injection for humidified gas turbines, *Applied Energy*. 251 (2019). doi:10.1016/j.apenergy.2019.113334.
- [62] B. Mei, X. Zhang, S. Ma, M. Cui, H. Guo, Z. Cao, Y. Li, Experimental and kinetic modeling investigation on the laminar flame propagation of ammonia under oxygen enrichment and elevated pressure conditions, *Combustion and Flame*. 210 (2019) 236–246. doi:10.1016/j.combustflame.2019.08.033.
- [63] A.A. Khateeb, T.F. Guiberti, X. Zhu, M. Younes, A. Jamal, W.L. Roberts, Stability limits and NO emissions of technically-premixed ammonia-hydrogen-nitrogen-air swirl flames, *International*

DELIVERABLE REPORT

- Journal of Hydrogen Energy. 45 (2020) 22008–22018. doi:10.1016/j.ijhydene.2020.05.236.
- [64] S. Wang, Z. Wang, A.M. Elbaz, X. Han, Y. He, M. Costa, A.A. Konnov, W.L. Roberts, Experimental study and kinetic analysis of the laminar burning velocity of NH₃/syngas/air, NH₃/CO/air and NH₃/H₂/air premixed flames at elevated pressures, *Combustion and Flame*. 221 (2020) 270–287. doi:10.1016/j.combustflame.2020.08.004.
- [65] S. Wiseman, M. Rieth, A. Gruber, J.R. Dawson, J.H. Chen, A comparison of the blow-out behavior of turbulent premixed ammonia/hydrogen/nitrogen-air and methane-air flames, *Proceedings of the Combustion Institute*. (2020) 1–8. doi:10.1016/j.proci.2020.07.011.
- [66] A. Hayakawa, Y. Hirano, E.C. Okafor, H. Yamashita, T. Kudo, H. Kobayashi, Experimental and numerical study of product gas characteristics of ammonia/air premixed laminar flames stabilized in a stagnation flow, *Proceedings of the Combustion Institute*. (2021) 1–9. doi:10.1016/j.proci.2020.07.030.
- [67] A. Goldmann, F. Dinkelacker, Experimental investigation and modeling of boundary layer flashback for non-swirling premixed hydrogen/ammonia/air flames, *Combustion and Flame*. 226 (2021) 362–379. doi:10.1016/j.combustflame.2020.12.021.
- [68] Z. Li, S. Li, Kinetics modeling of NO_x emissions characteristics of a NH₃/H₂ fueled gas turbine combustor, *International Journal of Hydrogen Energy*. 46 (2021) 4526–4537. doi:10.1016/j.ijhydene.2020.11.024.
- [69] S. Mashruk, H. Xiao, A. Valera-Medina, Rich-Quench-Lean model comparison for the clean use of humidified ammonia/hydrogen combustion systems, *International Journal of Hydrogen Energy*. 46 (2021) 4472–4484. doi:10.1016/j.ijhydene.2020.10.204.
- [70] H. Kobayashi, A. Hayakawa, K.D.K.A. Somarathne, E.C. Okafor, Science and technology of ammonia combustion, *Proceedings of the Combustion Institute*. 37 (2019) 109–133. doi:10.1016/j.proci.2018.09.029.
- [71] K.D.K.A. Somarathne, E. C. Okafor, A. Hayakawa, T. Kudo, O. Kurata, N. Iki, H. Kobayashi, Emission characteristics of turbulent non-premixed ammonia/air and methane/air swirl flames through a rich-lean combustor under various wall thermal boundary conditions at high pressure, *Combustion and Flame*. 210 (2019) 247–261. doi:10.1016/j.combustflame.2019.08.037.
- [72] E.C. Okafor, K.D.K.A. Somarathne, A. Hayakawa, T. Kudo, O. Kurata, N. Iki, H. Kobayashi, Towards the development of an efficient low-NO_x ammonia combustor for a micro gas turbine, *Proceedings of the Combustion Institute*. 37 (2019) 4597–4606. doi:10.1016/j.proci.2018.07.083.
- [73] O. Kurata, N. Iki, T. Inoue, T. Matsunuma, T. Tsujimura, H. Furutani, M. Kawano, K. Arai, E.C. Okafor, A. Hayakawa, H. Kobayashi, Development of a wide range-operable, rich-lean low-NO_x combustor for NH₃ fuel gas-turbine power generation, *Proceedings of the Combustion Institute*. 37 (2019) 4587–4595. doi:10.1016/j.proci.2018.09.012.
- [74] R.C. Rocha, M. Costa, X.-S. Bai, Combustion and Emission Characteristics of Ammonia under Conditions Relevant to Modern Gas Turbines, *Combustion Science and Technology*. (2020) 1–20. doi:10.1080/00102202.2020.1748018.
- [75] MAN Energy Solutions, MAN B&W two-stroke engine operating on ammonia, 2020.
- [76] R.S. Laursen, Ship Operation Using LPG and Ammonia As Fuel on MAN B&W Dual Fuel ME-LGIP Engines - Using low carbon ammonia fuel, in: ME-LGPI Event 2018, 2018.
- [77] M. Koike, H. Miyagawa, T. Suzuoki, K. Ogasawara, Ammonia as a hydrogen energy carrier and its application to internal combustion engines, in: Institution of Mechanical Engineers - Sustainable Vehicle Technologies 2012: Driving the Green Agenda, Woodhead Publishing Limited, 2012: pp.



DELIVERABLE REPORT

- 61–70. doi:10.1533/9780857094575.2.61.
- [78] S. Kojima, N. Nakamura, R. Shimizu, T. Sugimoto, K.-O. Kim, Ammonia burning combustion engine, US 2011/0265463 A1, 2011.
- [79] Hydrofuel, (n.d.). <https://www.nh3fuel.com/> (accessed January 19, 2021).
- [80] E. Kroch, Ammonia - A fuel for motor buses, *Journal of the Institute of Petroleum*. 31 (1945) 213–223.
- [81] W. Cornelius, L.W. Huellmantel, H.R. Mitchell, Ammonia as an engine fuel, *SAE Technical Papers*. (1965) 650052. doi:10.4271/650052.
- [82] J.T. Gray, E. Dimitroff, N.T. Meckel, R.D. Quillian, Ammonia fuel - Engine compatibility and combustion, *SAE Technical Papers*. (1966) 660156. doi:10.4271/660156.
- [83] E.S. Starkman, G.S. Samuelsen, Flame-propagation rates in ammonia-air combustion at high pressure, *Symposium (International) on Combustion*. 11 (1967) 1037–1045. doi:10.1016/S0082-0784(67)80230-3.
- [84] E.S. Starkman, H.K. Newhall, R. Sutton, T. Maguire, L. Farbar, Ammonia as a Spark Ignition Engine Fuel: Theory and Application, *SAE Technical Papers*. (1967) 660155. doi:10.4271/670946.
- [85] E.S. Starkman, R.F. Sawyer, R. Carr, G. Johnson, L. Muzio, Alternative fuels for control of engine emission, *Journal of the Air Pollution Control Association*. 20 (1970) 87–92. doi:10.1080/00022470.1970.10469379.
- [86] R.F. Sawyer, E.S. Starkman, L. Muzio, W.L. Schmidt, Oxides of nitrogen in the combustion products of an ammonia fueled reciprocating engine, *SAE Technical Papers*. (1968) 680401. doi:10.4271/680401.
- [87] T.J. Pearsall, *Ammonia Application in Reciprocating Engines*, 1967.
- [88] T.J. Pearsall, C.G. Garabedian, Combustion of Anhydrous Ammonia in Diesel Engines, *SAE Technical Papers*. (1967) 670947.
- [89] P.G. Grimes, Energy Depot Fuel Production and Utilization, *SAE Transactions*. 74 (1966) 650051.
- [90] C.S. Mørch, A. Bjerre, M.P. Gøttrup, S.C. Sorenson, J. Schramm, Ammonia/hydrogen mixtures in an SI-engine: Engine performance and analysis of a proposed fuel system, *Fuel*. 90 (2011) 854–864. doi:10.1016/j.fuel.2010.09.042.
- [91] C. Lhuillier, P. Brequigny, F. Contino, C. Mounaïm-Rousselle, Experimental study on ammonia/hydrogen/air combustion in spark ignition engine conditions, *Fuel*. 269 (2020) 117448. doi:10.1016/j.fuel.2020.117448.
- [92] C. Lhuillier, P. Brequigny, F. Contino, C. Mounaïm-Rousselle, Combustion Characteristics of Ammonia in a Modern Spark-Ignition Engine, in: *Conference on Sustainable Mobility*, Oct 2019, Catane, Italy, 2020: p. hal-02322493.
- [93] S. Frigo, R. Gentili, F. De Angelis, Further insight into the possibility to fuel a SI engine with ammonia plus hydrogen, *SAE Technical Papers*. 32 (2014) 0082. doi:10.4271/2014-32-0082.
- [94] M. Comotti, S. Frigo, Hydrogen generation system for ammonia-hydrogen fuelled internal combustion engines, *International Journal of Hydrogen Energy*. 40 (2015) 10673–10686. doi:10.1016/j.ijhydene.2015.06.080.
- [95] C. Lhuillier, P. Brequigny, F. Contino, C. Mounaïm-Rousselle, Performance and Emissions of an Ammonia-Fueled SI Engine with Hydrogen Enrichment, in: *14th International Conference on Engines & Vehicles*, Sep 2019, Capri, Italy, 2020: p. hal-02322439.
- [96] S. Frigo, R. Gentili, N. Doveri, Ammonia plus hydrogen as fuel in a S.I. engine: Experimental results, *SAE Technical Papers - 2012 Small Engine Technology Conference & Exhibition*. 32 (2012) 0019.



DELIVERABLE REPORT

- doi:10.4271/2012-32-0019.
- [97] S. Frigo, R. Gentili, Analysis of the behaviour of a 4-stroke Si engine fuelled with ammonia and hydrogen, *International Journal of Hydrogen Energy*. 38 (2013) 1607–1615. doi:10.1016/j.ijhydene.2012.10.114.
- [98] P. Dimitriou, R. Javaid, A review of ammonia as a compression ignition engine fuel, *International Journal of Hydrogen Energy*. 45 (2020) 7098–7118. doi:10.1016/j.ijhydene.2019.12.209.
- [99] A.J. Reiter, S. Kong, DIESEL ENGINE OPERATION USING AMMONIA AS A CARBON-FREE FUEL, in: *Proceedings of the ASME 2010 Internal Combustion Engine Division Fall Technical Conference, ICEF2010-35026*, 2010.
- [100] A.J. Reiter, S.C. Kong, Combustion and emissions characteristics of compression-ignition engine using dual ammonia-diesel fuel, *Fuel*. 90 (2011) 87–97. doi:10.1016/j.fuel.2010.07.055.
- [101] F.R. Westlye, A. Ivarsson, J. Schramm, Experimental investigation of nitrogen based emissions from an ammonia fueled SI-engine, *Fuel*. 111 (2013) 239–247. doi:10.1016/j.fuel.2013.03.055.
- [102] Y. Niki, D.-H. Yoo, K. Hirata, H. Sekiguchi, Effects of ammonia gas mixed into intake air on combustion and emissions characteristics in Diesel engine, in: *Proceedings of the ASME 2016 Internal Combustion Engine Fall Technical Conference, ICEF2016-9364*, 2016: pp. 1–6.
- [103] R. Halseid, P.J.S. Vie, R. Tunold, Effect of ammonia on the performance of polymer electrolyte membrane fuel cells, *Journal of Power Sources*. 154 (2006) 343–350. doi:10.1016/j.jpowsour.2005.10.011.
- [104] T. Hejze, J.O. Besenhard, K. Kordesch, M. Cifrain, R.R. Aronsson, Current status of combined systems using alkaline fuel cells and ammonia as a hydrogen carrier, *Journal of Power Sources*. 176 (2008) 490–493. doi:10.1016/j.jpowsour.2007.08.117.
- [105] J.C. Ganley, An intermediate-temperature direct ammonia fuel cell with a molten alkaline hydroxide electrolyte, *Journal of Power Sources*. 178 (2008) 44–47. doi:10.1016/j.jpowsour.2007.11.093.
- [106] G. Meng, C. Jiang, J. Ma, Q. Ma, X. Liu, Comparative study on the performance of a SDC-based SOFC fueled by ammonia and hydrogen, *Journal of Power Sources*. 173 (2007) 189–193. doi:10.1016/j.jpowsour.2007.05.002.
- [107] Y. Lin, R. Ran, Y. Guo, W. Zhou, R. Cai, J. Wang, Z. Shao, Proton-conducting fuel cells operating on hydrogen, ammonia and hydrazine at intermediate temperatures, *International Journal of Hydrogen Energy*. 35 (2010) 2637–2642. doi:10.1016/j.ijhydene.2009.04.019.
- [108] Gencell, Gencell A5 - Off-grid power solution, (n.d.). <https://www.gencellenergy.com/our-products/gencell-a5/> (accessed November 16, 2020).
- [109] AFC Energy, HydroX-Cell (L), (n.d.). https://www.afcenergy.com/products/hydrox-cell_l/ (accessed November 16, 2020).
- [110] AFC Energy, HydroX-Cell (S), (n.d.). <https://www.afcenergy.com/products/hydrox-cell-s/> (accessed November 16, 2020).
- [111] E. Satomi, H. Iwai, S. Suzuki, T. Koide, Y. Takahashi, E. Eguchi, Development of Ammonia-Fueled SOFC, *ECS Transactions*. 78 (2017) 2537–2540. doi:10.1149/07801.2537ecst.
- [112] M. Kishimoto, H. Muroyama, S. Suzuki, M. Saito, T. Koide, Y. Takahashi, T. Horiuchi, H. Yamasaki, S. Matsumoto, H. Kubo, N. Takahashi, A. Okabe, S. Ueguchi, M. Jun, A. Tateno, T. Matsuo, T. Matsui, H. Iwai, H. Yoshida, K. Eguchi, Development of 1 kW-class Ammonia-fueled Solid Oxide Fuel Cell Stack, *Fuel Cells*. 20 (2020) 80–88. doi:10.1002/face.201900131.
- [113] Alkammonia - Project description, (n.d.). <http://alkammonia.eu/2014/project-description/>



DELIVERABLE REPORT

- (accessed January 19, 2021).
- [114] G. Finkelshtain, GenCell's ammonia-fuelled, off-grid power generation solution, in: Ammonia Energy Conference 2020, 2020.
 - [115] B. Cox, K. Treyer, Environmental and economic assessment of a cracked ammonia fuelled alkaline fuel cell for off-grid power applications, *Journal of Power Sources*. 275 (2015) 322–335. doi:10.1016/j.jpowsour.2014.11.023.
 - [116] C.G. Vayenas, R.D. Farr, Cogeneration of electric energy and nitric oxide, *Science*. 208 (1980) 593–594. doi:10.1126/science.208.4444.593.
 - [117] C.T. Sigal, C.G. Vayenas, AMMONIA OXIDATION TO NITRIC OXIDE IN A SOLID ELECTROLYTE, *Solid State Ionics*. 5 (1981) 567–570.
 - [118] N.J.J. Dekker, G. Rietveld, Highly efficient conversion of ammonia in electricity by solid oxide fuel cells, *Journal of Fuel Cell Science and Technology*. 3 (2006) 499–502. doi:10.1115/1.2349536.
 - [119] L. ZHANG, Y. CONG, W. YANG, L. LIN, A Direct Ammonia Tubular Solid Oxide Fuel Cell, *Chinese Journal of Catalysis*. 28 (2007) 749–751. doi:10.1016/S1872-2067(07)60062-X.
 - [120] B. Stoeckl, M. Preininger, V. Subotić, C. Gaber, M. Seidl, P. Sommersacher, H. Schrottner, C. Hochenauer, High Utilization of Humidified Ammonia and Methane in Solid Oxide Fuel Cells: An Experimental Study of Performance and Stability, *Journal of The Electrochemical Society*. 166 (2019) F774–F783. doi:10.1149/2.0781912jes.
 - [121] B. Stoeckl, M. Preininger, V. Subotić, S. Megel, C. Folgner, C. Hochenauer, Towards a wastewater energy recovery system: The utilization of humidified ammonia by a solid oxide fuel cell stack, *Journal of Power Sources*. 450 (2020). doi:10.1016/j.jpowsour.2019.227608.
 - [122] J. Yang, A.F.S. Molouk, T. Okanishi, H. Muroyama, T. Matsui, K. Eguchi, A Stability Study of Ni/Yttria-Stabilized Zirconia Anode for Direct Ammonia Solid Oxide Fuel Cells, *ACS Applied Materials and Interfaces*. 7 (2015) 28701–28707. doi:10.1021/acsami.5b11122.
 - [123] T. Okanishi, K. Okura, A. Srifa, H. Muroyama, T. Matsui, M. Kishimoto, M. Saito, H. Iwai, H. Yoshida, M. Saito, T. Koide, H. Iwai, S. Suzuki, Y. Takahashi, T. Horiuchi, H. Yamasaki, S. Matsumoto, S. Yumoto, H. Kubo, J. Kawahara, A. Okabe, Y. Kikkawa, T. Isomura, K. Eguchi, Comparative Study of Ammonia-fueled Solid Oxide Fuel Cell Systems, *Fuel Cells*. 17 (2017) 383–390. doi:10.1002/fuce.201600165.
 - [124] O. Grasham, V. Dupont, M.A. Camargo-Valero, P. García-Gutiérrez, T. Cockerill, Combined ammonia recovery and solid oxide fuel cell use at wastewater treatment plants for energy and greenhouse gas emission improvements, *Applied Energy*. 240 (2019) 698–708. doi:10.1016/j.apenergy.2019.02.029.
 - [125] W.Y. Tan, Numerical simulation on the performance of a solid oxide fuel cell with direct ammonia internal decomposition, *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*. 36 (2014) 2410–2419. doi:10.1080/15567036.2011.569837.
 - [126] Y. Wang, J. Yang, J. Wang, W. Guan, B. Chi, L. Jia, J. Chen, H. Muroyama, T. Matsui, K. Eguchi, Low-Temperature Ammonia Decomposition Catalysts for Direct Ammonia Solid Oxide Fuel Cells, *Journal of The Electrochemical Society*. 167 (2020) 064501. doi:10.1149/1945-7111/ab7b5b.
 - [127] Y. Wang, Y. Gu, H. Zhang, J. Yang, J. Wang, W. Guan, J. Chen, B. Chi, L. Jia, H. Muroyama, T. Matsui, K. Eguchi, Z. Zhong, Efficient and durable ammonia power generation by symmetric flat-tube solid oxide fuel cells, *Applied Energy*. 270 (2020) 115185. doi:10.1016/j.apenergy.2020.115185.
 - [128] G. Cinti, L. Barelli, G. Bidini, The use of ammonia as a fuel for transport: Integration with solid oxide fuel cells, *AIP Conference Proceedings*. 2191 (2019) 020048. doi:10.1063/1.5138781.



DELIVERABLE REPORT

- [129] G. Cinti, G. Discepoli, E. Sisani, U. Desideri, SOFC operating with ammonia: Stack test and system analysis, *International Journal of Hydrogen Energy*. 41 (2016) 13583–13590. doi:10.1016/j.ijhydene.2016.06.070.
- [130] Weidner, E., Ortiz Cebolla, R., Davies, J. "Global deployment of large capacity stationary fuel cells", JRC Technical Report, <https://publications.jrc.ec.europa.eu/>, 2019.

