Trabajo Fin de Grado

Grado en Ingeniería de Tecnologías Industriales

Techno-economic assessment of green hydrogen production: study of ammonia production in Huelva

Autor: Laura Romero Piñeiro

Tutor: Pedro García Haro

Dpto. Teoría de la Señal y Comunicaciones
Escuela Técnica Superior de Ingeniería
Universidad de Sevilla

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Autor:
Laura Romero Piñeiro

Tutor:
Pedro García Haro
Profesor Titular de Universidad

Dpto. de Ingeniería Química y Ambiental
Escuela Técnica Superior de Ingeniería
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El tribunal nombrado para juzgar el Proyecto arriba indicado, compuesto por los siguientes miembros:

Presidente:

Vocales:

Secretario:

Acuerdan otorgarle la calificación de:

Sevilla, 2022

El Secretario del Tribunal

Acknowledgments

Foremost, I would like to express my gratitude to my mother for her encouragement and support throughout these years.

I would also like to extend my gratitude to my tutor Pedro García Haro for his guidance and attentiveness.

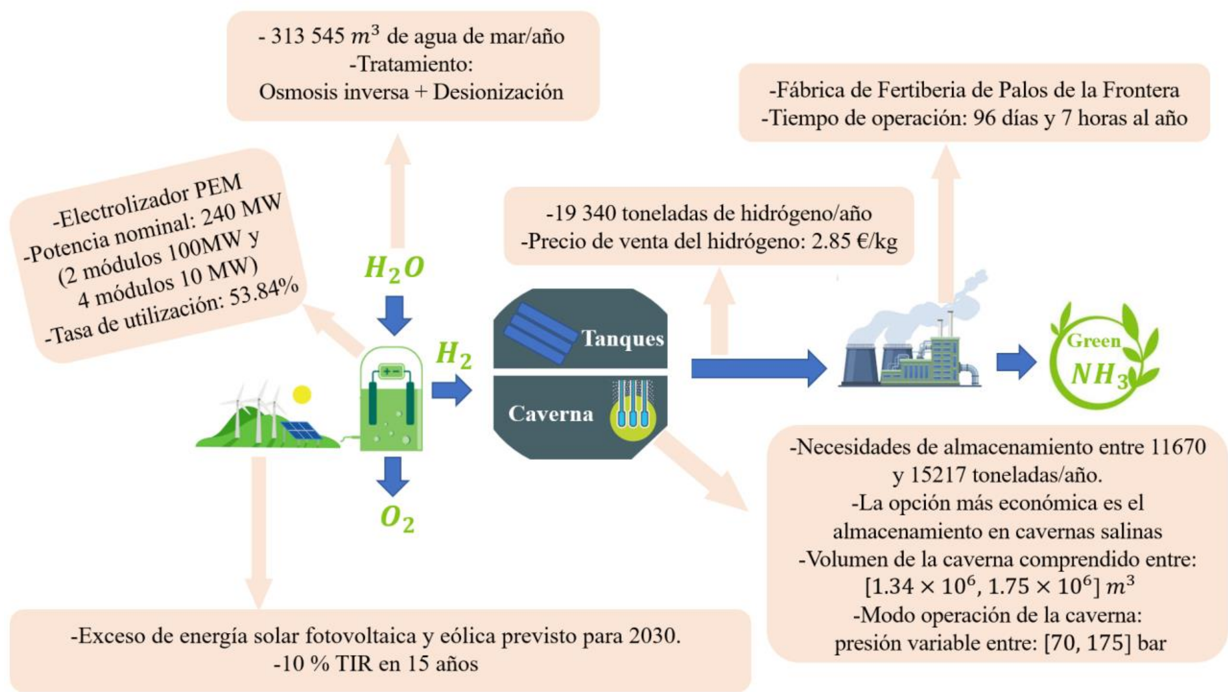
Resumen

El presente trabajo de fin de grado tiene como objetivo realizar un estudio tecno-económico de la producción de hidrógeno utilizando el excedente de energía solar fotovoltaica y eólica previsto para 2030. Este hidrógeno verde se suministrará a la fábrica de Palos de la Frontera de Fertiberia, que actualmente se abastece con hidrógeno gris, producido mediante reformado de metano con vapor (SMR). El hidrógeno será utilizado como materia prima para la producción de amoniaco verde que actualmente la fábrica vende como materia prima en la producción de fertilizantes.

Se ha analizado la tecnología necesaria para la producción de este hidrógeno y, posteriormente, se ha comparado el CAPEX y el OPEX de 4 casos diferentes, uno optimista y otro pesimista para el almacenamiento en cavernas salinas y en tanques presurizados. El menor coste se obtiene para el almacenamiento en cavernas salinas. Sin embargo, si se pretende alcanzar una TIR del 10% en 15 años, el hidrógeno producido no será competitivo con el precio de mercado esperado para el año 2030, incluso si el excedente de energía renovable fuera gratuito.

Finalmente, se han incluido los principales indicadores para la realización de un estudio del impacto ambiental del proyecto.

A continuación, se incluye un resumen gráfico con los principales resultados del proyecto.



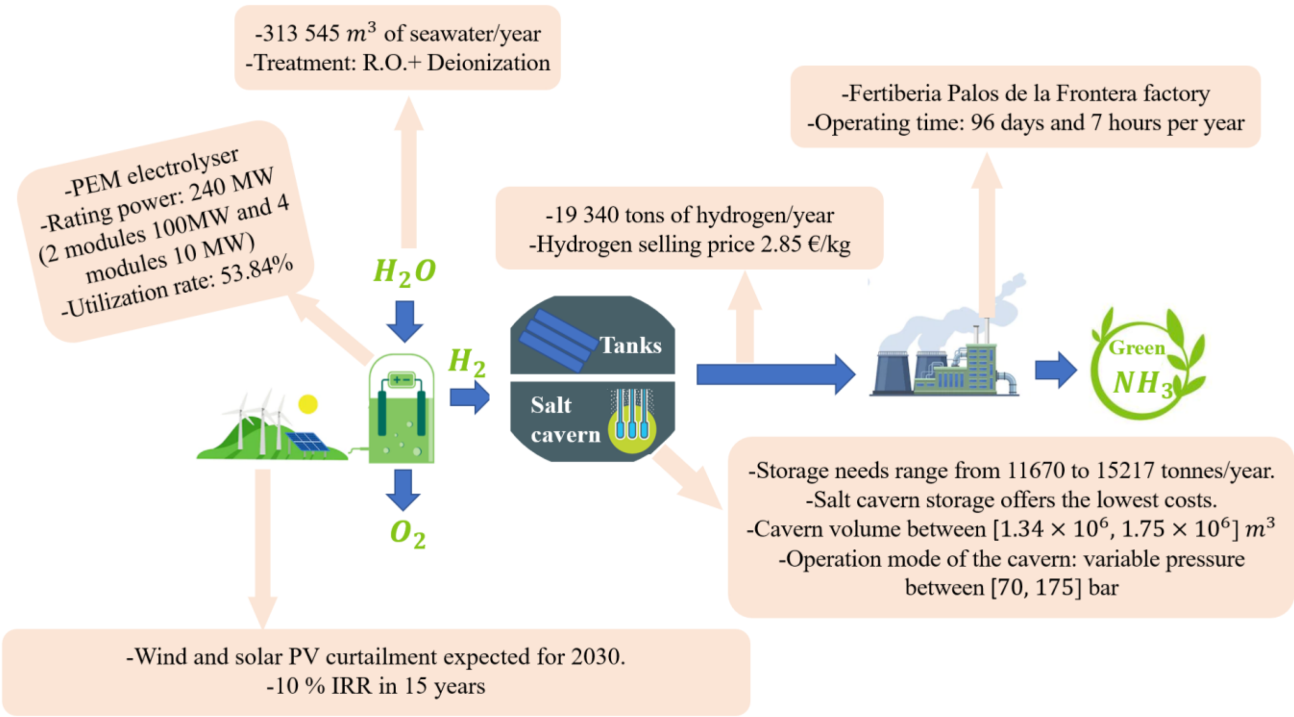
Abstract

The aim of this final degree project is to carry out a techno-economic study of the production of hydrogen using the expected wind and solar PV curtailment for 2030. This green hydrogen will be provided to Fertiberia's Palos de la Frontera factory, which is currently supplied using grey hydrogen, produced by SMR. This hydrogen will be used as feedstock to produce green ammonia, which is currently sold by the factory as fertiliser.

The technology needed to produce hydrogen has been analysed and, subsequently, the CAPEX and OPEX of 4 different scenarios have been compared, an optimistic and a pessimistic one for the storage in salt caverns and in pressurised tanks. The lower costs are obtained for salt cavern storage. Nevertheless, if an IRR of 10% is to be achieved in 15 years, the produced hydrogen will not be competitive with the expected market price in 2030, even if the surplus renewable energy were free of charge.

Finally, the most relevant indicators for carrying out an environmental impact study of the project have been included.

A graphical abstract with the main results of the project is included below.



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Abbreviations

CCS	Carbon capture and storage
IRR	Internal rate of return
LPG	Liquefied petroleum gas
NPV	Net present value
PEM	Proton exchange membrane
PFSA	Perfluoroacidsulfonic
PV	Photovoltaic
RES	Renewable energy source
SMR	Steam methane reforming
VRE	Variable renewable energy
YSZ	Yttria-stabilized Zirconia

1 INTRODUCTION AND MOTIVATION

Growing concerns about global warming, air pollution, fossil fuel depletion and geopolitical fears about their future availability are prompting massive investment in the quest to meet the future energy needs in a sustainable way. Hydrogen-based technologies, if sustainable, are increasingly being seen as an essential element of this energy transition.

Nowadays, more than 90 % of hydrogen is produced through carbon-intensive methods using fossil fuels. However, green hydrogen is expected to experience a dramatic cost reduction this decade as the cost of renewable electricity and electrolyzers fall, up to the point where it could compete with grey hydrogen even without a carbon tax [20].

Solar PV and wind are expected to be the mainstay of the energy transition. Both technologies have already experienced substantial cost reductions due to scale effects. Thus, they are now competitive with conventional power plant technologies, and they are expected to account for a significant share of the European energy mix by 2030 [63]. However, the large fluctuation of wind and solar power plants poses a challenge for implementing a sustainable energy economy. At certain times, when production exceeds demand, the operator may be obligated to allow less wind and solar generation than available. This wasted energy is known as curtailment, and it is expected to increase along with the penetration of variable renewable energy (VRE).

This work conducts a techno-economic assessment to study the viability of producing hydrogen via electrolysis using this electricity that would otherwise be wasted. In this project hydrogen will be used to produce ammonia but this is just one of the wide range of applications of hydrogen.

All in all, green hydrogen is expected to play a key role in the decarbonization of the energy system and Huelva has an enormous potential to lead its production in Spain.

1.1. The chemical cluster of Huelva

Figure 1 shows the distribution of the different companies that form the chemical cluster of Huelva. Aiqbe (Asociación de Industrias Químicas, Básicas y Energéticas de Huelva) currently has 19 members, which account for 20 production plants in Huelva and Palos de la Frontera. They constitute the most relevant centre of industrial activity in Andalusia and one of the most significant in Spain [31].

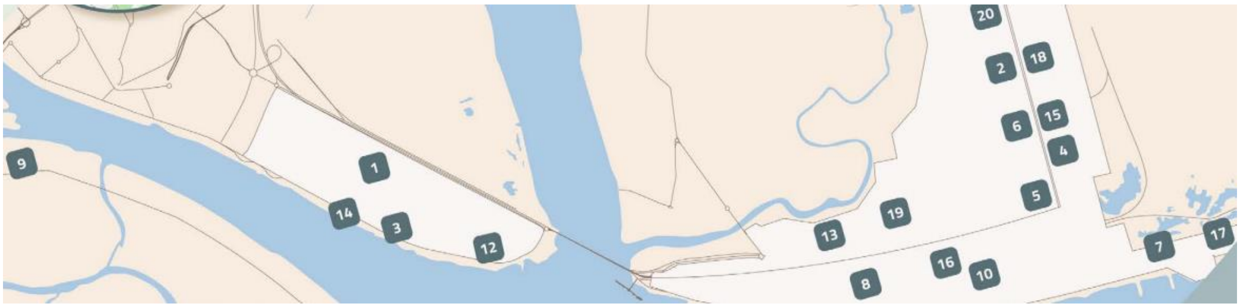

Figure 1. Location of the companies that constitute the chemical cluster of Huelva. Source: [21].

The list of companies is described in Table 1.

Table 1. Companies that constitute the chemical cluster of Huelva and their production. Source: [21]

Company	Production
1-Air Liquide	Oxygen, argon, carbon dioxide, nitrogen
2-Algry Química	Choline salts and its derivatives, active ingredients
3-Atlantic Copper	Cu cathodes and anodes, sulphuric acid, precious metals in anodic sludges, iron silicate, copper telluride, nickel carbonate, calcium sulphate
4-Bio Oils	Biodiesel, refined oil, glycerin
5-Cepsa. Refinería. La Rábida	Cyclohexane, xylene, propane, naphtha, sulfur, asphalts, butane, propylene, benzene, hydrogen, gasolines, kerosenes, gas oils, fuel oil
6-Cepsa Química. Palos	Phenol, acetone, cumene, AMS
7-Decal	Fuels, oils, Sandach fats
8-Electroquímica Onubense	Chlorine, sodium hypochlorite, sosa causticum, hydrochloric acid, hydrogen, salt
9- Electroquímica Onubense Salinas	
10-Enagás	Offloading, storage and regasification of liquefied natural gas, small scale services
11-Ence	Electric power
12-Endesa	Electric power
13-Exolum	Fuels
14-Fertiberia. Fábrica de Huelva	NPK complex fertilisers
15-Fertiberia. Fábrica de Palos	Ammonia, urea, AdBlue
16-Gunvor	Second generation biofuels from waste oils from waste oils, glycerine
17-Lipsa Huelva	Refined animal and vegetable fats and oils
18-Naturgy	Electric power
19-Repsol	Butane gas, autogas, propane, LPG
20-Venator	Titanium dioxide, ferric sulphate, caparrosa, fertilizers, ferrous and ferric salts, pigments

1.2. Grupo Fertiberia

Fertiberia is a leading producer of agricultural and industrial chemicals in the Iberian Peninsula and in Europe. It was founded in 1995 but its predecessor companies date back to the 1950s [68].

Fertiberia produces and distributes a wide range of fertilizer products, among them innovative solutions such as micronutrient-enriched fertilizers, as well as coated, liquid and soluble products. Furthermore, the firm produces a variety of chemical products that are used in industrial processes and as environmental solutions, intended mainly for the industrial and transport sectors.

The Fertiberia Group's customers are present in around 80 countries, and number nearly a thousand. Customers range from large retail groups, cooperatives industrial companies (especially in the chemical industry), to farmers.

Fertiberia's headquarters are located in Madrid. The company owns 13 production centers: 9 in Spain, 3 in Portugal and 1 in France, with a total production capacity of 9 million tons of fertilizers. It also has 10 logistics centers with a storage capacity of 290000 tons and 10 commercial offices in these three countries [6].

In 2020, the company's net revenues reached 672.9 million euros, while generating a total of 1546 direct jobs. The firm's total assets are estimated at 708 million euros.

Grupo Fertiberia produced 5.3 million tonnes of chemicals in 2020 (Figure 2). The largest production was that of nitrates (24.2%), followed by nitric acid (17.1%), ammonia (9.6%) and NPK (9.6%).

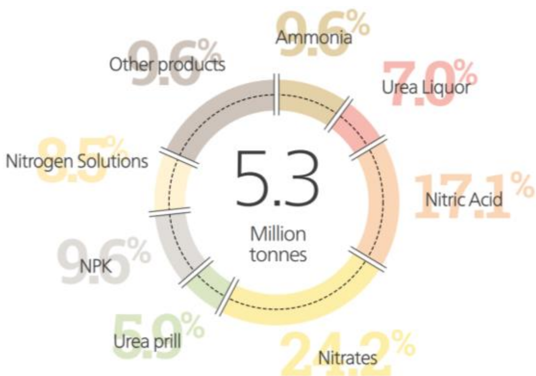

Figure 2. Fertiberia 2020 production. Source: [6]

1.3. Fertilizer industry in Spain

Figure 3 shows the fertilizer companies that consume ammonia in Spain based on [34]. It has been attempted to include the amount of NH_3 that each firm consumes, as well as the fertiliser industries that consume H_2, but this has not been possible due to lack of information.

Figure 3. Ammonia consumers in Spain.

2 AN OVERVIEW OF HYDROGEN

2.1. Types and uses of hydrogen

There are nine different colours to describe how hydrogen has been produced. Table 1 explains the characteristics of the most well-known types: green, blue, and grey hydrogen.

Table 2. Types of hydrogen. Source: [10]

Hydrogen Type	Production method	Carbon footprint
Grey hydrogen (Derived from fossil fuels)	SMR	330 $g\ CO_2/kWh_{H_2}$
Blue hydrogen (Low-carbon)	SMR + CCS	30-120 $g\ CO_2/kWh_{H_2}$
	Electrolysis using partially renewable electricity	
Green hydrogen (Renewable)	Electrolysis using renewable electricity	30 g CO_2/kWh_{H_2}

Grey hydrogen accounts for 95 % of the hydrogen production in the EU [10]. Nonetheless, green hydrogen will increase its competitiveness due to the rising prices of fossil fuels. On average, the production costs of green hydrogen will be the same as those of grey hydrogen by 2040. In certain countries, such as Germany, prices are expected to even out by 2030 [25].

Figure 4 shows that the share of non-carbon-capture SMRs in global hydrogen supply will fall from 81% in 2019 to 63% in 2030 and 15% in 2050. On the other hand, coal gasification will maintain its absolute production levels, but will reduce its relative share from 19% in 2019 to 5% in 2050, as other methods of producing hydrogen take hold, such as hydrogen supplied by electrolysis using electricity from grid and via off-grid dedicated renewable-based electrolysers.

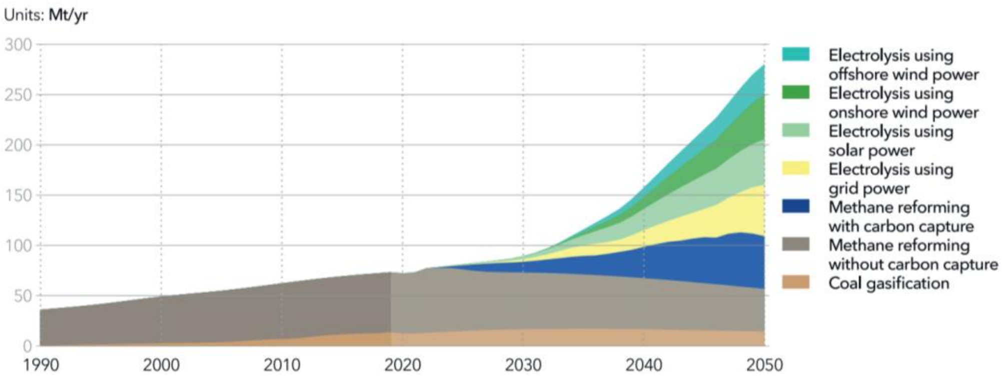

Figure 4. World hydrogen production by source. Source: [58]

At present, hydrogen is used in refineries to reduce the sulfur content of diesel and to convert heavy waste oils into higher-value petroleum products. It is also used for producing ammonia, which accounts for 65% of the industrial use of hydrogen [35]. Moreover, some applications, such as methanol and the direct production of reduced-iron steel, use hydrogen as part of a gas mixture, such as synthesis gas, for fuel or feedstock [58].

Figure 5 shows that 30% of global demand for hydrogen and synthetic fuels in 2050 is for industrial heating, 16% for ships, 6% for heavy long-haul road transport, 12% for aviation and 9% for buildings. The rest 27% is consumed for non-energy purposes.

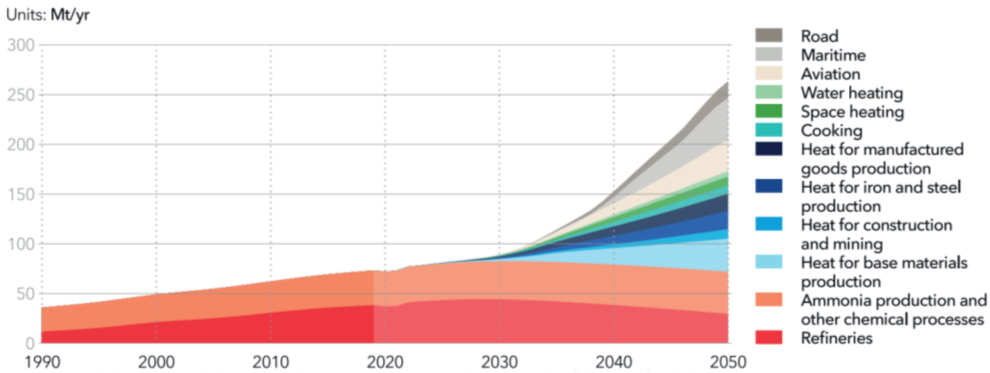

Figure 5. World hydrogen demand by sector. Source: [58].

2.1.1. Ammonia

At present, ammonia production is highly energy and emissions intensive: ammonia production consumes around 2% of the world's primary energy and generates 1% of total CO_2 emissions [73]. Its production is dependent on fossil fuels: more than 70% of ammonia is produced via SMR, while most of the remaining is produced via coal gasification.

On the other hand, less than 0.02 Mt of renewable ammonia was produced in 2021 [74]. Figure 6 summarises a way of producing green ammonia as well as some of its end uses.

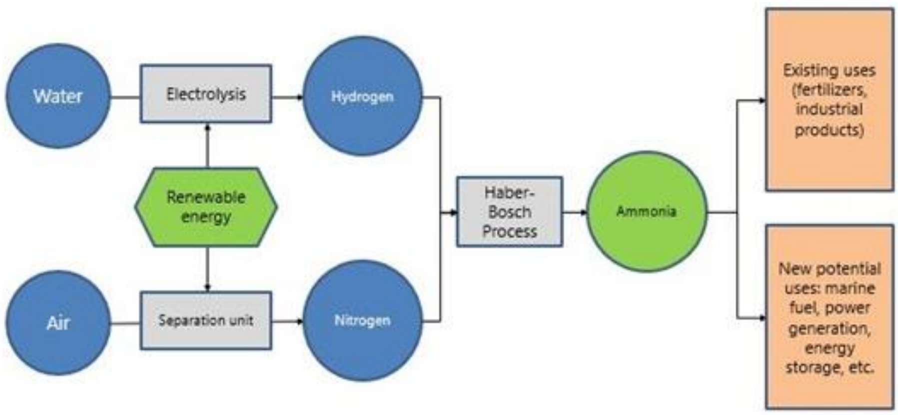

Figure 6. Green ammonia production and end uses. Source: [71].

183 Mt of ammonia were produced worldwide in 2020 (Figure 7), where China accounts for 29% of global production. 70 % of this ammonia is used for fertilisers, where the production of urea represents more than half of ammonia demand. The remaining is used in different industrial applications like plastics, explosives, or synthetic fibres. [69].

According to an IEA study, ammonia demand will nearly triple by 2050 from its 2020 levels [70] due to its potential uses as a:

- **Energy carrier:** The main advantage of ammonia over pure hydrogen is its greater volumetric energy content and its liquefaction temperature, which facilitates its transportation and storage. Indeed, the same amount of energy that is accumulated in one tank of ammonia would require two tanks of liquid hydrogen [30]. In addition to this, the infrastructure and practices to support reliable storage, distribution and export are already highly developed for ammonia.

- **Zero-carbon fuel:** Ammonia is especially suitable to serve as a shipping fuel, which represents an opportunity for the decarbonization of the maritime sector [27]. Its main drawback is that its use can lead to NOx and N_2O emissions [69].

- **Hydrogen carrier:** Ammonia is easier and cheaper to store and transport [72]. However, these transformations from H_2 to H_2 passing through NH_3 involve losses of 40% [10].

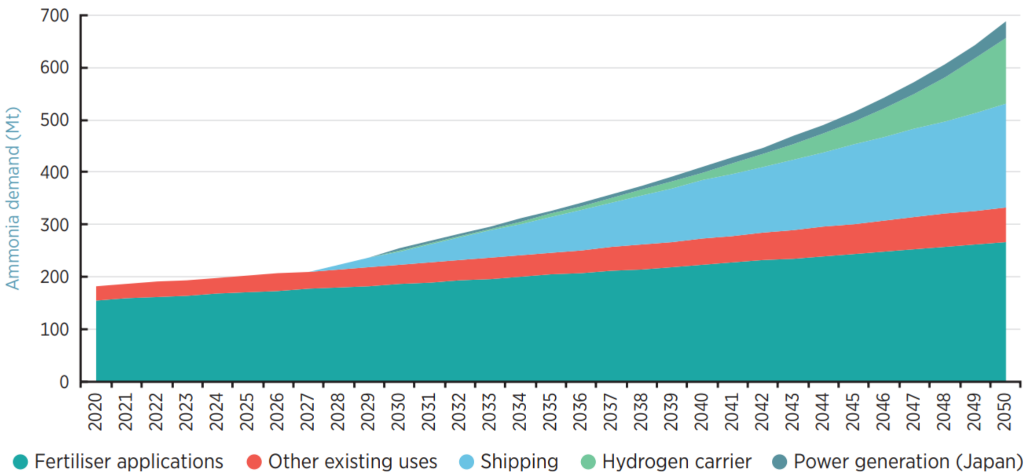

Figure 7. Expected ammonia demand up to 2050 for the 1.5°C scenario. Source: [74]

2.2. Risks of hydrogen

As it is shown in Table 3, the properties of hydrogen are quite different from conventional gaseous fuels like natural gas and liquified petroleum gas (LPG). However, if these differences are taken into account, hydrogen can be used as safely as any other fuel [76].

The main risks of hydrogen are the following:

- **Hydrogen leakage:** Due to its low viscosity and its high diffusivity, adequate sealing interfaces and suitable components must be used to prevent hydrogen systems from developing leaks [76].

  When hydrogen reaches the atmosphere, it reacts with hydroxile radicals, depleting atmospheric OH levels and delaying the neutralization of methane, ozone, and water vapor [64], contributing to an increase in global warming. However, the potential climate impacts of hydrogen-based energy systems would be significantly smaller than those of fossil fuel-based energy systems. A global hydrogen economy with a leakage rate of 1% of the hydrogen produced would result in a climate impact of 0.6% of the fossil fuel system it replaces, whereas a leakage rate of 10% would have an impact of 6% of that of the fossil fuel system [75].

- **Propensity to cause embrittlement:** Hydrogen embrittlement is a metal's loss of ductility and reduction of load bearing capability due to the absorption of hydrogen molecules by the metal. Hydrogen can cause embrittlement of high strength steels, titanium alloys and aluminium alloys producing cracks and fracture of the metals at stress under the yield stress.

- **Propensity to ignite:** As it is shown in Table 3, the range of hydrogen/air mixtures that can explode is wider than the ones for natural gas and LPG, ranging from 4 % v/v up to 75 % v/v. Nevertheless, the lower explosive limit is considered to be more important in hazard ranking than the width of the fuel's flammable range, and it is similar for natural gas (5.3% v/v), LPG (2.1 % v/v) and hydrogen (4 % v/v). Moreover, in the case of low momentum emissions, the dispersion characteristics of hydrogen will make the formation of a flammable mixture less likely.

On the other hand, hydrogen's ignition energy is only 0.02 mJ, whereas natural gas needs 0.29 mJ and LPG requires 0.26 mJ. This means that even tiny sparks like those generated by wearing certain types of clothing could ignite hydrogen/air mixtures and cause an explosion. Furthermore, hydrogen can spontaneously ignite when it is released from pressurized containers. However, the reason behind these spontaneous ignitions is not fully understood [76].

- **Propensity to detonate:** Detonations produce much more damage than ordinary explosions. Hydrogen/air mixtures are more likely to detonate than other common flammable fuels. Nevertheless, because of the fast speed at which hydrogen disperses, most detonations occur only in confined spaces.
- **Invisible flame:** Hydrogen flames are nearly invisible, making it difficult to detect and fight them.
- **Rapid burning rate:** As it is shown in Table 3, the maximum burning velocity of hydrogen is much greater than those of natural gas and LPG. This makes it difficult to confine hydrogen flames and results in higher explosion pressures [76].

Table 3. Properties of dry natural gas, LPG and hydrogen at 1 atm and 20 ºC. Source: [76]

Property	Dry natural gas (methane)	LPG (propane)	Hydrogen
Density $\left[\frac{kg}{m^3}\right]$	0.65	1.88	0.09
Diffusion coefficient in air $\left[\frac{cm^2}{s}\right]$	0.16	0.12	0.61
Viscosity $\left[\frac{g}{cm \times s}\right]$	0.651	0.819	0.083
Ignition energy in air [mJ]	0.29	0.26	0.02
Ignition limits in air [vol %]	5.3 - 15.0	2.1 - 9.5	4.0 – 75.0
Auto ignition temperature [ºC]	540	487	585
Flame temperature in air [ºC]	1875	1925	2045
Thermal energy radiated from flame to surroundings [%]	10 – 33	10 – 50	5 - 10
Detonability limits [% vol in air]	6.3 – 13.5	3.1 – 7.0	13 - 65
Maximum burning velocity [m/s]	0.43	0.47	2.6

2.3. Projects and investments in Spain

In October 2020 the Spanish Government published *la Hoja de Ruta del Hidrógeno: Una Apuesta por el Hidrógeno Renovable*, which details the action plan for hydrogen in Spain for 2030 and 2050.

The 2030 Vision foresees an installed capacity of 4 GW of electrolysers which will require investments estimated at 8.9 billion euros from public and private funds. However, [44] concludes that the investment in renewable hydrogen in Spain up to 2030 estimated in *la Hoja de Ruta* does not match the inversion announced by the energy companies (Figure 8). Using the data collected from the press:

- The sum of the investments of all projects is 14,493 million euros [44], 63% greater than the estimation in *la Hoja de Ruta.*
- The average specific investment is 6.18 M€/MW. If 4 GW of electrolysers are installed, the total investment would be of € 24.72 billion [44], 178% greater than the estimation in *la Hoja de Ruta.*
- The median specific investment is 4.21 M€/MW. For 4 GW, the investment would be €16.84 billion [44], 89% higher than the estimation in *la Hoja de Ruta.*

It should also be noted that the final investment will probably be lower than the estimation made from the projects announced at press, as the vast majority of the projects depend on the funds from Next Generation EU.

All in all, either the investment in *la Hoja de Ruta del Hidrógeno* is underestimated, or energy companies will not be able to undertake the investments they plan to make.

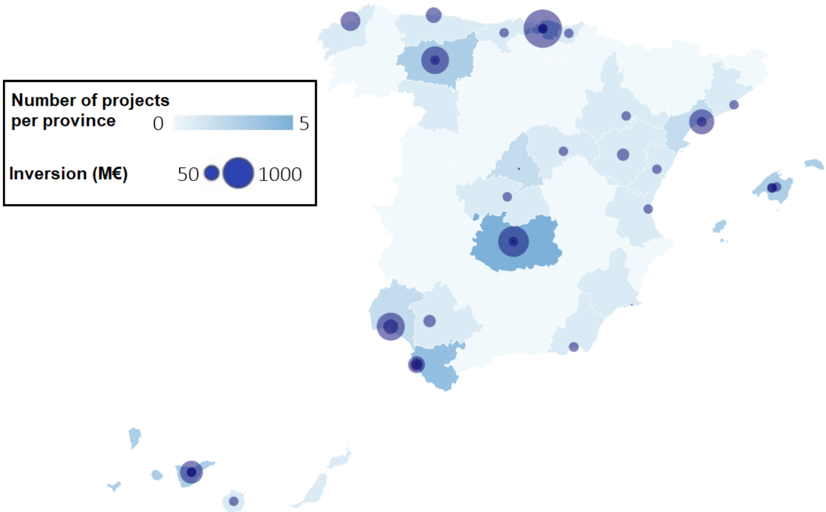

Figure 8. Projects announced in the press regarding hydrogen until December 2021. Adapted from [44]

2.4. Green hydrogen deployment potential in Huelva

Huelva has an enormous potential to lead the production of green hydrogen for its ideal climatic conditions, being one of the European cities with more sunny days per year, as well as for its water resources, land availability and industrial infrastructure [67], to which is added the huge availability of land in the port of Huelva, since it is Spain's largest port, with 1700 hectares [33].

Fertiberia produces and consumes 30% of all hydrogen converted into fuel in Spain and Palos' factory accounts for two thirds of this consumption [30]. In addition to this, the chemical cluster of Huelva represents the industrial cluster with the highest hydrogen consumption in Spain [26]. A common structure could be created, establishing a system of synergies among the different companies of the chemical cluster.

Moreover, as Fertiberia produces NH_3, hydrogen can be exported from the port of Huelva in the form of ammonia in ships that could be fuelled by NH_3. Furthermore, Huelva could become an ammonia bunkering spot, as it will be discussed at the end of the next section.

2.4.1. Projects in Huelva

Endesa plans to install a 100 MW electrolyser and to construct the associated renewable generation plants with a capacity of 430 MW in the province of Huelva, which will require an investment of 413 million euros [45].

In addition to this, Iberdrola and Fertiberia plan to install two electrolysers in Palos de la Frontera, the first with a capacity of 210 MW that can be in operation in 2024 [29] and will require an investment of 523 million euros [46], and the second one with a capacity of 370 MW which will be operational in 2027 [29] and will need an inversion of 701 million euros [46].

Finally, as part of the Positive Motion Plan, Cepsa will invest 3500 million euros in Huelva. The investment is earmarked for the production of biofuels and green hydrogen at two plants that are to be built on the company's land in Palos de la Frontera. Its construction is expected to begin in 2023 [47]. Cepsa plans to turn Huelva into the leader of the production of green ammonia for the maritime supply of all the ships that circulate in the Strait of Gibraltar. Huelva would thus make use of its strategic position in one of the busiest routes in the world, so that bunkering operations of this new type of fuel would skyrocket. This will position Huelva as one of the key nodes in global production [28].

3 CURTAILMENT

Curtailment describes any action that reduces the amount of electricity generated to maintain the balance between supply and demand. There are two main reasons behind renewable energy curtailment [61]:

- System-wide oversupply: It occurs when, on a large scale, there is not sufficient demand for all the available renewable electricity.
- Local transmission constraints: It occurs when there is insufficient transmission infrastructure to deliver the renewable electricity generated in a local area to a place where it could be used.

Variable renewable energy (VRE) is an intermittent non dispatchable technology. Thus, for increasing the generation of VRE, it is necessary to increase the flexibility of the power system. Some ways of increasing flexibility are grid expansion, energy storage and optimal ratios between wind and solar generation [60].

Increasing the exchange capacity in Europe helps the integration of renewables by providing more opportunities for the use of renewable energy. In fact, without network reinforcements, in 2030 49 TWh/year would be curtailed, while this volume increases to 244 TWh/year in 2040. This amounts to more than 1 % of annual RES generation in 2030 and 5 % in 2040. Germany and Spain are the most affected countries because of their high national share of RES generation [64].

The main challenge that powers systems with a high share of VRE will have to face is the reduction of inertia, which decreases the ability of the system to withstand power imbalances [60]. Inertia is the kinetic energy stored in synchronous generators which can be absorbed or injected into the grid to compensate momentary imbalances between demanded and generated power. This is essential for instantaneously balancing this mismatch until power plants are able to vary their output and restore the balance of the system [62]. However, these synchronous generators are being replaced by converted connected generators such as wind and solar, which do not provide inertia and results in a higher rate of change of frequency.

Two months have been selected to show how curtailment could develop during a regular day in the summer and in the winter of 2030 in Spain. Figure 9 and Figure 10 show the average curtailment in January and July respectively. It has been calculated from data provided by [39] as the average curtailment during each hour of the month. It can be seen that in both cases peak curtailment occurs around 15:00 pm. In addition to this, both wind and solar PV curtailment is greater during the summer.

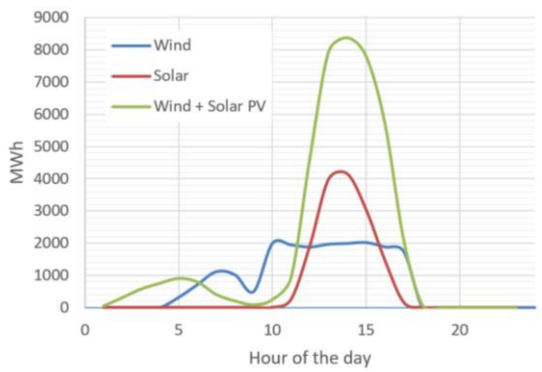

Figure 9. Curtailment in January. Based on [39]

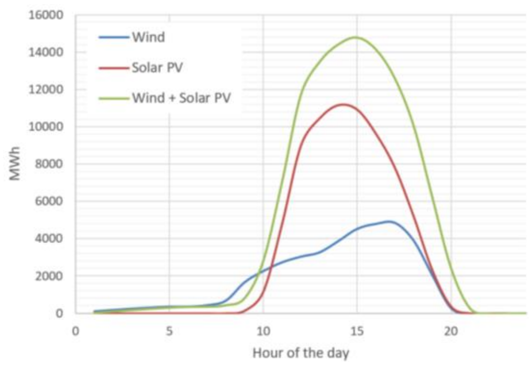

Figure 10. Curtailment in July. Based on [39]

4 PRODUCTION PROCESS

4.1. Overview of the process

Figure 11 shows a schematic representation of the process.

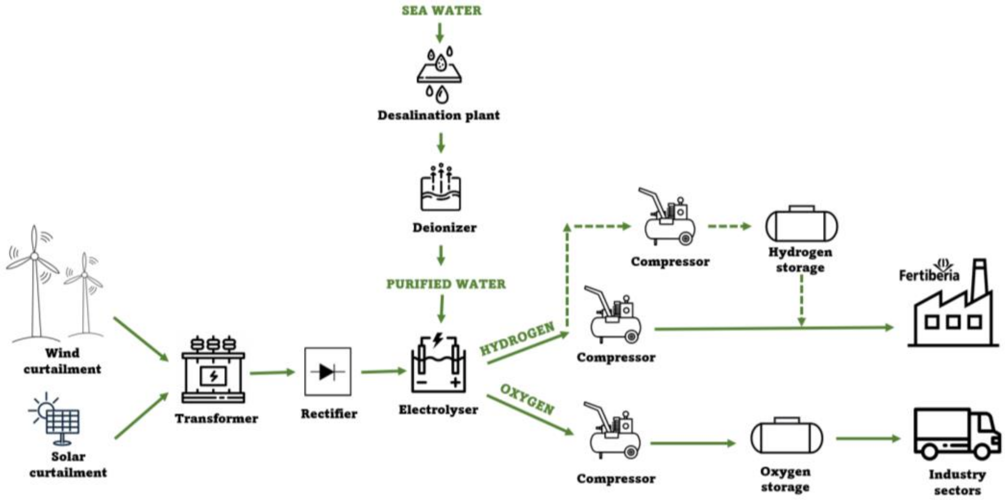

Figure 11. Production of electrolytic hydrogen from curtailed electricity

4.2. Hydrogen storage

4.2.1 Fertiberia storage needs

4.2.1.1 Annual demand of hydrogen

The Fertiberia Group annual ammonia production in 2020 was 508800 tonnes [6]. The annual report only provides data on ammonia production at Puerto Llano (400,000 tonnes). Assuming that Fertiberia only produces ammonia at the Palos de la Frontera and Puerto Llano plants, the annual production at Palos was 108800 tonnes of ammonia. Supposing that the production in 2020 will be the same as that of 2030, 19340 tonnes of hydrogen will be needed every year.

4.2.1.2 Operating time

The nominal capacity of Fertiberia's plant at Palos de la Frontera is 1130 t/day of anhydrous ammonia [23]. The optimum way of operating is by avoiding start-ups and shutdowns of the reactors, therefore, based on the nominal capacity and annual production data of the plant, it has been estimated that the factory operates only for 96 days and 7 hours consecutively at full load.

4.2.1.3 Hourly material balance in the storage system

An hourly material balance has been conducted to determine the maximum tonnes of hydrogen that will need to be stored throughout the year 2030 to size the storage system.

For each hour in which hydrogen is produced:

$$H_2\,produced\,[i] = \frac{Installed\ power\ [MW] \times 1\ h}{\eta \left[\frac{MWh}{t}\right]}$$

- The entire hydrogen production is stored during the hours in which the chemical facility is not operating:

$$H_2\,stored\,[i+1] = H_2\,stored\,[i] + H_2\,produced\,[i]$$

- During the hours in which the plant is operating, the hydrogen produced will be transported directly by pipeline from the electrolyser to the factory until the hourly demand is met. If less tonnes are produced in hour I, the remaining hydrogen will be transported from the storage system to the factory also via pipeline. If the production exceeds the hourly demand, the surplus is stored.

$$H_2\,stored\,[i+1] = H_2\,stored\,[i] - (Hourly\ H_2\,demand - H_2\,produced\,[i]\,)$$

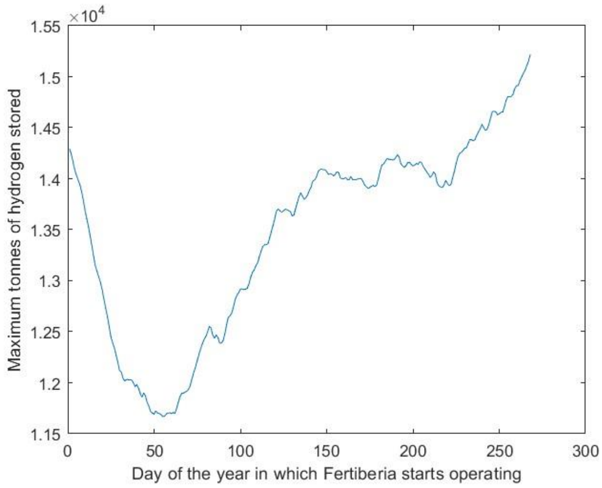

Figure 12. Tonnes of hydrogen vs day in which Fertiberia starts operating.

Figure 12 shows the maximum amount of hydrogen that needs to be stored as a function of the day of the year in which Fertiberia starts operating.

- The minimum amount of hydrogen that needs to be stored are 11670 tonnes, when the factory starts operating on the 55th day of the year.
- The maximum amount of hydrogen are 15217 tonnes, when Fertiberia begins to operate on the 268th day of 2030.

Figure 13 and Figure 14 show the evolution of the amount of hydrogen stored during 2030, if Fertiberia starts operating on the 55th and the 268th day respectively. If hydrogen is stored in a salt cavern, the curve will be shifted upwards, as there is minimum amount of hydrogen that needs to remain in the cavern for ensuring its stability[1].

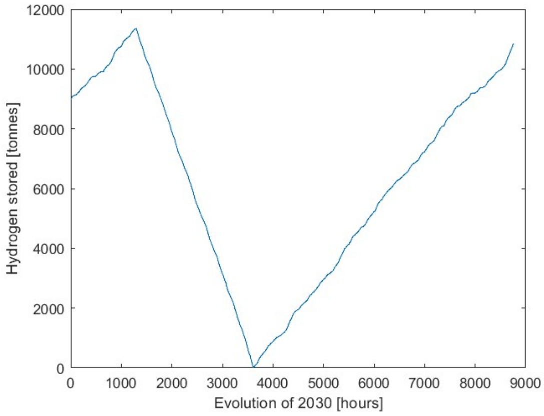

Figure 13. Hydrogen stored starting on the 55th day

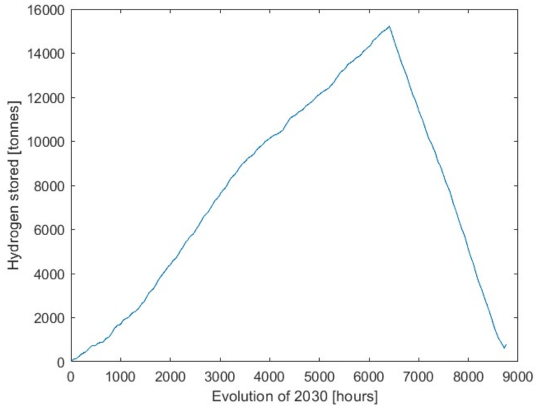

Figure 14. Hydrogen stored starting on the 268th day

Hydrogen storage allows decoupling its production from its consumption. Hydrogen is generated throughout the whole year, but it is only consumed during a few months (Figure 15), which results in large storage needs.

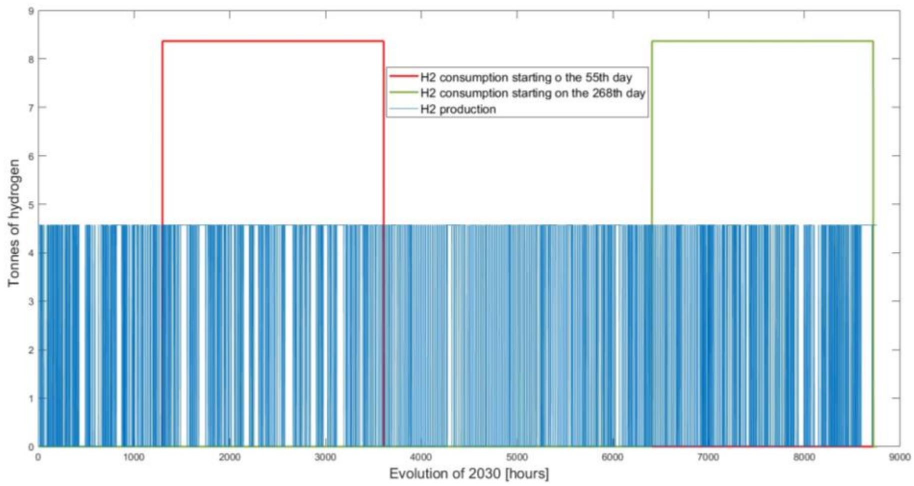

Figure 15. Production and consumption of hydrogen

4.2.2 Selection of the storage method

For storing large quantities of hydrogen, underground storage offers the best prospects. However, for small-scale applications, the most common way to store this gas is in compressed hydrogen gas tanks [49]. Table 4 shows the characteristics of the different types of underground storage methods. Salt caverns appear to be the most promising underground storage method due to their low construction cost, low risk of leakage, fast gas injection and extraction rates, and their low need for cushion gas. In addition to this, salt structures do not react with hydrogen. Therefore, two alternatives will be considered in this project: storing gaseous hydrogen in compressed tanks and in salt caverns.

[1] Further explanation can be found in section 4.2.2.1.3.

Table 4. Underground storage. Adapted from [2].

Storage type	Depleted field	Aquifer	Salt cavern	Lined rock cavern
Depth	300-2700 m	400 – 2300 m	300 – 1800 m	1000 m
Operating pressure	15 – 285 bar	30 – 315 bar	35 – 210 bar	20 – 200 bar
Cost of development (relative)	Low	Low	Low	High
Cost of operation (relative)	Low	Low	Medium	Medium
Geological availability	Most of Europe	Most of Europe	Primarily northwest Europe; 9 EU member states, the UK, Norway, Bosnia & Herzegovina, and Albania	Anywhere with igneous or metamorphic rock
Working gas capacity / Total gas capacity	50 -60 %	20 – 50 %	70 %	+70%
General suitability for hydrogen	Site-specific	Site-specific	High	High

4.2.2.1 Salt cavern

4.2.2.1.1. Salt cavern construction

Salt deposits are usually found in two forms: salt domes and bedded salt deposits. Salt domes are the best option as the salt mass is large and homogeneous, facilitating the design of the cavern.

When the layer of the bedded salt is not very thick (60-100 m) horizontal drilling techniques are required. However, salt caverns are usually built in salt domes and bedded salt deposits by solution mining. It consists in dissolving the salt by pumping water into the salt deposit until it becomes saturated. Around 7-8 m^3 of fresh water are required for dissolving 1 m^3 of salt [9]. The brine is pumped to the surface, creating a cavity in the salt formation. This leaching process may take from 2,5 to 4 years [3].

Firstly, a vertical borehole is drilled from the surface to the depth of the salt deposit, which is then equipped with two free hanging pipes known as casings, creating three annular spaces. The outer space is used for the injection of a blanket medium which prevents the salt in the roof area from being accidentally leached. Nitrogen or oil are commonly used as a medium blanket [4] as they both have a lower density than water and do not dissolve the salt.

Depending on which space is used for injecting water, two operational procedures are distinguished (Figure 16):

- Direct circulation: Water is pumped through the central pipe and brine is withdrawn through the space between the inner and outer leaching strings. A lower concentration of brine is obtained, and the resulting shape is cylindrical with larger diameters at the base of the cave.
- Reverse circulation: Water is injected between the inner and outer leaching strings, while brine circulates through the central tube. Caverns constructed using reverse circulation present an inverted cone shape and have less geomechanical stability [8].

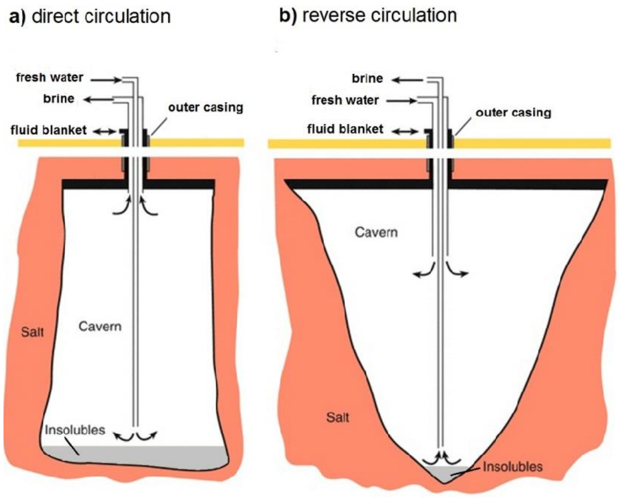

Figure 16. Direct and reverse circulation.

A combination of both methods is frequently implemented in order to achieve the desired cavern shape. The shape is monitored regularly by sonar surveys and once the cavern reaches the required size, the leaching strings are withdrawn.

4.2.2.1.2. Hydrogen leakage

Hydrogen leakage in a salt cavern depends on the depth at which the cavern is located. Rock salt is one of the geological materials with the lowest permeability, and consequently, these small leakages have been considered negligible. Assuming that the cavern is located 1000 meters underground, it would have a leakage rate of only 0.03% [48].

4.2.2.1.3. Volume of the cavern

To maintain the minimum pressure in the cavern and ensure its stability, 30% of the stored hydrogen has to remain in the cavern. This gas is known as cushion gas. Therefore, the tonnes (m_{cavern}) that have been considered for its dimensioning are:

$$m_{cavern} = \frac{m_{max}}{0.7}$$

Where m_{max} is the maximum of the vector $H_2\, stored\ [i]$, i.e., the maximum amount of operational gas required to be stored in a given hour of 2030.

Due to the lack of characterisation of the geometrical shape of the cavern, it will be assumed that the temperature remains constant in the cavern. The higher the height of the cavern, the greater the deviation in the volume obtained, as temperature gradients between the highest and lowest part of the cavern increase.

- Temperature: A surface temperature of 15ºC has been supposed and a gradient of 25ºC/km has been assumed as in reference [1].

$$T[°C] = 15 + 0.025 \times Depth\ [m]$$

For a depth of 1000 metres, the temperature obtained is 40ºC.

- Pressure: The cavern will operate at variable pressure. This is the most frequently used mode of operation for gas storage. The maximum pressure has a value lower than the fracture pressure of the halite and the minimum pressure must ensure the stability of the cavern.

  It is also possible to operate at constant pressure, but this mode of operation requires compensating the extracted gas by displacing brine. In addition, the hydrogen removed from a cavern operating at constant pressure contains a high proportion of water and salts [3].

  From Figure 17 it was derived that the cavern will operate between 70 and 175 bar.

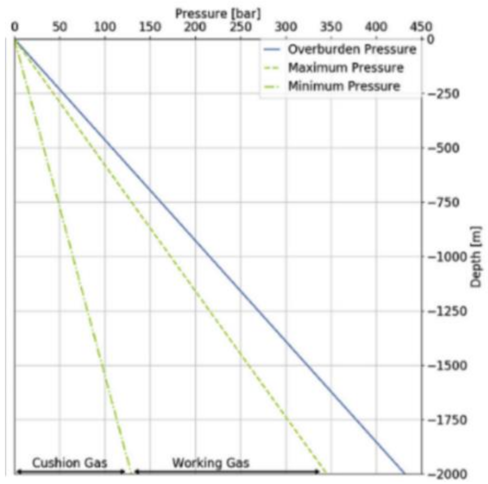

Figure 17. Depth [m] vs pressure [bar]. Source: [1].

$$Size\ of\ the\ cavern\ [m^3] = m_{cavern} \times \frac{1}{\rho_{H_2}}$$

$$\rho_{H_2} = \frac{P \times M}{Z \times R \times T} = 12.39\,\frac{kg}{m^3}.$$

Z=1.1 [43]

Therefore, the minimum and the maximum size of the cavern are $1.34 \times 10^6\ m^3$ and $1.75 \times 10^6\ m^3$.

4.3. Electrolyzer

4.3.1 Selection of the electrolyzer technology

Table 5 summarises the characteristics of the most used electrolyser technologies at present:

Table 5. Electrolyser technologies. Adapted from [22],[66].

	Alkaline	**PEM**	**SOEC**
Electrolyte	Potassium hydroxide (KOH)	PFSA membranes	YSZ
Operating temperature	70-90 ºC	50-80ºC	700-850 ºC
Operating pressure	1-30 bar	< 70 bar	1 bar
Cold-start time [min]	< 60	< 20	< 60
Stack lifetime [h]	60000-90000	20000-60000	< 10000
Cell voltage [V]	1.8-2.4	1.8-2.2	0.7-1.5
System response	Seconds	Milliseconds	Seconds
Lower dynamic range [2][%]	10-40	0-10	>30
Capital cost $\left[\frac{€}{kW_e}\right]$	1000-1200	1860-2320	>2000

A PEM electrolyzer will be installed as it is the natural choice for an intermittent energy supply due to its cold start capability, its fast start-ups and shutdowns and because PEM electrolysers are the ones that have the highest operational flexibility.

On the other hand, even though PEM electrolyzers use noble metals and complex membrane materials, they do not use aggressive chemicals (e.g.. KOH in Alkaline electrolyzers) [14].

4.3.2 Minimum power that meets hydrogen demand

In order to calculate the minimum power that satisfies the demand of Fertiberia, it has been assumed that the electrolyser only operates at nominal capacity, i.e.. hydrogen will only be produced in the hours in which the surplus of renewable energy is greater than the installed power.

$$\frac{Installed\ power\ [MW] \times i^*[h]}{\eta \left[\frac{MWh}{t}\right]} = H_2 annual\ demand\ [t] + H_2\ losses\ during\ compression\ [t]$$

[2] Minimum operable hydrogen production rate relative to maximum specified production rate.

- $i^*[h]$ is the number of hours in which the electrolyser is operating. It has been obtained that the using the following if statement:

$$\text{If } curtailment\ [i] \geq Installed\ power\ [MW]$$

$$i^* = i^* + 1$$

  - Where curtailment [i] is a vector that contains the hourly surplus of wind and solar energy estimated for 2030 provided by [39].

- η=52.5 MWh/t, as current electrolysers can produce 1 kg of hydrogen from 52.5 kWh [37].
- H_2 losses are estimated in the next section.

It has been obtained that the minimum power that meets the demand of Fertiberia is 240 MW, and that the electrolyser only operates for 4716 h every year, which results in a utilization rate of 53.84%. According to [14] 100 MW modules will be available by 2023. Thus, 2 modules of 100 MW and 4 modules of 10 MW will be installed.

4.3.2.1 Hydrogen losses during compression

- For underground storage compression losses represent approximately 8.5% molar while for tank storage at 250 bar they can be estimated at 9% [22].
- Today's hydrogen pipelines associated with industrial facilities such as oil refineries and chemical plants, operate at around 500–1200 psi [40]. Assuming hydrogen will be transported at 1200 psi, compression losses would be around 7% molar [22]. They only need to be included when hydrogen is transported from the electrolyser to Fertiberia. When hydrogen is transported from the storage system to the factory, it will be decompressed at the outlet of the storage unit until the required pressure in the pipeline is reached.

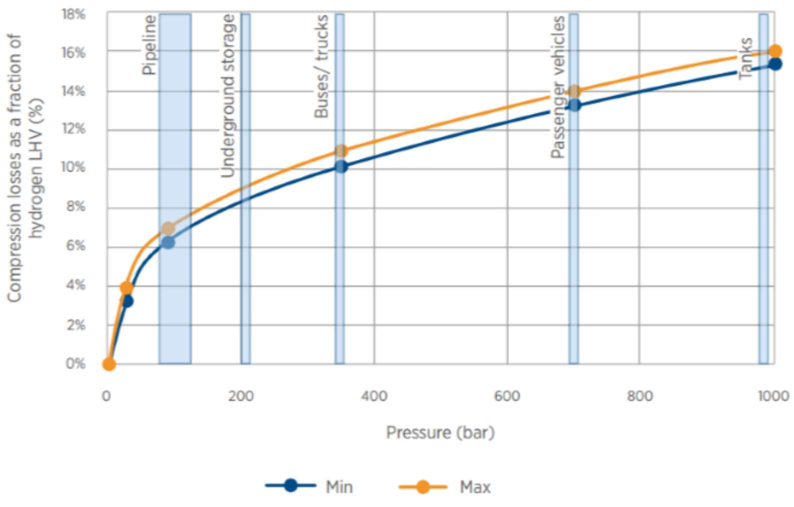

Figure 18. Hydrogen losses during compression. Source: [22].

4.3.3 Oxygen production

From the annual demand of hydrogen, knowing that by each mole of hydrogen half a mole of oxygen is produced, we can obtain that 154720 tons of oxygen are generated each year.

One strategy to cut down the cost of hydrogen production is effective utilization of this by-product. Some of the potential uses for oxygen are blast furnaces, food manufacturing, electric arc furnaces, medical care[3] [10] and wastewater treatment [11].

4.3.4 Water consumption

Hydrogen production is highly dependent on water resources and can be vulnerable to water shortages. Some potential water sources include sea water, water from the public grid, water from rivers or ground water. Since Huelva has limited water resources and environmental restrictions are expected to increase due to climate change, sea water will be chosen as feedstock.

In order to produce 19340 tons of hydrogen, 174060 tons of water are required every year considering the stoichiometry of the reaction. However, water needs are estimated to be 85% higher than the stochiometric requirements because of transport losses (10%), collection losses (5%), water losses during the desalination process via reverse osmosis (35%), losses owing to evaporations and leaks at the electrolyser input (10%), water needed for cleaning (25%) and an additional 10% of water has been considered to ensure there are not any shortage risks [17]. Taking this into account, 322011 tons of sea water are needed yearly.

4.4. Water treatment

Currently available desalination technologies on the market are based on thermal processes, membrane processes or a combination of these. Examples of membrane processes are reverse osmosis (RO) and electro-dialysis (ED). Some examples of thermal processes are vapor compression distillation (VCD), multiple-effect distillation (MED), membrane distillation (MD) and multi-stage flash evaporation (MSF) [38].

In this project, sea water will be treated via reverse osmosis, as it is the most widespread and advanced system at present, as it is used by 69% of the world's desalination facilities [16]. However, in many cases, the resulting purity of RO water still does not reach the high purity electrolysers require. Type I or II water as defined by the ASTM is needed in some cases, with a conductivity lower than 0.056 and 1 μS/cm respectively, whereas other electrolyzers require a less demanding purity (<5 μS/cm) [17]. Therefore, a deionization unit will be added after the water desalination.

It should be noted that direct sea water splitting has not been considered in this project because it is not economically meaningful, as the CAPEX and OPEX of water purification are insignificant compared to those of water electrolysis [79].

4.4.1 Water desalination

Figure 19 shows a representation of how water is desalinated via reverse osmosis. The next steps need to be followed:

1) Water is collected from an ocean depth of at least five meters at a very slow pace (0.1 m/s) so that the fish can swim against the flow.

2) Pre-treatment: Water passes through filters which can be sand-based, or materials called ultrafiltration

[3] The sale of oxygen is not considered in this project. However, reference [52] indicates that medical oxygen can be sold for 4,32 €/kg at 200 bar and 6,51 €/kg at 300 bar. This would result in profits of 668 390,4€/year and 1 007 227,2 €/year respectively (from which compression costs would have to be deducted).

membranes. Then, water is pumped through a cartridge filter to make sure there are not any impurities left in the salt water.

3) Reverse osmosis and energy recovery: Water is pressurised so that it passes through a series of very thin membranes with approximately atom sized holes, whereas salty water remains on the other side. In order to get back the energy from this salty water, it passes through an energy recovery device before returning it back to the ocean.

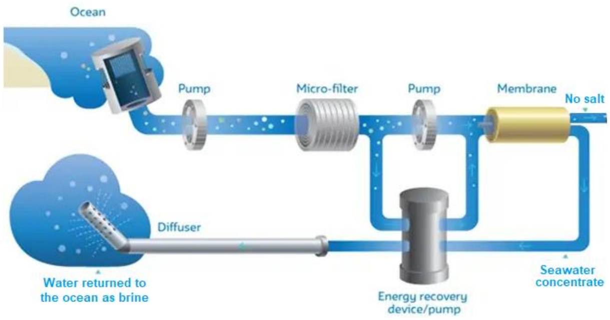

Figure 19. Water desalination. Adapted from [15].

4.4.2 Deionizer

A deionizer uses two opposing charged resins:

- A cationic resin that removes the cations. It is precharged with hydrogen ions on its exchange sites and it is usually made from styrene containing sulfonic acid groups [36].
- An anionic resin that removes the anions. It is precharged with hydroxide ions on its exchange sites and it is usually made from styrene containing quaternary ammonium groups [36].

Mixed bed resin is a mix of both cation and anion resin, whereas in a dual bed system the cationic resin and the anionic resin are in separate vessels. A mixed bed resin has been selected instead of a dual bed system, as it produces water with lower conductivity[4] [50].

Reference [51] indicates that water to be treated in a polishing mixed bed should have a conductivity ≤5 µS/cm. As the conductivity of water treated with a two-stage reverse osmosis machine is 2-3 µS/cm [57], there is no need to install a working mixed bed before the polishing mixed bed.

Subtracting from the total water requirement transport losses (10%), collection losses (5%) and water losses during the desalination process via reverse osmosis (35%), the flow that arrives at the deionizer is 26,8 $\frac{m^3}{h}$.

The model Deyolit AMB 7500 from the Spanish company Culligan was chosen. It is a mixed bed that can treat 6,8 $\frac{m^3}{h}$ [53]. Hence, 4 deionizers are needed.

[4] Technical data of a mixed bed in reference [51] indicates that the conductivity obtained is ≤ 0.08 µS/cm.

5 PROCESS FLOW DIAGRAM

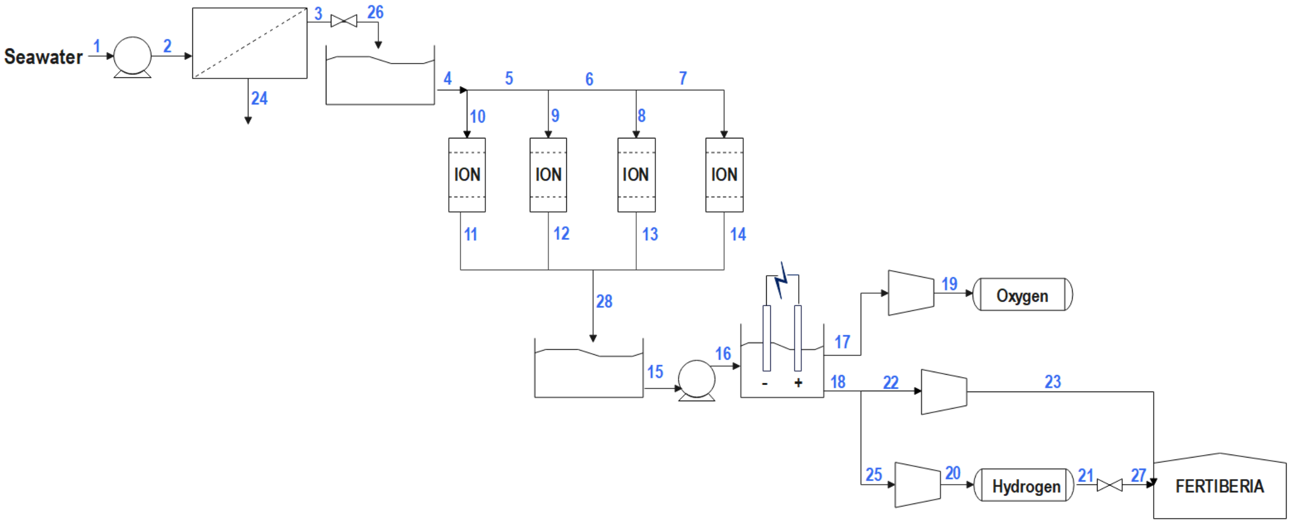

Figure 20. Process flow diagram.

Table 6 shows the flow, temperature, pressure, composition, and relevant parameters of all currents.

- Numbers shown in italics indicate that the value has been estimated.
- For all the streams in which a range appears, the left value indicates the flow if Fertiberia starts operating on the 55th day, and the right one is the value of the flow if the factory starts on the 268th day.
- The pressure exerted by the water column has been neglected in all flows except for flow number 1 which has been calculated assuming that water is collected from an ocean depth of five meters [17].
- Pressure of current 19 has been estimated considering that oxygen will be used for medical purposes.

Table 6. Flows

Number	Flow $\left[\frac{tons}{year}\right]$	Temperature [ºC]	Pressure [atm]	Composition	Relevant information
1	313308	*25*	1.5 [17]	Seawater	5% collection losses
2	295902	*25*	120 [78]	Seawater	10 % water losses during transportation
3	234981	*25*	55 [78]	Desalinated water	Conductivity: 2-3 µS/cm
4	234981	*25*	1	Desalinated water	Conductivity: 2-3 µS/cm
5	176235.75	*25*	1	Desalinated water	Conductivity: 2-3 µS/cm

6	117490.5	*25*	1	Desalinated water	Conductivity: 2-3 μS/cm
7	58745.25	*25*	1 [80]	Desalinated water	Conductivity: 2-3 μS/cm
8	58745.25	*25*	1 [80]	Desalinated water	Conductivity: 2-3 μS/cm
9	58745.25	*25*	1 [80]	Desalinated water	Conductivity: 2-3 μS/cm
10	58745.25	*25*	1 [80]	Desalinated water	Conductivity: 2-3 μS/cm
11	58745.25	*25*	1*	Purified water	Conductivity: ≤ 0.08 μS/cm
12	58745.25	*25*	1*	Purified water	Conductivity: ≤ 0.08 μS/cm
13	58745.25	*25*	1*	Purified water	Conductivity: ≤ 0.08 μS/cm
14	58745.25	*25*	1*	Purified water	Conductivity: ≤ 0.08 μS/cm
15	234981	*25*	1	Purified water	Conductivity: ≤ 0.08 μS/cm
16	234981	*25*	35	Purified water	Conductivity: ≤ 0.08 μS/cm
17	154720	*25*	30 [77]	Oxygen	-
18	19340	*25*	30 [77]	Hydrogen	-
19	154720	*25*	136 [81]	Oxygen	-
20	[11670, 15217]	*25*	From 70 to 175	Hydrogen	Cavern operates at variable pressure
21	[11670, 15217]	*25*	From 70 to 175	Hydrogen	Cavern operates at variable pressure
22	[7670, 4123]	*25*	30 [77]	Hydrogen	-
23	[7670, 4123]	*25*	82 [40]	Hydrogen	-

24	60921	*25*	120*	Brine	35 % water losses during desalination
25	[11670, 15217]	*25*	30 [77]	Hydrogen	-
26	234981	*25*	1	Desalinated water	-
27	[11670, 15217]	*25*	82 [40]	Hydrogen	-
28	234981	*25*	1	Purified water	-

*Assuming there is no pressure drop.

6 LOCATION

6.1. Estimation of the area

- **Desalination:** Reference [55] treats 124 445 m^3/day and the total constructed area of the desalination plant is 4420 m^2. Applying a scaling factor of 0,4, the area required for the desalination plant is 610,4 m^2.
- **Deionization:** As the area occupied by each deionizer Deyolit AMB 7500 is 1 m^2 [53], 4 m^2 are needed.
- **Electrolyzer:** In 2018, McPhy proposed that a 100 MW facility composed of five modules of 20 MW each would occupy 4500 m^2 [22]. As the nominal power of the electrolyzer is 240 MW, the area that the electrolyzer will require could be estimated as 2.2 times 4 500 m^2, which amounts to a total area of 9900 m^2.
- **Tanks:** In section 7.1.2.1 it is estimated that the maximum number of tanks needed to store hydrogen is 69 169. As each tank has a length of 12.2 m and a diameter of 1.1 m [18], assuming that tanks will be stacked on top of each other forming four rows, 232 061 m^2 would be needed.

  In addition to the large amount of space they occupy, tanks will be discarded because of their high cost, as it will be discussed in section 7. Therefore, tanks have not been considered for the calculation of the area.

Taking this into account, the minimum area of the plot should be 10 514,4 m^2.

6.2. Facilities location and hydrogen pipelines

All the equipment previously mentioned will be located in the red section shown in Figure 21, whose coordinates are (37.17, -6.89) and has a total area of 13 956 m^2. This the project will be carried out on a greenfield site, as the project starts from scratch and the required infrastructure is not present yet.

Figure 21 also includes a blue line that represents the pipelines that transport hydrogen from the electrolyzer to the chemical plant.

Figure 21. Palos de la Frontera

6.3. Seawater pipelines

Figure 22 shows the path from the sea to the desalination plant when pipelines cross the river Odiel, while Figure 23 shows a different path that goes around the river. The former needs 4.51 km, whereas the latter requires 13.3 km, assuming in both cases that water will be collected 1 km away from the coast.

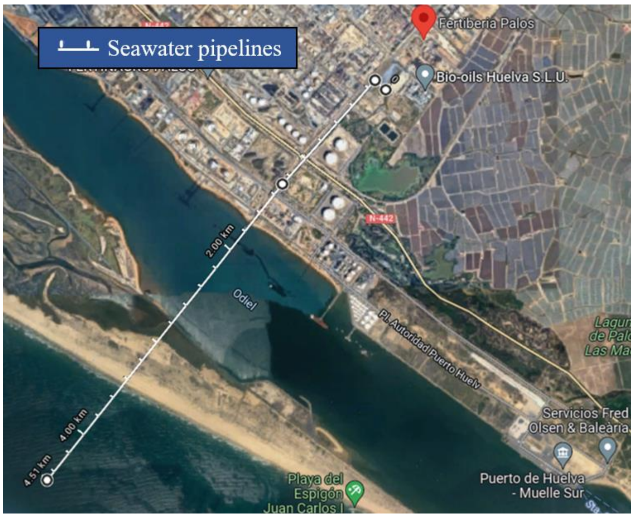

Figure 22. Pipelines crossing Odiel.

Figure 23. Pipelines going around Odiel.

7 ECONOMIC ANALYSIS

The CAPEX and OPEX have been calculated in four different scenarios:

- Case 1 is the best-case scenario that provides the minimum investment that would have to be undertaken: the amount of hydrogen to be stored is the minimum (the factory starts operating on the 55th day), and in addition to this, it uses the most economic estimates for the different costs.
- Case 2 is the worst-case scenario. It gives an estimate of the maximum investment to be undertaken: the amount of hydrogen that needs storage is the maximum (Fertiberia starts operating on the 268th day) and the most expensive estimations are used for the calculation of the different costs.
- Case 3 is the same as case 1 except that hydrogen is stored in pressurised tanks.
- Case 4 is like case 2 but hydrogen is stored in pressurised tanks.

7.1. CAPEX

7.1.1 Compressors

The electrical power of the three different compressors can be estimated with the following formula:

$$W_{elec} = \left[\dot{m} \times \left[\frac{R \times T_{in} \times \gamma}{(\gamma - 1)} \times \left[\left(\frac{P_{out}}{P_{in}} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \right] \right] \times \eta_g$$

Where:

- $R = 8{,}314 \frac{J}{mol \times K}$.
- $\gamma = 1{,}41$.
- $\dot{m} = 1{,}16 \frac{kmol}{s}$, considering that Fertiberia operates for 96 days and 7 hours and that 19340 tons of hydrogen are produced yearly.
- η_g was assumed to be 0.93.
- T_{in} was assumed to be 25 ºC.

Reference [13] does not provide information on the type of compressor but it should be a positive displacement compressor as it works with large volumes of hydrogen.

Table 7 shows the results for the minimum and maximum price using data from reference [13]. It provides two prices per MW: $1{,}07 \frac{M€}{\text{MW}}$ (Bafumé et al) and $0{,}65 \frac{M€}{\text{MW}}$ (Jacobs, Element Energy).

Table 7. Compressor costs.

Compressor	W_{elec}	**Minimum cost** $[M€]$	**Maximum cost** $[M€]$
Tank compressor	40,96 MW	26,63	43,83
Cavern compressor	35,92 MW	23,35	38,43
Pipeline compressor	26,73 MW	17,37	28,60

7.1.2 Hydrogen storage

7.1.2.1 Tanks

Reference [18] provides the cost for buying 400 vessels of 220 kg each at 76 851 $/vessel.

- The minimum number of vessels needed are:

$$\frac{11670 \times 10^3\ [kg]}{220\ \frac{kg}{vessel}} = 53046\ vessels$$

52800 vessels will be bought at 76851$/vessel. For the remaining 246 vessels, a scaling factor of 0.6 was applied:

$$Minimum\ cost\ [€] = \left[52\ 800\ vessels \times \frac{76\ 851\$}{vessel} + 246\ vessels \times \left[\frac{76\ 851\ \$}{vessel} \times \left[\frac{246}{400}\right]^{0,6}\right]\right] \times \frac{0,95\ €}{1\ \$}$$

$$= 3,86826 \times 10^9\ €$$

- The maximum number of vessels are:

$$\frac{15217 \times 10^3\ [kg]}{220\ \frac{kg}{vessel}} = 69169\ vessels$$

69800 vessels will be bought at 76851 $/vessel. For the remaining 369 vessels, a scaling factor of 0.6 was applied.

$$Maximum\ cost\ [€] = \left[68\ 800\ vessels \times \frac{76\ 851\ \$}{vessel} + 369\ vessels \times \left[\frac{76\ 851\ \$}{vessel} \times \left[\frac{369}{400}\right]^{0,6}\right]\right] \times \frac{0,95\ €}{1\ \$}$$

$$= 5,04865 \times 10^9\ €$$

7.1.2.2 Salt cavern

The price of the salt cavern can be estimated as 334 $\left[\frac{€}{MWh_{H2\,stored}}\right]$ [13].

$$[M€] = 334\left[\frac{€}{MWh_{H2\,stored}}\right] \times \frac{1\,M\,€}{10^6€} \times \frac{1\,h}{3600\,s} \times PCI\left[\frac{MJ_{H2}}{tons_{H2}}\right] \times Storage\ capacity[tons_{H2}]$$

- The minimum price is 129.9 $M€$
- The maximum cost is 169.4 $M€$

7.1.3 Water desalination

Reference [17] considers a flow of 700 $\frac{m^3}{day}$, which is similar to the electrolyzer demand: 882$\frac{m^3}{day}$. Thus, [17] can be considered as a good estimate of the investment costs of desalinating water in this project.

- 80 000 € for water abstraction (pipes, sand removal, pump and accessories, infrastructure).
- 218 584 €/km for water transport.
- 380 000 € for water storage.
- 675 000 € for water treatment (Pre-treatment and reverse osmosis).
- 150 000 € for the disposal of brine.

Taking this into account, the total investment cost for water desalination is 2.27 $M€$ if pipelines are 4.51 km long and for 13.3 km, an investment of 4.19 $M€$ is required.

7.1.4 Deionizer

The price of four deionizers Deyolit AMB 7500 amounts to a total cost of 186 648 € [53].

7.1.5 Electrolyzer

Table 8 summarizes the investment costs of PEM electrolyzers in 2030 from four different sources.

Table 8. PEM electrolyzer investment cost in 2030. Adapted from [13].

Source	Min [€/$MW_{H2\ out}$]	Max [€/$MW_{H2\ out}$]
IEA	0.841	2.095
IRENA	1.037	1.037
JRC	0.998	2.457
Schmidt	0.772	2.739
Average	0.912	2.082

$$[M€] = \frac{Price\ per\ MW\left[\frac{€}{MW_{H2\ out}}\right] \times PCI\left[\frac{MJ_{H2\ out}}{ton}\right] \times Installed\ capacity[MW_e]}{\eta\left[\frac{MW_e h}{kg}\right] \times \frac{1000\ kg}{1\ ton} \times \frac{3600\ s}{1\ h}}$$

- The minimum price is 0.139 $M€$. It was calculated using the minimum average price from Table 8 and the minimum storage needs of hydrogen estimated in section 4.2.1.3.
- The maximum price is 0.317 $M€$. It has been calculated using the maximum average price from Table 8 and the maximum hydrogen storage needs.

7.1.6 Results

Table 9 and Figure 24 show that for all cases, hydrogen storage represents, by far, the most significant cost, ranging form 129.9 $M€$ in case 1 to 5058.7 $M€$ in case 4. Thus, the option that has lower investment costs is, by far, the storage of hydrogen in salt caverns.

Table 9. Delivered-equipment investment cost summary.

	Case 1 [$M€$]	**Case 2** [$M€$]	**Case 3** [$M€$]	**Case 4** [$M€$]
Compressor	40.7 (23.5%)	67.0 (27.8%)	44.0 (1.1%)	72.4 (1.4%)
Storage	129.9 (75.0%)	169.4 (70.3%)	3868.3 (98.8%)	5058.7 (98.5%)
Desalination	2.3 (1.3%)	4.2 (1.7%)	2.3 (0.1%)	4.2 (0.1%)
Deionization	0.2 (0.1%)	0.2 (0.1%)	0.2 (0.0%)	0.2 (0.0%)
Electrolyzer	0.1 (0.1%)	0.3 (0.1%)	0.1 (0.0%)	0.1 (0.0%)
Total	173.3	241.2	3914.9	5125.8

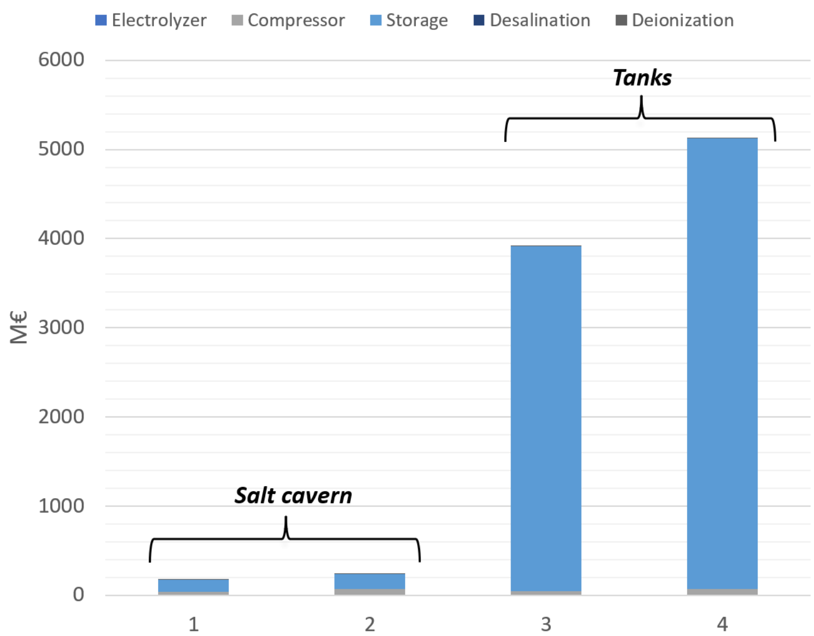

Figure 24. Delivered-equipment investment cost.

The total capital investment can be obtained by multiplying the equipment cost by a Lang factor of 6 [82]. Table 10 summarises the results.

Table 10. CAPEX

	Case 1 $[M€]$	**Case 2** $[M€]$	**Case 3** $[M€]$	**Case 4** $[M€]$
CAPEX	1039.8	1447.2	23489.4	30754.8

7.2. OPEX

7.2.1. Compressors

The variable OPEX is zero as compressors operate consuming hydrogen.

Reference [42] suggests that the fixed OPEX for a hydrogen compressor can be calculated as 3% of its CAPEX. Therefore:

- The minimum fixed OPEX of the compressor that pressurizes hydrogen into the pipeline is 521.2 $k€$ and the maximum OPEX is 857.9 $k€$.
- The minimum fixed OPEX of the compressor that pressurizes hydrogen into the tanks 798.8 $k€$, whereas the maximum is 1314.9 $k€$.

The OPEX of the salt cavern compressor is included in section 7.2.2.2.

7.2.2. Hydrogen storage

7.2.2.1. Tanks

Reference [42] suggests that the OPEX can be calculated as 1.5% of the CAPEX. Therefore, the OPEX lies between 58.0 $M€$ and 75.7 $M€$.

7.2.2.2. Salt cavern

The operational cost of the salt cavern can be estimated as 4 % of the investment cost required for constructing the salt cavern [13]. This 4% includes compression costs. In this way, the OPEX obtained is between 5.2 $k€$ and 6.8 $k€$.

7.2.3. Water desalination

The cost of electricity has been assumed to be 0.2075 €/kWh [54].

- The OPEX for the disposal of water treatment waste can be calculated as 10% of the CAPEX plus the energy consumed for sludge pumping [17] (180 kWh/day).
- The operating costs of water transportation include pumping energy costs. They can be estimated by the following equation:

$$C_{pumping} = \frac{1{,}248 \times 10^{-4} \times {q_f}^{2{,}84} \times \rho^{0{,}84} \times \mu_c^{0{,}16} \times K \times (1+J) \times H_y}{D_i^{4{,}84} \times E} + B'$$

Where:

- B' and J are constants that have been assumed to be negligible.
- H_y is the number of operating hours per year.
- q_f is the flow in $\frac{m^3}{s}$.
- ρ is the density in $\frac{kg}{m^3}$.
- μ_c is the viscosity in $Pa \times s$.
- D_i is the internal diameter which has been assumed to be 0,05 m.
- K is the cost of electricity, which has been estimated as 0.2075 €/kWh.
- E is the pump efficiency, which has been assumed to be 0,7.
- $C_{pumping}$ is the pumping costs in € per year per meter of pipe length.

There is a discrepancy regarding the cost estimated in the paper [17] and the cost we obtained for the very same flow using the formula proposed by this article. It could be due to the parameter H_y, as we consider that water is transported every hour of the year and perhaps this paper contemplates fewer operating hours. Thus, for taking into account this inconsistency, the price will also be calculated correcting the value of 5.744 €/year/m estimated in the paper. The following formula is the one that will be included for the calculations of the best-case scenarios (1 and 3), as the cost obtained is lower than the price that the previous equation provides. In addition to this, cases 1 and 3 have been calculated assuming that pipelines are 4.51 km long as it was estimated in section 6.3, whereas cases 2 and 4 assume that pipelines are 13.3 km long.

$$C_{pumping} = 5.744 \times \frac{q_f}{{q_f}'} \times \frac{K}{K'}$$

Where ${q_f}'$ and K' are the flow and the price of electricity used in reference [17], and q_f and K are the flow and the cost of electricity considered in this work.

- The OPEX of water treatment include:
  - The energy consumed for pumping: [17] estimates an electricity consumption of 1680 kWh/day.
  - 240 kWh/day for other motors and lighting.
  - 10 % of CAPEX for maintenance.
  - Reference [17] indicates that there are charges on Water Resources in Portugal, however, no information has been found in Spain and, thus, they have not been considered in this work.

7.2.4. Deionizer

7.5 k€/year are required assuming that the OPEX is 4% of the CAPEX.

7.2.5. Electrolyzer

The variable OPEX is zero as it includes costs associated with:

- Electricity: The electrolyzer operates with curtailed electricity, and it has been assumed for the calculation of the OPEX its price is zero. In section 7.3 a sensitivity analysis varying the cost of curtailed electricity has been conducted.
- Water: It will be estimated in the OPEX of the desalination and deionization unit.

[41] adopts a fixed OPEX of 47,5 €/kW. Therefore, the OPEX of the electrolyzer is 11 400 €/year.

7.2.6. Results

Table 10 and Figure 25 show that the option that provides lower operational costs is hydrogen storage in salt caverns (Cases 1 and 2). It should also be noted that, again, hydrogen storage represents the most expensive portion of the project.

Table 11. OPEX summary.

	Case 1 [k€]	**Case 2** [k€]	**Case 3** [k€]	**Case 4** [k€]
Electrolyzer	11.4 (0.2%)	11.4 (0.1%)	11.4 (0.0%)	11.4 (0.0%)
Tube compressor	521.2 (8.6%)	857.9 (8.6)	521.2 (0.9%)	857.9 (1.1%)
Tank compressor	-	-	798.8 (1.3 %)	1314.9 (1.6%)
Cavern + cavern compressor	5197.5 (85.8%)	6777.3 (68.1%)	-	-
Tanks	-	-	58023.9 (97.2%)	75729.8 (94.4%)
Desalination	317.9 (5.3%)	2299.8 (23.1%)	317.9 (0.5%)	2299.8 (2.9%)
Deionization	7.5 (0.1%)	7.5 (0.1%)	7.5 (0.0%)	7.5 (0.0%)
OPEX	6055.6	9953.9	59680.8	80221.4

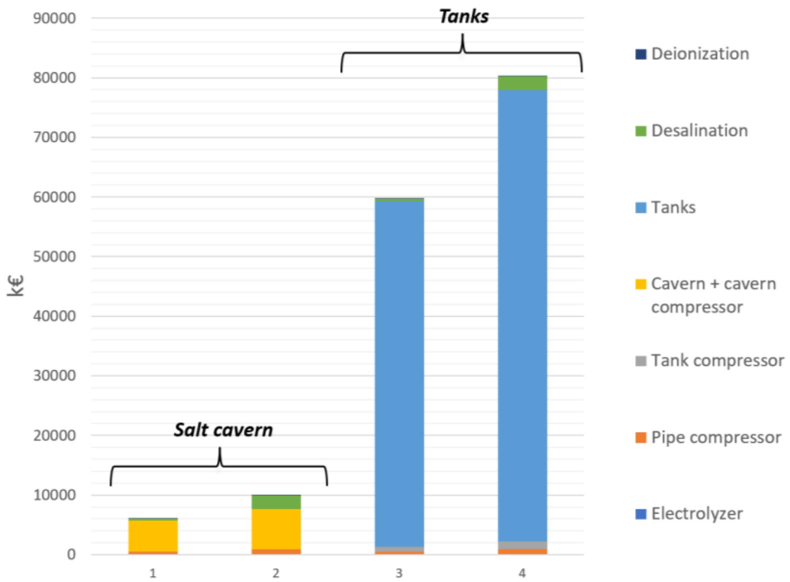

Figure 25. OPEX.

7.3. Hydrogen selling price

Figures 26 and 27 have been obtained for an IRR of 10%, considering a period of 15 years. Taking into account that green hydrogen produced from electrolysis with grid electricity is expected to cost 2.85 €/kg in 2030[5] [58], it can be deduced from Figure 26 that none of the cases are competitive with the market price, even if curtailed electricity is free.

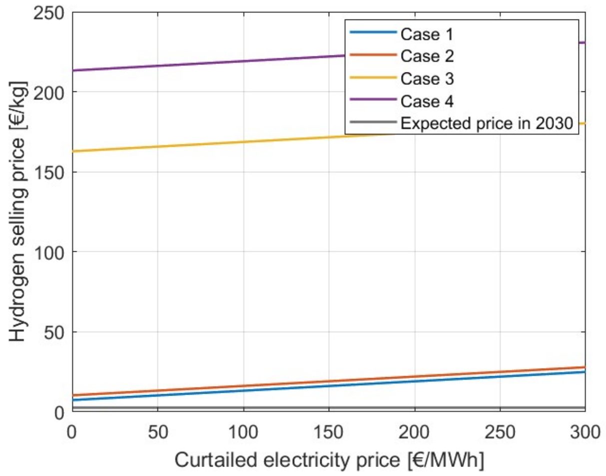

Figure 26. Hydrogen selling price.

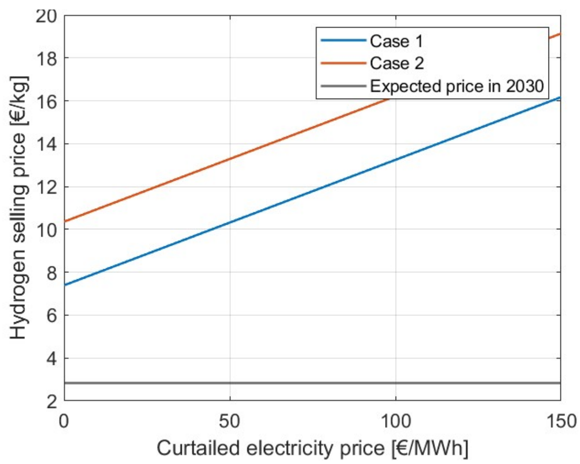

Figure 27. Hydrogen selling price zoomed in.

[5] Assumming that 1 $ = 0,95 € [19].

8 INDICATORS FOR THE ENVIRONMENTAL ASSESSMENT

Currently Fertiberia produces hydrogen via steam reforming. The emissions of grey hydrogen are estimated at 330 $\frac{g\ CO_2}{kWh_{H_2}}$ [10]. As green hydrogen emissions are 30 $\frac{g\ CO_2}{kWh_{H_2}}$ [10], producing hydrogen from electrolysis at Fertiberia factory in Palos de la Frontera would save 193 418 tonnes of CO_2 every year.

The indicators for the environmental assessment can be summarized by the following bullet points:

- Every year 322 011 tons of sea water are consumed in the electrolyzer. In addition to this, around 7-8 $m^3$of fresh water is required for dissolving 1 m^3 of salt [9], therefore 9,4-14 tons of fresh water are needed to construct the cavern.
- 112 704 tons of brine are generated every year owing to seawater desalination.
- Electricity consumption
  - From curtailed electricity: 240 MW during 4716 h, a total of 1 131 840 MWh every year.
  - From the grid:
    - 180 kWh/day for the disposal of water treatment waste.
    - 1.25 MWh/day for cases 1 and 3 and 27.4 MWh/day for cases 2 and 4. It has been estimated using the following formula:

      $$Consumed\ electricity\ \left[\frac{kWh}{year}\right] = \frac{C_{pumping} \times Distance}{K} \frac{[€/year]}{[€/kWh]}$$

    - 1680 kWh/day for water treatment
    - 240 kWh/day for motors and lighting.
    - It has been assumed that the electricity consumed by the deionizer is negligible compared to the electricity needed for desalination.
- Inorganic acids are consumed for regenerating the resin of the mixed bed deionizers.
- As the electrolyzer rated power is 240 MW, it will be connected to the high voltage grid, specifically, to a 220 kV line [56].
- No nearby protected areas have been identified.

9 CONCLUSIONS AND FUTURE WORK

This work carried out a study of the technologies needed to produce green hydrogen via electrolysis using curtailed electricity expected for 2030.

It has been concluded that in order to achieve the high purity required by the electrolysers, water will have to be treated by reverse osmosis and subsequently by deionisation. Furthermore, the electrolyser type that best adapts to the intermittent energy source of this project is a PEM electrolyzer, and it should have a nominal power of 240 MW.

Four different scenarios have been analysed, one optimistic and one pessimistic for the storage in salt caverns and in pressurised tanks. Salt cavern storage proved to be the option that produces hydrogen at a lower cost. However, none of the alternatives were competitive with the market price, even if the surplus of renewable energy were free.

It should also be noted that the largest costs to be incurred are storage ones: they account for between 70.3 and 75.0 % of CAPEX, and between 68.1 and 85.8 % of OPEX for salt caverns, while for pressurised tanks account for between 98.5 and 98.8 % of CAPEX and between 94.4 and 97.2 % of OPEX. Therefore, it might be more convenient for the Fertiberia to operate all year round and the amount not consumed by the plant could be exported from the port of Huelva, i.e., as ammonia as the most appropriate way to transport hydrogen over long distances.

The following lines could be proposed as future work:

- An analysis of other modes of operation more in line with Fertiberia's production to reduce storage costs.
- The development of the environmental impact assessment.
- Present the results to Fertiberia to propose a continuation of this study adapted to their specific needs.
- Extending the study to other industries that require hydrogen, especially in cases of continuous operation so than storage costs are not that high.
- Provide a much more detailed study of all possible industries that might be interested in the oxygen obtained as a by-product and its potential selling price.

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ANNEX 1

CAPEX

Electrolyzer	min [M€]	max [M€]
	0.139	0.317
Rated power [MW]	240	
LHV [MJ/ton]	120011	
η [MWh/ton]	52.5	
Source:	min [M€/MWH2]	max[M€/MWH2]
IEA	0.841	2.095
IRENA	1.037	1.037
JRC	0.998	2.457
Schmidt	0.772	2.739
Average	0.912	2.082

Salt cavern	min [M€]	max [M€]
	169.4	129.9
min storage needed [ton]	11670	
max storage needed [ton]	15217	
Price [€/MWh2]	334	

Deionizer	
Four deionizers [€]	186648

Tanks	min [M€]	max [M€]
	3868.26	5048.65

Compressors	min [M€]	max [M€]	Hourly demand [ton/h]	Flow [kg/s]	Flow [kmol/s]	P in [atm]	P out [atm]	Wesp,is[KJ/kmol]	Electric power [MWe]
Tank compressor	26.63	43.83	8.37	2.32	1.16	1	250	32777.5	40.9600
Cavern compressor	23.35	38.43	8.37	2.32	1.16	1	175	28737.1	35.9200
Pipe compressor	17.37	28.6	8.37	2.32	1.16	1	81.65	21386.3	26.7300
η [%]	93								
Source:									
Baufumé et al [M€/MWe]	1.07								
Jacobs, Element Energy [M€/MWe]	0.65								

Water desalination	min [M€]	max [M€]
	2.27	4.19
Water abstraction [€]	80000	
Water storage [€]	380000	
Water treatment [€]	675000	
Brine disposal [€]	150000	
Water transport [€/km]	218584	
min distance [km]	4.51	
max distance [km]	13.3	
Min water transport [k€]	985.8	
Max water transport [k€]	2907.2	

ANNEX 2

OPEX

Electrolyzer	[€]
	11400
[€/kW]	47.5
Rated power [MW]	240

Compressors	min [k€]	max [k€]
Pipeline	521.2	857.9
Tank	798.8	1314.9
3% of CAPEX		

Cavern + cavern compressor	min [k€]	max [k€]
4% of CAPEX	5197.5	6777.3

Tanks	min [M€]	max [M€]
3% of CAPEX	58.02	75.73

Deionizer	[k€]
4% of CAPEX	7.46

Desalination	min [k€]	max [k€]
	317.9	2299.8

qf[m^3/s]	0.01021
rho[kg/m^3]	1023.6
mu [Pa*s]	0.00089
K[eur/kWh]	0.2075
Hy [hours]	8760
Di [m]	0.05
E (%/100)	0.7
Distance [m]	13300
C pumping max [€/year/m]	156.12

Project flow [m^3/day]	882
Reference flow [m^3/day]	700
Project cost of electricity [€/kWh]	0.2075
Reference cost of electricity [€/kWh]	0.0716
Distance [m]	4510
C pumping min [€/year/m]	20.97

HYDROGEN STORAGE NEEDS

```
ult_dia_inicio=365-97; "Fertiberia operates during almost 97 days";
Potencia_instalada=240;
horas_funcionamiento=4716;
Eta=52.5; "MWh/ton";
H_almacenado=zeros(8760,ult_dia_inicio);
h2_producido=zeros(8760,ult_dia_inicio);
H_min=zeros(1,ult_dia_inicio);
H_max=zeros(1,ult_dia_inicio);
Matrix=xlsread('curtailment');
curtailment=Matrix(1:8760,5);
for z=1:ult_dia_inicio
    Numero_dia_fin=96+z;

            for i=1:8760
                if curtailment(i)>=Potencia_instalada; "It only operates at full
load";
                    h2_producido(i,z)=Potencia_instalada/Eta;
                end

                  if(i<(z*24-23)||i>=(Numero_dia_fin*24-23+6))
                  "23: first hour of the day, 6: hours of the last day";
                  "If Fertiberia is not operating";
                  H_almacenado(i+1,z)=H_almacenado(i,z)+h2_producido(i,z)*0.915;
"compression losses";

                          if(H_min(z)>H_almacenado(i,z))
                          H_min(z)=H_almacenado(i,z);
                          end

                         if(H_max(z)<H_almacenado(i,z))
                         H_max(z)=H_almacenado(i,z);
                         end

                    else
                   "If fertiberia is operating";
                 H_almacenado(i+1,z)=H_almacenado(i,z)+h2_producido(i,z)-8.368671571;

                          if(H_min(z)>H_almacenado(i+1,z))
                          H_min(z)=H_almacenado(i+1,z);
                          end
                          if(H_max(z)<H_almacenado(i+1,z))
                          H_max(z)=H_almacenado(i+1,z);
                          end
                  end
            end

Toneladas_max_en_caverna(z)=H_max(z)+abs(H_min(z));
end
[Almacen_maximo_segun_dia_operacion,dia_inicio_alm_max]=max(Toneladas_max_en_caverna)
[Almacen_minimo_segun_dia_operacion,dia_inicio_alm_min]=min(Toneladas_max_en_caverna)
plot(1:268,Toneladas_max_en_caverna)
```

ANNEX 4

HYDROGEN SELLING COST

```
"Million EUR";
CAPEX=1039.8;

OPEX_sin_coste_curtailment=6.0556;

MWh_al_anio=240*4716;
eur_kg=zeros(1,300);
kg_al_anio=19340000;


for i=0:300
EUR_entre_MWh=i;
bandera=0;
A=0;
    while (bandera==0)

Lado_izda=A/1.1+A/(1.1^2)+A/(1.1^3)+A/(1.1^4)+A/(1.1^5)+A/(1.1^6)+A/(1.1^7)+A/(1.1^8)
+A/(1.1^9)+A/(1.1^10)+A/(1.1^11)+A/(1.1^12)+A/(1.1^13)+A/(1.1^14)+A/(1.1^15);
        if(CAPEX<=Lado_izda)
        bandera=1;
        end
        A=A+0.1;
    end
     "A=-OPEX_sin_coste_curtailment-
MWh_al_anio*EUR_entre_MWh/(10^6)+eur_kg*kg_al_anio/10^6";

eur_kg(i+1)=((A+OPEX_sin_coste_curtailment+MWh_al_anio*EUR_entre_MWh/(10^6))/kg_al_an
io)*10^6;
end

plot(0:300,eur_kg)
hold on
```

HYDROGEN STORED (t)

```
Numero_dia_inicio=55; "Maximum possible value: 365-97";
Numero_dia_fin=96+Numero_dia_inicio;
N=1000; "Power variation range";
Y=zeros(1,N);

horas_funcionamiento=zeros(1,N);
Eta=52.5; "MWh/ton";
H_almacenado=zeros(N,8760);
h2_producido=zeros(N,8760);
consumo_Fertiberia_plot=zeros(N,8760);
Consumo_fertiberia=double(Y);
Horas_no_opera_Fertiberia=zeros(1,N);
Horas_opera_Fertiberia=zeros(1,N);
N_veces_consumo_completo=zeros(1,N);
H_min=zeros(1,N);
H_max=zeros(1,N);
Potencia_instalada=zeros(1,N);
Toneladas_max_en_caverna=zeros(1,N);
Produccion=zeros(1,N);
Perdidas_compresion_tuberia=zeros(N,8760);
Perdidas_tuberia_total=zeros(1,N);
Perdidas_compresion_almacenamiento=zeros(N,8760);
Perdidas_almacenamiento_total=zeros(1,N);
Gas_colchon=zeros(1,N);

Matrix=xlsread('curtailment');
curtailment=Matrix(1:8760,5);
bandera=1;


j=1;
while (bandera==1)
    Potencia_instalada(j)=10*j;

            for i=1:8760

                if curtailment(i)>=Potencia_instalada(j);
                    horas_funcionamiento(j)=horas_funcionamiento(j)+1;
                    h2_producido(j,i)=Potencia_instalada(j)/Eta;
                end


                 if(i<(Numero_dia_inicio*24-23)||i>=(Numero_dia_fin*24-23+7))
                 "If Fertiberia is not operating";

                 Perdidas_compresion_almacenamiento(j,i+1)=h2_producido(j,i)*0.085;
                 H_almacenado(j,i+1)=H_almacenado(j,i)+h2_producido(j,i)-
Perdidas_compresion_almacenamiento(j,i+1);

Perdidas_almacenamiento_total(j)=Perdidas_almacenamiento_total(j)+h2_producido(j,i)*0
.085;
                 Horas_no_opera_Fertiberia(j)=Horas_no_opera_Fertiberia(j)+1;
```

```
                    if(H_min(j)>H_almacenado(j,i+1))
                    H_min(j)=H_almacenado(j,i+1);
                    end

                   if(H_max(j)<H_almacenado(j,i+1))
                   H_max(j)=H_almacenado(j,i+1);
                   end


               else
              "If Fertiberia is operating";
               Horas_opera_Fertiberia(j)=Horas_opera_Fertiberia(j)+1;
                   Perdidas_compresion_tuberia(j,i+1)=h2_producido(j,i)*0.07;

      Perdidas_tuberia_total(j)=Perdidas_tuberia_total(j)+h2_producido(j,i)*0.07;
                    Consumo_fertiberia(j)=8.368671571+Consumo_fertiberia(j);
                   consumo_Fertiberia_plot(j,i)=8.368671571;
               H_almacenado(j,i+1)=H_almacenado(j,i)+h2_producido(j,i)-8.368671571;
"Negative tonnes of hydrogen stored values will be stored in a vector and afterwards
the storage curve will be shifted upwards";

                    N_veces_consumo_completo(j)=N_veces_consumo_completo(j)+1;

                if (h2_producido(j,i)>8.368671571)
               "Hourly demand will be sent to Fertiberia, the rest will be stored";
                  Perdidas_compresion_tuberia(j,i+1)=8.368671571*0.07;

            Perdidas_tuberia_total(j)=Perdidas_tuberia_total(j)+8.368671571*0.07;

      Perdidas_compresion_almacenamiento(j,i+1)=(h2_producido(j,i)-
      8.368671571)*0.085;

                  Perdidas_almacenamiento_total(j)=Perdidas_almacenamiento_total(j)
                  +(h2_producido(j,i)-8.368671571)*0.085;


                               else
                  "All the hydrogen produced will be sent to Fertiberia";

Perdidas_compresion_tuberia(j,i+1)=h2_producido(j,i)*0.07;
Perdidas_tuberia_total(j)=Perdidas_tuberia_total(j)+h2_producido(j,i)*0.07;
                               end


                             if(H_min(j)>H_almacenado(j,i+1))
                             H_min(j)=H_almacenado(j,i+1);
                             end
                             if(H_max(j)<H_almacenado(j,i+1))
                             H_max(j)=H_almacenado(j,i+1);
                             end

               end


           end

      Toneladas_max_en_caverna(j)=H_max(j)+abs(H_min(j));
      Produccion(j)=Potencia_instalada(j)*horas_funcionamiento(j)/Eta;
      Gas_colchon(j)=Toneladas_max_en_caverna(j)/0.7-Toneladas_max_en_caverna(j);
```

```
if(Produccion(j)>=Consumo_fertiberia(j)+Perdidas_tuberia_total(j)+Perdidas_almacenami
ento_total(j))
            bandera=0;
            fprintf("%d     %d\n",Potencia_instalada(j), j)
        end

        if (j==N)
           bandera=2;
        end
j=j+1;
end
a_Potencia_inst=(j-1)*10;
a_Toneladas_max_definitivas=Toneladas_max_en_caverna(j-1); "Not taking into account
the cushion gas";
a_Toneladas_max_definitivas_con_gas_colchon=a_Toneladas_max_definitivas/0.7;
a_Almacenamiento_inicial=H_almacenado(j-1,1)+abs(H_min(j-1));
a_H_almacenado=zeros(1,8760);
a_H_almacenado_curva=abs(H_min(j-1))+H_almacenado(j-1,1:8760);
a_h2_producido=h2_producido(24,1:8760);
a_consumo_Fertiberia_plot=consumo_Fertiberia_plot(24,1:8760);

plot(1:8760,a_h2_producido)
hold on
plot(1:8760,a_consumo_Fertiberia_plot)
hold off
```