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MASTER's Degree in Energy and Nuclear Engineering



MASTER's Degree Thesis

The decarbonization of a floating glass production plant: a cost comparison of alkaline and PEM electrolyzers

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Abstract

The decarbonization of the industrial sectors is crucial to reach the ambitious climate goals and the carbon neutrality. Heavy industries such as refining, iron and steel, chemicals and glass manufacturing are responsible of significant CO2 emissions due to the utilization of fossil-based energy sources and feedstock. Electrifying these energy-intensive processes is currently challenging due to both technical and economic barriers. In this context, a growing interest for green hydrogen is emerging in the recent years. Green hydrogen can effectively replace fossil fuels and fossil-based hydrogen in multiple industrial processes and its role is thus becoming pivotal in transforming hard-to-abate industries. This study aims to investigate the decarbonization of a float glass industry by installing a power-to-hydrogen (PtH) system. In the float glass manufacturing, hydrogen is already used to create an inert atmosphere (90% N_2 and 10% H_2) in the tin bath chamber and prevent the formation of defects. Thus, green hydrogen can be easily adopted without modifying the production process. In this work, a real production facility located in Larbaa (Algeria) was considered as case study. The PtH system was sized to continuously meet the hydrogen demand, which exhibits seasonal variation and results in 102 ton/y. In the design procedure, a techno-economic optimization based on minimizing the levelized cost of hydrogen (LCOH) was carried out by using the particle swarm optimization (PSO) algorithm. The optimal design tool implemented in MATLAB provided as outcome the size of the PV, the electrolyzer, the hydrogen tank and the hydrogen compressor. The main low temperature electrolyzer technologies were considered: the proton exchange membrane (PEM) and the alkaline (ALK). The techno-economic performances of these electrolyzers were assessed and compared in order to identify the most cost-effective solution. Furthermore, the effects of the lifetime of PEM electrolyzer, the modulation range of ALK electrolyzer, the interest rate and the annual operational expenditure (OPEX) were investigated to determine their impact on the LCOH. Finally, a further comparison with a grid-based scenario was performed. In this case, the electrolyzer was fed by electricity withdrawn from the national grid and a sensitivity analysis on the electricity price was conducted.

Keywords: Hydrogen, electrolysis, decarbonization, glass industry, optimal design

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Acronyms

ALK Alkaline **BoP** Balance of the Plant **CAPEX** Capital Expenditure **CCS** Carbon Capture and Storage **EL** Electrolyzer **EMS** Energy Management Strategy HC Hydrogen Compressor HER Hydrogen Evolution Reaction ${\bf HT}$ Hydrogen Tank **IRENA** International Renewable Energy Agency **KPI** Key Performance Indicator LCOH Levelized Cost of Hydrogen LOH Level of Hydrogen **MEA** Membrane Electrode Assembly NG Natural Gas **NPC** Net Present Cost **OER** Oxygen Evolution Reaction

- **OPEX** Operational Expenditures
- **PEM** Proton Exchange Membrane
- **PPA** Power Purchase Agreement
- PtH2 Power-to-Hydrogen
- **PSO** Particle Swarm Optimization
- ${\bf RES}$ Renewable Energy Sources
- ${\bf SMR}$ Steam Methane Reforming
- ${\bf SPE}$ Solid Polymer Electrolyte
- ${\bf TMY}$ Typical Meteorological Year
- **TRL** Technology Readiness Level
- **VRE** Variable Renewable Energy
- **YSZ** Yttria Stabilezd Zirconia

Chapter 1

Introduction

1.1 Background

The energy transition represents a crucial paradigm shift in the current context, as the world grapples with the challenges of environmental sustainability and the urgent need to mitigate climate change. This process involves transitioning from traditional energy sources based on fossil fuels to renewable and low-carbon sources. The importance of this transition is inherently linked to the need to reduce greenhouse gas emissions, mitigate environmental impacts and create a sustainable energy future [1]. One of the key agreements guiding this transition is the 2015 Paris Agreement [2]. This international accord, signed by numerous nations, sets the goal of limiting the increase in global temperature to well below 2 degrees Celsius above pre-industrial levels, with the aspiration to limit this increase to 1.5 degrees Celsius. This ambitious goal underscores the need for immediate global action to reduce greenhouse gas emissions and adopt more sustainable energy practices. The European Union (EU), in particular, has taken a leadership role in defining concrete objectives and milestones for the energy transition by 2050. In the context of its strategy for a fair and sustainable energy transition, the EU aims to achieve climate neutrality by 2050. This implies that greenhouse gas emissions should be balanced by carbon removals or offsets, drastically reducing the environmental impact of human activities. To achieve these goals, the EU has outlined a series of concrete actions and measures. The promotion of renewable energies, energy efficiency, technological innovation and the decarbonization of key sectors such as industry and transportation is at the core of this strategy. Specifically, the EU has set intermediate targets, such as a 55% reduction in greenhouse gas emissions by 2030 compared to 1990 levels, indicating a clear road map to achieve the ambitious 2050 milestones. [3]

1.2 Decarbonization of industrial processes

The target set by the 2015 Paris Agreement implies a huge decarbonization of all sectors of the economy by 2050. Undertaking this massive challenge means a great effort, particularly in fulfilling the lack of technologies in industrial sectors. Renewable energy sources (RES), along with energy storage systems such as batteries, are fundamental in this scenario, even though their potential it has been still not fully exploited [4]. Most of these technologies, unfortunately, are still not commercially mature or ready for wide adoption. It is clear that all energy systems must be designed through a multidisciplinary approach with the interaction of technical, environmental, economic and social factors. For this reason, IRENA has came up with different scenarios relying on a fusion of five reduction measures [4]: from the reduction of energy demand to the enhancement of energy efficiency in order to minimize or at least reduce energy waste. Furthermore, they focused their attention on the direct use of electricity produced by RES, and its indirect use via synthetic fuels and feedstocks like so-called *green* hydrogen.

As a Part along with other 195 members, Italy has been making its contribution. In this context, Italy has adopted the National Integrated Plan for Energy and Climate (PNIEC) [5] as a key strategy to reduce greenhouse gas emissions, promote a transition to a low-carbon economy and enhance RES penetration. PNIEC represents a clear and ambitious road map for the decarbonization of the Italian economy. Through targeted investments, the adoption of innovative technologies and the promotion of sustainable practices, Italy is committed to play a leading role in the transition to a low-carbon future, thereby contributing to global efforts to mitigate climate change.

One of the main dimensions that contributes to achieve the targets of PNIEC is the decarbonization. The aim is to completely forsake coal instead of electricity production. The main sources of carbon emissions include the use of fossil fuels for electricity generation, heating, transportation and industry. Decarbonization involves a transition to more sustainable and low-carbon energy sources, such as renewable energy (solar, wind, hydroelectric, geothermal), nuclear energy, and more energy-efficient technologies such as electrification or Carbon Capture and Storage (CCS).

Among many sectors, the industrial high-temperature heat one is very energy demanding [6] and responsible for 1.1 Gt_{CO_2} /year [7] Furthermore, industrial sectors are often characterized by energy-intensive production processes and are more complex to decarbonize compared to other sectors. Some of the industrial sectors, commonly referred to as "Hard to Abate", include chemical, steel, cement, and glass industries. The main points that make them so hard to green up are:

• High energy intensity: many industrial processes require significant energy consumption, often obtained through the combustion of fossil fuels;

- Complex chemical processes: some industrial sectors involve complex chemical processes that generate carbon emissions as byproducts;
- High-temperature requirements: sometime, due to the necessity to reach those specific high temperatures direct electrification may be challenging. However, electricity can be still used to produce energy carriers such as green hydrogen or new low-emission heating fuels;
- High cost: most of the current solutions are not feasible by an economic point of view. Only a few of them are cost-effective highlighting the importance of cooperation between technical and economic side;

Although decarbonizing these processes is challenging, central to this plan is the role of hydrogen in transforming sectors that are hard to decarbonize with electrification alone. Decarbonization through the use of hydrogen has several consequences based on the end-use sector. Industries with the highest hydrogen consumption potential are: paper, chemicals, steel, ceramic, cement and glass. European Commission intends to support the deployment of green hydrogen technologies by increasing the installed capacity up to 2X40 GW in 2030 (40 GW in Europe and 40 GW in neighborhood countries) aiming at providing 13-14% of hydrogen in the final energy consumption mix at 2050 [8]. The EU's hydrogen strategy, "A Hydrogen Strategy for a Climate-Neutral Europe", released in July 2020 [9], outlines a road map for developing a hydrogen economy that contributes to the decarbonization of sectors difficult to electrify. The strategy emphasizes the importance of green hydrogen, produced using RES, and low - carbon hydrogen, produced with CCS technologies. These distinctions reflect Europe's commitment to ensuring the environmental sustainability of hydrogen production.

1.3 Hydrogen production

Hydrogen, the most abundant element in the universe, has long been recognized as a potential clean energy carrier. Unlike conventional fossil fuels, hydrogen produces no greenhouse gas emissions when consumed, making it a promising solution for decarbonizing various sectors. At ambient temperature, hydrogen is a colorless and odorless gas that is practically insoluble in water. After helium, it is the most difficult gas to liquefy. Generally less reactive at cold temperatures, hydrogen undergoes numerous chemical reactions when heated or in the presence of catalysts.

As it is possible to see from Table 1.1, hydrogen has a low density with respect to methane but at the same time a higher specific heat. The latter enables the same amount of heat generated with a lower final temperature but at the same time to have a high specific work during compression, thus, explaining the reason why

Properties	Methane	Hydrogen
Density $[kg/m^3]$	0.717	0.084
Specific heat at constant pressure $[kJ/kgK]$	0.16	0.61
Flammability level in air [%vol]	$5.3 \div 15.0$	$4.0\div75.0$
Ignition energy in air $[mJ]$	0.29	0.02
Autoignition temperature [°C]	540	585
Flame temperature in air [°C]	1875	2045
Flame emissivity [%]	38	21
Energy density [MJ/kg]	55.5	142
Energy density $[MJ/m^3]$	37.3	12

 Table 1.1:
 Thermo-physical properties of methane and hydrogen

storing, compressing, and liquifying hydrogen is quite challenging. Furthermore, hydrogen is a flammable and highly volatile gas that can detonate in a certain mix with air. Its upper flammability level is greater than methane resulting in a wider concentration range with air that produces fire in presence of a source of ignition. Additionally, the almost-invisibility when it burns and the higher flame temperature and velocity makes hydrogen tough to manage.

On the other hand, combustion products are less toxic since are CO-free. The lowest emissivity reduces the heat transfer by irradiation, the high diffusion coefficient in air and the low density make hydrogen to have an escape velocity higher with respect to other gasses. Indeed, hydrogen disperses at a rate 2.8 faster than methane. All these features have implications, especially regarding the safety of adopting this gas. The design of a plant using hydrogen as fuel or raw material should take into account its flammability, ventilation against unintended mixing processes, safe transportation and storage.

Similar to electricity, hydrogen is an energy carrier rather than an energy source and it can be produced from multiple energy sources. There are several ways of producing it and a color-code nomenclature is commonly used as in Figure 1.1. The most common are blue and green hydrogen and in some instances grey, black and brown are used interchangeably referring to fossil fuels in general. Moreover, hydrogen versatility lies in its ability to be produced through various methods, including electrolysis, steam methane reforming (SMR) and gasification of biomass, each with its own environmental footprint. Overall, in terms of materials, H_2 can be extracted from fossil fuels (CH₄, coal, oil or other higher hydrocarbons), biomass or biogas and water. In terms of energy, the process is sustained by renewables



Figure 1.1: Hydrogen nomenclature based on its production process

producing electricity, nuclear and fossil fuels itself [10].



Figure 1.2: Indicative production of hydrogen from natural gas, biomass, and electrolysis using RES [11]

The term green hydrogen means hydrogen produced cleanly via water electrolysis powered by renewable electricity or through the gasification of biomass[12]. It offers a sustainable energy solution for sectors that are hard to electrify directly, including transportation and heavy industry. Additionally, it contributes to the production of clean feedstock for syngas or synthetic fuels, and it finds applications in various industrial processes, such as the manufacturing of iron, steel, and chemicals. The use of green hydrogen as an energy carrier broadens the scope of renewable power applications, outperforming batteries in certain scenarios due to its higher energy density [4]. Furthermore, green hydrogen, transported through pipelines, presents an economically viable option for distribution and energy storage. Lastly, the controlled production of green hydrogen through electrolysis serves as a flexible and controllable source of electricity demand, offering adaptability within power systems.

Its production via electrolysis can be performed using different electrolysis technologies such as: alkaline electrolysis, proton exchange membrane electrolysis or through the use of solid oxide electrolyzer. Anyway, a deeper overview of how it is produced will be better explained in the next chapter.

Despite its immense potential, challenges persist in the widespread of its adoption. Hydrogen production carries energy losses, 20-35% energy loss for green hydrogen [13] increasing the electricity capacity needed as more end uses shift to hydrogen or its derived products. The current cost of producing green hydrogen (3.5-6.8 USD/kg [14]) remains a significant barrier, 5-10 times more expensive than natural gas and 2-3 times more than grey hydrogen (0.7-2.51 USD/kg [14])necessitating substantial investments in research and development and the scaling up of production capacities [4]. However, according to IRENA, in 2050 the LCOH can decrease up to 1.38 USD/kg if the cost of electrolyzers will reduce too [14]. Additionally, the development of a robust infrastructure for hydrogen storage and transportation is crucial for seamless integration into existing energy systems. Usually, hydrogen is produced close to where it is used so there is a huge lack in existing dedicated pipelines, storages and refuelling station. Part of this need can be compensated by repurposing the existing natural gas infrastructure. However, mixing hydrogen in natural gas infrastructure without affecting final appliances and infrastructure itself may be feasible only if gas interchangeability is guaranteed. Not considering that hydrogen atoms can permeate into steel pipelines causing the embrittlement phenomena. Moreover, not all regions or nations can rely on such existing facilities and that is the reason why it should be performed a place-by-place assessment.

For all those reasons mentioned above, the Italian Authority established in the D.M 3^{rd} of June 2022 [15] that to inject into the national gas network, the gas mixture under consideration must meet some eligibility ranges based on their properties. Specifically, in terms of hydrogen, the gas cannot overcome the limit of 2% of hydrogen in volume in the mixture.

1.4 Literature review

Decarbonization, in particular in energy-intensive sectors like industrial processes, represents a worldwide challenge. In this section, an overview, especially in Italy, of the current state towards greener industry, hydrogen penetration, pros and cons of proposed technologies that will be used, and feedback from different Off-takers will be provided. In addition, it will be presented a literature review about some particular applications using green hydrogen in order to reduce CO_2 emissions. Confindustria in partnership with ENEA [16] reviewed the national Italian industry sector hydrogen potential in the energy transition mapping the possible hydrogen off-takers. Based on several meetings and data-sharing with industrial stakeholders, the review aims to give a detailed national overview of the development and spread of current and future technologies in the main industrial sectors (Hard to Abate). The highest potential sectors are steel, ceramic, glass, refinery, concrete, chemicals, paper, and food.

As reported by Federacciai, the steel industry has a keen interest in hydrogen with potential uses in furnace processes and direct reduction of iron (DRI process). Nevertheless, main issues related to its use could be plant-related aspects of adapting pipes and components to new features of the greener gas mixture, shorter lifespan of the furnaces and lack of proper legislation.

On the other hand, since the refinery sector already works with grey hydrogen as a feedstock, UNEM claims cost, large amount of green hydrogen availability together with the subsequent lack of inadequacy and flexibility due to RESs as limiting constraints for green hydrogen switching.

Assocarta, representing the paper industry, highlights that their business essentially depends on natural gas (NG). Therefore, the necessity to design suitable and mature technology that ensures better performance for hydrogen-feed burners and combustors is crucial for their companies.

Instead, according to concrete sector stakeholders, Federbeton, the best decarbonization option is CCUS whereas hydrogen has still a higher cost and can cause refractory embrittlement and negative aspects due to the high quantities of steam produced too.

The chemicals industry, represented by Federchimica, has already a well-established confidence with hydrogen production, transport and utilization as they use it to produce chemicals like ammonia, hydrogen peroxide or chlorinated compounds. They already exploit hydrogen, usually produced by SMR, for heating purposes. In the latter application, there may be difficulties in combustor substitution, plant adaptation engineering and potential increase in NO_x .

Regarding the ceramic sector, Confindustria Ceramica, the commercial furnaces use NG to make ceramics. In addition, to the high hydrogen cost, plant adaptation problems and regulation, ceramic companies are worried about the quality of their products using hydrogen, since their manufacture is in direct contact with the combustion environment and the flame temperature and the different ways to irradiate of the hydrogen can affect creation processes. Introduction

The glass sector, represented by Assovetro, is the one that best explains its involvement with hydrogen. The most energy-intensive process (70% of the primary energy consumption) is glass melting. In this step, hydrogen may be employed replacing NG, but it could have a further minor application as a reducing agent to neutralize air infiltration into the electric oven. As well as previous sectors, the glass division suffers the changes in final product quality, plant adaptation components problems and their safety, NO_x increasing potential, the shorter service life of refractory due to corrosion, SO_x stripping and high alkaline vapor content.

Even the food and non-ferrous metals industries, Unionfood and Assomet respectively, share, along with the ceramic and glass ones, the same worries about availability, costs, product quality and blending and distribution facilities. In addition, In the production of thin aluminum sheets, hydrogen is considered as something to strictly avoid.

Furthermore, it is important to stress that all Hard to Abate fields, that want to use hydrogen as fuel for combustion, are currently able to withstand and use, without any significant problems or any change in the infrastructure, a mixture of NG-H2 ranging from 5% to 20% in volume of hydrogen. To resume, using a 20% hydrogen blending in the gas mixture can cover up to 34% of the MiTe's target and each sector can benefit from an avoided cost ranging from 2 M \in to 41 M \in (ETS share 60 $\in/tonCO_2$). However, to be profitable the specific production cost of the hydrogen should be around 3.7 \in/kg .

A more general overview is given by the 2023 Global Hydrogen Review by IEA [8] that every year tracks worldwide hydrogen production and demand, as well as progress in critical areas such as infrastructure development, policy, regulation, investments and innovation. In 2022 the main consumer of hydrogen was China while Europe, due to the war in Ukraine, decreased its use.

Neuwirth et al [17] aims to estimate the technical potential of hydrogen demand applied to Germany. The paper adopts a process-specific and site-specific bottomup approach to energy-intensive industries considering fossil fuel replacement with hydrogen. They come up with a predicted German future hydrogen demand of 326 TWh/a. If the non-energy-intensive industries are taken into consideration, the demand grows to 482 and 534 TWh/a.

The study presented by Schmitz et al [18] aims at reporting the CO2 emissions together with the energy consumption of the entire European glass industry gathering the data from EU ETS. As an added value, they assess the energy intensity for some EU aggregates and some selected Member States.

Zier et al [19] investigated how the technical decarbonization options affect the future CO2 budget targets according to the Paris climate goal. The analysis is conducted focusing on the German glass industry, particularly to container and flat glass industry. The predicted bottom-up model designed by authors shows that any simulation is not able to achieve CO2 targets, but they can significantly decrease consumption pointing out how important political decisions are.

Gärtner et al [20] proposed an interesting publication on the integration of a Power-To-Hydrogen plant integrated into oxyfuel glass furnace. The plant exploits both the hydrogen and oxygen from the electrolyzer to drive the combustion process. Outcomes demonstrated successful aspects such as compatibility, however, the main constraint remains the too high economic indicators.

Marocco et al [21] assessed with their publication the key role of hydrogen as fuel in the decarbonization process. Through the auxiliary of an optimization framework, they evaluated the best configuration to satisfy the thermal demand of a scrap-based electric arc furnace steel plant, coming out with a sensitivity analysis of the LCOH based on the hydrogen share in the fuel mixture.

1.5 Aim of the thesis

The thesis aims to study the decarbonization of a real float glass industry based in Larbaa, Algeria, that uses hydrogen in its manufacturing process. To start, two main in-depth literature reviews were performed. The first one was based on the main green hydrogen solutions that nowadays help to green up and reduce CO2 emissions in the industrial sectors and towards which direction are energy policies moving in this respect. The second was done on current state-of-arte of splitting water electrolyzers delving into technical and economic barriers, coupling with RES, techno-economic applications using Power-to-X. Then, once the hydrogen load and the meteorological data were estimated, a techno-economic optimization was carried out in MATLAB environment using a PSO algorithm in order to know the optimal configuration (PV field, electrolyzer, hydrogen tank and hydrogen compressor) that minimizes LCOH exploiting only green hydrogen. The optimal design was performed by testing PEM and alkaline electrolyzer. Then, they were compared with the purpose of showing which is more profitable from an economic point of view. In the second part of the thesis, several scenarios were investigated with a sensitivity analysis in order to point out differences among technologies and their effects on the LCOH.

Chapter 2

Water electrolysis

2.1 Introduction

Hydrogen is the most abundant element but at the same time, its molecular structure is not present in nature other than in presence of other atoms. Therefore it must be produced using primary source of heat and extrapolating it from other elements which have hydrogen atoms. Starting from that, based on the raw material, hydrogen production technologies can be primarily classified into conventional or renewable. As already said in the previous chapter, conventional production refers to the one that use fossil sources (e.g. coal, oil, gas, etc) and has CO_2 as by-product. One of the most known technologies is the steam methane reforming. This process occurs within a processing component known as a reformer, where steam at elevated temperatures (~ 700 - 1100 °C) reacts with a fossil fuel, in the presence of a metal-based catalyst, typically nickel returning a low purity hydrogen [22]. The presence or not of CCS systems makes hydrogen production commonly called *grey* or *blue* respectively.

In contrast, renewable production starts from materials such as water and biomass. While the latter produces CO_2 as a conventional production, the first one exploits electricity in order to split the water. According to thermodynamics, the water-splitting reaction is inherently non-spontaneous. Nonetheless, external energy input, such as electricity, can drive this process[23]. The electro-chemical conversion of water into hydrogen and oxygen occurs through a process called water electrolysis. The reaction involved with splitting water is the following:

$$H_2O_{(l)} + 237.2 \ kJmol_{electricity}^{-1} + 48.6 \ kJmol_{heat}^{-1} \rightarrow H_2 + 1/2 \ O_2$$

where the full reaction can be divided into two half-reactions also called hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) that decompose water into hydrogen and oxygen gas respectively [24]. That process makes high-purity hydrogen ($\sim 100\%$ hydrogen) and when electricity that feeds electrolysis



comes from RES, hydrogen is named green.

Figure 2.1: Hydrogen production using water electrolysis [25]

Water electrolysis presents a promising approach to produce green hydrogen using renewable sources. It involves the utilization of electricity and the reaction takes place in a device known as an electrolyzer. Electrolyzers typically consist of multiple cells (stack) containing an anode and a cathode, separated by an electrolyte material. The various water electrolysis technologies are distinguished by the type of electrolyte used and the operating temperature. Three are the most mature water electrolysis technologies: Alkaline water electrolysis (AWE), Proton Exchange Membrane water electrolysis (PEMWE), and Solid Oxide electrolysis (SOEL). Further low Technology Readiness Level (TRL) electrolysis types are: Anion Exchange Membrane water wlectrolysis (AEMWE) and Proton Conducting Ceramic electrolysis (PCCEL). Below, a brief overview of each of these technologies is provided.

2.2 Alkaline water electrolysis

Alkaline stands as the current most mature among electrolyzer technologies and it has long been considered a standard for large-scale industrial hydrogen production [26]. Figure 2.2 illustrates the operational principle of alkaline electrolyzers. The operating temperature of the cell usually ranges from 70°C to 90°C to maximize

the electrical conductivity [27]. The half-reactions are shown below:

Anode:
$$4OH^- \longleftrightarrow 2H_2O + O_2 + 4e^-$$

Cathode: $4H_2O + 4e^- \longleftrightarrow 2H_2 + 4OH$





Within the cell, two gas-evolving electrodes are immersed in a liquid electrolyte, separated by a porous separator (diaphragm) that selectively permits ions while hindering gas bubbles. Typically, the electrodes comprise an electrically conductive porous metal framework, often coated with a catalyst layer. Unlike the corrosive conditions in PEM electrolyzers, the alkaline environment allows for the widespread use of non-platinum group metal (PGM) electrodes as both catalysts and electrode materials. Various combinations of transition metals have been extensively explored in research literature, demonstrating superior performance compared to PGM catalysts. Additionally, the utilization of robust porous separators contributes to the high durability and impurity tolerance of alkaline electrolyzers, resulting in longer estimated lifetimes compared to other available electrolyzer technologies [29]. Each cell can be connected in two different configurations to form a stack for industrial uses: parallel connection (monopolar assembly) or series connection (bipolar assembly). The first has the advantage of ensuring a homogeneous current feeding, the second is more efficient from an energetic point of view [24].

The diaphragms positioned between the electrodes are frequently formed by asbestos, porous ceramics, polymers, and their composites thereof. One instance of a composite separator is Zirfon PerlTM, a blend of zirconia and polysulfone network known for preserving the high wettability of the zirconia and its shape retention while harnessing the flexibility of polymer. Zirfon materials are presently

and extensively employed and are regarded as cutting-edge separators in alkaline electrolyzers. The electrolyte solution usually is composed of 25-30% of potassium hydroxide (KOH) that recirculates throughout the unit. Its main role is wetting the electrodes and diaphragm both and cooling down the temperature of the cell. Since water consumption occurs at the cathode side and production at the anode side, it is necessary to blend streams from both sides before reintroducing them into the cell. This is done essentially to prevent electrolyte concentration or dilution within the cell. However, these streams may contain amounts of dissolved gases $(H_2 \text{ and } O_2 \text{ bubbling})$, potentially contaminating the product gases during mixing. This issue restricts operation at higher pressure levels. To avoid the problem thicker separators or spacers between electrodes and separators may be possible solutions. Nonetheless, increased thickness leads to elevated cell ohmic-drop across the electrodes, potentially reducing current density. Advanced designs now employ zero-gap electrodes with thinner separators and enhanced electrocatalysts to boost current density. To address gas mixing concerns, auxiliary methods such as catalytic gas purification processes may be employed.

However, alkaline electrolyzers have several drawbacks. They present a low partial load range of operability (20-100%) due to the cross-diffusion of product gases. This event not only reduces the efficiency of the electrolyzer but threatens the operation safety leading to an unwanted concentration of hydrogen. Furthermore, its intrinsic design for fixed process conditions due to the long time to reach the steady-state operation, in terms of current density, temperature and electrolyte flow, limits its compatibility with certain types of renewables. While the use of batteries and control systems can partially mitigate this limitation, alkaline electrolyzers may not be the optimal choice for variable renewable energy sources like solar PV or wind.

At system level, alkaline electrolyzers necessitate the circulation of electrolyte within the stack components, resulting in a pressure drop and an almost negligible efficiency reduction. In addition, After exiting the stack, the circulating electrolyte solution requires a gas separation process. It passes through a gas/water separator positioned above the stack at a specified height, where the liquid phase is extracted at the bottom and returned to the stack, while the gas is extracted at the top. The water column within the gas/water separator also serves as a buffer storage for accommodating load specification changes. The water level in each gas/water separator is controlled by the water management system, with water permeation through the diaphragm also taken into account.

Commercially accessible alkaline electrolyzers often produce hydrogen with lower purity compared to alternative options (e.g. PEM electrolyzers), while consuming more energy. Moreover, the employment of corrosive alkaline electrolytes poses safety risks in the event of leakage or gas mixing (given the highly flammable nature of hydrogen and oxygen mixtures), necessitating meticulous system design and maintenance. In conclusion, the ongoing challenges for alkaline electrolyzers lay on:

- Increasing current density without affecting efficiency;
- Reducing the diaphragm thickness taking under control safety issues due to the gas diffusion;
- Re-designing catalyst compositions and electrode architectures into electrodes with a high specific surface area;
- New concept of porous transport layer (PTL) and electrode concept;
- Increasing the operational temperature [28];

2.3 Proton Exchange Membrane water electrolysis

Proton exchange membrane (or polymer electrolyte membrane) water electrolyzer is a promising solution that aims to overcome the drawbacks of the alkaline electrolyzer [30]. As its name says, it uses a solid polymer as electrolyte [31], thus, having no consumption of electrolyte. The half-reactions are slightly different with respect to alkaline as at the anode, water molecules undergo electrolysis, resulting in the separation of oxygen (O_2) and protons (H^+), with the release of electrons (e^-). The protons move through the proton exchange membrane (PEM), while the electrons travel through an external circuit, eventually recombining at the cathode to produce hydrogen [31].

Anode: $2H_2O \longleftrightarrow O_2 + 4H^+ + 4e^-$

$$Cathode: 4H^+ + 4e^- \longleftrightarrow 2H_2$$



Water electrolysis

Figure 2.3: PEM water electrolyzer [28]

The primary structure within the cell consists of a solid polymer electrolyte (SPE), approximately 0.2 μ m in thickness [30] [32], capable of conducting protons. These cells allow a compact design and exhibit high efficiency in the process of water splitting. The membrane has a dual role: facilitating the movement of ionic charges and ensuring the separation of electrolysis byproducts (molecular hydrogen and oxygen), thereby averting their spontaneous exothermic recombination into water. The prevailing choice for membrane material is a sulphonated tetrafluoroethylenebased fluoropolymer–copolymer also called Nafion[®] developed by DuPont in the 1960s [23]. The central part is the membrane electrode assembly (MEA) that is composed in the middle by the SPE membrane, then, by two porous layers of electrocatalysts which act as coating of the PEM. One at the anode for OER and the other at the cathode for HER. Typically, the MEA is encased between two porous current distributors comprised of sintered titanium particles in order to be resistant to corrosion since its acidic conditions during operations [23]. Furthermore, in order to transport electric current to the cell and isolate adjacent cells, two hollow bipolar plates (BPPs) are employed. Channels are incorporated to transport water to the anode and to collect liquid-gas mixtures in each cell compartment [23]. In addition, together with the MEA gas diffusion electrodes complete the electro-chemical cell. According to IRENA [28] the catalytic layers commonly utilize precious group metal compositions: iridium oxide (IrO_2) at the anode that shows a high metallic conductivity and platinum nanoparticles supported on a carbon substrate (Pt/C) at the cathode. Concerning OER, IrO_2 is considered the state-of-the-art in PEM electrolyzer, being less active but more stable and showing less corrosion with respect to RuO₂. On the other hand, for HER, the catalyst was adopted starting from studies based on PEM fuel cells without any deep research due to the predominance of the OER. PEM are able to work at high

current density beyond 2 A cm⁻². The thin membrane can provide great proton conductivity too, thus, reducing the operational cost of the cell [30] [33]. RES can be easily coupled with PEM electrolyzers since their load range can cover from 10 to 100% of their nominal power density. The reason can be found in the fact that the gas cross-over rate through the solid electrolyte is much lower. This allows to avoid high concentrations of hydrogen in the anode and have safer and wider operation. Modern PEM electrolyzers can achieve up to 5% as lower bound and 125% as upper bound [28]. Additionally, PEM electrolyzers can operate at high pressure (~ 130 bars [34]) due to the robustness given by the solid membrane. The benefits that high pressure brings, are the reduction in energy consumption for end-users to further compress and store the hydrogen after electrolysis [35] and the reduction in dehydration of the SPE preserving its aging [36]. However, high pressure can also negatively affect the cross-permeation and sometimes may need a thicker membrane in order to stand at pressures above 100 bars [37] [38]. The selection of component materials must be appropriate considering the corrosive environment of the membrane and has to stand to high over-voltage. For this reason, expensive materials are used making in turn PEM slightly costlier than ALK electrolyzers affecting their penetration in the market. At system level, the balance of the plant (BoP) includes: heat exchangers, pressure control unit and recirculation pumps. To manage and separate hydrogen, on the cathode side, gas separator, de-oxygenation component, gas dryer and a compressor are present [31]. The plant typically can operate at constant atmospheric pressure, having two different pressures at anode and cathode (differential pressure) or with the same pressure on both sides (balanced pressure). Future scenarios expect a huge development in PEM. The research focuses its attention on the reduction in the thickness membrane, on a novel concept of electrodes able to use less quantity of catalyst and on introducing new cost-effective coating on PLTs [28].

2.4 Solid Oxide water electrolysis

The solid oxide electrolysis cell (SOEC) is an electrolyzer unit that works at hightemperature ($\sim 800 - 1000$ °C) [24]. This characteristic makes the electrochemical process reversible (from electrolyzer mode to fuel cell mode and vice versa) and highly efficient. The cell presents an electrolyte made usually with yttria stabilized zirconia (YSZ) or gadolinium doped ceria (GDC) [39]. All of these are ceramic materials that show good ionic conductivity at high temperatures. The anode is composed by a composite of Nickel and YSZ with 30% porosity where Nickel makes electronic phase and acts as catalyst too while YSZ makes ionic phase. On the other hand, the cathode has to be a good ionic and electronic conductor, has to be porous and should have similar thermal expansion with respect to the electrolyte layer. The current state-of-art for the cathode is a perovskite oxide such as $La_{1-x} Sr_x MnO_3$ (LSM) or $La_{1-x} Sr_x Co_{1-y}Fe_yO_3$ (LSCF) [40]. The electrochemical reactions are described as in follow:

Anode:
$$O^{2-} \longleftrightarrow 1/2O_2 + 2e^-$$

Cathode: $H_2O + 2e^- \longleftrightarrow H_2 + O^{2-}$



Figure 2.4: Solix Oxide water electrolyzer [28]

The assembly of the cell can be defined as electrolyte-supported cell or anodesupported cell. The first has a thicker electrolyte leading to a more robust cell with a high durability but there is the necessity to work at a higher temperature to ensure good conductivity through the electrolyte. The second is mechanically supported by the anode and it provides better efficiencies and performances at lower temperatures. The use of high-temperature cells has several advantages: all transport processes are improved enhancing the efficiency, there is no need of precious catalysts at the electrodes, can operate reversibly without any difficulties, multiple fuels can be used (H₂, CO, CH₄, biogas, etc.) and the heat is recovered at high temperature and can be exploited for other purposes. In contrast, there is the necessity to have higher quality components in the BoP, it is not proper for fast start-up operation, idle mode held at 700-900 °C and suffers thermal cycles. Nevertheless, SOECs are still under research trying to develop more thermo-mechanically stable materials but an increasing interest is gaining.

2.5 Power-to-Hydrogen

Renewable energy sources such as wind, solar and hydro-electric are subject to environmental, seasonal and daily cycles, which may constrain their utilization or

effectiveness. Consequently, renewable energy cannot continuously generate power throughout the day, operating intermittently rather than on demand. For this reason, they are also called variable renewable energy (VRE) and this intrinsic characteristic limits their penetration [31]. Energy storage provides the capability to store excess energy generated during periods of high renewable energy production or low demand. This stored energy can then be utilized during periods of low renewable energy production or high demand, effectively balancing supply and demand dynamics [41]. While batteries could be suitable for short-term storage (load demands in a daily perspective) [42], the need to store large amounts of renewable energy shifts the attention towards chemical storages. Chemicals can result appealing for the industrial sectors. They can be exploited in several final uses (e.g. manufacturing, stationary systems, automotive, etc.) and can rely on existing distribution and utilization infrastructure. A potential strategy for widespread and sustainable integration of RES across different end users involves the production of synthetic chemicals to be fed into the existing grids. These chemicals could be generated using RES-based processes, such as electrochemical, thermochemical, or biochemical methods. This solution is also called Power-to-X where *power* means electricity and X stands for all the other forms or energy carriers in which electricity can be stored. It allows large size and long-term storage, the possibility of chemically fixing the carbon recycled from CO_2 and high flexibility and duration to match the fluctuation of RES [43]. The storage of electricity can be done using hydrogen as chemical energy carriers in PtH_2 system. The process involves a water splitting reaction through the use of an electrolyzer driven by RES electricity to have as outputs H_2 and O_2 . Hydrogen, besides the final storage product, can in turn be used as an intermediate medium to further produce synthetic gas in Power-to-gas or to synthesize Dimethyl ether (DME) in Power-to-liquid process.



Figure 2.5: Hydrogen as an energy carrier or precursor for complex processes [25]

In literature, there are countless researches that study PtH_2 plants with the aim of assessing their techno-economic feasibility. In the current section, a literature review is presented focusing mainly on applications that use green hydrogen from a PtH_2 plant to decarbonize a specific process.

Henry et al. [44] investigate the final hydrogen selling price under three different scenarios using PEM and ALK technologies. In the first two, H₂ is produced using electricity from the national grid when electricity price is under a specific setpoint (100 £/MWh) and during low demand periods respectively, while the last scenario exploits a wind turbine owned by the user located in Killybegs, Donegal. The selling prices of hydrogen having a production setpoint of 500 kg/hr in scenario 1 are 5.98 £/kg and 5.12 £/kg, in scenario 2 are 17.24 £/kg and 13.48 £/kg, in scenario 3 are 5.60 £/kg and 4.85 £/kg for PEM and ALK respectively.

Gökçek and Kale [45] carried out a techno-economic analysis of a hydrogen refueling station (HRFS) powered by a hybrid wind-PV-battery and hybrid wind-battery system in Gökçeada, Turkey. The hybrid wind-PV-battery has 904 kW of PV, 800 kW of wind and 347 kWh battery with a final LCOH of 8.92 \$/kg. The second optimal configuration has 2.4 MW of wind and 550 kWh battery resulting in 11.08 \$/kg of LCOH.

Ibagon et al. [46] performed a techno-economic optimization to size a PtH₂ in Uruguay able to produce a 250 $tons_{H_2}/day$ minimizing the LCOH. At the end of the analysis, the system is composed of 1059 MW of PV, 975 MW of wind, 811 MW of electrolyzer and the LCOH result in 3.58 USD/kg.

Ibanez et al. [47] studied an off-grid green hydrogen production system in Finland comprising of a 10.4 kW solar PV installation and a 7.05 MW wind farm for electricity generation, a 100 MW alkaline water electrolyzer and a battery energy storage system. The LCOH result in 2.34 €/kg.

Matute et al. [48] assessed the feasibility of PtH_2 with the peculiarity that the electrolysis is fed by PV power-purchase agreement (PPA) located in Spain. The size of the electrolyzer is 5 MW and must meet 600 tons of H_2 /year and the PPA price is 35 €/MWh. The final LCOH is equal to 3.33 €/kg

Fragiacomo et al. [49] propose a sensitivity analysis of a hydrogen refueling station based in Reggio Calabria, Italy, changing the PPA price and the potential hydrogen delivery rate of the daily production for the Hydrogen Mobility.

Matute et al. [3] provide a techno-economic feasibility of a spanish PV-electrolysis plants in a self-consumption regime to produce green hydrogen. The optimal dispatch model proposes to calculate plant dispatch and schedule the operation with a model that takes into account the predictability of PV, the electricity market and the dynamic operational states of the electrolyzer.

Moradpoor et al. [50] carry out a economic analysis of a green hydrogen production fed by a wind farm for oil refining in Finnish, Finland. Several scenario were analyzed changing both electrolyzers and the way of providing electricity. In the end, it was found that using ALK electrolyzer in baseload PPA the average operational cost is $2.79 \notin kg$.

It is important to stress that, all of these researches are highly affected by boundary conditions. The availability of renewable sources can change a lot based on the location. The choices such as the type of renewables used, the type of electrolyzers, the possibility of considering storage for both electricity (battery) and hydrogen (hydrogen tank) have an influence on the LCOH. In addition, the technical and economic assumptions that can be made, the operational state and the degradation along the component lifetime, the way in which LCOH is calculated, the assumption on the economical factor have an impact on the final result.

Chapter 3

Methodology

3.1 Introduction

In this chapter, it will be provided the methodology used to develop the thesis. Firstly, the description of the case study will be presented. Then, meteorological data assessment based on the location of the real floating glass industry and its hydrogen demand will be carried out. To conclude, there will be described the optimization tool together with the main assumptions and methods used to perform the techno-economic analysis.

3.2 Case study description

The floating glass manufacturing facility, used as a reference in this work, is a real plant called CEVITAL and located in Larbaa, Algeria. Boudries et al. [51] in 2014 already studied the glass factory with the aim of replacing the existing conventional electric power generation of the hydrogen production unit with a PV system. CEVITAL uses hydrogen in the floating glass manufacturing process in a mixture with nitrogen (about 10% H₂ and 90% N₂) into the tin bath in order to make the environment inert, preventing the generation of defects. The hydrogen unit is already a PtH₂ system but in this case, the electrolysis is driven by electricity from the grid.

For its needs, the plant has a nominal production capacity of 600 tons/day and withdraws water at a rate of 60 m³/h. At nominal rate, it consume hourly 1600 m³ and 150 m³ of nitrogen and hydrogen respectively [51]. The current hydrogen unit is composed of an electrical station, which includes a transformer, a rectifying cabinet and a regulation unit, a water treatment unit and an electrolyzer. However, for the thesis purpose, it is supposed to have a PtH₂ system that takes into account:

- **PV field**: it includes interconnected PV modules designed to generate renewable electricity in direct current (DC). The amount of energy produced depends on factors such as solar irradiance, PV cell technology, meteorological conditions, especially temperature, which impacts module efficiency.
- **Electrolyzer**: the choice of the electrolyzer type will be the fundamental part of the study because it will affect performances and costs both.
- Hydrogen tank: the pressurized storage tank is used to store the amount of hydrogen in excess and to smooth the fluctuation in hydrogen demand. Moreover, it is assumed not to have a battery. Therefore, the system exploits as much electrical energy as possible coming from PV, storing hydrogen during low-demand or high production periods and discharging it when it is necessary. Its minimum and maximum pressure are 20 and 200 bars respectively.
- Hydrogen compressor: in order to compress the gas at the suitable pressure of the hydrogen tank. It is an ancillary component but needful for the system. It is assumed that its specific consumption to compress hydrogen is equal to 4 MJ/kg.

Furthermore, all the remaining auxiliary components are included in their respective constituents.



Figure 3.1: Hydrogen as an energy carrier or precursor for complex processes

3.3 Solar energy resource assessment

The meteorological data are carried out using PVGIS tool. It provides several meteorological variables on a hourly, daily or monthly basis such as solar irradiance, air temperature and wind speed based on data from satellites and reanalysis. Starting from that, it is able to return the power produced by PV at a certain azimuth and orientation with the possibility of changing features of the cell. In order to have a valid assessment, the most representative meteorological variables are needed. For this reason, the Typical Meteorological Year (TMY) dataset from 2005 to 2020 is used. Knowing typical months, it is possible to extract the global irradiance on the array plane and the air temperature every hour for a year. The data are calculated assuming a crystalline silicon cell fixed at its optimized slope and azimuth with an installed peak power of 1 kW_p and a system loss of 14%.

According to HOMER help manual [52], to calculate the PV power produced the equation (3.1) is used considering a time-step of 1 hour.

$$P_{PV} = P_{PV,STC} \cdot f_{PV} \cdot \left(\frac{G_T}{G_{STC}}\right) \cdot \left[1 + \alpha_p \cdot (T_C - T_{STC})\right]$$
(3.1)

Where G_{STC} is 1000 W/m² and T_{STC} is equal to 25 °C.

This equation takes into account the effect of the global irradiance and the ambient temperature. Moreover, f_{PV} is the so-called derating factor, a coefficient that scales the PV output power due to different sources of losses. However, since the cell temperature is unknown, using [52] it is possible to express it as a function of the air temperature through the power balance of the PV array.

$$T_c = T_a + G_T \cdot \left(\frac{\tau\alpha}{U_L}\right) \cdot \left(1 - \frac{\eta_c}{\tau\alpha}\right)$$
(3.2)

The terms $\left(\frac{\tau\alpha}{U_L}\right)$ can be written as:

$$\left(\frac{\tau\alpha}{U_L}\right) = \left(\frac{T_{c,NOCT} - T_{a,NOCT}}{G_{T,NOCT}}\right)$$
(3.3)

Resulting in the final expression:

$$T_c = T_a + G_T \cdot \left(\frac{T_{c,NOCT} - T_{a,NOCT}}{G_{T,NOCT}}\right) \cdot \left(1 - \frac{\eta_c}{\tau\alpha}\right)$$
(3.4)

Where:

- $G_{T,NOCT} = 800 \text{ W/m}^2;$
- $\tau \alpha = 0.9;$

• $T_{a,NOCT} = 20^{\circ}\mathrm{C}$

In this context, it is assumed that PV always works at its maximum power point, thus, having that:

$$\eta_c = \eta_{mpp} \tag{3.5}$$

But the η_{mpp} in turn depends on the cell temperature:

$$\eta_{mpp} = \eta_{mpp,STC} \cdot \left[1 + \alpha_p \cdot (T_C - T_{STC})\right] \tag{3.6}$$

Finally, the complete equation of the cell temperature expressed in °K.

$$T_{c} = \frac{T_{a} + \left(T_{c,NOCT} - T_{a,NOCT}\right) \cdot \left(\frac{G_{T}}{G_{STC}}\right) \cdot \left[1 - \frac{\eta_{mpp,STC} \cdot \left(1 - \alpha_{p} \cdot T_{STC}\right)}{\tau \alpha}\right]}{1 + \left(T_{c,NOCT} - T_{a,NOCT}\right) \cdot \frac{G_{T}}{G_{STC}} \cdot \left(\frac{\eta_{mpp,STC} \cdot \alpha_{p}}{\tau \alpha}\right)}$$
(3.7)

To make explicit T_c , the commercial PV LG365Q1C-A5 is chosen with the following characteristics:

Cell type	Monocrystalline silicon
P_{rated} [W]	365
$\eta_{mpp,STC}[-]$	0.21
NOCT [°C]	44 ± 3
$\alpha_p \; [\%/^{\circ}\mathrm{C}]$	-0.30
Operating temperature [°C]	$-40 \div + 90$

 Table 3.1: PV technical specification

Having T_c , the power output from the PV array can be calculated. Although from PVGIS it can be already possible to extract P_{PV} , the method used by HOMER seems to be more accurate even if it still tends to overestimate the PV system power output [53].

3.4 Hydrogen demand

The floating glass facility uses hydrogen mainly between 10 am and 5 pm while during the rest of the day, the consumption is pretty stable. The hydrogen demand is constant throughout the month but seasonally changes, in January, April, June and October. In this case, the hydrogen demand is provided by [51] as it is possible to see in Figure 3.2. The total demand is equal to $102 \text{ tons}_{\text{H}_2}/\text{year}$.

Methodology



Figure 3.2: Evolution of the average hourly hydrogen consumption

3.5 Sizing procedure and economic analysis

Hydrogen demand and PV output power are the input parameters in the optimization design. The coupling design between PV and the hydrogen production unit was carried out using a techno-economic optimization tool employing a methodology divided into two main parts. In the first one, an energy management strategy (EMS) is defined in order to describe how the system operates. Meanwhile, in the second part, the particle swarm optimization (PSO) algorithm is applied to provide a feasible system configuration.

Energy management strategy

The aim of the EMS defined in this thesis, is to exploit as much as possible RES and, at the same time, meet the hydrogen demand without relying on the help of the grid or external/grey hydrogen. At each time step (1 hour), PV power is considered:

• If PV production is lower than the hydrogen demand and lower than the minimum electrolyzer operating power (according to its modulation range), the demand is met using the hydrogen storage and the remaining produced
electricity is exported to the grid. The electrolyzer is turned off because it is not able to work within its operating range. In case green hydrogen from the tank is still not sufficient, a grey hydrogen backup system is used.

- If PV production is lower than the hydrogen demand but higher than the minimum electrolyzer operating power, the demand is met primarily by the PV and then partially by the tank. In case green hydrogen from the hydrogen tank is still not sufficient, a grey hydrogen backup system is used.
- If PV output is higher than the hydrogen load, the electricity produced will feed the electrolyzer that, in order of priority, firstly meets the demand and then, in case of surplus of electricity, charges the storage with the excess of hydrogen. In case the tank is already charged, the electrolyzer produces just the proper amount of hydrogen to fulfill the demand and then, the excess electricity will be sold to the grid.



Figure 3.3: Energy management strategy

It is important to remember that in this configuration no batteries are taken into account as well as grid-based electricity. In addition, even if a grey hydrogen backup system is introduced according to the EMS, in practice, configurations that exploit it will be discarded during the optimization since it is assumed to meet the demand only using green hydrogen.

Techno-economic optimization

As second part of the methodology, the techno-economic optimization is performed in MATLAB environment. It includes the control logic based on the EMS and uses a Particle Swarm Optimization algorithm. This algorithm is a population-based stochastic optimization technique inspired by the social behavior of bird flocking. In PSO, a population of potential solutions, referred to as particles, moves through the search space to find the optimal solution. Each particle represents a potential solution and has its own position and velocity in the search space. The movement of particles is influenced by their own best-known position and the global best-known position found by any particle in the population. This cooperative behavior allows particles to quickly converge towards promising regions of the search space. It is one of the most suitable algorithms for the design of renewable energy systems. The objective function of the PSO is the minimization of the LCOH of the system. In addition, it has to satisfy at the same time a couple of constraints. During the entire lifetime of the project (20 years) the PtH_2 system must rely 100% on the RES. The Level of Hydrogen (LOH) in the tank, defined as the ratio between the amount of hydrogen in the storage and the maximum capacity of the tank, at any time interval, must be maintained among its range of operation that can be seen in Table 3.4. The size of each component must be in a certain range from zero up to an upper bound, high enough to not affect the optimization.

The levelized cost of hydrogen is a useful KPI to compare different technologies for hydrogen production. It is used to evaluate and compare the long-term unit costs of various baseload technologies throughout their operational lifetimes. It includes all the costs of the project: from the initial cost of investment to operation and maintenance expenditures. By calculating the levelized cost of hydrogen, stakeholders can evaluate the economic viability of different hydrogen production technologies and determine the competitiveness of hydrogen as an energy carrier compared to other fuels. The lower will be the LCOH, the more cost-effective the system. It is defined as:

$$LCOH = \frac{C_{NPC,tot}}{\sum_{n=1}^{N} m_{H_2} \cdot (1+i)^{-n}}$$
(3.8)

Where:

- m_{H_2} is the yearly hydrogen demand [kg];
- N is the system lifetime [-];
- i is the interest rate [%];
- $C_{NPC,tot}$ is the Net Present Cost (NPC) [\in];

The Net Present Cost (NPC) is a financial KPI used to evaluate the total cost of a project or investment over its entire life span, adjusted for the time value of money. It represents the sum of all cash outflows and inflows discounted to their present value using an appropriate discount rate. The NPC is useful for comparing different investment alternatives or projects, as it provides a single measure of their economic viability. A project with a lower NPC is generally considered more economically favorable, as it indicates lower overall costs or higher returns relative to the initial investment. It includes the capital expenditure (CAPEX) and the operating expenditures (OPEX). The latter in turn takes into account the operating and maintenance costs, and the replacement costs for the j-th component and the revenues from the grid when electricity is injected.

$$C_{NPC,tot} = \sum_{j} C_{inv,j} + \sum_{n=1}^{N} \left(\frac{\sum_{j} C_{O\&M,j,n} + \sum_{j} C_{rep,j,n} - C_{sell,n}}{(1+i)^{j}} \right)$$
(3.9)

The $C_{inv,j}$ or CAPEX, represents the total investment cost of each component and includes the installation and the transport cost. It is a cash flow that is considered once at the beginning of the project. $C_{O\&m,j,n}$ refers to the expenses for the ongoing operation, upkeep, and maintenance of the j-th component in the n-th year. The replacement cost $C_{rep,j,n}$ is an occasional cost that incurs at the end of each component lifetime. It may happen that some components are assumed to operate as long as the lifespan of the system, thus not needing a replacement (see Table 3.2). $C_{sell,n}$ refers to the revenues due to the exported electricity in the n-th year and it is considered a negative cashflow in the NPC. The interest rate *i* has a huge relevance since represents the rate at which future cash flows are discounted to their present value. In this work, instead of calculating the real one, the interest rate will be assumed as 5%. However, a sensitivity analysis will be carried out to investigate the effect on the LCOH.

All the costs that belong to OPEX $(C_{inv,j}, C_{O\&m,j,n}, C_{rep,j,n}, C_{sell,n})$ are evaluated over the entire lifetime of the system on a yearly basis. Moreover, all the costs in equation 3.9 are expressed in euros referring to the n-th year.

All the techno-economic assumptions and input data are summarized in Table 3.2, Table 3.3 and Table 3.4. They contain the specifications of each component. According to [54], PV investment cost can be assumed $800 \notin kW$ while the yearly O&M is expressed as a percentage of the CAPEX. About electrolyzers, the table shows the characteristics of both PEM and alkaline. In the thesis, it will be studied the decarbonization options using both of them. Moreover, they operate at a pressure of 30 bar while they have a nominal efficiency of 54% and 55% respectively. The efficiency curves of the electrolyzers are represented according to [55]. During the operation of the electrolyzers, based on their operating power, the efficiency changes accordingly to Figure 3.4. The modulation range, due to the reason described in Chapter 2 is different among electrolyzers as well as the lifetime with

PEM having more flexibility and alkaline having a higher lifetime. In addition, the CAPEX of electrolyzers per unit of power does not take into account installation and civil works and it is not assumed fixed at the beginning but evaluated through a cost function expressed in %W that depends on the size and the technology maturity expressed in year according to [56]. Then, the other costs are summed considering them as 10% of the specific EL CAPEX thus having the total EL investment cost.

$$C_{inv,EL} = \left(k_0 + \frac{k}{P_{EL,rated}} \cdot (P_{EL,rated})^{\alpha}\right) \cdot \left(\frac{V}{V_0}\right)^{\beta}$$
(3.10)

With:

- k and k_0 curve coefficients [-];
- $P_{EL,rated}$ the nominal size of the electrolyzer [kW];
- V and V_0 plant installation year and reference year [-];
- α and β scaling and learning factor respectively [-];



Figure 3.4: Alkaline (left) and PEM (right) efficiency curve [55]

As already said before, the hydrogen tank must always be within an acceptable range in order to continuously supply hydrogen without problems. The storage is chosen among I-type tank ($200bar \leq p_{tank} \leq 300bar$) with a maximum operating pressure of 200 bar. Additionally, as final assumptions, the system time horizon is set at 20 years and revenues that come from selling the electricity are calculated according to the Algerian price of electricity for businesses updated in March 2022 and then converted in \notin /kWh [57]. The initial LOH at the start of the operation (t = 0) is set at 20% to simulate a starting reservoir.



Figure 3.5: Alkaline (left) and PEM (right) cost function curve [56]

Once all the input parameters are estimated and calculated, it is possible to proceed with the implementation of the techno-economic optimization into the MATLAB environment. According to the constraints on the component size, after assuming random size values, the optimization code simulates with a time-step of 1 hour over 20 years the hydrogen production and relative costs and revenues of the PtH_2 . At the end of the simulation, it returns the NPC and LCOH based on the sizes hypothesized before. At this point, the PSO algorithm starts a new simulation changing sizes and trying to minimize the LCOH. When the global optimum is found the code stops. Although the algorithm tries its best to reach the minimum without violating the constraints, sometimes could happen that for a certain set of sizes, the hydrogen production from PV is not enough to meet the demand and when even the hydrogen tank is not able to fulfill the request, the systems withdraws grey hydrogen, according to the EMS. Nevertheless, this study aims to analyze the decarbonization of a real flat glass facility relying only on RES. For this reason, although it is possible to use grey hydrogen according to the code, if a simulation uses it, automatically a penalty will be assigned to the LCOH of that configuration resulting in a much higher LCOH. The additional malus has a double reason. Firstly, to discard solutions that break the constraints and, on the other hand, to move solutions away from the *swarm* incentivizing the PSO to find another better solution.

Parameter	Value	Ref
PV		
f_{PV}	0.86	[58]
α_p	-0.3 %/°C	
CAPEX	800 €/kW	[54]
annual $O\&M \ [\% \text{ of CAPEX}]$	2%	
Lifetime	20 years	
PEM Electrolyzer		
Efficiency curve	-	[55]
Nominal efficiency	55%	[55]
Modulation range	10-100%	[21]
Operating pressure	30 bar	
Lifetime	40000 h	[3]
Stack replacement cost [$\%$ of the CAPEX]	30%	[55]
Annual OPEX [% of the CAPEX]	3%	[59]
Installation cost [$\%$ of the CAPEX]	10%	[21]
BoP lifetime	20 years	[58]
α	0.622	[56]
β	-158.9	[56]
k	9458.2	[56]
k_0	585.85	[56]
V_0	2020	[56]
V	2020	

 Table 3.2:
 Techno-economic input data:
 PV and PEM electrolyzer

Parameter	Value	Ref
Alkaline Electrolyzer		
Efficiency curve	-	[55]
Nominal efficiency	56%	[55]
Modulation range	20 - 100%	[55]
Operating pressure	30 bar	
Lifetime	80000 h	[55][60]
Stack replacement cost [$\%$ of the CAPEX]	30%	[48]
Annual OPEX [% of the CAPEX]	4%	
Installation cost [$\%$ of the CAPEX]	10%	[21]
BoP lifetime	20 years	[58]
lpha	0.649	[56]
eta	-27.33	[56]
k	11603	[56]
k_0	301.04	[56]
V_0	2020	[56]
V	2020	
Hydrogen tank		
p_{min}	20 bar	
p_{max}	200 bar	[21]
SOC_{min}	p_{min}/p_{max}	
SOC_{max}	1	
CAPEX	500 €/kg	[61]
Replacement cost	500 €/kg	
Annual $O\&M$ [% of CAPEX]	2%	[21]
Lifetime	20 years	

 Table 3.3:
 Techno-economic input data: alkaline electrolyzer and hydrogen tank

Parameter	Value	Ref
Hydrogen compressor		
Specific energy consumption	$4 MJ/kg_{H_2}$	[62]
CAPEX	1600 €/kg	[62]
Replacement cost	1600 €/kg	[62]
Annual OPEX [% of CAPEX]	2%	[21]
Lifetime	20 years	
LOH $(t=0)$	0.2	
Other assumptions		
interest rate	5%	
Price of sold electricity	0.032 €/kWh	[57]
Cost of grey hydrogen	4€/kg	[63]
System lifetime	20 years	
Level of hydrogen	$LOH_{min} \leq LOH \leq LOH_{max}$	
$m_{H_2,grey}$	0	

 Table 3.4:
 Techno-economic input data of hydrogen compressor and main assumptions

Chapter 4

Results

4.1 Introduction

In this chapter, the result of the techno-economic optimization will be discussed. Firstly, a PV-based scenario will be investigated. Results will be shown presenting one simulation using PEM electrolyzer and another one with ALK electrolyzer. At this point, a sensitivity analysis will be performed in order to make a comparison among these two technologies. The KPIs interested in the analysis are: the lifetime for PEM and the modulation range for ALK, the interest rate and the annual electrolyzer OPEX for both. Additionally, another comparison will be made but in this scenario, the EL CAPEX will be considered fixed. The reason behind the comparison lies in the research of the impact that certain parameters have on the LCOH and on the feasibility of a PtH₂ system. In the second part of the chapter, a grid – based scenario will be introduced. This further scenario wants to highlight the economic difference of using a different source of electricity. Finally, a sensitivity analysis on the electricity price will be carried out.

The choice of using PEM and alkaline electrolyzer was made because, as lowtemperature electrolyzers, they are the most suitable technologies for this kind of application as well as the most mature units used in PtH₂. Compared to solid oxide electrolyzers, they have more flexibility and can be better coupled with RES. At this point, the thesis want to investigate which one between PEM and ALK is the most cost-effective and in which conditions, what are their advantages or disadvantages, strengths and limits. However, this study wants to go even beyond that and deeply research what affects the LCOH and in which way. Furthermore, through a what - if logic it wants to develop and analyze future scenarios and see their trend.





Figure 4.1: Comparison between **Figure 4.2:** Comparison between PEM and Alkaline efficiency curve PEM and Alkaline cost function curve

4.2 PV-based scenario

4.2.1 PtH₂ system with PEM electrolyzer

The hourly hydrogen demand over a year is represented in Figure 4.1. All the input parameters are described in Table 3.2, recalling that the EL CAPEX is variable based on the volume production (see eq. 3.10). On purpose, it is not assumed to include the effects of the year ($V = V_0 = 2020$) since it is an assumption based on future forecast that could not be sure.



Figure 4.3: Hydrogen demand over a year

The optimization code, for this configuration, returns a LCOH of $9.20 \notin kg$ with 8684 kW of PV, 2721 kW of electrolyzer, 2014 kg capacity of hydrogen tank and 37 kW of compressor.

LCOH [€/kg]	PV [kW]	EL [kW]	HT [kg]	HC [kW]	NPC [€]
9.20	8684.23	2721.04	2014.76	37.00	11710225

Table 4.1: PEM base case

PEM works 3952 hours per year, thus, lasting about 10 years and needing only one stack replacement. The total investment cost for the EL is $1061 \notin kW$. The net present cost in Fig. 4.4 is characterized based on its components. The major contribute of the NPC is the PV due to its large size and consequent cost. Even if the specific cost of PV is lower than PEM, the ratio between them in terms of size is exactly 3.19.



Figure 4.4: Net present cost of the system

As result of the optimization, it is possible to know even the instant electrolyzer operating power and the LOH per hour over one year. The LOH (Fig. 4.5) increases a lot during summer up to its maximum level due to the high productivity of PV and then it is discharged on a daily basis during the night and during cold seasons. The electrolyzer, when it is not turned off, often reaches its maximum power leading to a good exploitation.



Figure 4.5: LOH in hydrogen tank



Figure 4.6: EL operating powers

In addition, all the hydrogen flow rates based on their destination or origin are reported in Fig 4.7. According to the EMS, when hydrogen production is higher than demand the surplus is stored in the tank. In the opposite case, the demand is satisfied using hydrogen from the storage.

Another important result that has to be shown is Fig. 4.8. It represents the yearly duration curve for PEM and PV. For each point on the Y-axis, the abscissa of the curve stands for the number of hours when the power is equal to or larger





Figure 4.7: Hydrogen flow rates

than the coordinate. Therefore, for high power, the number of hours will be lower and vice versa. Nevertheless, it is important to notice that for the electrolyzer, the trend of the duration curve is quite different compared to the PV. Starting from the lowest part of the curve, at 3952 hours there is a vertical line that represents the number of hours when the power of the PEM is higher than 0. This lower bound highly depends on the minimum power required by the PEM to turn on itself and, thus, on its modulation range. Then, the EL curve follows the same trend of PV with a perfect coupling among them. Afterward, a linear (almost horizontal) behavior occurs. The reason why EL is no longer coupled with PV can be found in the LOH of the hydrogen tank. When the storage is full, even if the solar electricity production is high, the electrolyzer just works with enough power to meet the demand. Therefore, this behavior can be seen as a shift in the PEM curve due to this constraint. Indeed, going towards higher powers the trend starts to rise similarly to the PV curve up to the maximum electrolyzer power point (\approx 1200 hours) that marks the upper bound. Above that point, the number of hours higher than that power becomes 0.

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Figure 4.8: PEM duration curve

4.2.2 PtH₂ system with alkaline electrolyzer

In this scenario, alkaline unit is used as electrolyzer. It has a higher lifetime but at the same time less flexibility with respect to PEM. From an economic point of view for high powers, it is way cheaper than PEM. All its features used in the simulation are listed in Chapter 3. According to the optimization, Table 4.2 reports the results. Furthermore, due to the liquid electrolyte, the alkaline annual operating expenditures usually are higher than PEM and assumed as 4% of the CAPEX.

LCOH [€/kg]	PV [kW]	$\mathbf{EL}\ [\mathbf{kW}]$	HT [kg]	HC [kW]	NPC [€]
8.93	8747.24	2702.15	1941.62	37.00	11359888

 Table 4.2:
 ALK base case

Concerning the size component almost nothing changes except for the slightly smaller hydrogen tank. However, using ALK the LCOH is reduced mainly due to its lifetime. ALK works 3611 hours per year and with its 80000 hours of life span, it can easily operate for more than 20 years. Therefore, it is not necessary a stack replacement. The savings from the avoided replacement cost affect the LCOH by about 30 cents per kilo of H_2 .



Figure 4.9: LOH in hydrogen tank



Figure 4.10: EL operating powers

The investment cost of ALK electrolyzer is marginally reduced and results in $1025 \notin kW$. According to Fig. 4.2, around 2 MW the two cost functions overlap so that there is no big difference in specific cost between ALK and PEM electrolyzer. The NPC is lower than PEM base case due to the reduction in EL CAPEX as is possible to see in Figure 4.11.



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Figure 4.11: Net present cost of the system

Nevertheless, another contribution that accounts for the NPC is the narrower modulation range of alkaline. The minimum ALK operating power is 20% of the rated power. For this reason when the power from PV is not enough all the electricity is injected into the grid increasing annual revenues.



Figure 4.12: Hydrogen flow rates

The duration curve is slightly changed. Certainly, the upper bound of the curve is adapted to the maximum power of the ALK while the almost horizontal step

should not have significant variations. However, the main point is the shift towards left of the vertical line due to the higher ALK minimum operating power. If the upper bound matches with the maximum power, the lower bound matches with the operating hours of the EL. As a consequence of its limit, the electrolyzer works less reducing in turn the power coupling with PV.



Figure 4.13: ALK duration curve

4.2.3 PEM - alkaline comparison

The base cases with PEM and ALK electrolyzer are carried out. Adopting ALK results more cost-effective with respect to PEM. In literature, however, many technoeconomic analyses were performed using different lifetimes for PEM or modulation ranges for ALK and assuming different values for the economic optimization. For this reason, to understand the robustness of the model and to examine how changes in certain parameters impact the outcomes, the sensitivity analysis is introduced. A sensitivity analysis is a technique used to assess how changes in the input variables affect the output of a model, system, or decision. The process typically involves varying one or more input parameters within a certain range, while keeping other variables constant and observing the corresponding changes in the output. This allows to identify which factors have the most significant influence on the results (in this case the LCOH) and to assess the overall stability and reliability of the system.

4.2.3.1 Sensitivity analysis on PEM lifetime

Different studies assess that future trends are willing to increase the lifetime of PEM electrolyzers to 60000 up to 80000 hours and even beyond that [3] [31]. Hence, for the sake of completeness, the sensitivity analysis is performed with: 30000, 40000, 60000 and 80000 hours.



Figure 4.14: Sensitivity analysis on PEM lifetime and alkaline comparison

Figure 4.14 shows the LCOH using a PEM electrolyzer with different lifespans. It is clear to see that the trend is descending as the lifetime increases. Actually, the scenarios with 40000 and 60000 hours are quite similar while the others present a more evident change. The main factor that affects the LCOH is the replacement cost. Indeed, in the lowest lifetime scenario, the stack needs two replacements while in the opposite case (80000 h) no replacement is required. The impact can be quantified so that each replacement weighs on the LCOH roughly 35 cents/kg. Despite the economic considerations, from a technical point of view, component sizes, operating hours per year and the EL investment cost do not change significantly. In addition, in the figure above, the dashed red line represents the LCOH of ALK base case. In this case, it is used as benchmark to make a comparison among technologies. In order to be more cost-competitive than ALK, PEM electrolyzers need to increase their lifetime. The only scenario that returns a LCOH lower than the ALK one is the 80000 h scenario.

		Results		
Scenario	30000 h	40000 h	60000 h	80000h
LCOH [€/kg]	9.53	9.20	9.12	8.85
PV [kW]	8651.05	8684.23	8508.17	8457.50
EL [kW]	2727.13	2721.04	2754.35	2764.35
$\mathrm{HT}~[\mathrm{kg}]$	2019.70	2014.76	2040.53	2047.88
HC [kW]	37.00	37.00	37.00	38.00
NPC [€]	12122664	11710225	11608431	11260756

 Table 4.3:
 Sensitivity analysis on PEM lifetime: optimization outputs

4.2.3.2 Sensitivity analysis on alkaline modulation range

In alkaline electrolyzer, the most important constraint that limits performances is the low partial load range. The diaphragm does not inhibit the product gases from diffusing across it [30]. The diffusion of oxygen in the cathode reduces the efficiency while the diffusion of hydrogen in the anode can detonate within a certain range. The latter diffusion is particularly important in partial range when the oxygen production rate decreases leading to a too-high hydrogen concentration in the anode. Therefore, not all the ALK units can go down to 20%. Sometimes for safety reasons, the lower bound can be 30% [64] or even 40% [65] of the rated power.

Figure 4.15 shows that the LCOH increases as the modulation range restricts. The flexibility of the electrolyzer impacts its operating hours. The less it works, the less it will produce hydrogen. For this reason in the 30-100% scenario, all the sizes increase with the PV to EL ratio almost equal to the base case (≈ 3.3). To be noticed, if the size of EL increases, the minimum EL power rises too. Therefore, in the design phase, it is important to size the PV taking into account this effect. The last scenario (40-100%) is the worst from an economic point of view. According to Table 4.4, the PV/EL ratio decreases with a larger EL and HT but a smaller PV unit. In this case, the optimization tool designs a configuration where the EL operates few hours per day but when it turns on, it produces much more hydrogen than that hourly demand. Thereby, the system mainly relies on the hydrogen tank and on its capacity to store the surplus of hydrogen produced, fulfill the demand during the remaining hours of the day when the EL is not working. This is possible to see even from the size of the hydrogen compressor that is much greater than the other scenarios due to the larger hydrogen flow rate that it has to compress in a shorter period. On the other hand, for this scenario, it is possible to see a step decrease in ALK investment cost (988.4 \in /kW) due to its larger size. The



Figure 4.15: Sensitivity analysis on alkaline modulation range and PEM comparison

blue dashed line refers to the base case LCOH using PEM electrolyzer. It allows to understand that to be more profitable than in PEM scenario, ALK should operate at 20-100% of its modulation range.

Scenario	20-100%	30-100%	40-100%
LCOH [€/kg]	8.93	9.37	9.67
PV [kW]	8747.24	9355.14	9103.81
EL [kW]	2702.15	2797.38	3139.21
$\mathrm{HT} \; [\mathrm{kg}]$	1941.62	2216.05	2319.70
HC [kW]	37.00	39.00	45.00
NPC [€]	11359888	11924053	12307683

Table 4.4: Sensitivity analysis on ALK modulation range: optimization outputs

With different flexibility even the duration curve changes. From Fig 4.16 the two duration curves share the same X-axis to better see differences. What is possible to see is the difference in the shift towards fewer operating hours. In a

40-100% scenario, the EL is no longer coupled with PV leading to a higher amount of electricity not used. The main cause of this wasted electricity is related to the modulation range but a minor contribution is provided by the greater size of the electrolyzers too. The time spent by the ALK to just produce the amount of hydrogen equals the demand is reduced since the storage is much more used.



Figure 4.16: Comparison between alkaline duration curves: 20-100% modulation range scenario (top), 40-100% modulation range scenario (bottom)

4.2.3.3 Sensitivity analysis on interest rate

The interest rate is one of the most important KPIs in a techno-economic analysis. It represents the rate at which future cash flows are discounted to their present value. This rate is essential for evaluating the economic viability of a system. In the economic evaluation of an investment, the discount rate can be chosen among several options. For instance, it may be equal to the weighted average cost of capital (WACC) or may be calculated taking into account the nominal interest rate and the escalation rate. However, the interest is as fundamental as tough to forecast since it can depend on several factors such as the cost of debt, cost of equity, the project risk or market conditions. The sensitivity analysis here conducted wants to



Figure 4.17: Comparison between 5% and 8% interest rate

investigate the effect that the interest rate has on both PEM and ALK scenarios varying it between 4% and 8% which could be assessed as a viable range for these applications.

Scenario	i = 4%	i=5%	$\mathbf{i}=6\%$	i = 8%
PEM	8.49	9.20	9.93	11.47
ALK	8.22	8.93	9.67	11.22

Table 4.5: Sensitivity analysis on the interest rate: LCOH comparison betweenPEM and alkaline

As it is expected, higher will be the interest rate, higher will be the LCOH according to eq. 3.8. More precisely, there is a constant proportion as the interest rate increases. Both LCOHs rise by 7-8% for each percentage point. These results agree with the recent 2023 Global Hydrogen review by IEA [8] that assesses the rising from 5% to 8% raises the project cost by nearly one-third.

4.2.3.4 Sensitivity analysis on electrolyzer annual OPEX

As for the interest rate, it is difficult to know in advance during the design phase the exact value that accounts for the annual electrolyzer OPEX. It may depend on numerous factors based on the management of the component, its performances and the type used. For this reason, based on estimation, it is expressed as a percentage of the CAPEX. Usually, from literature, it is known that the OPEX for alkaline is slightly higher compared to PEM due to the difficulty of managing a liquid electrolyte.



Figure 4.18: Sensitivity analysis on the electrolyzer annual OPEX and PEM-ALK comparison

The trend shows a linear decrease in LCOH as the OPEX diminishes too. OPEX is closely related to the NPC which in turn is related to LCOH. However, at fixed annual EL OPEX, alkaline electrolyzer remains more profitable than PEM. As a matter of fact, the 2% OPEX scenario with PEM has an almost equal LCOH of the ALK scenario with 4% of annual OPEX. Every percentage point leads to a reduction in the LCOH of around 25-30 cents per kilo.

Scenario		OPEX=2%	OPEX=3%	OPEX=4%
PEM		8.91	9.20	9.49
ALK	LCOH [€/kg]	8.38	8.66	8.93

 Table 4.6:
 Sensitivity analysis on the electrolyzer annual OPEX: LCOH comparison between PEM and alkaline

4.2.3.5 PEM-alkaline base case comparison with fixed CAPEX

The use of a cost function allows to calculate the CAPEX of the electrolyzer taking advantage of the scale effect. This decision may be reliable, however, in order to provide an overview as complete as possible, a further base case scenario is investigated with fixed CAPEX. According to [55], the fixed CAPEX for PEM and ALK is 1400 \notin /kW and 1100 \notin /kW respectively.

PEM	ALK
10.72	9.51
9240.20	8845.99
2625.10	2677.72
1949.71	1942.44
35.00	37.00
13637470	12101747
	PEM 10.72 9240.20 2625.10 1949.71 35.00 13637470

 Table 4.7: PEM-ALK comparison with fixed electrolyzer CAPEX: optimization outputs

The results are not so different compared to the variable CAPEX scenario. While for ALK, the fixed CAPEX and the one calculated with the cost function have a small difference, the assumed fixed CAPEX for PEM differs more than 400 \notin /kW leading to a substantial difference. In both PEM and ALK cases, even if the sizes are similar, the weight that fixed EL CAPEX has on the final NPC is greater due to its value. This scenario and the one with the cost function one suggest that nowadays PEM technologies cannot be competitive with ALK despite their advantages.

4.3 Grid-based

The second main part of the results focuses their attention on a grid-based scenario. The aim is to investigate the production of hydrogen when no RES are used but electricity withdrawn from the grid directly feeds the electrolyzer. Both PEM and alkaline electrolyzer will be tested using the cost function to evaluate the CAPEX. The average electricity price is set at $0.1 \notin /kWh$. However, taking into account its high volatility, a further sensitivity analysis will be undertaken to better investigate all possible scenarios.

4.3.1 PtH₂ system with PEM electrolyzer

According to the optimization result, there is no need for hydrogen tank and compressor in this configuration. The electrolyzer withdraws the exact amount of electricity directly from the grid based on the hourly demand without surplus or deficit. Indeed, both storage and compressor are components that help to smooth the intermittent nature of RES. In the grid-based scenario, the source follows the load (see Fig 4.20) while in PV-based scenario the electrolyzer must adapt itself to the solar availability. The EL size is considerably dropped leading to a steep increase in the EL CAPEX. Furthermore, without storage, the electrolyzer works continuously along the entire year (8760 h per year). In this way, the plant needs three stack replacements that contribute to the already high annual OPEX. Despite that, the LCOH is quite low, even if it has a strong dependence on the electricity price.

LCOH $[\epsilon/kg]$	EL [kW]	HT [kg]	HC [kW]	NPC [€]
7.57	822.64	0	0	9625469



Table 4.8: Grid-based scenario: PEM base case

Figure 4.19: Hydrogen flow rate in the system





Figure 4.20: Electrical power used by electrolyzer and withdrawn from the grid

4.3.2 PtH₂ system with alkaline electrolyzer

The scenario here presented shows similar characteristics compared to the previous one. No storage and compressor are used, and the electrolyzer is never turned off as the hydrogen demand is always higher than zero. The modulation range does not affect negatively the performances since the operating power is always within the flexibility limits. LCOH is slightly lower than the PEM one according to the results based on the scenario with PV. Despite its 80000 hours lifetime, one stack replacement is needed due to the constant operation of electrolyzer.

LCOH [€/kg]	EL [kW]	HT [kg]	HC [kW]	NPC [€]
7.31	909.60	0	0	9302257

 Table 4.9:
 Grid-based scenario: alkaline base case

Results



Figure 4.21: Hydrogen flow rate in the system



Figure 4.22: Electrical power used by electrolyzer and withdrawn from the grid

4.3.3 Sensitivity analysis on electricity price: PEM-ALK comparison

Electricity prices can be subject to significant volatility due to various factors including fuel prices, weather conditions, energy policies, market structures and geopolitical events. Due to this reason, simulating a scenario with only one fixed electricity price may result meaningless. Conducting a sensitivity analysis on electricity prices helps designers to assess the potential impacts of various factors and scenarios and make more informed decisions with respect to this uncertainty effect. Therefore, the electricity price ranges from 5 c \in /kWh up to 20 c \in /kWh, further scenarios with a higher price will not be considered as their final LCOHs are inconvenient.



Figure 4.23: Sensitivity analysis on the electricity price and PEM-ALK comparison

It is clear from Fig 4.23 that exploiting low-cost electricity leads to lower operating expenditures and, thus, lower LCOH. Buying electricity at $0.05 \notin$ /kWh, the LCOH becomes quite profitable, $4.55 \notin$ /kg and $4.38 \notin$ /kg for PEM and ALK respectively. These values can reasonably compete with fossil-fuel hydrogen production costs. However, it is almost impossible to buy electricity at that cost throughout the entire system lifetime. A possible solution could be using a fixed-volume baseload PPA contract at that price [66]. However, increasing the electricity price, the size of the electrolyzer rises too. This effect implies a reduction in the total investment cost as it is possible to see in Table 4.10 and Table 4.11.

Results							
	LCOH $[\epsilon/kg]$	EL [kW]	${\rm C_{inv,EL}}~[{\rm {\ensuremath{\in}}}/{\rm kW}]$	NPC $[\in]$			
$C_{el} = 0.05 \in /kWh$	4.55	766.45	1354.05	5783645			
$C_{el} = 0.10 \ \text{e}/\text{kWh}$	7.57	822.64	1333.78	9625469			
$C_{el} = 0.15 \ \text{e}/\text{kWh}$	10.50	966.94	1289.45	13352270			
$C_{el} = 0.20 \ \text{\&/kWh}$	13.36	1070.21	1262.98	16998117			

Table 4.10: Sensitivity analysis on electricity price: PEM optimization outputs

	LCOH [€/kg]	EL [kW]	$C_{inv,EL}$ [€/kW]	NPC [€]
$C_{el} = 0.05 \ \text{\&/kWh}$	4.38	754.00	1435.04	5577372
$C_{el} = 0.10 \ \text{e}/\text{kWh}$	7.31	909.60	1362.77	9302257
$C_{el} = 0.15 \ \text{e}/\text{kWh}$	10.11	1084.01	1299.37	12860638
$C_{el} = 0.20 \ \text{\&/kWh}$	12.84	1213.00	1260.74	16337327

 Table 4.11:
 Sensitivity analysis on electricity price: alkaline optimization outputs

4.3.4 PV-based and grid-based comparison

In this section, the thesis wants to highlight the difference between PV-based scenario and grid-based scenario. The chart below illustrates PEM LCOH according to the electricity prices used in the sensitivity analysis. The LCOH of PEM base case with PV is used as a benchmark and it is represented with the black dashed line. When the system purchases electricity at a price equal or higher than 0.15 \notin /kWh, the most cost-effective solution becomes the one that exploits PV. On the contrary, the grid-based scenario starts to be profitable below the PV-based line.

The same trend can be observed in Fig. 4.25 using alkaline electrolyzer. In this case, the threshold is slightly lower, however, as for PEM, scenarios with 0.10 \notin /kWh or less as electricity price still remain more affordable than PtH₂ fed by PV.

An additional interesting point that can be assessed, is the different way of operation if the electrolyzer works with RES or if it is fed by the national grid. In PV-based scenarios, what really weighs is the huge investment cost (CAPEX) while the operational expenses are relatively low and when there is a surplus of electricity there can be revenues that balance costs. On the other hand, using electricity from the grid, the CAPEX is considerably reduced as the only sized component is the electrolyzer. OPEX, on the contrary, are relevant due to the continuous purchase of electricity.





Figure 4.24: Sensitivity analysis on the electricity price and PV-based scenario comparison for PEM electrolyzer

These effects can be clearly seen in Fig. 4.26. In the chart, the LCOH is decomposed into its main contributions related to CAPEX and OPEX. In PV-based scenario, the costs of running, managing and maintaining the system are limited with respect to the investment cost while this situation is reversed in scenarios with only grid and that can be seen in Fig 4.26 (a) for PEM and (b) for ALK electrolyzer. Specifically, the percentage of CAPEX and OPEX in the LCOH in grid-based scenarios ranges between 82%-92% and 18%-8% respectively as the electricity price increases. For electrolyzers coupled with PV, the CAPEX share is almost 94% of the total LCOH.



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Figure 4.25: Sensitivity analysis on the electricity price and PV-based scenario comparison for alkaline electrolyzer



Figure 4.26: CAPEX vs OPEX PEM: PV-based and grid-based comparison



Figure 4.27: CAPEX vs OPEX ALK: PV-based and grid-based comparison

Chapter 5 Conclusion

The urgent need to address climate change and reduce greenhouse gas emissions has led the world to explore cleaner and more sustainable energy alternatives. In this context, hydrogen has emerged as a key player in the decarbonization process of energy-intensive industries such as steel, aluminum, chemical, refinery, ceramic and glass. Some of them require high-temperature heat making direct electrification challenging while others emit CO_2 as a result of complex chemical reactions. In addition, they require significant capital investment, face intense cost competition and are highly sensitive to the quality of their final product. Hydrogen, as a clean energy source, can replace current fossil fuels in high-temperature heat sectors and can be used as feedstock and reducing agent. Moreover, it can be produced from RES through a *Power – to – Hydrogen* system, representing not only a promising electricity chemical storage but also an energy carrier to be involved in further conversion processes.

This thesis work aims to decarbonize a real floating glass facility based in Larbaa, Algeria. The industry already uses hydrogen in their manufacturing process together with nitrogen to make the environment inert. However, the current hydrogen production occurs via water electrolysis using electricity from the grid. The floating glass industry consumes 102 $tons_{H_2}/year$ and has a constant monthly demand that changes seasonally throughout the year. The decarbonization applied to this case study consists of producing green hydrogen using a PtH₂ system exploiting the high solar energy availability in that area through a PV field. In the hydrogen production unit, PV produces electricity that will be used to run the water-splitting reaction. The electrolyzer generates hydrogen to satisfy the demand according to PV power available and, in case of surplus, hydrogen will be compressed and stored in a hydrogen tank using a compressor. In the design procedure, a techno-economic optimization based on minimizing the levelized cost of hydrogen was carried out by using the particle swarm optimization algorithm. The optimal design tool implemented in MATLAB provides as outcomes: the size

of the PV, the electrolyzer, the hydrogen tank and the hydrogen compressor. As electrolyzer, PEM and alkaline unit were considered. Alkaline electrolyzer operates at low temperature and it is the most mature technology. It adopts inexpensive materials such as catalysts, leading to a low CAPEX and a low-cost hydrogen production. It has a longer lifetime with respect to PEM due to its robustness and it can adequately tolerate impurities. However, it has low flexibility due to the gas cross-diffusion issues, the produced H_2 gas has low purity compared to other electrolyzers, it suffers corrosion and its maximum current density is limited. The annual OPEX are higher due to the liquid electrolyte and the coupling with RES is challenging. PEM is a low-temperature electrolyzer, relative established technology with a compact design using a solid polymer as electrolyte. It produces high-purity hydrogen and can achieve high current density with relatively low operational costs. It has better flexibility with a faster load response that enables high compatibility with RES intermittency. On the other hand, the main disadvantage is the corrosive acidic regime that affects the lifetime and components performances leading to more expensive catalysts, collectors and separator plates and, thus, to a higher CAPEX.

The techno-economic optimization was performed by assessing the solar energy production through the use of PVGIS tool. The latter is able to extract meteorological data based on the typical meteorological year. Starting from that, the PV power output is evaluated taking into account the effect of the air temperature that could improve PV performances. Along with the optimization, the other goal of the thesis is to study and compare the PEM and ALK electrolyzer from an economical point of view. Electrolyzer CAPEX is evaluated using a cost function based on the designed size while OPEX are estimated as a percentage of CAPEX. In the initial scenario, alkaline returns the lowest LCOH, 8.93 \notin /kg, compared to PEM, 9.20 \notin /kg. The stack replacement cost has a remarkable impact on the final result and it can account for up to 35 cents/kg. Due to its shorter lifetime for the reason already discussed above, PEM needs at least one stack replacement while alkaline can last the entire lifetime of the project. Results appear differently if future developments will enhance the lifetime of PEM according to the 2050 target proposed by IRENA [28]. With the same duration, PEM becomes cheaper than alkaline electrolyzer due to its wider partial operation range. On the contrary, the main barrier of alkaline remains its flexibility: lower will be its minimum load, better will be its exploitation and, thus, the LCOH. Once performed the sensitivity analysis on the main technical parameter related to electrolyzer, the effect of the economic factors is investigated for the two technologies. Firstly, the interest rate is considered. According to the optimization result, even if it depends on several factors, it must be evaluated as precise as possible since each point variation can add or remove to the LCOH up to 70 cents/kg. Nevertheless, the sensitivity analysis performed on the interest rate agrees with the results found by

[8]. Then, the focus was shifted towards the annual electrolyzer OPEX. Based on the results, it is intuitive that a lower annual expenditure leads to a lower LCOH. It is important to remember that in all of the considered scenarios, on an equal economic basis, alkaline is more cost-effective than PEM electrolyzer. A further scenario is studied considering the electrolyzer CAPEX as fixed, 1400 \in /kW for PEM and 1100 \in/kW for alkaline. The optimization outputs emphasize even more the difference between PEM and alkaline due to higher investment cost, suggesting that without the discount effect due to the scale-up size, PEM is currently not profitable compared to ALK. To conclude, the PtH_2 is analyzed in a grid-based scenario where the electrolyzer is no longer fed by PV but by electricity withdrawn from the grid. However, since the electricity price is usually unstable, a sensitivity analysis is conducted and compared to scenarios that exploit PV energy. The optimization design in this scenario returns a configuration where no storage and compressor are needed. The electrolyzer uses electricity according to the amount of hydrogen required to meet the demand. For both PEM and alkaline electrolyzer, the PV-fed PtH_2 becomes profitable when the electricity price is equal to or higher than $0.15 \notin kWh$. On the other hand, when the electricity price is lower than this threshold, from an economical point of view, the grid-based scenario is more affordable. A further difference between these two scenarios lies in the contribution that total CAPEX and OPEX have on the LCOH. In PV-based scenario, CAPEX is the predominant element as the model includes more components and there is no need to buy electricity so the only operational expenses are the ones used to run, maintain and sometimes replace components. On the other hand, in grid-based scenario, CAPEX is extremely reduced since only electrolyzer is required. Instead, OPEX account for the main contribution due to the electricity purchase cost.

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