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"Renewable energy systems"

Master Thesis

PRODUCTION OF GREEN HYDROGEN BY ELECTROLYZER FROM A LARGE-SCALE AGROVOLTAIC POWER PLANT

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ABSTRACT

Climate change represents one of the most urgent challenges that humanity must face in the 21st century. It refers to long-term changes in Earth's climate statistical patterns, which include increasing global average temperature, rising sea levels, intensification of extreme weather events, and modification of ecosystems. These changes are primarily attributed to the increase in greenhouse gas emissions, mainly caused by human activities such as fossil fuel combustion, industry, and intensive agriculture. Energy demands are closely linked to climate change. The growing global energy demand has led to an increase in the extraction and consumption of fossil fuels, which contribute significantly to greenhouse gas emissions. Today, the energy transition and the decarbonisation of the economy are one of the main global objectives. In Europe, the adoption of the «Green New Deal», sets the challenging goal of completely zero net emissions of Green House Gas (GHG) to 2050, with the intermediate target to reach in 2030 a reduction of 55% compared to 1990 values: to achieve these ambitious goals will require a radical change in the fuel mix with the potential adoption of hydrogen. Italy has translated these objectives into the Integrated National Energy and Climate Plan (PNIEC).

In 2020, the MISE (Ministry of Economic Development), adopted the National Integrated Energy and Climate Plan (PNIEC), which is a fundamental tool to turn the energy and environmental policy of our country towards decarbonisation.

The objectives are therefore multiple also in the light of the PNRR that also makes the Italian system more sustainable in the long term, through the progressive decarbonisation of all sectors. This objective implies accelerating energy efficiency; increasing the share of electricity produced from renewable sources, both with decentralized and centralized solutions (including innovative and offshore); developing a more sustainable mobility; start the gradual decarbonisation of the industry, including the start of the adoption of hydrogen-based solutions, in line with the European Strategy. Moreover, we focus at full environmental sustainability, which also involves improving waste management and the circular economy, the adoption of smart agriculture, the defence of biodiversity and the strengthening of the management of natural resources, starting with water.

In more detail, the PNIEC expects that in Italy to achieve the targets set should install about 50 GW of photovoltaic systems by 2030, with an average of 6 GW per year.

The current annual installed power is less than 1 GW, so it is clear that is necessary to find alternative solutions to accelerate the pace; in Italy the annual need for

electricity is equal to 320 TWh (Terna data) and only 24 TWh derive from photovoltaic systems.

These targets will be achieved both through the repowering of existing plants and the construction of new plants. Given the ambitious goals, timing and expected demand for electricity, a rapid and significant growth of photovoltaic capacity is needed. To date, there are three localization options:

- Industrial and residential roofs;
- Industrial land;
- Agricultural land;

Initial assessments, carried out as part of the PNIEC research, conclude that only roof surfaces will not be sufficient to achieve the objectives set. In addition, due to the lack of support measures and an often unfavourable location (for example near watercourses or on hillsides), industrial land are, in many cases, considered uneconomic or not feasible. Consequently, solutions outside roofs and industrial land must be evaluated. To achieve these ambitious goals, it will require an environmentally sustainable use (involving local communities) of a small part of uncultivated or underutilized agricultural land (agro-voltaic).

The project I will discuss in this document falls into the third category mentioned above (agro-voltaic plants) with the foresight of integrating agricultural activity to the production from renewable sources and also the production of green hydrogen through water electrolysis process in order to make the whole cycle truly environmentally sustainable to the benefit of the reduced emissions, local production and the socio-economic impact on the territory. More in detail, the first part of this paper provides a general analysis of the hydrogen topic, its various production methods, and its utilization in hard-to-abate sectors. The concept of green hydrogen is examined in greater detail, providing an overview of commercially available electrolyzers used for its production and analyzing potential strategies to reduce their costs. In the second part, a study of a real project for the production of green hydrogen through water electrolysis from an agrovoltaic plant is analyzed. The annual productivity of the agrovoltaic plant, the electrolyzer's consumption, and its hydrogen productivity are examined. A mapping of all potential end consumers around the power plant was conducted, highlighting their specific consumption patterns in detail. Finally, through an evaluation of the capital expenditures (CAPEX) and operational expenditures (OPEX) related to the PV (photovoltaic) and PTG (power-to-gas) plant, it was possible to assess the levelized cost of hydrogen production (LCOH).

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1 <u>Hydrogen</u>

Hydrogen is the most abundant element in the world, but only available to us locked up in compounds like fossil fuels, gasses and water. It requires a lot of energy to liberate those hydrogen molecules; either as "blue" hydrogen via steam methane reforming of natural gas with CCS, or as "green" hydrogen from water and renewable electricity via electrolysis. Today, the overall demand for hydrogen in Europe is about 8.4 Mton annual where the refining industry with 49% is the main user, followed by production of ammonia by 31% and from production of methanol, equal to 5% of the total. The annual production of hydrogen in Europe is around to 10.5 Mton, mainly through steam methane reforming (SMR) located in major sites of consumption, such as refineries and production facilities of ammonia. Italy, with about 0.6 Mton of hydrogen consumption, represents the fifth European country where over 70% of demand comes from the refining sector, about 14% from the sector ammonia while the remaining part from the other sectors of the chemical industry. From a technological point of view, there are no particular constraints on the passage to blue or green hydrogen. In fact, these industries already produce and consume hydrogen to meet their needs. However, in case of switch to blue hydrogen it must be consider critical issues in relation to the storage of carbon dioxide, while in case of transition to green hydrogen, one of the main obstacles is the need of a continuous feed of the production processes. [12]

Low-carbon hydrogen can also be produced from methane pyrolisis, where the carbon ends up as solid rather than as CO2, with 4-5 times lower electricity consumption than electrolysis and potentially lower hydrogen production cost.

Steam methane reforming with CCS does not lead to zero emissions, requires significant infrastructure for the CO2, is still exposed to the price fluctuations characteristic of fossil fuels, and could face social acceptance issues. Moreover, methane leakages associated with production and transportation of the gas can contribute to the acceleration of climate change. Methane has 86 times higher global warming potential compared to CO2 over a 20 years time horizon. Pyrolysis is still at the pilot scale stage and would require high temperature renewable or low carbon heat. Hence, green hydrogen is one of the most attractive options.

Hydrogen has significant cost, complexity, and often safety disadvantages compared with direct electrification, however it is needed in those sectors which are difficult or impossible to electrify, like aviation, shipping, and high heat industrial processes. Renewable and low carbon hydrogen is crucial for meeting the Paris Agreement goals to decarbonize hard-to-abate sectors. To meet the targets, hydrogen would need to meet around 15% of world energy demand by 2050.

In the figures below are represented the breakdowns of hydrogen demand by sector in Europe and Italy.



Figure 1 Hydrogen demand by sector in Europe [12]





1.1 Properties of hydrogen

As with electricity, hydrogen is an energy carrier that can be produced via renewable energy. Like a fossil fuel, hydrogen is explosive and produces heat when combusted; it can be extracted from hydrocarbons, held in tanks, moved through pipelines, and stored long term; it can be transformed between gaseous and liquid states and converted into derivatives.

The main characteristics of hydrogen are:

1. Abundant, but costly to produce as a low-carbon and renewable energy carrier

Hydrogen is the most abundant element in the universe, but on Earth it is found only as part of a compound, most commonly together with oxygen in the form of water but also in hydrocarbons.

For use as an energy carrier or zero-emission fuel, hydrogen must be released from its bond with oxygen or extracted from hydrocarbons. Hydrogen is the simplest of all elements, but processes to produce it in its pure form are not so simple: they are energy intensive and involve large energy losses, have significant costs, and can produce their own carbon emissions.

2. Low energy density is an issue

Hydrogen's energy density is very low compared to other fuels. This makes hydrogen more difficult to store and transport. Low energy density also reduces the feasibility of hydrogen, at least in its gaseous form, for use cases not connected directly to the grid, such as shipping and aviation. The solution is to condense hydrogen to a liquid, which only partly solves the challenge, or convert it to derivatives such as ammonia, methanol or synthetic fuels.

3. Liquid hydrogen and derivatives can overcome limitations, but conversion is inefficient and can be costly

Compressed hydrogen is in general the most cost effective way of transporting large volumes over long distances, but this requires pipelines and presents technical challenges. Hydrogen may need to be operated at different pressures (or velocity) than natural gas/biomethane and could have a negative effect on materials (in pipes and valves).

To match some of the density and flexibility benefits of liquid fuels, such as gasoline and diesel, hydrogen can be condensed into a liquid, but the temperature point for hydrogen liquefaction is extremely low at -253°C, requiring significant energy. Even in its liquid state hydrogen is not as energy dense as comparable fossil fuels. Hydrogen can be converted to derivatives such as ammonia, which has a higher energy density per volume than liquid hydrogen and can be stored and transported as a liquid at low pressures or in cryogenic tanks at around -33°C at 1 bar. Ammonia can be transported at low cost by pipelines, ships, trucks, and other bulk modes. The warning is that the ammonia synthesis, and its subsequent dehydrogenation to release hydrogen, requires significant energy.

4. Combustible, but behaves differently to natural gas

Hydrogen is combustible and gaseous at normal atmospheric pressure and temperature, but it behaves differently to natural gas, requiring adaption or development of infrastructure, appliances, and safety standards. Hydrogen ignites with very low energy and has a wide flammability range. The dispersion behaviour is different to other gases due to the small size of hydrogen atoms. Hydrogen is colourless, tasteless, and odourless, meaning that specific sensors or odorization are required to detect it, and additives are needed to produce the familiarity of a visible colour flame when burning hydrogen.

5. Great potential, but also significant challenges

Producing and converting hydrogen is inefficient and involves large losses. Hydrogen is also generally more energy intensive to store and transport than other conventional fuels. One major consideration is the relationship between greater electrification and widescale hydrogen use. Where decarbonization through direct electrification of a sector is feasible, this is the first priority due to the inefficiencies of converting electricity to hydrogen. Where electrification is not an option, then hydrogen is the best alternative, as is the case in many so-called hard-to-abate sectors. [13]

1.2 Ways of producing hydrogen

Hydrogen can be produced using different methods with varying efficiencies and environmental impacts, and is typically classified into colours depending on the method and feedstock used. A summary of the different colours of hydrogen, including feedstock, production technology and emission levels, is given in Figure 3.



Figure 3 Different types of hydrogen [12]

The production processes mentioned above and the respective incoming energy sources are characterized by very significant environmental impacts different from each other, and, in particular, the production of brown hydrogen is the most polluting with values in the range of 18-20 tCO2/tH2, while green hydrogen is neutral in terms of carbon footprint.

As we can see from the figure 4, the hydrogen produced today is almost exclusively produced from fossil fuels (grey and brown hydrogen, from natural gas and coal respectively). However, carbon prices are rising, particularly in Europe, and all industries are moving to decarbonize. The transition from grey/brown hydrogen to blue and green (produced from fossil fuels with carbon capture, or by renewable energy) in oil refining, ammonia production, and other industrial uses could ensure demand for low-carbon hydrogen in the next years.



Figure 4 Hydrogen production by different types of process in Europe [12]

1.2.1 Hydrogen from fossil fuels: methane reforming and coal gasification

- Grey hydrogen

Grey hydrogen produced from natural gas can be produced by methane reforming, which includes steam methane reforming (SMR) and autothermal reforming (ATR). The SMR process works by introducing natural gas, mainly methane, and steam into a reactor supplied by heat from a surrounding furnace. Natural gas is converted to hydrogen and carbon monoxide, which is then sent through a water gas shift reactor and a pressure swing adsorber to convert carbon monoxide to carbon dioxide and then separate the hydrogen out from the syngas.

1) Steam methane reforming reaction	$CH_4 + H_2O \rightarrow CO + 3H_2$
2) Water gas shift reaction	$\text{CO} + \text{H}_2 \text{O} \rightarrow \text{CO}_2 + \text{H}_2$

The final reaction is:

$$CH_4 + H_2O \rightarrow CO_2 + 4H_2$$

In figure 5 we can observe the process scheme. Firstly, there is the feed of natural gas in a desulphurisation unit, where it will be cleaned by acids. Then the desulphurised methane will enter the reactor where the steam methane reforming takes place, it will be cooled in order to enter the catalysts of water gas shift at about 350 °C and finally it will pass through the PSA (pressur swing adsorbtion) from which hydrogen will be extracted.



Figure 5 Process scheme of SMR

On the other hand, the ATR (Autothermal reforming) process is less commercially advanced than SMR. It differs from SMR since the heat is supplied in the process itself, eliminating the need for a furnace.

-Brown hydrogen

Brown hydrogen, produced from coal, is generally produced through gasification. Coal gasification is based on partial oxidation (POX), where coal is burnt with a selected amount of oxygen under pressure in a gasifier. The output of this gasification step is a syngas containing a mixture of hydrogen, carbon monoxide, carbon dioxide and other gases. In a second step, the addition of steam enables the water gas shift reaction with carbon monoxide, producing additional hydrogen. In figure 6 it is described the overall process.

 $C + \frac{1}{2}O_2 \rightarrow CO$

 $CO + H_2O \rightarrow CO_2 + H_2$



Figure 6 Process scheme of coal gasification [9]

- Blue hydrogen

1) Coal gassification

2) Water Gas Shift reaction

Adding CCS (carbone capture and storage) to any of the before-mentioned technologies (SMR and coal gasification) will create blue hydrogen, and 0,5% of hydrogen today is produced as blue hydrogen.

For SMR, there are different options for the placement of a carbon capture plant that affect the overall capture rate and the efficiency of the plant. For the ATR, the capture plant will typically follow the water gas shift reactor. In coal gasification, the carbon and hydrogen can be separated with pressure swing adsorption. It is important to know that capture plants do not capture 100% of the CO_2 and there are also concerns regarding upstream emissions, which include both carbon dioxide and methane.

Cost-wise, SMR is currently the most economic production method. However, the overall cost of SMR with CCS is expected to increase towards 2050, despite a decrease in the CAPEX, because fuel and carbon costs are likely to increase. Regarding emissions from blue hydrogen technologies, ATR is the technology with the lowest emissions; It has also high efficiency and is hence a promising option for blue hydrogen. In the figure below, different parameters are shown for each production method.

		SMR	SMR with CCS	ATR	ATR with CCS	Coal gasification	Coal gasification with CCS
Efficiency	%	66-76	69-79	67-85	74-80	60-66	58
Emissions	kg CO ₂ /kg H ₂	8.9-9.4	0.5-2	7.4-9.8	0.3-1.3	16.5-20.2	1.8-2.1
LCOH	USD/kg H ₂	0.8-2.7	1.8-4.1	0.8-2.7	1.3 - 3.0	2.2 - 4.1	3.7 - 5.2

Figure 7 Comparison of efficiency, emissions and levelized cost of hydrogen (LCOH) across production methods [13]

1.2.2 Hydrogen from electricity: electrolysis

- Green hydrogen

At a basic level, electrolysis splits water (H2O) into hydrogen (H2) and oxygen (O2) by applying an electric current. Hydrogen is produced at the cathode while oxygen at the anode. Researchers and developers have optimized this process and currently there are four main technologies; Alkaline, Proton Exchange Membrane (PEM), Solid Oxide Electrolysis (SOE) and Anion Exchange Membrane (AEM).

Regardless of the technology, the overall electrolysis reaction is the same:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2$$

A typical electrolysis process diagram is shown in Figure 8 below. It is important to know that different processes will use different pieces of equipment. For example, PEM units will not require the KOH mixing tank, as no electrolytic solution is needed for these electrolyzers. Another example involves water purification equipment. Water quality requirements differ across electrolyzers. Some units include water purification inside their hydrogen generation unit, while others require an external deionizer or reverse osmosis unit before water is fed to the cell stacks. For systems

that do not include a water purifier, one is added in the process flow. A water storage tank may be included to ensure that the process has adequate water in storage in case the water system is interrupted. Each system has a hydrogen generation unit that integrates the electrolysis stack, gas purification and dryer, and heat removal. Electrolyte circulation is also included in the hydrogen generation unit in alkaline systems. Oxygen and purified hydrogen are produced from the hydrogen generation unit; Moreover, a compressor and hydrogen storage can be added to the system. Typical utilities that the electrolysis systems need include electricity for electrolysis and other peripheral equipment; cooling water for the hydrogen generation unit; pre-pressurization gas; and inert gas.



Figure 8 Process flow diagram [14]

1.3 Hydrogen for hard-to-abate sectors: industrial sector.

The hard-to-abate industrial sectors, that are difficult to electrify, already use hydrogen as feedstock within the production processes. In particular, the sectors considered are refining, ammonia production, methanol production and steel production. Today, almost all the hydrogen used comes from fossil fuels (grey or brown hydrogen) and the options for the supply of decarbonised hydrogen are respectively the electrolysis process (green hydrogen) or the Steam Methane Reforming coupled to a CO₂ capture system (blue hydrogen).



Figure 9 Hard-to-abate industrial sectors [12]

For each sector, it is provided a description of the main production processes estimating the amount of hydrogen required per equivalent unit of finished product/process output.

- Refining

The refining sector is the largest producer and consumer of hydrogen in Europe. Hydrogen is typically produced by steam or autothermal reforming processes, using natural gas as feedstock. In refineries hydrogen is mainly used within hydrotreating and hydrocracking processes.



Figure 10 Production and hydrogen demand in refining sector [12]

-**Hydrogen demand**: the hydrotreating process requires about 20 - 50 Nm³ of H_2 per ton of distilled product. Instead, the hydrocracking process requires about 300 Nm³ of H_2 per ton of distilled product.

The hydrotreating process is one of the fundamental steps of refining. It is intended to remove the contaminants in crude oil, including mainly sulphur, oxygen, nitrogen and metals. The hydrocracking process, however, aims to break the long chains of hydrocarbons transforming them into lighter products with low sulphur content (for example kerosene, diesel). The scheme of operation of the two processes is rather similar: both, in fact, use high pressure hydrogen and catalysts. However, with equal feed input to the process, hydrocrackers use a greater amount of catalysts and operate at higher pressures.



Figure 11 Process scheme of refining [12]

- Ammonia production

Ammonia is one of the chemical products with the highest rate global production and is mainly used for the production of fertilizers, such as urea and ammonium salts, and for the food industry.



Figure 12 Production and hydrogen demand for ammonia production [12]



The Haber-Bosch process is the technological solution for the industrial synthesis of ammonia using nitrogen and hydrogen as reagents and a heterogeneous iron-based catalyst.



Figure 13 Process scheme of ammonia production [12]

These gaseous reagents, nitrogen and hydrogen , constitute what is defined pure of synthesis. The pure synthesis is obtained by exploiting natural gas which can be reformed with steam or, in alternative, to autothermal process; the latter implies partial oxidation of the hydrocarbon into monoxide of carbon (CO) and hydrogen (H₂) through the use of an appropriate amount of air. Nitrogen and hydrogen react in a ratio of 1:3 with temperature between 350-550 $^{\circ}$ C and optimum pressure of 140-320 atm.

 $N_2 + 3H_2 \rightarrow 2NH_3$

It is necessary to introduce a catalyst (mixture of iron, potassium oxide and aluminum oxide) to accelerate the reaction, as the high temperatures, which would be necessary to accelerate the reaction kinetics of the cleavage of N_2 bonds, do not favor thermodynamically the synthesis reaction that becomes endoergonomic at high temperature (from the products to the reagents). The ammonia produced is cooled with water and collected in a cooling chamber at -33 °C, which corresponds to its temperature condensation. Hydrogen and nitrogen molecules that have not reacted remain in the gas phase and can be recirculated for a new synthesis. The efficiency of the process is around 62-66%.

-Methanol production

Methanol is the base product of many chemical compounds, such as formaldehyde, methyl-ter-butyl ether (MBTE) and acetic acid. It is mainly produced by steam reforming of natural gas.



Figure 14 Production and hydrogen demand for methanol production [12]

```
-Hydrogen demand: 189 kg of H<sub>2</sub> per ton of methanol produced.
-Emissions: 1,49 tCO<sub>2</sub>/tMeOH
```

Methanol can be produced from both carbon monoxide (CO) and carbon dioxide (CO₂). Stoichiometry of methanol synthesis reaction is:

- Hydrogenation of CO: CO + $2H_2 \rightarrow CH_3OH$
- Hydrogenation of CO_2 : $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$

Focusing on the process, the first step is the purification of natural gas, mainly through desulphurisation. Then, the flow is pre-heated, steam is added and enters the reformer where, at a pressure of 20 bar and at a temperature of 800-950 °C, takes place the production of syngas. Usually carbon dioxide is added to the syngas to increase the efficiency of the next process methanol synthesis. The syngas produced by reforming is compressed to be converted inside the reactor. The conversion rate of methanol is in the order of 5% per pass, so the syngas that does not undergo the reaction is again used at the level of input to the synthesis process. Methanol synthesis is a process that requires temperatures relatively low and high pressure. The temperature can be controlled to 200-300 °C by using catalysts, while the pressure at 50-100 bar. The catalysts are used to accelerate the kinetics of the reaction, and typically copper catalysts (CU) are adopted. Finally, methanol is separated from water by distillation. The process flow is shown in the figure 15.



Figure 15 Process flow of methanol production [12]

-Steel production

The Direct Reduced Iron process is one of the main alternatives for decarbonising the steel industry.



Figure 16 Production and hydrogen demand for steel production [12]



Direct Reduced Iron (DRI) is obtained by the reduction of ferric oxide, contained in minerals ferrous. The reduction reaction takes place inside a reactor where CO and H_2 transform iron ore into DRI. The reduction process requires a temperature around 800 °C and can occur in two different configurations:

- In one case, CO and H_2 are produced from natural gas by reforming process and are subsequently introduced into the reactor DRI.

- Alternatively, there is the integrated process in which the methane is introduced directly into the reactor reduction, and inside carbon monoxide and the hydrogen are produced.

The DRI produced is then sent to an electric furnace or blast furnace to be further processed and transformed into steel. The whole process is represented in the figure below.



Figure 17 Process flow of steel production [12]

1.4 Hydrogen for hard-to-abate sectors: transport sector

Within the transport sector, several «sub-categories» can be considered «Hard-to-Abate» and mainly refer to: heavy transport by road, shipping, air transport and rail transport.



Figure 18 Different means of transport [12]

The use of electricity to limit GHG emissions from long-haul heavy transport is not always technologically actionable. Therefore, hydrogen together with other synthetic fuels produced from hydrogen as «feedstock» (e-Gasoline, e-Diesel, e-Metano, e-GNL, e-Ammoniaca, e-Methanol, e-DME/e-OME and e-jet), despite different technological and infrastructural problems, are currently being considered as potential solutions for the decarbonisation of the sector.

These e-fuels (electrofuels) can be both liquid and gaseous as we can see from the figure 19.



Figure 19 Different types of e-fuels [12]

Unlike conventional fuels, they do not release additional CO_2 and can therefore be considered climate neutral. Moreover, thanks to their compatibility with internal combustion engines, they can be used to feed road vehicles, airplanes and ships, allowing them to continue to use existing technologies and infrastructure (especially for e-gasoline, e-diesel, e-kerosene) while limiting the impact on the environment. For the production of e-fuels, the starting point is the use of electricity produced from renewable sources that through the use of appropriate production processes can be converted into chemical energy.



Figure 20 Production process of e-fuels [12]

The e-fuels can be used in three alternative technological solutions:

- The **Fuel Cell** is a system of direct conversion of chemical energy into electricity. Unlike internal combustion engines, where the fuel is mixed with air, in the Fuel Cell

there is a separation of the fuel from the oxidant, without combustion of the fuel. To date, PEMFC - «Proton Exchange Membrane Fuel Cell» is the most used technology in road transport, by achieving system efficiency between 40-65%.

- Internal combustion engines are currently the most used technological solution for the transport sector. For the adoption of e-hydrogen, e-Ammoniaca, e-Methanol and e-DME/e-OME it is necessary a retrofit of the existing propulsion systems while regarding the use of e-Gasoline, e-Diesel, e-Methane and e-GNL do not require significant retrofit actions of existing propulsion systems.

- As regards the **turbines**, the most widely used technological solution in long-haul air transport, in the case of e-hydrogen feeding, retrofit actions are required while, if they are powered by e-Jet, there is no need retrofit actions to existing propulsion systems.



Figure 21 Technological solutions for e-fuels [12]

With regard to long haul heavy transport, there are different technological solutions depending on the subsector:

- In the **heavy transport by road**, besides the electrification of the vehicles, the more promising initiatives relatively to e-fuels regard the adoption of e-hydrogen in the Fuel Cell or the adoption of e-Diesel and e-Metano/ e-GNL in the current engines.

- In the **shipping** the research is mainly concentrated on the use of e-hydrogen in the Fuel Cell or the adoption of e-Diesel, e-Metano/e-GNL, e-Ammoniaca and e-Methanol in current engines.

- Air transport is characterized by more limited initiatives for the decarbonisation of the sector, at least in the short term. In the medium-long term, instead, the

initiatives that have found greater interest of search regard the adoption of e-hydrogen in the Fuel Cell or the adoption of e-hydrogen and e-jet in the turbines.

- In the **rail transport**, by considering the railway sections not yet electrified, the various initiatives have focused only on the adoption of e-hydrogen in Fuel Cell.

2 Electrolyzers

Water electrolysers are electrochemical devices used to split water molecules into hydrogen and oxygen by passage of an electrical current.



Figure 22 Electrolysis system [6]

They can be fragmented in three levels:

- The cell is the core of the electrolyser and it is where the electrochemical process takes place. It is composed of the two electrodes (anode and cathode) immersed in a liquid electrolyte or adjacent to a solid electrolyte membrane, two porous transport layers (which facilitate the transport of reactants and removal of products), and the bipolar plates that provide mechanical support and distribute the flow.

- The stack has a broader scope, which includes multiple cells connected in series, spacers (insulating material between two opposite electrodes), seals, frames (mechanical support) and end plates (to avoid leaks and collect fluids).

- The system level (or balance of plant) goes beyond the stack to include equipment for cooling, processing the hydrogen (e.g. for purity and compression), converting the electricity input (e.g. transformer and rectifier), treating the water supply (e.g. deionization) and gas output (e.g. of oxygen). Purified water is fed into the system using circulating pumps, or also by gravity. The water then reaches the electrodes by

flowing through the bipolar plates and through the porous transport layers. At the electrode, the water is split into oxygen and hydrogen, with ions (typically H⁺ or OH⁻) crossing though a liquid or solid membrane electrolyte. The membrane or diaphragm between both electrodes is also responsible for keeping the produced gases (hydrogen and oxygen) separated and avoiding their mixture.



SYSTEM LEVEL

Figure 23 Balance of plant configuration [15]

Ī STACK LEVEL Manifold frame and sealing ÷ Membrane or Seperator Membrane or Seperator 4 Н, 02 **Bipolar Plate** ipolar Plate Electrode Repeat until end plate H₂O H₂O Porous Porous Transport Transport Manifold frame and sealing Layer Layer ķ ł

Figure 24 Stack level configuration [15]



Figure 25 Cell level configuration [15]

2.1 Electrolyser Technologies

Electrolysers are typically divided into four main technologies. Alkaline and polymer electrolyte membrane (PEM) are already commercial, while anion exchange membrane (AEM) and solid oxide, now at lab scale, promise a major step forward.

Solid oxide and anion exchange membrane (AEM) have high potential, but are much less mature technologies, with only a few companies and original equipment manufacturers (OEMs) involved in their manufacture and commercialisation. These are mostly based in Europe. These four electrolysers are distinguished based on the electrolyte and temperature of operation. The basic principle of a water electrolysis cell consists of two electrodes separated by an electrolyte. The electrolyte is the media responsible for transporting the generated chemical charges (anions (-) or cations (+)) from one electrode to the other. In the alkaline type, the electrolyte responsible for transporting the OH⁻ anions is typically a highly concentrated potassium hydroxide solution. The electrodes and produced gases are physically separated by a porous inorganic diaphragm (also called separator) that is permeable to the KOH solution. In PEM, AEM, and solid oxide electrolysers, the electrodes are separated by an electron-insulating solid electrolyte, which is responsible for transporting ions from one electrode to the other and at the same time physically separating the produced gases. For these, there is no need to add a liquid electrolyte solution, and the ion transport happens within the PEM, AEM or solid oxide component. Figure 25 summarizes the operating conditions and the most important components for the four types of electrolysers.

	Alkaline	PEM	AEM	Solid Oxide
Operating temperature	70-90 °C	50-80 °C	40-60 °C	700-850 °C
Operating pressure	1-30 bar	< 70 bar	< 35 bar	1 bar
Electrolyte	Potassium hydroxide (KOH) 5-7 molL ⁻¹	PFSA membranes	DVB polymer support with KOH or NaHCO3 1molL ⁻¹	Yttria-stabilized Zirconia (YSZ)
Separator	ZrO ₂ stabilized with PPS mesh	Solid electrolyte (above)	Solid electrolyte (above)	Solid electrolyte (above)
Electrode / catalyst (oxygen side)	Nickel coated perforated stainless steel	Iridium oxide	High surface area Nickel or NiFeCo alloys	Perovskite-type (e.g. LSCF, LSM)
Electrode / catalyst (hydrogen side)	Nickel coated perforated stainless steel	Platinum nanoparticles on carbon black	High surface area nickel	Ni/YSZ
Porous transport layer anode	Nickel mesh (not always present)	Platinum coated sintered porous titanium	Nickel foam	Coarse Nickel-mesh or foam
Porous transport layer cathode	Nickel mesh	Sintered porous titanium or carbon cloth	Nickel foam or carbon Cloth	None
Bipolar plate anode	Nickel-coated stainless steel	Platinum-coated titanium	Nickel-coated stainless steel	None
Bipolar plate cathode	Nickel-coated stainless steel	Gold-coated titanium	Nickel-coated Stainless steel	Cobalt-coated stainless steel
Frames and sealing	PSU, PTFE, EPDM	PTFE, PSU, ETFE	PTFE, Silicon	Ceramic glass

Figure 26 Characterisation of the four types of water electrolysers [15]

We analyze in detail every single type of electrolyser.

Alkaline electrolysers: These have a simple stack and system design and are relatively easy to manufacture. Currently, they have electrode areas as high as 3 square metres (m^2). They operate with high concentrate KOH (typically 57 moles of solute per litre of solution [mol/L]) as electrolyte, robust ZrO_2 based diaphragms and nickel (Ni) coated stainless-steel for the electrodes. The ionic charge carrier is the hydroxyl ion OH⁻, with KOH and water permeating through the porous structure of the diaphragm to provide functionality for the electrochemical reaction. This allows the intermixing of the produced gases (hydrogen and oxygen H₂ and O₂) that are dissolved in the electrolyte, limiting lower power operating range and the ability to operate at higher pressure levels. To prevent this, thicker (0.252 millimetre [mm]) diaphragms are used, but this creates a higher resistance and lower efficiencies.

Spacers are sometimes included by some manufacturers between electrodes and diaphragms to further avoid the intermixing of gases. These thick diaphragms and added spacers result into high ohmic resistances across the two electrodes, drastically reducing current density at a given voltage. Today's advanced designs, using zerogap electrodes, thinner diaphragms and different electrocatalyst concepts to increase current density.



Figure 27 Alkaline electrolyser [15]

Regardless of the technology, the overall electrolysis reaction is the same:

$$H_2O \rightarrow \ \ ^\prime \!\! ^2 O_2 + H_2$$

However, reaction at each electrode differs between the four electrolysers. In an Alkaline system the reactions at the electrodes are:

Alkaline hydrogen production at the cathode

$$4 \text{ H}_2\text{O} + 4\text{e}^- \rightarrow 2\text{H}_2 + 4\text{OH}^-$$

Alkaline oxygen production at the anode

$$4 \text{ OH}^{-} \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^{-}$$

Polymer Electrolyte Membrane (PEM) electrolysers: These use a thin (0.2 mm) PFSA membrane and electrodes with advanced architecture that allows achieving higher efficiencies (i.e. less resistance). The perfluorosulfonic acid (PFSA) membrane is also chemically and mechanically robust, which allows for high pressure differentials. Thus, the PEM cells can operate at up to 70 bar with the oxygen side at atmospheric pressure. Titanium-based materials, noble metal catalysts and protective coatings

are necessary, not only to provide long-term stability to cell components, but also to provide optimal electron conductivity and cell efficiency. These requirements have caused PEM stacks to be more expensive than alkaline electrolysers. PEMs have one of the most compact and simplest system designs, yet they are sensitive to water impurities such as iron, copper, chromium and sodium and can suffer from calcination. Today, electrode areas are quickly approaching 2000 square centimetres (cm²), yet this is still far from future concepts of large MW stack units using single stack concepts.



Figure 28 Proton Exchange Membrane system [15]

In a PEM system the reactions at the electrodes are:

PEM hydrogen production at the cathode

 $4H^+ + 4e^- \rightarrow 2H_2$

PEM oxygen production at the anode

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^{-1}$$

Solid oxide electrolysers (SOEC): These operate at high (700-850°C) temperatures. This enables: the favourable kinetics that allow the use of relatively cheap nickel electrodes; electricity demand decreases and part of the energy for separatio is provided through heat (waste heat can be used and apparent efficiencies based on electricity can be higher than 100%); the potential for reversibility (operating as fuel cell and electrolyser); coelectrolysis of CO2 and water to produce syngas (which is

the basic building block for the chemical industry). SOECs are today only deployed at the kW-scale, although some current demonstration projects have already reached 1 MW.



Figure 29 Solid oxide system [15]

In a Solid Oxide system the reactions at the electrodes are:

Solid Oxide hydrogen production at the cathode

 $2H_2O + 4e^- \rightarrow 2H_2 + 2O^{2-}$

Solid Oxide oxygen production at the anode

 $20^{2-} \rightarrow 0_2 + 4e^{-}$

Anion Exchange Membranes (AEM): This is the latest technology with only a few companies commercialising it, with limited deployment. The AEM membrane has chemical and mechanical stability problems, leading to unstable lifetime profiles. Moreover, performance is not yet as good as expected, mostly due to low AEM conductivity, poor electrode architectures and slow catalyst kinetics. Performance enhancement is typically achieved by tuning membrane conductivity properties, or by adding a supporting electrolyte(e.g. KOH, or sodium bicarbonate [NaHCO₃]).


Figure 30 Anion Exchange Membrane system [15]

In Anion Exchange Membrane system the reactions at the electrodes are:

AEM hydrogen production at the cathode

 $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$

AEM oxygen production at the anode

$$40H^{-} \rightarrow 2H_{2}O + O_{2} + 4e^{-}$$

2.2 PEM and Alkaline electrolysis comparison

Here we take a look at two of the most dominant means of electrolysis in the market today, Alkaline electrolyzers (AE) and Proton Exchange Membrane (PEM) electrolyzers. They are both types of devices used to split water molecules into hydrogen and oxygen by passage of an electrical current. While they serve the same purpose, there are several differences between the two technologies. Let's explore the comparison and advantages of each:

Alkaline Electrolyzers:

1. Structure and operation: The alkaline electrolyzer uses a liquid alkaline electrolyte. The water in this electrolyte is split into hydrogen and hydroxide

ions at the cathode pole. These ions are then brought into contact with a membrane, after which they are oxidized to water and oxygen at the anode pole.

- 2. Efficiency: Alkaline electrolyzers typically have a higher efficiency compared to PEM electrolyzers, typically ranging from 60% to 70%. This means they can convert a higher percentage of the electrical energy into hydrogen.
- 3. Cost: Alkaline electrolyzers are generally more affordable than PEM electrolyzers due to their simpler design and the use of inexpensive materials like nickel and steel.
- 4. Durability: Alkaline electrolyzers tend to have a longer lifespan compared to PEM electrolyzers. They can operate for tens of thousands of hours, making them suitable for continuous operation.
- 5. Flexibility: Alkaline electrolyzers can handle variable loads and are more tolerant of fluctuations in the power supply. This makes them suitable for applications where electricity availability varies.
- 6. Large-scale applications: Alkaline electrolyzers are well-suited for large-scale hydrogen production due to their robustness and lower capital costs. They are commonly used in industrial applications and centralized hydrogen production facilities.

PEM Electrolyzers:

- 1. Structure and operation: A PEM electrolyzer uses a polymer membrane as electrolyte that allows only hydrogen ions to pass through. The water is split into oxygen, hydrogen ions, and four electrons at the anode. The hydrogen ions and the four electrons then pass through the membrane and are converted to hydrogen at the cathode.
- 2. High-pressure operation: PEM electrolyzers can operate at higher pressures, typically up to 30 bar or more. This allows for the production of high-purity hydrogen without the need for an additional purification step.

- 3. Compactness and portability: PEM electrolyzers have a more compact design and are lighter compared to alkaline electrolyzers. This makes them suitable for decentralized or on-site hydrogen production, where space and mobility are important factors.
- 4. Response time: PEM electrolyzers can start and stop quickly, often within seconds, allowing for rapid adjustments to changing power demands. This makes them suitable for applications with dynamic power availability, such as renewable energy integration or grid balancing.
- 5. Efficiency at low loads: PEM electrolyzers tend to have higher efficiency at low loads compared to alkaline electrolyzers. This means they can effectively operate at part-load conditions and are more efficient when power supply fluctuations occur.
- 6. Safety: PEM electrolyzers operate at lower temperatures and pressures compared to alkaline electrolyzers, reducing the risk of hydrogen leakage or explosions.

Both alkaline and PEM electrolyzers have their unique advantages and are suitable for different applications. Alkaline electrolyzers excel in large-scale, continuous hydrogen production with variable power supply, while PEM electrolyzers are more suitable for compact, decentralized systems with rapid response times and high-purity hydrogen requirements. [7]



Figure 31 PEM and Alkaline electrolyser structures [6]

Technology		ALK		PEM	
	Unit	2017	2025	2017	2025
Efficiency	kWh of electricity/ kg of H₂	51	49	58	52
Efficiency (LHV)	%	65	68	57	64
Lifetime stack	Operating hours	80 000 h	90 000 h	40 000 h	50 000 h
CAPEX – total system cost (Incl. power supply and Installation costs)	EUR/kW	750	480	1 200	700
OPEX	% of initial CAPEX/year	2 %	2 %	2 %	2%
CAPEX – stack replacement	EUR/kW	340	215	420	210
Typical output pressure*	Bar	Atmospheric	15	30	60
System lifetime	Years	20		2	20

Figure 32 Techno-economic characteristics of ALK and PEM electrolysers [8]

2.2.1 Strategies for cost reduction

Green hydrogen is still 2-3 times more expensive than blue hydrogen (produced from fossil fuels with carbon capture and storage) and further cost reductions are needed.

The largest single cost component for on-site production of green hydrogen is the cost of the renewable electricity needed to power the electrolyser unit. This renders production of green hydrogen more expensive than blue hydrogen, regardless of the cost of the electrolyser. A low cost of electricity is therefore a necessary condition for producing competitive green hydrogen. This creates an opportunity to produce hydrogen at locations around the world that have optimal renewable resources, in order to achieve competitiveness. Low electricity cost is not enough by itself for competitive green hydrogen production, however, and reductions in the cost of electrolysis facilities are also needed. This is the second largest cost component of green hydrogen production and is the focus of this paragraph, which identifies key strategies to reduce investment costs for electrolysis plants from 40% in the short term to 80% in the long term. Figure 30 shows how up to 80% of green hydrogen production of cheaper

electricity and electrolyser capex investment, in addition to increased efficiency and optimised operation of the electrolyser.



Figure 33 Green hydrogen production costs [15]

Today signifies an electrolyser investment cost of USD 770/kilowatt (kW), electrolyser efficiency of 65%, an electricity price of USD 53/MWh, full load hours of 3200, and a weighted average cost of capital (WACC) of 10% (relatively high risk). On the other hand, in the future (2050), the electrolyser investment cost could be of USD 130/kW, efficiency of 76%, electricity price of USD 20/MWh, full load hours of 4200, and a WACC of 6%.

Regarding the electrolyser investment cost, despite their market availability and maturity, PEM and Alkaline water electrolysers are still considered highly expensive from both CAPEX and OPEX perspectives, compared to fossil fuel-based hydrogen production. PEM water electrolysers are 50%-60% more expensive than alkaline. Today, the main contributor to system costs is still the stack, which represents 40%-50% of the total, for both alkaline and PEM electrolysers. Figure 31 and Figure 32 show a breakdown of cost components for both PEM and Alkaline electrolysers.



Figure 34 Cost breakdown for 1 MW PEM electrolyser [15]

For PEM electrolysers the stack represents slightly less than half of the electrolysis system cost. For the balance of plant, power supply represents a very significant cost component. For PEM stacks, bipolar plates are a significant cost component, as they are often built to provide multiple functions and require advanced materials such as gold or platinum coated titanium.



Figure 35 Cost breakdown for 1 MW alkaline electrolyser [15]

For alkaline electrolysers, within the stack, over 50% of the costs relate to electrodes and diaphragms, as opposed to 25% of the cost in the CCM for PEM. Bipolar plates for alkaline, however, account for only a small part of stack costs, as opposed to over 50% in the case of PEM, due to a simpler design, simple manufacturing and cheaper materials (nickel coated steel).

At the stack level, there are mainly two strategies to achieve lower costs:

1) **Stack design and cell composition**: This includes using less critical materials, redesigning the stack to achieve a higher efficiency (i.e. lower electricity cost), higher durability (longer lifetime to distribute the investment) and increase the current density (higher production rate).

2) Increase the module size.

Concerning stacks for alkaline electrolysers, the key areas to focus on are the electrodes and the diaphragms.

• Increase current densities: The current densities of the stacks can be increased, from the current, 0.5 A/cm² to more advanced units of 2-3 A/cm². This current density increase cannot be made, however, at the penalty of lower efficiency. Power densities of 2-3 W/cm² could be achieved by demonstrating thinner diaphragms or membranes for alkaline electrolysers. As with PEM, alkaline electrolysers also need to improve their voltage efficiency levels, reducing ohmic losses and increasing electrode kinetics.

• Reducing diaphragm thickness: This could improve efficiency and reduce electricity consumption. The thinner the diaphragms, the lower the resistance to transporting the OH⁻ species from the cathode to the anode. However, this comes at a cost of higher gas permeation, which contributes to higher safety concerns. Overall, the diaphragm thickness should reach values that approach those of PEM. State-of-the-art membranes for PEM are about 125-175 micrometres (μ m) with a potential decrease to 20 μ m or lower. For alkaline electrolysers, the current diaphragm thickness is about 460 μ m. Decreasing this to 50 μ m would contribute to improving the efficiency from 53% to 75% at 1 A/cm².

For PEM stacks, the focus areas are bipolar plates and PTLs, given their large cost contribution and large potential for reduction. Re-designing the stacks can achieve

large cost reductions, since it enables the reaching of higher power densities, from the current 2 A/cm² to 6 A/cm² or more in the next few decades. Next, electrodes should be scaled up from the current 1 500-2 000 cm², up to 5 000 cm² and eventually 10 000 cm².

• Reducing membrane thickness: This allows an increase in efficiency, which in turn enables a reduction in electricity consumption. Thick membranes (Nafion N117 with approximately 180 μ m thickness,) are still responsible for efficiency losses of about 25% (at 2 A/cm²). There are much thinner membranes that are commercially available, with thicknesses as low as 20 μ m. This thickness reduction would allow a reduction in efficiency losses to about 6% (at 2 A/cm²).

Figure 33 and 34 show the KPIs (Key Performance Indicators) for the electrolysis technologies, both for the state of-the-art in 2020 and as targets for 2050.

	2020	Target 2050	R&D focus
	PEM electrolysers		
Nominal current density	1-2 A/cm ²	4-6 A/cm2	Design, membrane
Voltage range (limits)	1.4-2.5 V	< 1.7 V	Catalyst, membrane
Operating temperature	50-80°C	80°C	Effect on durability
Cell pressure	< 30 bar	> 70 bar	Membrane, reconversion
			catalysts
Load range	5%-120%	5%-300%	Membrane
H ₂ purity	99.9%-99.9999%	Same	Membrane
Voltage efficiency (LHV)	50%-68%	>80%	Catalysts
Electrical efficiency (stack)	47-66 kWh/Kg H ₂	< 42 kWh/Kg H ₂	Catalysts/membrane
Electrical efficiency (system)	50-83 kWh/Kg H ₂	< 45 kWh/Kg H ₂	Balance of plant
Lifetime (stack)	50 000-80 000 hours	100 000-120 000 hours	Membrane, catalysts,
			PTLs
Stack unit size	1 MW	10 MW	MEA, PTL
Electrode area	1 500 cm ²	> 10 000 cm ²	MEA, PTL
Cold start (to nominal load)	< 20 minutes	< 5 minutes	Insulation (design)
Capital costs (stack)	USD 400/kW	< USD 100/kW	MEA, PTLs, BPs
minimum 1 MW			
Capital Costs (system)	700-1400 USD/kW	< 200 USD/kW	Rectifier, water
minimum 10 MW			purification

Figure 36 Future KPIs for PEM electrolyser [15]

For PEM water electrolysers, significant development of the technology can be obtained by:

- replacing thick membranes;
- reducing catalyst quantities after reengineering electrode concepts;
- removing or substituting expensive coatings on PTLs;

	Alkaline electrolysers		
Nominal current density	0.2-0.8 A/cm ²	> 2 A/cm ²	Diaphragm
Voltage range (limits)	1.4-3 V	< 1.7 V	Catalysts
Operating temperature	70-90°C	> 90°C	Diaphragm, frames,
			balance of plant
			components
Cell pressure	< 30 bar	> 70 bar	Diaphragm, cell, frames
Load range	15%-100%	5%-300%	Diaphragm
H ₂ purity	99.9%-99.9998%	> 99.9999%	Diaphragm
Voltage efficiency (LHV)	50%-68%	> 70%	Catalysts, temperature
Electrical efficiency (stack)	47-66 kWh/Kg H ₂	< 42 kWh/Kg H ₂	Diaphragm, catalysts
Electrical efficiency (system)	50-78 kWh/Kg H ₂	< 45 kWh/Kg H ₂	Balance of plant

Lifetime (stack)	60 000 hours	100 000 hours	Electrodes
Stack unit size	1 MW	10 MW	Electrodes
Electrode area	10 000-30 000 cm ²	30 000 cm ²	Electrodes
Cold start (to nominal load)	< 50 minutes	< 30 minutes	Insulation (design)
Capital costs (stack)	USD 270/kW	< USD 100/kW	Electrodes
minimum 1 MW			
Capital costs (system)	USD 500-1 000/kW	< USD 200/kW	Balance of plant
minimum 10 MW			

Figure 37	' Future	KPIs for	Alkaline	electrolvser	[15]
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For alkaline electrolysers, the focus on increasing efficiency can be achieved by:

- increasing the limit for the operating temperature;
- replacing thick diaphragms;
- redesigning catalyst compositions;
- moving electrode architectures into high area electrodes;
- introducing novel PTL/electrode concepts.

2.3 Water and land use for green hydrogen production

Green hydrogen production uses water as feedstock and renewable electricity as energy source to separate hydrogen and oxygen from water in an electrolyser. Water, as pure as possible, is therefore a key input. From a stoichiometric perspective, 1 kg of hydrogen requires 9 kg of water as input. Due to some inefficiencies in the process, however, taking into account the process of water demineralisation, with typical water consumption, the ratio can range between 18 kg and 24 kg of water per kg of hydrogen. The largest water consumption is actually upstream and it is the highest when the electrolyser is coupled with PV. Water consumption for green hydrogen from PV can vary between 22 and 126 kg of water per kg of hydrogen depending on the solar radiation, lifetime and silicon content. Considering a very large 1 GW electrolyser, operating with an efficiency of 75% for 8 000 hours per year, the annual hydrogen production would be 0.15 million tonnes of hydrogen and 3 million tonnes of water (assuming 20 kg of water used per kg of hydrogen). For the expected 19 exajoules (EJ) of green hydrogen (approximately 160 megatonnes [Mt]) in the Transforming Energy Scenario of the IRENA Global Renewables Outlook, we would require around 3 billion m³ of water per year in 2050. This is 0.08% of the current global consumption of freshwater. For the land area, there are no real projects of more than 100 MW in water electrolysis (the largest one, as of November 2020, is 20 MW, in Becancour, Canada). Thus, so far, land area estimates rely on engineering estimates, rather than plot optimisation based on real experience.

- A study funded by the German government in 2014 estimated that a 100 MW electrolyser plant would occupy about 6300 m².

- Siemens estimated in 2017 that a 300 MW electrolyser plant would occupy about 180 m x 80 m (15 000 m²).

- ITM estimated in 2017 that one 100 MW electrolyser would occupy about 40 m x 87 m (3500 m^2), with the possibility of using multiple layout options to fit different applications.

- In 2018, McPhy proposed a 100 MW facility (composed of five modules of 20 MW each) with a plot size of 4500 m².

More recently, given the various multi-GW national strategies, there are studies looking at what it could mean to have these multi-GW facilities. One study comes from the Institute for Sustainable Process Technology (ISPT) in the Netherlands, which made a detailed bottom-up study for a 1 GW alkaline and PEM plant. As a result, the maximum area requirements were 13 ha and 17 ha (0.13 km² - 0.17 km²)

for a PEM and an alkaline electrolyser plant respectively, with the potential to decrease the land requirements with compact designs of 8 ha and 10 ha respectively (Figure 30 left for the plot size of an alkaline electrolyser). The bulk of this space (65%-75%) is for the electrolyser building and the electrical equipment (e.g. switchgears and transformers), with the least space used by the hydrogen processing section. [15]



Figure 38 Plot size for an Alkaline 1 GW electrolyzer plant (left) and for a 100 MW Alkaline electrolyser (right) [15]

2.4 Different scenarios for green hydrogen production, transport and

consumption

In the installation of electrolysers exist different scenarios.

- The decentralized off-grid scenario;
- The decentralized grid-connected scenario;
- The grid-connected transport of electricity scenario;
- The grid-connected transport of hydrogen scenario;
- 1) Decentralized off-grid scenario

Decentralized off-grid scenario assumes that electrolyzers and RES power plants are both installed at consumption centers (i.e., factory, town, etc.) in the same location. In this off-grid scenario, RES power plants are not connected to the grid. Therefore, the RES capacity factor depends on the location of consumption centers, and the absence of network connection implies that the surplus of generation or the insufficient hydrogen production cannot be managed through the power grid. In terms of costs and feasibility, the decentralized off-grid scenario should be considered viable only in particular contexts (e.g., remote areas in extra-EU countries). In fact, it has the highest cost if compared with the cases that consider electrolyzers and the related renewable source plants connected to the grid. In this scenario, a substantial increase in renewable installed capacity is required, much higher than the size of the electrolyzer, in order to allow a stable production of hydrogen generation. Moreover, additional batteries are required to reach the electrolyzer target.



Figure 39 Decentralized off-grid scenario [16]

Pros

As the connection to the grid is not provided, there are no extra costs related to transmission networks Cons

The energy producibility of RES, may not be satisfactory. In this scenario, the RES plants are located exclusively in correspondence with the demand for hydrogen and not in areas where renewable energy producibility is more favorable. Furthermore, storage equipment (e.g., batteries) is needed. The increase in renewable installed capacity implies higher costs compared to the other scenarios.

2) Decentralized grid-connected scenario

The decentralized grid-connected scenario assumes also in this case that electrolyzers and RES are both at consumption centers, in the same location, but in this configuration the renewable power plants are connected to the grid. Also in this scenario, the RES capacity factor depends on location of demand sites, with the consequent risk of being forced to increase the installed RES capacity.



Figure 40 Decentralized grid-connected scenario [16]

Pros

Due to the presence, in the same location, of RES and electrolyzers, this scenario entails lower costs for investments in power transmission and there is no need of hydrogen transmission cost since the electrolyzers are located close to hydrogen demand sites.

Cons

RES capacity factors could be lower in hydrogen demand locations, just as reminded in the previous scenario (1). Furthermore, there is a potential additional cost related to exporting the exceeding power from RES, in all occurrences where renewable energy generation is higher than the local electrolyzer demand.

3) Grid-connected transport of electricity scenario

The grid-connected transport of electricity scenario assumes that the RES power plants are in the most favorable areas in terms of producibility; the electricity is then transmitted through the network infrastructure to the electrolyzers, which are installed close to hydrogen demand sites.



Figure 41 Grid-connected transport of electricity scenario [16]

Pros

Due to the flexibility in locating them, RES can be installed in the most convenient sites enabling higher capacity factors; moreover, in this case there is no need of hydrogen transport, avoiding consequently the related transport costs.

Cons

Considering the necessity to transport renewable electricity from the power plants to the hydrogen consumption centers, there could be a potential additional cost for transmission system reinforcements to relieve grid congestions between RES power plants and electrolyzers.

4) Grid-connected transport of hydrogen scenario

The grid-connected transport of hydrogen scenario assumes that electrolyzers and RES power plants are installed in the same location and the hydrogen is supplied through new hydrogen pipelines or repurposed gas pipelines to the demand sites, potentially located in different areas. In this scenario, the additional cost for hydrogen transmission from electrolyzers to demand sites is compensated by the possibility to exploit the most favorable RES sites.



Figure 42 Grid-connected transport of hydrogen scenario [16]

Pros

RES can be installed in the most convenient sites enabling higher capacity factors and electrolyzers can better exploit zonal energy surplus avoiding RES curtailment and providing flexibility services. Cons

There could be additional costs related to hydrogen transport from electrolyzers to demand sites.

As expected, the **off-grid decentralized scenario** (1) has the highest cost in comparison to other cases. According to this scenario, an oversizing of the renewable installed capacity is required, much higher than the size of the electrolyzer, in order to allow a stable generation output. Furthermore, additional batteries are needed to reach the high capacity factor target of the electrolyzer (the equivalent of 7,000 hours per year). This scenario shows the highest levelized cost of hydrogen (LCOH2) equal to $4.7 \notin / \text{kgH2}$. The other three scenarios have been simulated in a grid-connected context. Therefore, in case of connection to the power grid, the impact on costs is different depending on the scenarios. The **grid-connected decentralized scenario** (2) needs higher investments in renewables compared to the other grid-connected scenarios, due to the potential lower capacity factor in some

consumption sites. This scenario estimates an overall LCOH of $3.8 \notin /kgH2$. The **transport of electricity scenario** (3) requires lower investments in renewables thanks to the selection of location with higher RES producibility. Investments in transmission grid and batteries are significant due to the power infrastructure needed to transport electricity to the electrolyzers. Also in this case the overall LCOH is 3.8 $\notin /kgH2$.

The **transport of H2 scenario** (4) is the only scenario where the cost for hydrogen infrastructures is present, since it requires a dedicated grid to convey hydrogen from RES power plants to consumption centers. For hydrogen transport the assumption is based on the average investment cost given by the European Hydrogen Backbone Initiative 2021 which estimates a range between 1,000 and 2,000 k€/km. The total cost for this scenario is between 4.1 and 4.4 €/kgH2, higher than the other grid-connected cases, mainly due to the cost of hydrogen infrastructure. In conclusion, the connection with the power grid (scenarios 2-3-4) is the best solution compared to off-grid installation (scenario 1), as the grid allows to export RES generation when their production exceeds the electrolyzer consumption. The same grid can also supply green energy to the electrolyzer when local RES generation does not reach the energy needed for hydrogen production.

3 Agrovoltaic

Agro-voltaic systems, also known as agrivoltaic systems or solar farming, refer to the integration of agricultural activities with solar energy production. These systems combine the cultivation of crops or raising of livestock with the installation of solar panels on the same land. The concept behind agro-voltaic systems is to optimize land use and maximize the benefits of both agriculture and solar energy generation.



Figure 43 Agro-voltaic plant

Here are some key aspects and benefits of agro-voltaic systems:

• Dual Land Use: Agro-voltaic systems enable the simultaneous use of land for agricultural purposes and solar energy production. By utilizing the same area for both activities, farmers can make efficient use of limited land resources.

• Increased Land Productivity: The shading provided by solar panels can have positive effects on certain crops, reducing water evaporation and improving crop yields. The panels can also protect delicate crops from harsh weather conditions, such as excessive sunlight or hail.

• Renewable Energy Generation: Agro-voltaic systems contribute to the production of clean and renewable energy. Solar panels capture sunlight and convert it into electricity, reducing reliance on fossil fuels and helping to mitigate climate change.

• Diversification of Income: Farmers can benefit from the dual income streams generated by agriculture and solar energy. They can sell the harvested crops or livestock products while also receiving revenue from the electricity generated by the solar panels, either through direct consumption or by selling it to the grid.

• Environmental Sustainability: Agro-voltaic systems promote sustainable land use practices by utilizing renewable energy sources and minimizing the environmental impact of agriculture. They can help reduce greenhouse gas emissions, conserve water, and improve soil quality.

• Local Community Benefits: Agro-voltaic systems can bring economic and social benefits to local communities. They create opportunities for job creation, stimulate the local economy, and contribute to energy independence and resilience.

• Research and Development: Agro-voltaic systems offer opportunities for research and development in optimizing the coexistence of agriculture and solar energy. Scientists and agricultural experts can study different crop-solar panel configurations, microclimate effects, and crop responses to various light conditions.

Although agro-voltaic systems have great potential, they also present challenges and considerations. These include the selection of appropriate crops that can grow under shaded conditions, the design and maintenance of the system to ensure optimal sunlight exposure, and the integration of the energy produced with existing power grids or storage systems. Overall, agro-voltaic systems represent an innovative approach to sustainable agriculture and renewable energy production, providing multiple benefits for farmers, the environment, and local communities. [17]

3.1 Desciption of the project

The project under consideration describes an agrovoltaic plant with consequent production of green hydrogen through electrolyzer. More in detail, it is a ground-mounted agro-photovoltaic power plant with single-axis tracking system, monocrystalline double-sided modules, battery energy storage (BESS) and power-to-gas conversion (PTG), operating in "market parity".



Figure 44 The overall layout of the project

The analysed project will be in Tuscany Region and the site has an extension of 210 hectares. The area, from a grid point of view, is not saturated and the proximity of energy infrastructures let the site be ideal for the constitution of the so-called Energy District. The project consists of two main steps:

• The realization of a first agro-photovoltaic 50 MWp PV power plant;

• The implementation of a second 80 MWp PV power plant with a 25 MWe electrolysis section to produce H2 (Power-to-Gas or PTG) and a further expansion with a 100 MW * 2h storage system (Battery Energy Storage System or BESS).

In the figure below is shown the location of the interest site where our plant will be located.



Figure 45 Territorial classification of the plant

3.1.1 FV and hydrogen production

From a point of view of the production, the plant will have about 1500 equivalent hours of operation per year and an annual yield of about 195 GWh. To carry out this analysis, different datasets from PVGIS have been utilized to obtain specific values of the production. More in detail, I explain how I have calculated the annual productivity of the agro-voltaic plant. By using PVGIS, I have set the location of the plant (Pisa), the PV technology (Crystalline silicon), the installed peak PV power (1 KW), system loss (18%) and no slope of the inclined axis;



Figure 46 PVGIS representation

With these informations, I obtained in output the hourly production values of an overall year for 4 different solar radiation database (SARAH, CMSAF, ERA5, COSMO) obtaining then a single value doing the average. I recalculated the production on the current value of our plant (130 MW) and finally knowing the maximum power of the electrolyzer (25MW) I calculated its annual consumption.

Annual FV production [MWh/year]	194650
Annual electrolyser consumption[MWh/year]	96510
Grid supply [MWh/year]	98130

Figure 47 Production FV numerical value

More in detail, I simulated a typical day for each trimester in order to analyze more precisely the FV production and consumption of the electrolyzer.

1° Trimester	FV	Electrolyser
[hours]	production	consumption
	[MWh]	[MWh]
1	0	0
2	0	0
3	0	0
4	0	0
5	0	0
6	13	13
7	22	22
8	27	25
9	36	25
10	38	25
11	38	25
12	38	25
13	37	25
14	36	25
15	31	25
16	17	17
17	3	3
18	0	0
19	0	0
20	0	0
21	0	0
22	0	0
23	0	0
24	0	0



Figure 48 Plot 1° trimester production

2° Trimester	FV	Electrolyser
	production	consumption
	[MWh]	[MWh]
1	0	0
2	0	0
3	0	0
4	0	0
5	11	11
6	30	25
7	47	25
8	59	25
9	66	25
10	69	25
11	68	25
12	67	25
13	67	25
14	66	25
15	63	25
16	57	25
17	44	25
18	26	25
19	5	5
20	0	0
21	0	0
22	0	0
23	0	0
24	0	0



Figure 49 Plot 2° trimester production

3° Trimester	FV production [MWh]	Electrolyser consumption [MWh]
1	0	0
2	0	0
3	0	0
4	0	0
5	7	7
6	31	25
7	52	25
8	63	25
9	68	25
10	70	25
11	69	25
12	69	25
13	68	25
14	69	25
15	67	25
16	62	25
17	48	25
18	25	25
19	4	4
20	0	0
21	0	0
22	0	0
23	0	0
24	0	0



Figure 50 Plot 3° trimester production

4°	FV	Electrolyser
Trimester	production	consumption
	[MWh]	[MWh]
1	0	0
2	0	0
3	0	0
4	0	0
5	0	0
6	0	0
7	20	20
8	35	25
9	41	25
10	41	25
11	39	25
12	38	25
13	38	25
14	37	25
15	34	25
16	22	22
17	4	4
18	0	0
19	0	0
20	0	0
21	0	0
22	0	0
23	0	0
24	0	0



Figure 51 Plot 4° trimester production

From these graphs, we can see how the profiles, related to 2° and 3° trimester so a period from April to September, show a fairly similar trend with a wide range of daily production (from 6 a.m. to 19 p.m.) and the maximum production can reach 70 MWh especially in the hottest hours (between 11 a.m. and 14 p.m.). Powered the electrolyzer, it remains an high energy surplus that can be supply into the grid or power several final consumers located in the area around the plant. On the contrary, the profiles related to 1° and 4° trimester, which span a period from October to March, show a similar trend but completely different from the 2° and 3° trimesters. In this case the daily production range is narrower (from 7 a.m. to 16 p.m.), the maximum production can reach 40 MWh (between 10 a.m. and 12 p.m.) and the energy surplus is lower than the previous profiles.

For what concerns the annual hydrogen production of our plant several parameters were taken into account and are listed in the table below. The analysis was conducted based on an alkaline electrolyzer, assuming the most optimal condition with an efficiency of 70%. The alkaline electrolyzer is more suitable for the characteristics of the project under consideration compared to the PEM electrolyzer because our system is centralized, meaning that the power plant (PV + electrolyzer) is not located near the consumption centers but rather at a distance from them.

Alkaline electrolyser efficiency [%]	70
LHV _{H2} (Lower heating value) [MJ/kg]	120
LHV _{H2} [MWh/kg]	0,0333
Density H_2 [kg/m ³], 0°C and 1 bar	0,089
Power electrolyser [MW]	25
h _{eq} electrolyser [h/year]	3860

Figure 52 Alkaline electrolyser parameters [11] – [8]

•
$$h_{eq}$$
 electrolyser $\left[\frac{h}{year}\right] = \frac{Annual \ electrolyser \ consumption\left[\frac{MWh}{year}\right]}{Power \ electrolyser[MW]} = \frac{96510}{25} = 3860 \frac{h}{year}$

To obtain the annual hydrogen production I applied these relations:

• $Hydrogen \ production[\frac{MWh}{year}] = (Efficiency * Power [MW] * h_{eq} \ electrolyser [h])$ = (0,7 * 25 * 3860) = 67550 MWh/year

•*Hydrogen production* $\left[\frac{kg}{year}\right] = \frac{Hydrogen \, production \left[\frac{MWh}{year}\right]}{LHV \, H2 \left[\frac{MWh}{kg}\right]} = \frac{67550}{0,0333} = 2026484 \, Kg/year$

•*Hydrogen production*
$$\left[\frac{t}{year}\right] = \frac{Hydrogen \, production\left[\frac{kg}{year}\right]}{1000} = 2026 \, t/year$$

•Hydrogen production
$$\left[\frac{m^3}{year}\right] = \frac{Hydrogen \, production[\frac{kg}{year}]}{Density H_2[\frac{kg}{m^3}]} = \frac{2026484}{0,089} = 22769481 \, m^3/year$$

Hydrogen Production [kg/year]	2026484
Hydrogen Production [t/year]	2026
Hydrogen Production [MWh/year]	67550
Hydrogen Production [m ³ /year]	22769481

Figure 53 Hydrogen production values

Among the various commercial electrolyzers, the model A series Atmospheric Alkaline Electrolyzer (1 bar) is the most suitable one to meet the requirements and parameters of the project under consideration.



Figure 54 Alkaline electrolyser A series model [10]

The electrolyzer must be able to deliver a flow rate of 5898 m^3/h .

•Hydrogen production
$$\left[\frac{m^3}{h}\right] = \frac{Hydrogen \ production\left[\frac{m^3}{year}\right]}{h_{eq} \ electrolyser\left[\frac{h}{year}\right]} = \frac{22769481}{3860} = 5898\frac{m^3}{h}$$

The most optimal configuration of electrolyzers to deliver this flow rate consists of two A 1000 models, each with a capacity of 4 MW, and one A 3880 model with a capacity of 17 MW, totaling 25 MW, which is the design specification.

The choice to have multiple smaller electrolyzers instead of a single 25 MW electrolyzer offers several advantages.

1) Redundancy: With multiple electrolyzers, there is redundancy in the system. If one electrolyzer fails or requires maintenance, the other can continue to operate, ensuring a more reliable and continuous hydrogen production process. In contrast, if the single 25 MW electrolyzer fails, the entire production capacity is affected.

2) Flexibility: Having multiple smaller electrolyzers allows for greater flexibility in operation. It becomes easier to scale up or down the production capacity based on the demand. If the demand for hydrogen decreases, one or more electrolyzers can be temporarily shut down, saving energy and operational costs.

3) Efficiency: Smaller electrolyzers tend to have higher efficiency compared to larger ones. The efficiency of an electrolyzer typically decreases as its size increases.

4) Maintenance and Serviceability: Maintenance and service operations are generally easier to carry out on smaller units.

5) Risk Mitigation: Distributing the hydrogen production capacity across multiple smaller electrolyzers reduces the risk associated with a single point of failure. In the event of a failure or malfunction in one unit, the impact on overall production capacity is limited. This approach provides a higher level of risk mitigation and ensures continuity in hydrogen supply.

In summary, having smaller electrolyzers offers advantages in terms of redundancy, flexibility, efficiency, maintenance, and risk mitigation compared to a single 25 MW electrolyzer. These benefits contribute to a more reliable, adaptable, and efficient hydrogen production system.

3.1.2 Mobility and industrial consumers

After calculating the electricity and hydrogen production of our plant, I analyzed the possible final consumers considering a radius of 15/20 km around the plant and calculating in detail the quantities required.



Figure 55 Final consumers around the plant

• Ship transport

With regard to shipping I analyzed the two main routes:

- Livorno \rightarrow Capraia (2,45 h)

- Piombino \rightarrow Portoferraio (1h)

while for the consumptions I considered a ferry/ship container (Toremar) from 100 mt approximately. [3]



Figure 56 Sea routes Livorno- \rightarrow Capraia, Piombino \rightarrow Portoferraio



Figure 57 Ferry used for the sea routes [3]

Imagining that a daily route is to make the round trip twice a day for 180 days a year, what you get is that with a production of 2026 tons per year of hydrogen you can cover the needs of about 4 ferries for the first route (Livorno \rightarrow Capraia) or 11 ferries for the second (Piombino \rightarrow Portoferraio). The steps to obtain these results are shown below. By analyzing the Livorno \rightarrow Capraia route we have that:

• Daily energy required[MJ] = Daily diesel consumption[kg] * $LHV_{DIESEL}\left[\frac{MJ}{kg}\right] =$ = 2750 * 42,68 = 234740 MJ

- Daily hydrogen required[l] = $\frac{\text{Daily energy required}[k]}{\text{Energy density } H_2[\frac{kJ}{l}]} * \frac{1}{\text{efficiency electrolyser}} = \frac{234740000}{6240} * \frac{1}{0,7} = 53740,841$
- Daily hydrogen required[kg] =

= Daily hydrogen required[l] * Density H_2 at 700 bar $\left[\frac{kg}{l}\right]$ =

= 53740, 84 * 0, 052 = 2794, 52 kg

- Annual hydrogen consumption[kg] =
 - = Daily hydrogen required[kg] * 180 gg = 2794, 52 * 180 = 503014, 3 kg
- Number of powered ferries = $\frac{Annual hydrogen produced[kg]}{Annual hydrogen consumption[kg]} = \frac{2026484}{503014} = 4$

The same procedure is applied for the Piombino \rightarrow Portoferraio route. So, in conclusion we have deduced that:

- Number of powered ferries for the Livorno \rightarrow Capraia route = 4
- Number of powered ferries for the Piombino \rightarrow Portoferraio route = 11

TRAGHETTI							
Consumo Gasolio [kg/h]	Durata Tratta Liv-Cap [h]	Consumo Gasolio per tratta [kg]	Consumo Gasolio Andata/Ritorno [kg]	Gasolio potero calorifico inferiore [Mi/kg]	Energia richiesta x giorno [MJ]	Energia richiesta [kl]	
500	2,75	1375	2750	42,68	234740	234740000	
Volume H2 richiesto per tratta Liv Cap [l]	1 Massa richiesta H2 [kg]	SUU Consumo annuale idrogeno [kg]	100	42,68	85360 Numero Traghetti alimentabili [-]	8536000	
53740,84249	2794,52381	503014,2857			4		
Volume H2 richiesto per tratta Piomb Port [I]	Massa richiesta H2 [kg]	Consumo annuale idrogeno [kg]			Numero Traghetti alimentabili [-]		
19542,12454	1016,190476	182914,2857			11		

Figure 58 Ferries numerical results [21]

• Railway transport

The study on railway transport was conducted considering only the non-electrified lines by analyzing the number of trains that can be powered by the amount of hydrogen produced from my plant.



Figure 59 Tuscany railway lines [1]

Linee Fondamentali



Linee complementari

Sistema di Trazione

non elettrificate a doppio binario
 non elettrificate a semplice
 binario

Non-electrified line with an average journey time of 2 hours \rightarrow approximately 150/200 km of route. [20]

Assuming that a daily route for a typical train is a round trip (150 km each way) done twice a day, every day, throughout the year, what we get is that with a hydrogen production of 2026 t per year, the demand for approximately 20 trains can be covered. More in detail, the various steps are shown:

• Daily energy required [kJ] = Power Fuel Cell[kW] * 8 h * 3600 s = 800 * 8 * 3600 = 23040000 kJ

•Daily hydrogen required[l] =
$$\frac{\text{Daily energy required }[k]}{\text{Energy density }H_2[\frac{k}{l}]} * \frac{1}{\text{efficiency electrolyser}} = \frac{23040000}{6240} * \frac{1}{0.7} = 5274, 7 \text{ }l$$

•Daily hydrogen required[kg] =

= Daily hydrogen required[l] * Density
$$H_2$$
 at 700 bar $\left\lfloor \frac{kg}{l} \right\rfloor$ =
= 5274, 7 * 0,052 = 274,28 kg

• Annual hydrogen consumption[kg] =

= Daily hydrogen required[kg] * 365 gg = 274, 28 * 365 = 100114, 28 kg

•Number of powered trains =
$$\frac{Annual hydrogen produced[kg]}{Annual hydrogen consumption[kg]} = \frac{2026484}{100114,28} = 20$$

TRENI							
Chilometri totali non elettr. [km]	Idrogeno totale prodotto [kg]	Distanza giornaliera x treno [Km]	Distanza annuale x treno [Km]	Consumo chilometrico [km/kgH2]			
503	2.026.484	600	219000	5,7			
Potenza Media Fuel Cell a Idrogeno Treno Medie Dimensioni [kW]	Tempo percorrenza per tratta [s]	Energia richiesta per tratta [kWh]	Energia richiesta per tratta [kJ]	Energia richiesta totale per 4 tratte [kJ]	Densità di energia H2 [K]/I]	Densità H2 a 700 bar [kg/l]	
800	7200	1600	5760000	23040000	6240	0,052	
Volume H2 richiesto [I]	Massa H2 richiesta [kg]	Massa H2 richiesta annuale [kg]	Numero di treni alimentati [-]				
5274,725275	274,2857143	100114,2857	20				

Figure 60 Trains numerical results

• Road transport

Regarding road transport (cars, trucks, buses), after identifying the average annual mileage of each vehicle [km], the hydrogen consumption per kilometer [km/kg], and the annual hydrogen consumption, I have deduced that with the amount of hydrogen produced by our plant (2026 tons), I can meet the needs of 18420 cars or 225 trucks or 660 buses, by generating a reduction of CO_2 . In the figure below, I have highlighted the diesel-hydrogen equivalence for each means of transport.

```
For cars: [2]
4 l of gasoline → 1 kg of hydrogen→ 100 km
For trucks around 25 t: [2]
30 l of diesel → 7,5 kg of hydrogen → 100 km
For buses (assuming 50 passengers, urban): [4]
25 l of diesel → 5,1 kg of hydrogen → 100 Km
```

Figure 61 Diesel-Hydrogen equivalence

For cars:

Annual hydrogen consumption for a single car[kg] =
=
$$\frac{Average annual mileage[km]}{Consumption per Kilometer[\frac{km}{kg}]} = \frac{11000}{100} = 110 \ kg$$

• Number of powered cars $= \frac{Annual hydrogen produced [kg]}{Annual hydrogen consumption [kg]} = \frac{2026484}{110} = 18423$

•
$$CO_2$$
 avoided $[t] = \frac{CO_2 emissions \left[\frac{g}{km}\right] * Number of fed cars * Average annual mileage [km]}{10^6} = \frac{168 * 18423 * 11000}{10^6} = 34044,93 t$

For trucks:

•Annual hydrogen consumption for a single truck[kg] =

$$= \frac{Average annual mileage [km]}{Consumption per Kilometer \left[\frac{km}{kg}\right]} = \frac{120000}{13,33} = 9002,25 \ kg$$

• Number of powered trucks = $\frac{Annual hydrogen produced[kg]}{Annual hydrogen consumption[kg]} = \frac{2026484}{9002,25} = 225$

$$\bullet CO_{2}avoided[t] = \frac{CO_{2}emissions\left[\frac{g}{km}\right]*Number of fed trucks*Average annual mileage[km]}{10^{6}} = \frac{700*225*120000}{10^{6}} = 18909, 1 t$$

For buses:

•Annual hydrogen consumption for a single bus[kg] =
=
$$\frac{Average annual mileage[km]}{Consumption per Kilometer[\frac{km}{kg}]} = \frac{60000}{19,61} = 3059,66 kg$$

• Number of powered buses = $\frac{Annual hydrogen produced[kg]}{Annual hydrogen consumption[kg]} = \frac{2026484}{3059,66} = 662$

•CO₂avoided[t] =
$$\frac{CO_2 emissions\left[\frac{g}{km}\right] * Number of fed buses * Average annual mileage[km]}{10^6} = \frac{104 * 662 * 60000}{10^6} = 4132,89 t$$

Auto/Camion/Autobus							
ldrogeno totale prodotto [Kg/y]		0					
2.026.484		-2					
Percorrenza ann auto [km]	Consumo auto[Km/Kg]	Consumo ann h2[kg]	Numero di auto ricaricabili all'anno	Emissioni Ca2 (g/km)	Co2evitata [tonn]		
11000	10	0 110	18423	168	34044,93		
Percorrenza ann cami on [km]	Consumo camion [km/kg]	Corsumo ann h2 [kg]	Numero di cami on ricaricabili all'an	Emissioni Co2 (g/km)	Co2evitata [tonn]		
120000	13,3	3 9002,25	225	700	18909,1		
Percorrenza ann autobus [km]	Consumo bus [km/kg]	Corsumo ann h2 [kg]	Numero di autobus ricaribabili all'a	(Emissioni Co2[g/km]	Co2evitata[tonn]		
60000	19,6	1 3059,66	662	104	4132,89		

Figure 62 Road transport numerical results [5]

• Foundry "Carlo Gelli" and Refinery "ENI"

Other potential end consumers are the foundry and refinery sectors, which are hard-to-abate sectors that require the consumption of hydrogen in their production processes.

Foundry " Carlo Gelli"					
Production of steel and cast iron [t/y]	[18]	10000			
Hydrogen demand [kg/t]	[12]	70			
Annual hydrogen required [kg/y]		700000			
Annual hydrogen required [m ³ /y]	7865168,539				

Figure 63 Foundry numerical values

- Annual hydrogen required $\left[\frac{kg}{y}\right] =$ = Hydrogen demand $\left[\frac{kg}{t}\right]^*$ Production of steel $\left[\frac{t}{y}\right] = 70 * 10000 =$
 - = 700000

ENI refinery					
Hydrogen demand: process hydrotreating [m ³ /t _{prod}]	[12]	20			
Hydrogen demand: process hydrocracking [m ³ /t _{prod}]	[12]	300			
	tot	320			
Production of distilled products [barili/day]	[19]	84000			
Production of distilled products [tep/y]		4476360			
		143243520			
Annual hydrogen consumption [m ³ /anno]		0			

Figure 64 Refinery numerical values

- Annual hydrogen consumption $\frac{m^3}{y} =$
- = Production of distilled products $\left[\frac{tep}{y}\right]$ * Hydrogen demand $\left[\frac{m^3}{t_{prod}}\right]$ = = 4476360 * 320 = 1,43 * 10⁹
3.1.3 Economic aspects

From an economic standpoint, our goal is to calculate the LCOH (Levelized Cost of Hydrogen). To do this, I have calculated the CAPEX (Capital Expenditures) and OPEX (Operating Expenditures) related to the FV (Photovoltaic) plant and PTG (Power-to-Gas) plant.

FV Plant		CAPEX FV	€	OPEX FV	€
P (MW)	130	FV plant	90.000.000,00 €	Routine maintenance	1.500.000,00€
Operating hours (h/y)	1500	Extraordinary maintenance after 10 y	9.000.000,00€	EE auxiliaries	200.000,00€
Annual rate of decay (%/y)	0,5%	Extraordinary maintenance after 20 y	9.000.000,00€		
		TOTAL	108.000.000,00 €	TOTAL	1.700.000,00€

Figure 65 CAPEX and OPEX for FV plant [22], [23]

The cost item for the CAPEX FV plant includes development and construction costs.

PTG plant		CAPEX PTG	€	OPEX PTG	€
Total Electrolysers power (MW)	25	PTG plant	12.000.000,00€	Routine maintenance	800.000,00 €
Number of electrolysers	3	Compressor	4.000.000,00€	Electricity costs	4.825.500,00 €
Operating hours (h/y)	3860	Injection unit	600.000,00€	Water costs	23.709,40 €
PTG production (kg/h)	231	Pipelines H2	5.000.000,00€		
PTG production (kg/y)	2026484	Pipelines components H2	200.000,00€		
Annual rate of decay (%/y)	1,00%	Storage	3.500.000,00€		
		Extra maintenance after 10 y	8.000.000,00 €		
		Extra maintenance after 20 y	8.000.000,00 €		
		TOTAL	41.300.000,00€	TOTAL	5.649.209,40 €

Figure 66 CAPEX and OPEX for PTG plant [22], [23]

The CAPEX cost item for extraordinary maintenance concerns stack replacement, while the OPEX cost item for ordinary maintenance includes storage maintenance, injection maintenance and piping. The figures below show the percentage breakdown of CAPEX and OPEX for our facility. With its 108 000 000 €, the FV plant accounts for 72% of the total CAPEX, while the expenditure for the PTG plant is relatively lower (28% of the total CAPEX). On the contrary, concerning OPEX, the PTG plant has significantly higher costs (77% of the total OPEX) compared to the FV plant (23% of the total OPEX).

CAPEX	CAPEX TOTALE	CAPEX FV	CAPEX PTG
Power (MW)	0	13	0 25
Operating hours	0	150	0 3860
Number of electrolysers	-	-	3
e	149.300.000,00 €	108.000.000,00 €	41.300.000,00 €
%	100%	729	6 28%

Figure 67 Total CAPEX FV + PTG



Figure 68 Graphical breakdown of CAPEX

OPEX	OPEX TOTALE	OPEX FV	OPEX PTG
€	7.349.209,40 €	1.700.000,00 €	5.649.209,40 €
%	100%	23%	77%





Figure 70 Graphical breakdown of OPEX

Considering a production timeframe of 30 years, I have calculated the annual hydrogen production with an annual decay rate of 1% [24]. The PTG OPEX for subsequent years was calculated with an inflation rate of 3%. I recalculated the CAPEX by considering a Weighted Average Cost of Capital (WACC) of 6.5% and added it to the PTG OPEX for each individual production year. In conclusion, it was possible to calculate the Levelized Cost of Hydrogen (LCOH) as the ratio between CAPEX (WACC) + OPEX and the annual hydrogen production. Taking an average over the 30-year period, we can state that the average LCOH for our plant is $7,05 \notin$ /kg.

Year		1		2		28		29		30
Production H ₂ [kg]		2.026.483,79		2.006.218,95		1.544.875,15		1.529.426,40		1.514.132,14
		5.649.209,40		5.818.685,68		12.548.526,73		12.924.982,53		13.312.732,01
OPEX PTG	€		€		€		€		€	
CAPEX PTG adjusted for WACC + OPEX PTG	€	8.811.857,76	€	8.981.334,05	€	15.711.175,10	€	16.087.630,90	€	16.475.380,37
LCOH [€/kg]		4,348		4,477		10,170		10,519		10,881

Figure 71 LCOH (Levelized cost of hydrogen) numerical values

• CAPEX PTG adjusted for WACC
$$[\in] = CAPEX PTG * \left[\frac{\%WACC^*(\%WACC+1)^{30}}{(\%WACC+1)^{30-1}} \right] =$$

= 41 300 000 * $\left[\frac{6.5\%^*(6.5\%+1)^{30}}{(6.5\%+1)^{30-1}} \right] = 3$ 162 648, 36 \in

•
$$LCOH\left[\frac{\epsilon}{kg}\right] = \frac{CAPEX PTG adjusted for WACC[\epsilon] + OPEX PTG[\epsilon]}{Production H_2[kg]}$$

•
$$LCOH_{mean}\left[\frac{\epsilon}{kg}\right] = 7 \epsilon/kg$$

CONCLUSIONS

In conclusion, this master's thesis provides a comprehensive analysis of decarbonization strategies with a specific focus on the role of hydrogen as a key element in the transition to a low-carbon economy. The research sheds light on the various aspects of hydrogen production, utilization, and its potential in hard-to-abate sectors. The examination of green hydrogen, in particular, highlights the importance of electrolyzers in the commercial market and explores strategies to reduce their costs.

Furthermore, the thesis presents a case study of a real project involving the production of green hydrogen through water electrolysis from an agrovoltaic plant. The analysis considers the annual productivity of the agrovoltaic facility, the electrolyzer's consumption, and the resulting hydrogen output. Additionally, a thorough mapping of potential end consumers surrounding the power plant is provided, offering detailed insights into their specific consumption patterns.

By evaluating the capital and operational expenditures related to the PV and PTG plant, the thesis also assesses the levelized cost of hydrogen production (LCOH). This cost evaluation serves as a valuable indicator for the economic viability of hydrogen as a sustainable energy option.

Overall, the findings of this research underscore the significance of decarbonization efforts and the crucial role that hydrogen can play in achieving a sustainable and low-carbon future. The thesis contributes to the existing body of knowledge by providing insights into the feasibility, challenges, and potential solutions related to the utilization of hydrogen in decarbonization strategies. It is hoped that the outcomes of this study will inform policymakers, industry stakeholders, and researchers in advancing the adoption and implementation of hydrogen as a viable pathway towards decarbonization and a more sustainable future.

REFERENCES

- [1] https://www.rfi.it/it/rete/la-rete-oggi/La_rete_oggi_regione_per_regione/toscana.html
- [2] <u>https://www.h2it.it/wp-content/uploads/2019/12/Piano-Nazionale_Mobilita-Idrogeno_</u> integrale_2019_FINALE.pdf
- [3] https://www.ferryhopper.com/it/ferry-routes/direct/livorno-capraia
- [4] <u>https://www.corriere.it/motori/mobilita-sostenibile/22_febbraio_16/h2city-gold-arriva-italia-l</u> autobus-idrogeno-toyota-400-km-un-pieno-5ff37d5a-8e8f-11ec-a91e-e98defcaa657.shtml
- [5] https://viviamosostenibile.it/mezzi-di-trasporto-quali-preferire-per-muoversi-in-maniera-ecologica/
- [6] https://demaco-cryogenics.com/blog/about-hydrogen-electrolyzer/
- [7] Rob Cockerill, "Electrolyser technologies, PEM vs Alkaline electrolysis", November 2020
- [8] IRENA, "Hydrogen from renewable power, technology outlook for the energy transition", September 2018
- [9]http://newsimg.bbc.co.uk/media/images/41058000/gif/ 41058602 combo coal cycle 416.gif
- [10] <u>https://nelhydrogen.com/product/atmospheric-alkaline-electrolyser-a-series/</u>
- [11] https://elab.hysafer.ulster.ac.uk/accounts/signup/
- [12] Politecnico di Milano," Hydrogen Innovation Report 2022", Luglio 2022
- [13] DNV "Hydrogen forecast to 2050"
- [14] Johanna Ivy, "Summary of Electrolytic Hydrogen Production", September 2004
- [15] IRENA, "Green Hydrogen Cost Reduction"
- [16] CESI Studies, "Italian Hydrogen Strategy: What impact on the power system?"
- [17] "Linee guida in materia di impianti agrivoltaici", Giugno 2022
- [18] <u>www.fonderiagelli.it</u>
- [19] https://www.eni.com/it-IT/attivita/italia-livorno-raffineria.html
- [20] https://www.politesi.polimi.it/bitstream/10589/137355/5/2017_12_Peli.pdf
- [21] http://www.sardegnaindustriale.it/article.asp?ID=7164&IDmagazine=2011002
- [22] https://www.sciencedirect.com/science/article/pii/S2666386420302241
- [23] https://onlinelibrary.wiley.com/doi/full/10.1002/solr.202100487
- [24] Jolywood, "N type, same sunshine more value"