



ARENHA

ADVANCED MATERIALS AND REACTORS FOR ENERGY STORAGE THROUGH AMMONIA H2020 Grant Agreement Number: 862482

Start date of project: 01/04/2020

Duration: 5 years

WP5 – Plant validation

D5.6 Report on different benchmarking studies

Topic:LC-NMBP-29-2019: Materials for non-battery-based energy storageFunding scheme:Research and innovation actionsCall identifier:H2020-NMBP-ST-IND-2018-2020

Due date of deliverable:	Actual submission date:	Reference period:
31-03-2025	10-05-2025	01-04-2023 – 31-03-2025
Document cla	Prepared by ^(**) :	

Version	DATE	Changes	CHECKED	APPROVED
v0.1	07-04-2024	First Release	CNH2	C. Alonso
v0.2	24-04-2025	Review with Consortium comments	CNH2	C. Alonso
v0.3	09-05-2025	Review with Consortium comments	CNH2	C. Alonso
final	10-05-2025	Final (format review)	TEC	

This pro agreem use tha	This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 862482. The present publication reflects only the author's views. The Commission is not responsible for any use that may be made of the information contained therein					
	Dissemination Level					
PU	Public	X				
PP	PP Restricted to other programme participants (including the Commission Services)					
RE	RE Restricted to a group specified by the consortium (including the Commission Services)					
СО	CO Confidential, only for members of the consortium (including the Commission Services)					
CON	Confidential, only for members of the Consortium					

(*) for generating such code please refer to the Quality Management Plan, also to be included in the header of the following pages

(**) indicate the acronym of the partner that prepared the document



Content

1.	Executive summary	3
	1.1. Description of the deliverable content and purpose1.2. Brief description of the state of the art and the innovation brought	3 3
2.	Hydrogen production benchmarking	4
	 2.1. Solid Oxide Electrolysis Cell (SOEC)	4 4 5 6
3.	Ammonia production benchmarking	7
	3.1. Conventional Haber-Bosch3.2. ARENHA Enhanced Ammonia Synthesis Process	7 8
4.	Ammonia decomposition benchmarking	9
	4.1. Proton exchange membrane fuel cell (PEMFC)4.2. Solid oxide fuel cell (SOFC)4.3. Ammonia combustion process	9 11 14
5.	Ammonia storage benchmarking	15
	 5.1. Liquid ammonia storage	15 16 16 17 18 18
6.	Conclusions	19
	 6.1. Hydrogen production benchmarking conclusions	19 20 21 21 21 21 21 22 23
7.	References	23



1. Executive summary

1.1. Description of the deliverable content and purpose

The aim of this deliverable is to perform the benchmarking between the different solutions addressed in ARENHA project.

A H₂ production benchmarking between SOEC, PEM, Alkaline and Battolyser will be done in order to know what the best solution is.

On the other hand, a NH₃ production benchmarking between conventional Haber-Bosch process, ARENHA project innovative Haber-Bosch process will be done for knowing the most efficient option.

The NH₃ decomposition membrane reactor coupled with PEMFC will be compared vs ammonia reforming with SOFC and ammonia combustion process for determining the most efficient and cost-effective solution.

Finally, the ammonia storage benchmarking between solid and liquid storage will be done in terms of efficiency, cost and durability. All the benchmarking studies will be done at the same conditions in order that the results will be solid and consistent.

1.2. Brief description of the state of the art and the innovation brought

The innovation brought on the different ARENHA project solutions were:

- **IKTS:** modified electrolyte supported cells.
- ELCOGEN: modified cathode supported cells.
 This new approach to SOEC configuration materials aims to further improve the efficiency of the system with, thus, facilitating the implementation of this technology.
- Proton Ventures: innovative ammonia synthesis loop.
- **H2SITE:** NH₃ decomposition membrane reactor.



2. Hydrogen production benchmarking

All electrolyser technologies for hydrogen production are defined in this task.

2.1. Solid Oxide Electrolysis Cell (SOEC)

This technology is one of the newest electrolyser technologies and is therefore still maturing compared to other technologies.

The operation consists of supplying water to the cathode where it receives electrons to produce hydrogen gas and oxygen anions. These oxygen anions move toward the anode where they lose excess electrons to be emitted as oxygen gas, as it is shown in Figure 1.



Figure 1. SOEC electrolyser.

The typical SOEC electrolytes are based on ZrO₂ doped with yttria (YSZ) or scandia (SSZ).

The cathode generally contains Nickel and zirconia while the anode is lanthanum, strontium cobalt perovskites (LSCF) or lanthanum strontium cobalt (LSC). Ceria is also added as a catalyst often in doped form to increase the ionic conductivity and used with LSCF or LSC as a composite electrode or applied as an intermediate layer between the anode and the electrolyte to prevent interdiffusion of the elements and eliminate the zirconate formation.

During this process, high temperatures are required, which are beneficial since it reduces the cell equilibrium voltage necessary to split the water by providing the necessary residual energy in the form of heat. The water splitting reaction occurs in the vapor phase where the free energy required is lower. Another advantage of this technology is that some of the energy can be provided using waste heat (thermally) instead of electricity, which reduces electricity-related costs.

2.2. Polymer Electrolyte Membrane (PEM)

This technology works at a lower temperature than other technologies since it works with working temperatures of 50-100°C. Furthermore, this technology works at high pressures (20-30 bar) comparted to others.



The operation consists of supplying water to the anode to split into oxygen and hydrogen ions. As oxygen is discharged at the anode, hydrogen ions move across the proton-conducting membrane to the cathode and react with electrons to form hydrogen gas, as it is shown in Figure 2.



Figure 2. PEM electrolyser.

The electrocatalysts are coated directly onto the membrane forming a membrane electrode array (MEA). The use of a solid electrolyte eliminates both the need for liquid electrolyte circulation and the resistance caused by the formation of gas bubble on the electrodes. Because of this, the design of PEM technology is more compact ensuring a wide range of current densities.

Membrane electrode assembly (MEA) assemblies are compressed between porous transport layers that are combined with an interconnect (bipolar plate) and a gasket to from a PEM cell. The individual cells are connected electrically (in series) and hydraulically (in parallel) to achieve high hydrogen production rates.

Typical membranes used are perfluorinated sulphonic acid membranes. These membranes are quite thin (100-200µm thick), platinum nanoparticles are used as recombination catalyst in the membrane to avoid hydrogen permeation. A platinum-on-carbon catalyst is used in the cathode for efficient hydrogen production while iridium or ruthenium and/or their oxides are used in the anode.

Porous transport layers (PTLs) are necessary to ensure uniform distribution between the electrodes and the bipolar plate. For the cathode, carbon paper or non-woven carbon is used, while titanium is used for the anode due to its high conductivity and corrosion resistance. Bipolar plates are also usually made of titanium for the same reasons.

2.3. Alkaline electrolyser

This technology is the oldest and most widespread to date. It is a low-temperature process ($60-90^{\circ}C$) using an alkaline liquid electrolyte (20-40% by weight of potassium hydroxide or KOH) and operates in a pressure range of 1 to 30 bar. The alkaline electrolyser has been used for large-scale (MW) H₂ production in industrial applications.

Water is supplied to the cathode where it is split into H_2 gas and hydroxide (OH-) ions. These OH- ions pass through the membrane to become O_2 and water at the anode, as it is shown in Figure 3.



Alkaline electrolyser cells requite the separator and electrodes to be placed close to each other, which is called a zero-gap design or diaphragm electrode array (DEA). This decreases the ionic transportation resistance by reducing the distance between electrodes and the overpotential by evolving gas at the back of the electrode. All this improves the efficiency of the cell.

The cell components are press-fitted together and spacings are used between the electrodes and the cell housings which is beneficial to prevent leakage.

Electrodes are usually made of nickel or stainless steel due to their combination of high corrosion resistance, high electrical conductivity and high electrochemical activity. Electrocatalysts are added in the form of base substrates to further improve corrosion resistance and electrochemical activity.

Typical catalysts for the cathode are ruthenium dioxide (RuO₂), molybdenum (Mo), mixed metal oxides (MMO) and nickel alloys (Ni-Mo), while the catalysts used in the anode are mixed nickel and or/cadmium and cobalt oxide.

The most common diaphragm for this technology is composed of a ZrO₂ base supported by polymeric fabric in a meshed structure. This is mainly due to its high electrochemical, chemical and thermal resistance together with the desired ionic permeability. While the bipolar plates and spacers are made of nickel and/or nickel-coated steel for high corrosion resistance against electrolyte (KOH) to avoid leakage, the seals are made of polytetrafluoroethylene (PTFE) or ethylene propylene diene monomer (EPDM). The alkaline cells are connected in series (back of the cathode of one cell to the anode of the neighbouring cell) by concurrent pressing, so that the individual cells are clamped between the end plates and pressed together with threaded rods.

2.4. Battolyser

This technology is innovative and still under development. It consists of an electrolyser which produces green hydrogen (100% renewable) at a reduced price.

One of the most important features of this technology is the electrolyser. It can be switched on instantly and can also be switched off after intermittent energy production. This means that the electrolyser is running on renewable energy to obtain green hydrogen and when there is no renewable energy supply, it stops and stops producing to ensure that the hydrogen produced is 100% renewable.



The patented electrolyte of this technology is nickel-iron because it is robust, efficient and its lifetime is considerably longer than other materials. As they are easily found in the earth, their cost is lower than the other technologies.

The catalyst used is regenerative, this means that is does not degrade electro-chemically and therefore a higher efficiency is obtained, and the lifetime of the system is extended.

The catalytic converter is characterised by the fact that it can produce hydrogen or it can also feed energy into the grid. The battery of the electrolyser functions as a back-up energy source when renewable energy is not available in order to ensure 100% green hydrogen production.

The expected performance for this technology is 85% at an outlet pressure of 30bar. The modules are expected to be available in 2025-2026 with electrolysis capacity of 25MW.

3. Ammonia production benchmarking

3.1. Conventional Haber-Bosch

In this process, hydrogen react catalytically with nitrogen to form anhydrous liquid ammonia. Le Chatelier's principle predicts that the formation of NH3 will be favoured when pressure is increased. On the other hand, the reaction is exothermic, however, the equilibrium constant decreases with increasing temperature, which mean that at high temperatures small amounts of ammonia are obtained.

In conclusion, the maximum performance of ammonia will be obtained if the reaction is carried out at a temperature as low as possible. However, if the temperature is less than 300°C the performance would be very high but the reaction would be too slow. Due to this, the use of catalysts is used to significantly increase the reaction rate, reaching temperatures of 400-530°C.

The catalyst used in this process is an Iron catalyst, which ensures better conditions for the absorption and dissociation of N_2 . Aluminium or potassium oxides are normally added to these catalysts to improve performance by increasing the surface area of the catalyst.

Currently, other catalysts have been developed that provide the same effect in terms of performance, these are those shown in Table 1.

•	•
CATALYSERS	EXAMPLES
Cobalt-bases catalysts	Co/CeO ₂ Co ₃ Mo ₃ N Co-BaH ₂
Electride-based catalysts	Ru/[Ca ₂₄ Al ₂₈ O ₆₄] ⁺⁴ (e ⁻) ₄
Iron-bases catalysts	Fe ₃ O ₄ α-Fe ₂ -O ₃
Metal nitride based catalysts	γ-Mo ₂ NNi ₂ Mo ₃ N
Ruthenium-based catalysts	Ru/CaFH Ru/CeO ₂

Table 1. Example of catalysts.



The Haber-Bosch process is divided into several stages:

• Stage 1. Obtaining the reaction gases: Obtaining reaction gases from air and natural gas. Air being the main resource to obtain N2 and natural gas is used to obtain H₂. These gases are purified and mixed in the appropriate proportions, giving rise to the following reaction

$$3H_2(g) + N_2(g) \rightarrow 2NH_3(g)$$

- Stage 2. Compression and purification of gases: The reaction gases are compressed to increase pressure and purified to eliminate impurities. The N₂ is compressed to approximately 200 times atmospheric pressure and cooled to liquefy.
- Stage 3. NH₃ synthesis: It is carried out in the reactor, which contains an iron catalyst at high pressure and temperature. The catalyst increases the reaction rate and allows NH₃ to form from N₂ and H₂. The NH₃ formed is separated from the rest of the gases and collected in a container.
- Stage 4. Recycle waste gases: The gases that have not reacted are recovered and retreated in order to minimize costs and not cause damage to the environment.

The Figure 4 shows the complete cycle of Haber-Bosch for the production of ammonia.



Figure 4. Haber-Bosch process.

3.2. ARENHA Enhanced Ammonia Synthesis Process

In this task, the development of a process configuration for the ARENHA ammonia pilot plant was pursued with the following targets as lead:

- Liquid storage of the ammonia product
- Potential for application of a high-performance catalyst.
- Incorporation of ammonia sorption technology.
- Suitable for flexible operation with varying feed flow rate.



The new configuration of the ARENHA ammonia synthesis loop (shown in the deliverable D2.4 and deliverable D4.7 & D4.8) has a lot of advantages for use in an experimental environment.

- The flexibility of the process is enhanced by in-line sorbent regeneration, which make automation
 of the cycling between the sorption and regeneration stages straightforward, and capable of
 absorbing significant operational upsets.
- The performance of the catalyst can be investigated for a range of thermal operating conditions.
- Multi-stage sorption with intercooling avoids mechanically challenging design for internal cooling of the sorbent bed.
- The modular arrangement of the equipment allows for minor changes after the plant has been built, in order to test improvements suggested by experimental results.

4. Ammonia decomposition benchmarking

Ammonia could be directly used or as hydrogen energy carrier it could cracked to have H₂ for different applications. In this section, the use of ammonia in internal combustion engines and in two fuel cell technologies are defined: solid oxide fuel cell (SOFC) and proton exchange membrane fuel cell (PEMFC).

4.1. Proton exchange membrane fuel cell (PEMFC)

For the proton exchange membrane fuel cell (PEMFC) ammonia is a toxic gas. This is due to the fact that ammonia can envelop the acidic proton exchanger membrane and the cathode catalyst. The residual amount of ammonia must be less than 0.1 ppm and therefore cannot be used directly in PEMFC. therefore, the aim is to convert ammonia into pure hydrogen. Such a decomposition of ammonia to hydrogen requires high temperatures, thus increasing the complexity of the system.

There is another PEMFC technology which can use the ammonia decomposition gas directly, which reduces the complexity of the system. The performance obtained is 34-36%, which is lower compared to other technologies.

The main problems of this technology are the development of efficient ammonia decomposition and hydrogen purification. Some of the lines of research and improvement for this technology are:

- Ni-Loaded catalysts with Al₂O₃ are the most economical, stable and efficient catalyst for ammonia decomposition. Some combinations of Ru can give better results than the above, but they have a very short lifetime and are very expensive.
- The incorporation of the microfluidic reactor improves the heat transfer between the reaction unit and the heating unit, thereby improving the volumetric hydrogen production rate and energy efficiency of the reactor.
- The design of catalyst is conditioned by the study of reaction mechanisms and the optimisation of boundary conditions.
- Large-scale devices have an H₂ recovery rate of 90%. However, for small-scale hydrogen production equipment, there are some problems to high inlet pressures.
- The chilled adsorption requires a large amount of energy to keep temperatures low for large-scale production.
- The size of the separation equipment can be reduced and is therefore a solution for H₂ separation in small-scale systems.



Absorber is used for removing the residual ammonia after cracking although the use of membranes for H_2 separation/purification could be another option. The membranes are made of palladium with high permeability, but even if it is an expensive material they are better than the most common alternative made of vanadium. These membranes are somewhat cheaper to manufacture, but their performance is only about 32-36% of the Palladium ones. On top of that, Vanadium membranes are more prone to fragilization phenomena and are not as selective. This makes the Palladium membrane the best option for high purity hydrogen production.

An ammonia decomposition gas feeding process is shown in Figure *5*, which has undergone residual ammonia directly in the PEMFC.



Figure 5. Ammonia decomposition gas

- The ammonia gas evaporates and is preheated through the evaporator and recuperator 1. It subsequently enters the recuperator 2 with the objective of raising the temperature necessary for the decomposition reaction.
- It is introduced into the cracker for catalytic decomposition, the decomposition gas cools through recuperator 1 and the evaporator while providing energy for gasification and preheating of liquid of ammonia.
- The decomposition gas enters the absorber to eliminate residual ammonia and obtain a mixture of nitrogen and hydrogen for which it is sent to the PEMFC to react electrochemically and consequently generate electrical energy.
- The exhaust gas from the anode enters the combustor to generate high temperatures gas through catalytic combustion with air. The high temperature gas is sent to the cracker to provide the energy required for the ammonia decomposition reaction.
- Gas flows through recuperator 2 and 3 to heat the ammonia entering the cracker. Air and fuel enter the combustion chamber.
- The gas generated at high temperatures by the anode tail cannot satisfy the heat input from the ammonia decomposition reaction. Because of this, additional energy is needed which is provided by the introduction of ammonia gas and air into the combustion chamber.



4.2. Solid oxide fuel cell (SOFC)

These fuel cells are commonly based on cermet fuel electrode and either protonic or ionic conductor oxide electrolyte and requires the high temperatures for its operation which range from 500-900°C. Because of this, this technology has one of the highest efficiencies, with values of over 70%.

These cells do not require the fuel to be cleaned by external cracking or exhaustive cleaning. The high operating temperature of ammonia means that is can crack in the anode chamber, so SOFCs can operate in either internal or external cracking mode, as it is shown in .

• <u>External cracking</u>: A decomposition reaction takes place in an external reactor without direct heat transfer with the components of the electrochemical reaction. The NH3 is first decomposed into nitrogen and hydrogen in the external reactor and then fed to the SOFC.

$$2NH_3 \rightarrow N_2 + 3H_2$$

- <u>Internal cracking</u>: combining both the endothermic ammonia decomposition reaction and the exothermic electrochemical reaction allows for simpler design and higher thermodynamic efficiency. In the case of internal decomposition, it can be further decomposed into direct and indirect methods.
 - <u>Indirect internal decomposition</u>: The reactor is in contact with the fuel cell providing efficient heat transfer between the two units.
 - <u>Direct internal decomposition</u>: The cracking reaction take place in the anode chamber itself, using the heat generated by the exothermic electrochemical reaction as the heat. This means that no separate decomposition reactor is required. This method requires a multifunctional electrode that provides good catalytic activity for both the ammonia decomposition and the electrochemical reaction.



Figure 6. SOFC Decomposition.

SOFCs can be classified according to their electrolyte as either oxide ion conducting solid oxide fuel cells (O-SOFC) or proton conducting solid oxide fuel cells (H-SOFC). Comparison is shown in Figure 7.



Figure 7. SOFC electrolyte comparison.

• <u>O-SOFC</u>: Hydrogen is produced through the decomposition of ammonia and reacts with oxide ions to produce water. The direct electro-oxidation of ammonia occurs through the following reactions.

Anode side reactions

 $2NH_3 \rightarrow N_2 + 3H_2$ $H_2 + 0^{2-} \rightarrow H_20 + 2e^{-}$

Cathode side reactions

 $\frac{1}{2} \mathcal{O}_2 + 2 e^- \rightarrow \mathcal{O}^{2-}$

 <u>H-SOFC</u>: Hydrogen generated from the decomposition of ammonia at the anode is oxidised to protons, moves through the electrolyte and reacts with oxygen at the cathode through the following reactions.

> Anode side reactions $2NH_3 \rightarrow N_2 + 3H_2$ $H_2 \rightarrow 2H^+ + 2e^-$ Cathode side reactions

$$\frac{1}{2}O_2+2H^++2e^-\to H_2O$$

The electrochemical performance of the anode and cathode is defined as the sum of the polarisations associated with the charge transfer rates at the triple phase boundary (TPB), the effective ionic and electronic conductivity of the electrode and the gaseous species transported through a porous electrode. The chemical and structural stability of SOFC components affects service life as they can exhibit electrode catalyst poisoning, electrode microstructural changes and structural stresses at high operating



temperatures. The degradation rate should be less than 0.2% per thousand hours over the total lifetime of 40,000 hours.

The main components of SOFC are the anode, cathode, electrolyte and interconnectors. The following are the metals of which each of the above components is made up.

• <u>Electrolytes:</u> They are responsible for transporting the oxide ions or protons between the anode and the cathode to complete the electrochemical reactions. It is necessary that they have a similar coefficient of thermal expansion to the electrode materials, low electronic conductivity and high ionic/protonic conductivity. Typical materials of which electrolytes are composed are shown on Table 2 and Table 3 below.

ELECTROLYTE MATERIAL	TEMPERATURE (ºC)	Σ(SCM ⁻¹) IN AIR
(ZrO ₂) _{0.97} (Y ₂ O ₃) _{0.03}	800	0.018
(ZrO ₂) _{0.92} (Y ₂ O ₃) _{0.08}	800	0.052
(ZrO ₂) _{0.90} (Y ₂ O ₃) _{0.10}	800	0.037
(ZrO ₂) _{0.922} (Sc ₂ O ₃) _{0.078}	800	0.120
(ZrO ₂) _{0.91} (Sc ₂ O ₃) _{0.09}	800	0.109
(ZrO ₂) _{0.907} (Sc ₂ O ₃) _{0.093}	800	0.120
(ZrO ₂) _{0.90} (Sc ₂ O ₃) _{0.10}	800	0.072
(ZrO ₂) _{0.89} (Sc ₂ O ₃) _{0.10} (CeO ₂) _{0.01}	700	0.057
(ZrO ₂) _{0.88} (HfO ₂) _{0.01} (Sc ₂ O ₃) _{0.10} (CeO ₂) _{0.01}	800	0.140
(CeO ₂) _{0.80} (GdO _{1.5}) _{0.20}	800	0.093
(La _{1-x} Sr _x)(Ga _{1-y} Mg _y)O _{3-α}	800	0.11-17
BICOVOX	600	0.100

Table 2. O-SOFC electrolyte material.

Table 3. H-SOFC electrolyte material.

ELECTROLYTE MATERIAL	TEMPERATURE (⁰C)	Σ(SCM ⁻¹) IN AIR
BaCe _{0.8} Y _{0.2} O _{3-δ}	800	0.011
Ba _{0.9} K _{0.1} Ce _{0.6} Zr _{0.2} Y _{0.2} O _{3-δ}	800	0.012
$Ba_{0.8}Sr_{0.2}Ce_{0.6}Zr_{0.2}Y_{0.2} O_{3-\delta}$	800	0.009
BaCe _{0.4} Zr _{0.4} In _{0.2} O _{3-δ}	750	0.050
BaCe _{0.2} Zr _{0.7} Y _{0.1} O _{3-δ}	800	0.060
BaCe _{0.8-0.2} Ti _{0.2} Y _{0.2} O _{3-δ}	800	0.008
Ba _{0.95} Ce _{0.90} Y _{0.10} O _{3-δ}	1000	0.120
Ba _{0.995} Ce _{0.95} Y _{0.005} O _{3-δ}	900	0.001
SrCe _{0.9} Yb _{0.1} O ₃₋₅ (Li/K) ₂ CO ₃	700	0.100

• <u>Cathode materials for SOFC</u>: The materials used to manufacture the cathode need a similar thermal expansion coefficient to that of the electrolyte to avoid thermal stresses. The most commonly used are Perovskites (ABO₃), especially lanthanum manganite, cobalt-bases materials and ferrite due to their ionic electronic conductors' properties. The most common material for SOFC is Lanthanum strontium manganite (LSM) because it is thermally compatible with the electrolyte.



An alternative material is the composition of LSM with YSZ as it increases the electrochemical active area. However, the polarisation resistance of LSM cathodes is higher at lower temperatures, thus limiting their use to an intermediate temperature range.

 <u>Anode materials for SOFC</u>: The materials studied for use in anodes need a series of requirements such as adequate conductivity, porosity, resistance to catalyst poisoning, among others. These materials are fluorite, perovskite, pyrochlore, rutile, spinel and double perovskite. For ammonia SOFCs the focus is on materials for the development of catalyst materials for cracking, especially in direct electro-oxidation research for ammonia. One of the materials used in the anode for the ammonia SOCF is Ni-Fe cermet, this is because the iron gives it a higher catalytic activity for the decomposition of ammonia.

Ammonia decomposition is also affected by hydrogen poisoning, which occurs when hydrogen occupies the ammonia absorption site and consequently reduce the catalytic activity of decomposition. Hydrogen poisoning at the anode is common at low temperatures and as the temperature increases, hydrogen is absorbed in the active zone.

Vapour poisoning occurs when vapour is generated at the anode following the reaction of the electrooxidation of hydrogen. Such poisoning has a major effect on ammonia decomposition. It can be reduced by adding rare earth elements to a Ni-Al2O3 catalyst to increase ammonia conversion.

4.3. Ammonia combustion process

The combustion of ammonia in air is very difficult without the presence of a catalyst, because the flame temperature is generally lower than the ignition temperature of the ammonia-air mixture. The flammability range of ammonia in air is 16% to 25%.

When ammonia is left with oxygen, a yellowish-green flame is created. This combustion occurs when chlorine is converted to ammonium, forming nitrogen and hydrogen chloride. If the chlorine is in excess, the explosive nitrogen trichloride or trichloramine (NCl₃) is formed.

The combustion of ammonia results in nitrogen and water as an exothermic reaction.

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

Obtaining an enthalpy of reaction ($\Delta H^{\circ}r = -1267.20 \text{ kJ/mol}$) with a calorific value ($\Delta H^{\circ}c = -382.81 \text{ kJ/mol}$). To facilitate the combustion of ammonia it is necessary to restrict the exit velocity of the waste gas, in order to ensure that the ammonia has an adequate residence time for combustion with high destruction efficiency.

Tests carried out by Zeeco show a correlation between the stability of the ammonia flame and the exit velocity. This correlation is shown in Figure 8.



Figure 8. Typical Design Maximum Exhaust Velocity Versus Diameter nominal torch tip.

As can be seen, there is a relationship between the maximum design exit velocity for waste gases containing ammonia with respect to the diameter of the flare tip. The larger the diameter of the flare tip, the greater the volume of gas and therefore the greater the heat release from the flame. If a flare system is not designed in this way, there is a greater potential for incomplete combustion and thus an unignited release of residual gas.

There are different considerations for the correct design for ammonia combustion which are as follows:

- <u>Distribution of waste gases</u>: For proper uniform distribution of the waste gas throughout the torch nozzle body, it is necessary to include flow distribution devices to distribute the waste gas properly.
- <u>High stability and flame-stabilizing design</u>: The stability system provides a stable flame for initial ignition. For ammonia combustion the design of the windscreen has to be modified to minimize wind effects so that air and fuel are concentrated in that area.
- <u>Exit velocity strategies:</u> These consist of the correct dimensioning of the flares, especially their diameter, in order to be able to modify the exit velocity in the combustion of the residual ammonia gas.
- <u>Auxiliary equipment:</u> Liquid Seal Drums (LSD) are used as protection to separate the torch system from the upstream head and equipment. This is because ammonia is soluble in water and could form a corrosive ammonia solution.

5. Ammonia storage benchmarking

One of the drawbacks of hydrogen technology is that it is difficult to store and transport because it is a complicated gas. That is why ammonia is added since it has the ability to store and transport hydrogen much more efficiently in terms of complexity and costs. Therefore, at this point different ways of storing ammonia are studied depending on its state of form (liquid or gas).

5.1. Liquid ammonia storage

Storing ammonia in a liquid state is the most common way to store ammonia. Currently the main methods of storing ammonia in liquid state are pressure storage, semi-refrigerated storage, low-temperature storage.



5.1.1. Pressure storage

Pressurized storage tanks have a wide range of capacity (1kg-1500t). These containers can be cylindrical or spherical depending on the desired storage capacity. The cylindrical ones are usually horizontal, up to 150t and 25 bars, while the spherical one's rest on supports due to safety measures and reach capacities of 250-1500t, 16 bar and a thickness of no more than 30mm. The containers are protected from external overheating with water spray, paint or a recirculation of ammonia through a water cooler.

This storage system is suitable for:

- Store small quantities of ammonia
- Loading and unloading of tanker trucks
- Inlet and outlet piping systems

This equipment includes auxiliary flow meters for pressurised ammonia feed and effluent streams, centrifugal pumps for liquid ammonia streams discharge, piping for liquid ammonia loading and unloading, and pressure relief valves for ammonia vapour and inert.

The incorporation of 0.2% water in the ammonia reduce stress corrosion cracking. Additional protection can be obtained by coating with aluminium or zinc metal.

A vessel designed for ammonia storage should not operate below its transition temperature because there is no risk of brittle fracture in cracks or weld joint areas. It is for this reason that these vessels should not be filled with refrigerated ammonia, it must be first be heated to a transition temperature above that of the vessel's steel.

5.1.2. Semi-refrigerated storage

Semi-refrigerated system allows the storage of liquid ammonia at low pressures in an insulated container. It is kept at a temperature of 0°C with a pressure between 3 and 4 bar.

These containers are generally sphere-shaped with capacities of up 3000 tonnes. They consist of a cooling system in which the vapour in the container is compressed and liquefied by water cooling and the liquid is then returned to the tank, as it is shown on Figure 9. This type of refrigeration is not very sophisticated but very economical.



Figure 9. Semi-refrigerated storage loop.



5.1.3. Low temperature storage

This storage method is used for large quantities of ammonia where refrigerated tanks are used. These tanks are insulated cylindrical tanks with a flat bottom and a domed roof which operate at atmospheric pressure and a temperature of -33°C and a capacity of 50.000 tonnes.

The cooling is provided by a cooling unit which consist of 2 stages.

The first stage works with ammonia gas from outside the storage tank, which is compressed to less than 1 psig until it reaches a range of 2 to 4 bar. It is then cooled down in the flash tank while waiting for the second stage.

In the second stage, the condensing pressure is increased to 10-16 bar. The ammonia is then condensed and sent to a receiver, which, thanks to the level control built into the tank, directs the liquid to the flash tank.

The low temperature storage loop is shown in Figure 10 below.



Figure 10. Low temperature storage loop.

There are 2 types of ammonia refrigeration tanks, single-walled and double-walled.

The first consist of a single layer insulated on the outside to prevent freezing moisture. Such insulation has to be completely airtight and high standards of construction and maintenance are required to minimise risks. These panels are composed of foam glass, polystyrene, polyisocyanurate or polyurethane together with a layer of aluminium used as isolation.

The double-walled tanks consist of a lower tank designed for storage pressures and temperatures surrounded by a second tank with a 46cm space between the two tanks. The remaining space between the tanks is filled with insulating materials such as loose fill perlite while filling dry gas in order to protect the insulation. As a safety measure the inner and outer casing of the tanks are made of the same material so that if there is a failure inside the tank, the outside will be able to contain the ammonia.



The tanks can be placed on the ground or on a structure. In the first case, it is necessary to heat the soil in advance to avoid freezing. Using concrete platforms with ventilation at the bottom, can eliminate the requirement for soil preheating. In addition, to avoid cracking due to stress corrosion, stander materials (API 625) and certified manganese carbon are used.

Although, the investment cost for the double-wall tank is greater than for single-wall construction.

5.2. Solid ammonia storage

Due to the problems present in the storage of ammonia in the working liquid state at high pressure at room temperature and its toxicity, a solid-state material has been developed as ammonia storage. This increases safety as the risk of leaks is avoided.

Some materials used for solid storage of ammonia are amides/imide, halides, complex metal hydrides, metal fullerides, and borohydrides. Within these materials, metal halides stand out. However, these materials require practical improvements for their correct use for the ammonia storage.

One of the advantages of this type of storage is that the absorption/desorption of ammonia is completely reversible because it is less volatile and less ammonia is released at room temperature compared to liquid ammonia. This material is tested for road and air transport.

Currently, the metal amine salt $Mq(_{NH3})_6Cl_2$ is the best element due to the low vapor pressure of 2 mbar at room temperature and high gravimetric (9.19%) and volumetric (109g H₂/L) hydrogen density. However, it is difficult to achieve the balance of all these capabilities. The absorption capacity achieved is 1-5% of the equilibrium capacity. In addition to this, metal halides are unstable under absorption conditions and after each charge and discharge, which reduces the progress of the following cycles of use, making it currently impractical because this technology need even greater development so that be viable at commercial levels.

5.3. Storage comparison

Once all the ammonia storage technologies have been defined, the Table 4 shows the data obtained for each of them in order to make comparisons between them.

Table 4. Storage comparison						
	Pressure (bar)	Temperature (°C)	Capacity NH₃ (tons)	Cost		
Pressure storage	16-18	20-25	270-1500	Expensive		
Semi-refrigerated storage	3-5	0	450-2700	Cheap		
Low temperature storage	1	-33	4500-45000	Expensive		
Solid storage	1-30	20-250	No data (Developing)	No data (Developing)		

Table 4. Clarada asmusulasu



6. Conclusions

This task provides a comparison and analysis between all the technologies defined in this document with the main objective of to highlight the different characteristic of each of them and their correct use depending on the purpose.

6.1. Hydrogen production benchmarking conclusions

In Table 5 below it is shown the comparison data for the different technologies explained before.

		i dibite e		eg) eempaneen			
Technology	Temperature (ºC)	Pressure (Bar)	H₂ purity (%)	Performance (%)	Stack life (kh)	System life (year)	Stack Cost
SOEC	700-1000	1-5	99.9 ^[3]	81-86% ^[4]	25-40	N/A	N/A
SOEC IKTS (Arenha)	720-860	0,8-1,2	99.9**	86.6%*1	40	5* ³	~300 €/kW (~300 MW/y manufacturing) ~100 €/kW (~1GW/y manufacturing)
SOEC ELCOGEN (Arenha)	650-700	1-1,5	99.9**	86.1%*1	40	5* ³	~500 €/kW (~300 MW/y manufacturing) ~100 €/kW (~1GW/y manufacturing)
PEM	50-80	<35	99.99 ^[5]	50-70% ^[4]	60- 100	10-20	~270 €/kW ^[5]
Alkaline	60-80	<30	99.99 ^[5]	50-71% ^[4]	55- 120	20-30	~45-65 \$/kW HMC; ~130- 260 \$/kW LMC ^{*2[6]}
Battolyser	45-60	30	99.999	85%	-	-	N/A (technology in development)

Table 5. Technology comparison

[3] Source: Sunfire Hylink SOEC, Hydrogen purity after drying before cleaning

[4] Citation: IRENA (2020), Green Hydrogen Cost Reduction: Scaling up Electrolysers to Meet the 1.5°C Climate Goal, International Renewable Energy Agency, Abu Dhabi.

[5] Source: ISPT 2020, Gigawatt green hydrogen plant State-of-the-art design and total installed capital costs.

[6] Source: IEA Global Hydrogen Review

*¹ Values at system level in deliverable D2.7. Arenha SOEC performances are similar to "conventional" SOEC, the advantage is that to achieve same performances Arenha SOEC operates at lower temperatures.

*2 45-65 \$/kW High Manufacturing Capacity (HMC) / 130-260 \$/kW Low Manufacturing Capacity (LMC);

*³ 5 year operational demonstrated today, but potential for higher operation as other electrolysis systems.

**SOEC IKTS and SOEC ELCOGEN values should be confirmed with experimental results on Arenha project work package 5.

6.2. Ammonia synthesis benchmarking conclusions

In Table 6 below it is shown the comparison data for the different ammonia synthesis processes production.



Process	Temperature (ºC)	Pressure (Bar)	Performance (% LHV)	Specific Steam Production (tsteam/tNH ₃)	Cost
Conventional Haber- Bosch (Centralised)	360-480 ^[12]	100-200 ^[12]	~85 ^[13]	N/A	N/A
Conventional Haber- Bosch (Decentralised)	300-500	130	~75	[-]	~16 M€ (for 60t/d)
ARENHA Enhanced ammonia synthesis	300-475	80	67.7-80*	0.91	~14 M€ (for 60t/d)

Table 6. Process comparison

* Efficiency Enhanced Ammonia Synthesis Loop: 68% LHV efficiency, 80% if steam produced to SOEC considered as an energy gain.

*1Estimated.

^[12] Source: Topsoe

^[13] Used combining IEA – Global average levelised cost of hydrogen production by energy source and technology, 2019 and 2050 data for SMR and IRENA and AEA (2022), *Innovation Outlook: Renewable Ammonia*, International Renewable Energy Agency, Abu Dhabi, Ammonia Energy Association, Brooklyn.

6.3. Power-to-Ammonia benchmarking conclusions

In this section focus on the Power-to-Ammonia solution, the integration of SOE and Ammonia synthesis. According to the results presented in section 2.5.3 of deliverable D2.7, the integration of ARENHA's Solid Oxide Electrolysis (SOE) technology with ARENHA's ammonia synthesis process represents the most efficient solution for decentralized ammonia production with comparable performances with competitor blue ammonia solution as it showed hereafter.



Figure 11. Efficiency comparison between different centralised and decentralised ammonia production pathways. PEM and Alkaline data from [7], [8], Fossil fuel-based pathways data from [9].



6.4. Ammonia-to-Hydrogen benchmarking conclusions

In reference to the Ammonia-to-Hydrogen, Table 7 shown the different processes comparison, this information was deeply analysed on deliverable 2.7.

Table 7. Comparison between the key performance indicators (KPI) of the conventional packed bed and of the packed bed membrane reaction units for hydrogen production from ammonia.

	Conventional process Stationary applications	Conventional process Vehicle applications	MR-assisted process Stationary and vehicle applications
Reactor operating conditions			
Reaction temperature [°C]	450	450	400
Reaction pressure [bar]	5	5	5
Permeate pressure [bar]	-	-	0.1
KPI			
NH ₃ conversion	97.8%	97.8%	99.1%
H ₂ recovery	-	-	80.6%
Reactor efficiency (nreactor)	96.2%	96.2%	79.2% [*] (97.4% ^{**})
$\eta_{NH_3 to H_2}$	5.8 kg/kg	5.8 kg/kg	7.0 kg/kg* (5.7 kg/kg**)

6.5. Ammonia-to-Power benchmarking conclusions

This section presents the benchmarking for the three main pathways for electricity generation using ammonia.

6.5.1 Ammonia cracking + PEMFC

Ammonia-to-hydrogen modelling and main KPI were discussed in D2.7. Ammonia cracking technology can be combined with PEMFC for electricity generation. Considering that PEMFC systems require pure hydrogen reaching 54% electrical efficiency, 52.6% total efficiency for the Ammonia-to-Power solution could be achieved with membrane reactor.

6.5.2 Ammonia reforming with SOFC

According to IKTS characterization of SOFC system for power generation from ammonia, the performance map (NH₃) 10-cell-stack results is shown in Figure 12.



Figure 12. IKTS performance map (NH3) 10-cell-stack SOFC

IKTS reports 58% electrical efficiency for ammonia fed SOFC.

6.5.3 Ammonia combustion process

According to literature [10], gas turbines can be operated in a simple cycle mode, achieving around 35-40% (LHV) efficiency from fuel to electricity. When the gas turbine is combined with a steam turbine in a combined cycle mode, the overall efficiency is increased to the range 55-60% (LHV). This relatively high fuel conversion to electricity gives gas turbines an efficiency advantage over coal-fired thermal power plants (35-45% (LHV) efficiency range). Although the vast majority of existing gas turbines run on conventional, carbon-intensive fuels, the potential to retrofit these units to run on lower or zero-emission fuels presents a huge opportunity to decarbonize existing, high-efficiency power generation assets.

To conclude a summary of the presented pathways for electricity production from ammonia are presented in Table 8.

Process	Performance (% LHV)	Application
Membrane Reactor combined with PEMFC	52.6%	Small to medium scale
NH ₃ SOFC	58%	Small to medium scale
Gas Turbines	35-45%	Medium to big scale
Combined Cycle Gas Turbine (CCGT)	55-60%	Medium to big scale

Table 8. Ammonia-to-Power Pathways performance comparison.



6.6. Ammonia storage benchmarking conclusions

Table 9. Ammonia Storage comparison.			
Storage	Performance (%)	Durability (years)	Cost
Solid	40	Up to 5	~10USD/Kg
Liquid (Pressurized)	85	20-30	~3 USD/kg*
Liquid (Refrigerated)	90	20-30	~1 USD/kg

*3 USD/kg NH3 for pressurized tanks (small-medium scale); 0.56-1.06 USD/kg NH3 for refrigerated tanks (medium to big scale). [11] Source: Techno-Economic Aspects of Production, Storage and Distribution of Ammonia. R.M. Nayak-Luke • C. Forbes • Z. Cesaro • R. Bañares-Alcántara • K.H.R. Rouwenhorst.

7. References

[1] https://www.frontiersin.org/journals/energy-research/articles/10.3389/fenrg.2022.819939/full

[2] https://www.frontiersin.org/journals/energy-research/articles/10.3389/fenrg.2020.509052/full

[3] Source: Sunfire Hylink SOEC.

[4] Citation: IRENA (2020), Green Hydrogen Cost Reduction: Scaling up Electrolysers to Meet the 1.5°C Climate Goal, International Renewable Energy Agency, Abu Dhabi.

[5] Source: ISPT 2020, Gigawatt green hydrogen plant State-of-the-art design and total installed capital costs.

[6] Source: IEA Global Hydrogen Review

[7] 'Cummins Hylizer specsheet'. 2021. Accessed: Feb. 10, 2025. [Online]. Available: ttps://www.cummins.com/sites/default/files/2021-08/cummins-hylyzer-1000-specsheet.pdf

[8] Sunfire, 'Sunfire-HyLink Alkaline'. Accessed: Feb. 10, 2025. [Online]. Available: https://sunfire.de/en/products/pressurized-alkaline-electrolyzers-ael/

[9] IRENA, 'Innovation Outlook: Renewable Ammonia', 2022.

[10] Ammonia-fuelled gas turbines: a technology and deployment update

[11] Source: Techno-Economic Aspects of Production, Storage and Distribution of Ammonia. R.M. Nayak-Luke • C. Forbes • Z. Cesaro • R. Bañares-Alcántara • K.H.R. Rouwenhorst.

[12] Source: Topsoe

[13] Used combining IEA – Global average levelised cost of hydrogen production by energy source and technology, 2019 and 2050 data for SMR and IRENA and AEA (2022), Innovation Outlook: Renewable Ammonia,International Renewable Energy Agency, Abu Dhabi, Ammonia Energy Association, Brooklyn.