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START-UP AND CHARACTERIZATION OF A LAB SCALE ELECTROLYZER UNDER DIFFERENT OPERATIONAL CONDITIONS.

(PUESTA A PUNTO Y CARACTERIZACIÓN DE UN ELECTROLIZADOR A ESCALA DE LABORATORIO BAJO DIFERENTES CONDICIONES DE OPERACIÓN.)

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TÍTULO	PUESTA A PUNTO Y CARACTERIZACIÓN DE UN ELECTROLIZADOR A ESCALA DE LABORATORIO BAJO DIFERENTES CONDICIONES DE OPERACIÓN		
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PALABRAS CLAVE

Electrolizador PEM, electrólisis del agua, caracterización, energías renovables, Power-to-gas.

PLANTEAMIENTO DEL PROBLEMA

El hidrógeno está considerado como un vector energético. Esto se debe a que puede ser reconvertido en energía a través de múltiples maneras: empleando pilas de combustible, motores de combustión interna, transformándolo en metano o directamente inyectándolo en la red existente de gas natural [1]. Este último modo de empleo del hidrógeno se conoce como Power-to-gas (PtG) El objetivo del Power-to-Gas es generar hidrógeno a partir de excesos de energía renovable que la red eléctrica no puede asumir. De este modo, la intermitencia que actualmente sufren las energías renovables se puede ver aliviada, consiguiendo que la producción energética pueda llevarse a cabo en su totalidad mediante energías renovables [2]. El hidrógeno se obtiene mediante electrólisis del agua. La electrólisis puede realizarse empleando diferentes sistemas, pero el más interesante es aquel que emplea una membrana de intercambio de protones PEM (Proton Exchange Membrane). Este electrolizador, a diferencia de los tradicionales, no está compuesto por electrolitos altamente contaminantes y es más compacto y eficiente [3, 4]. Este estudio se encargará de elegir un electrolizador PEM en función de sus características tecnológicas y económicas. Posteriormente, se instalará caracterizará y se determinarán de manera experimental las variables que optimicen el rendimiento del equipo, como etapa previa a su acople a aerogeneradores.

RESULTADOS

Se estudió la influencia de la presión (0-12 bar), la intensidad (2-12 A) y la temperatura del agua (10-55 ºC) sobre la producción de hidrógeno.

El estudio de la presión se realizó en todo el rango de intensidades. Se observó que, en todos los casos, la producción de hidrógeno disminuía al aumentar la presión. Sin embargo, a altas intensidades (>7 A) el descenso porcentual en la producción es menor.

El estudio de la influencia de la intensidad sobre la producción se realizó en todo el rango de temperaturas. Se apreció que, a mayor intensidad, mayor producción, de manera directamente proporcional.

La influencia de la temperatura se estudió en todo el rango de intensidades. Se determinó que no influye en la producción de hidrógeno. Sin embargo, se observó que influye en el voltaje que es necesario proporcionar para el desarrollo de la electrólisis. Cuanto mayor era la temperatura, menor era el voltaje, como se puede observar en la Figura 1. De este modo, a temperaturas más altas, mejor eficiencia.

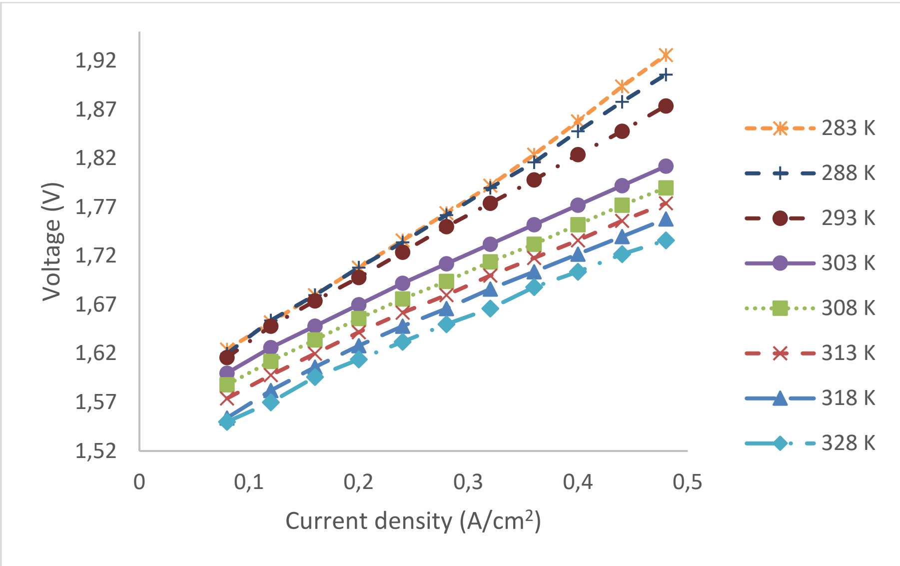

Figura 1 *Curva de polarización a diferentes temperaturas.*

CONCLUSIONES

Se eligió el electrolizador Hart 250 de Hidrógena debido a sus buenas prestaciones técnicas. Se determinó que los aumentos de presión influían de manera negativa en la producción de hidrógeno, pero que se veían atenuados conforme aumentaba la intensidad. A intensidades más altas, la producción era mayor. Para distintas temperaturas, la producción no se veía afectada, pero si el voltaje, que disminuía con el aumento de temperatura. A temperaturas más altas, la eficiencia era mayor, ya que es inversamente proporcional al voltaje.

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[4] Selamet, Ö.F. et al. (2011) *International Journal of Hydrogen Energy, 35,* pp.5043-5052.

TITLE	**START-UP AND CHARACTERIZATION OF A LAB SCALE ELECTROLYZER UNDER DIFFERENT OPERATIONAL CONDITIONS.**		
AUTHOR	**SERGIO SAN MARTÍN GÓMEZ**		
DIRECTOR	**ALFREDO ORTIZ SAINZ DE AJA**		
DEGREE	*Chemical Engineering*	DATE	September 25th, 2018

KEYWORDS

PEM Electrolyzer, water electrolysis, characterization, renewable energies, Power-to-gas.

SCOPE

Hydrogen is considered an energetic vector. It can be turned into electricity by several processes: using fuel cells, internal combustion engines, methanazing it or injecting into the existing natural gas network [1]. The last process is known Power-to-gas (PtG) The main goal of Power-to-Gas is generating hydrogen from the excess energy from renewable sources that the grid is unable to take. Thereby, the intermittency of the renewables nowadays can be relieved, obtaining energy from renewable sources only [2]. Hydrogen is obtained by water electrolysis. Electrolysis can be performed by several systems but the most interesting is the Proton Exchange Membrane (PEM) electrolyzer. As opposed to the traditional and widespread electrolyzers, PEM system does not use a highly pollutant electrolyte and it is more compact and efficient [3, 4]. This study will choose a PEM electrolyzer following technical and economic criteria. Then, it will be installed and characterized. After that, the variables that make the electrolysis efficient will be experimentally determined. This study will be a preliminary step of a project aimed to couple electrolyzers to wind turbines.

RESULTS

The main results can be outlined as:

The work was focused on the influence of several variables on hydrogen production, such as pressure (0-12 bar), intensity (2-12 A) and temperature (0-55 ºC)

The study of the pressure was performed for all the intensities. It was observed that, for all the cases, hydrogen production drop when the pressure was risen. Se observó que, en todos los casos, la producción de hidrógeno disminuía al aumentar la presión. However, the percentage drop at high intensities (>7 A) was lower.

The influence of the intensity on hydrogen production was studied in all the temperature range. The intensity was directly proportional to hydrogen production meaning that the higher the intensity, the higher the production.

The temperature did not influence hydrogen production. However, it influenced electrolysis voltage. When the temperature was risen, the voltage decreased as shown in Figure 1. Thus, the higher the temperature, the higher the efficiency (reversely proportional to the voltage).

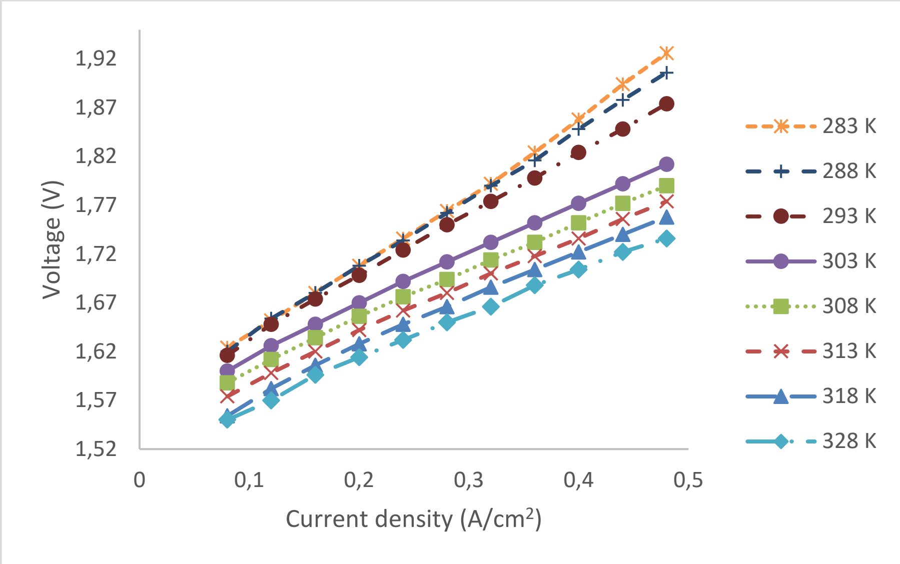

Figure 1 *Polarisation curve at different temperatures.*

CONCLUSIONS

Hart 250 electrolyzer was chosen due to its good performance. Pressure rise was determined to be negatively affecting hydrogen production, but this effect was attenuated as the intensity was risen. At high values of intensity, production was higher. For different temperatures, production was not affected. Nevertheless, it affected voltage. Voltage decreased when temperature was increased. At higher temperatures, efficiency was higher.

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1. Introduction

1.1 Climate change and renewable energies.

According to the European Union regulations and agreements, it is necessary to reduce the greenhouse gas emissions up to 80% by 2050 (compared to 1990) [1]. In order to reduce anthropogenic contribution to climate change, many countries in the EU and around the globe have committed to renewable energy and zero emission technologies [2]. Because of that, the use of renewable energies such as wind and solar power are increasing. Figure 1 represents the electricity production in Spain along the time [3].

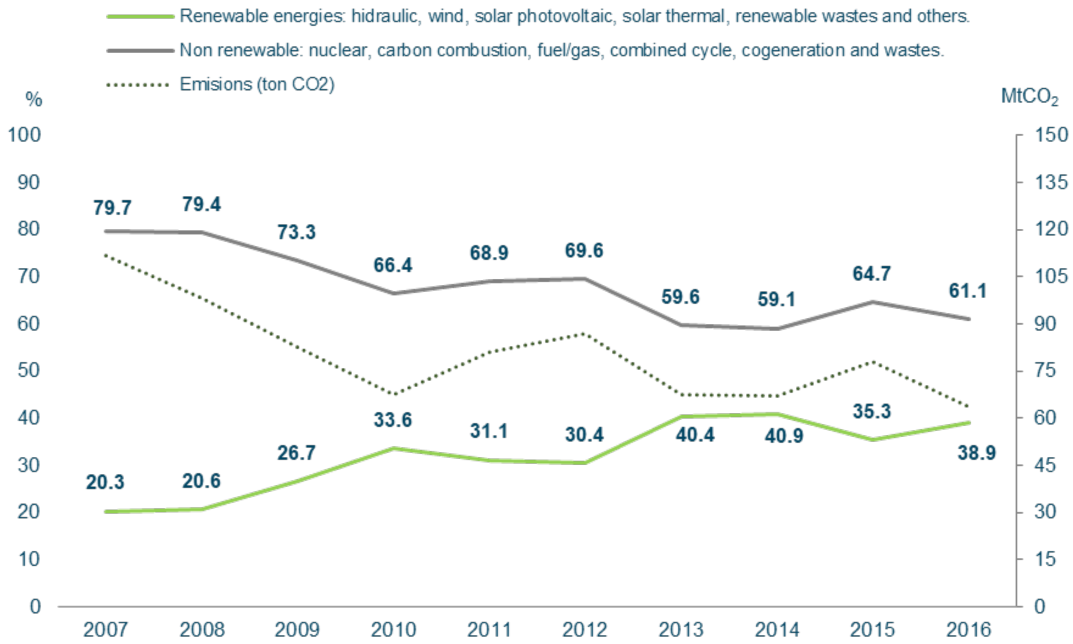

Figure 1 *Electricity production and emissions in Spain versus time.*

As it can be seen, renewable energies do not fulfil the whole energy demand. For example, in Spain, non-renewable energies represent more than the 60% of the total production (Figure 1).

In fact, the potential of renewable energies is foreseen much higher than the global demands in many countries, and it is usually well distributed in the territory [4]. In Spain, the installed capacity exceeds 90 GWh, while the maximum demand is below 50 GWh. In Germany, the amount of excess electricity was 1581 GWh, and this amount is expected to increase as the renewable system increases [2].

The intermittence of this energy sources is the biggest problem. Sometimes, renewable energy production does not meet the demand during peak times. On the other hand, the grid could not be able to take all the energy produced, resulting in loss of power.

Thus, it is necessary to balance the energy grid to increase the efficiency of the system and to fulfil the requirements of the European Union. However, that represents one of the most challenging steps.

As large amounts of electricity cannot be stored, maintaining the stability by fitting instantaneous power generation and power demand is fundamental. Nowadays this trade-off is accomplished by combining renewable power generation and non-renewable power generation at the same time because of the intermittence and variability of the renewable energies. For example, in Spain, the electricity is produced by joining nuclear power with wind power, solar power or cogeneration. Figure 2 shows the estimated electricity demand, the real energy production and the contribution of each kind of energy to cover the demand in a specific period of time [5].

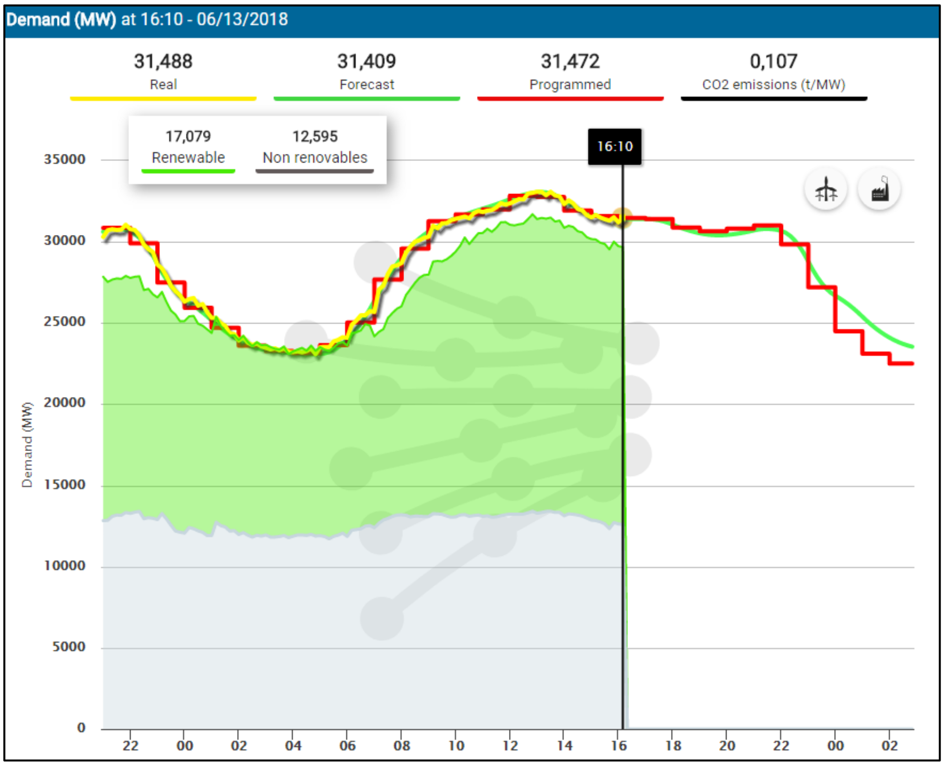

***Figure 2** Real and programmed electricity demand in Spain.*

Figure 3 details the kind of energy used, clearly stating that the most relevant renewable energy is wind power, closely followed by hydropower. The figure also shows the exchanges between the Iberian Peninsula and the Balearic Islands.

Wind energy contributes to the Spanish generation system by supplying more than 10% of the electricity demand, while its growth pattern is foreseeing a much faster penetration level in near future [6]. Wind energy is also the most widespread renewable energy, which make it the most interesting energy for this study.

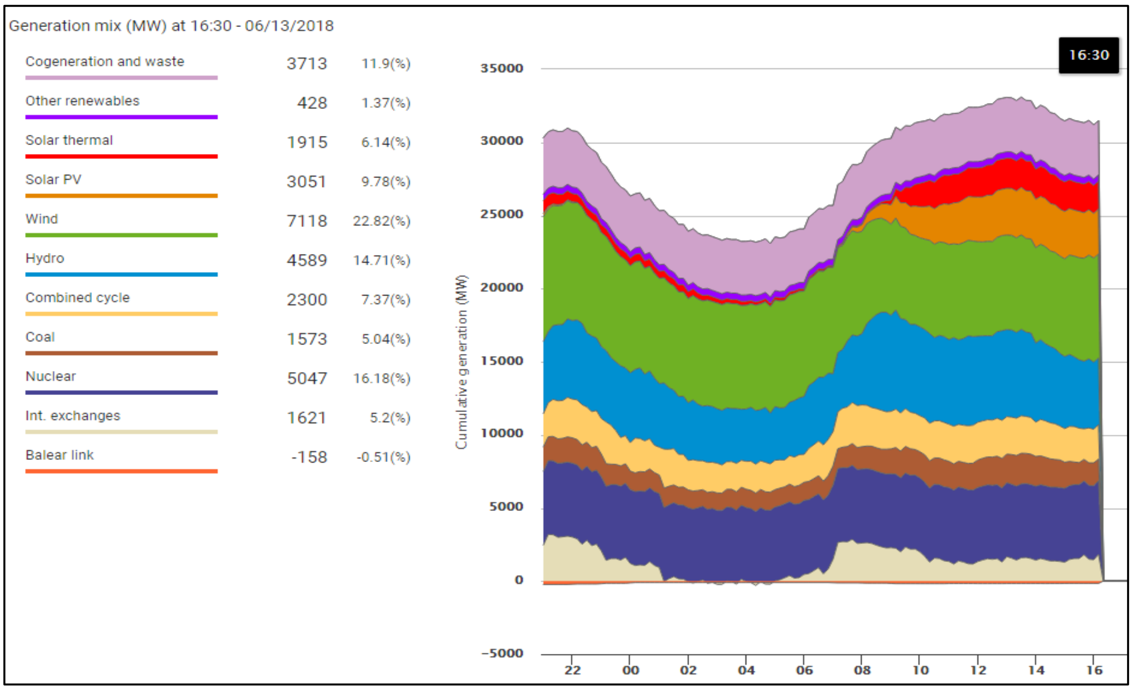

Figure 3 *Real energy production in Spain.*

1.2 Power-to-gas principles: hydrogen as an energetic vector.

To move to a zero-emission economy, hydrogen produced via water electrolysis from renewable electricity is commonly regarded to be a sustainable energy carrier with large potential for decarbonisation of many sectors.

Figure 4 shows the potential uses of hydrogen as an energetic vector. The first step is taking the excess of energy from renewables for producing H_2 by electrolysis. Then, hydrogen can be directly injected to the gas network. In other cases, H_2 is transformed back to electricity using a fuel cell, methanized, stored into pressure vessels or even used in internal combustion engine (ICE). For example, automotive companies such Hyundai or Toyota are now commercializing hydrogen powered cars.

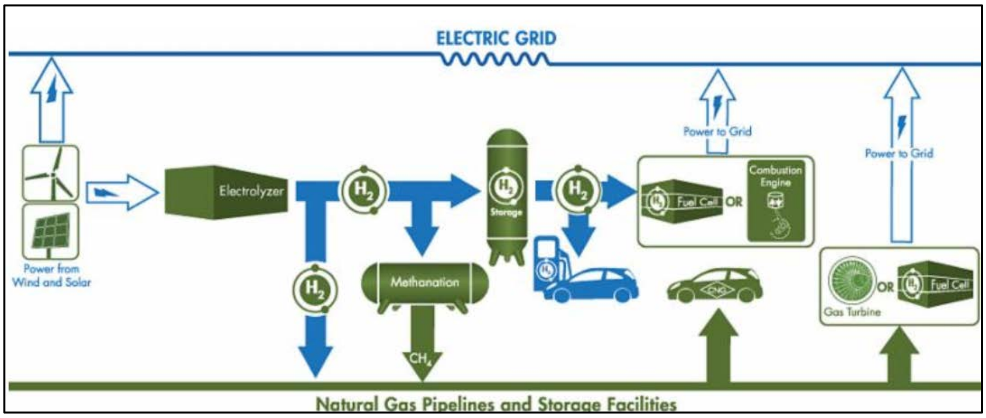

Figure 4 *Hydrogen as an energetic vector. (National Fuel Cell Research Center)*

The conversion of water to hydrogen by electrolysis and the use of the grid to storage and transport is known as Power-to-Gas (PtG). Hydrogen is injected into the natural gas network in a quantity and quality compatible with the gas safety regulations and thereby transported as a mixture of hydrogen and natural gas to demand centres (Figure 4). Once integrated into the electricity network, PtG systems provide flexibility to the power system and absorb excess electricity from renewables to produce hydrogen. Injection of hydrogen into the gas network reduces gas volumes supplied from terminals[7,8].

However, since PtG is still in development, there are several challenges to face[9], such as:

- The establishment of a proper legal and political framework for power-to-gas technology[8].
- Accurate PtG data in order to enhance and develop powerful simulations and models. Currently, the modelling of these systems is not solid because lack of data[10].
- Economic and social analysis about the impact of the PtG integration[9].

If these challenges are overcoming, the technology can be deployed into the market.

1.3 Water electrolysis. Electrolyzer fundamentals.

The essential technology in Power-to-gas to transform electricity into the energetic vector (H_2) is electrolysis.

There are three different types of electrolysis: alkaline, solid oxides and proton exchange membrane (PEM). Alkaline electrolysis is the most mature technology; it is well-known and widely used in the industry. However, it has several drawbacks such as electrolyte contamination, corrosion, low efficiency and high maintenance costs. Besides, it does have pollutant and hazardous components like the electrolyte. Solid oxides electrolyzer is a technology on its early steps of development, to be considered in a near feature[11].

On the other hand, proton exchange membrane (PEM) electrolyzer have many advantages. It is a compact device, easy to operate and it has a high working current and pressure. Since it can work at low DC currents, it can be directly connected to PV panels to produce hydrogen from renewables. Due to all these advantages, PEM electrolyzers will be under study in this work.

The working principles of a PEM cell are illustrated in Figure 5. As it is shown, the water molecule is dissociated in the anode, producing oxygen, protons and electrons. The protons then travel through the membrane to the cathode, where hydrogen is formed as a product of a reduction reaction.

The main parts of a PEM electrolyzer are:

- Proton exchange membrane.
- Anodic and cathodic catalyst layer.
- Gas diffusion layer.
- Bipolar plates.

The proton exchange membrane, commonly known as MEA (membrane electrode assembling) is made of a stable sulfonated tetrafluoroethylene-based fluoropolymer–copolymer: Nafion®. Nafion® based MEA’s have received plenty of attention as proton exchange membrane both in electrolyzers and fuel cells [12].

The membrane thickness varies from 100 to 300 µm and it is coated on each side with a catalyst generally made of precious metal (platinum) in the cathode, and metallic oxides as anodic catalyst [12–14]. The membrane should have:

1. Chemical, thermal and mechanical stability.
2. High proton conductivity.

3. Low gas permeability, specially to hydrogen and oxygen to avoid its diffusion to the cathode.
4. High permeability to water.

The membrane area determines the hydrogen production. It is a function of the current density per membrane area (in A/cm^2) Thus, a trade-off between the production and the membrane lifetime is needed, since high values of current density per membrane area make the membrane to degrade faster.

The gas diffusion layer allows the flow of the current and the movement of the gases. It is generally made of a porous, electrical conductor material, like titanium (Ti). This material must be corrosion-resistant and it must let the water into the catalytic sites[13].

The bipolar plates serve as electrodes and circulators for water and gas products. They also have channels where these elements circulate. They separate one cell from another [13].

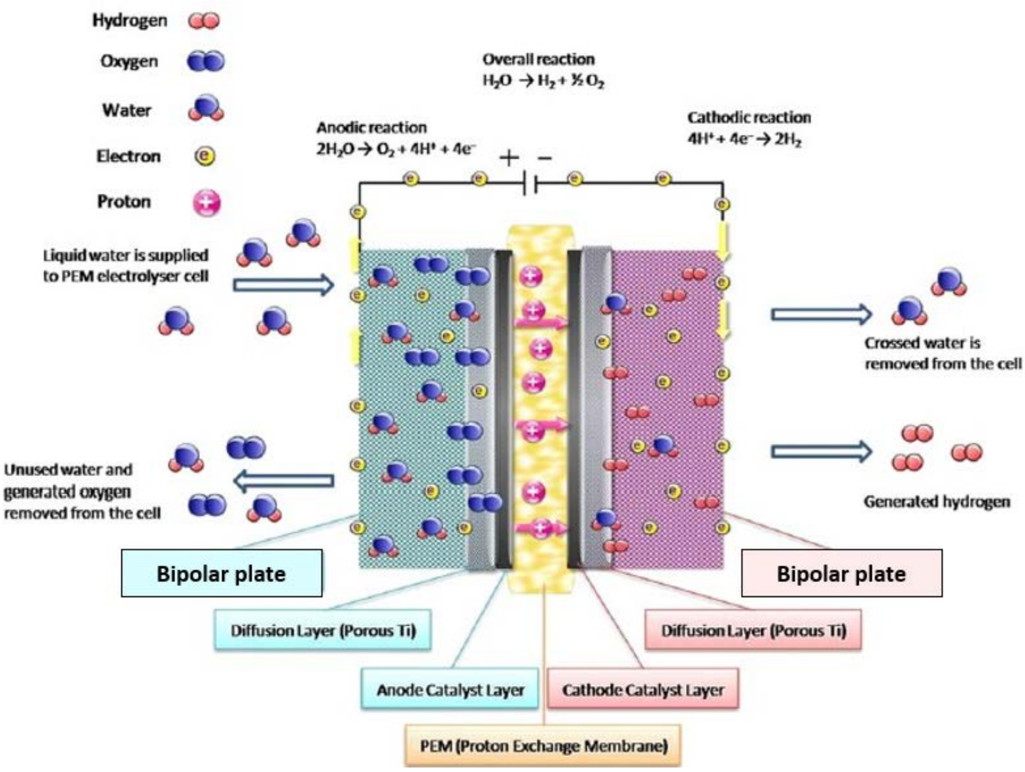

Figure 5 *Working principles and schematic of a PEM electrolyzer.*

All these parts form a cell. The assembly of several cells (from 2 in experimental set up to several tens in industrial equipment) is a stack. Industrial electrolyzers can have more than 100 stacks.

Depending on the wanted purity of the hydrogen, the electrolyzer may need auxiliaries. If a 99% pure H_2 is wanted it is necessary to remove water from the exiting gas. Since the membrane is hydrophilic, both water and protons reach the cathode. Then, the leaving hydrogen is saturated in water. Because of that, hydrogen is typically dried using silica gel columns.

Despite of this configuration, the best equipment performance will be reached after studying and setting the optimal operating parameters.

Many factors and variables have an influence over the electrolysis and thus the production of hydrogen. For a PEM electrolyzer, the most important are [13]:

- **Temperature.**
- **Pressure.**
- **Voltage (V)** plays a significant role in hydrogen production. It is necessary to apply a potential that exceeds the minimum one for the water decomposition, commonly 1.48 V/cell.
- **Intensity (A)** The current applied will determine the total amount of hydrogen produced.

All these factors and variables will affect electrolyzer performance and hence, the efficiency.

1.4 Cell efficiency.

The efficiency is reversely proportional to the cell voltage (V_{CELL}) [11,13,15]. Efficiency is also dependant on the thermoneutral voltage, defined as the minimum isothermal decomposition voltage of water under adiabatic conditions. It can be calculated from thermodynamic data [11,13,15,16]:

$$E^0_{cell} = -\frac{\Delta G^0}{n * F} \qquad (1)$$

Where $\Delta G^0$is the free energy change of Gibbs, n is the number of electrons involved (2) and F is the Faraday constant ($9.6485 \cdot 10^4$ C/mol).

The Gibbs-Helmholtz equation (eq. 2) allows to determine the free energy change of Gibbs under normal conditions (1 bar, 298 K) for the water electrolysis reaction.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (2)$$

Using the higher heating value for the water electrolysis, that considers all energy released by reaction between initial and final state at the same temperature, $\Delta H^0 = 285840\ J/mol$, knowing the entropy $T\Delta S^0 = 163\ J/mol$ and substituting in eq. 1, the thermoneutral voltage is 1.48 V.

For different temperature conditions, the values of enthalpy, entropy and Gibbs' free energy can be calculated as [17]:

$$\Delta H = \Delta H^0 + \int_{298}^{T} \Delta Cp_{components} * dT \qquad (3)$$

$$\Delta S = \Delta S^0 + \int_{298}^{T} \frac{\Delta Cp_{components}}{T} * dT \qquad (4)$$

Being the heat capacity of each component showed in Table 1 [17].

Table 1 *Heat capacity of each component as a function of temperature.*

Component	**Heat capacity (Cp, $J \cdot mol^{-1} \cdot K^{-1}$)**
Hydrogen (gas)	$(29.07-0.836) \cdot 10^{-3}\ T + 20.1 \cdot 10^{-7} T^2$
Oxygen (gas)	$(25.72+12.98) \cdot 10^{-3}\ T - 38.6 \cdot 10^{-7} T^2$
Water (liquid)	75.3
Water (gas)	$(30.36+9.61) \cdot 10^{-3}\ T + 11.8 \cdot 10^{-7} T^2$

Then, the ideal efficiency of a cell can be expressed as in Equation 5 [11,13,15].

$$\eta_{cell} = \frac{E^0_{cell}}{E_{cell,real}} \qquad (5)$$

1.5 State-of-the-art.

The electrolysis state-of-the-art research is aimed to improving the efficiency, costs and the lifetime of the electrolyzers, in order to make it a reliable technology. Continuous long-term operation of power-to-gas pilot plants and decreasing the auxiliary equipment are essential. It is also important to have a consistent standard and strategy of hydrogen production. Optimum system configurations and components shall be determined with regard to the available infrastructure and the type of application involved [18].

Most of the pilot plants are in Europe or North America. According to Gahleitner (2013), Germany is the country with the highest number of pilot plants. Germany is committed with the development of power-to-gas systems that will be operating in the future. Spain and the UK are also relevant, since they have a good number of plants.

Regarding the capacity of the plants, it seems that the installed power is following an ascendant trend. However, all the realized projects reviewed in Gahleitner (2013) are below 1 MW. Nevertheless, there are several promising projects that will lead to a 6.7 MW of installed power eventually.

An evidence of the immaturity of Power-to-gas is the mean operational time of the plants: most of them had a working period between a few months to four years [18]. Besides, others are not able to run with the sole power of renewable energies: the 32% of the studied plants are powered by the electricity from the grid. Other join renewable energies with the grid, to smooth variations and fluctuations.

In relationship with wind, this energy is one of the power sources in the half of the total plants studied in Gahleitner (2013). Moreover, in 9 of the 42 projects is the sole power source. The relevance of wind energy is noticeable.

About Spain, there are several different cases. In Gutiérrez-Martín (2010), the study designs a set of electrolyzers to be coupled to a real wind farm. The project predicts a potential production of nearly 10 Gwh of hydrogen per year. The electrolyzer estimated capacity is 21.3 MW and the expected efficiency is 62%, while the selected operation has resulted very versatile, as electrolyzers are able to run into a range from 1.7 to 100% of the maximum power, by using of an adequate control. There is also a high-pressure storage and a fuel cell system with a 70% efficiency.

The biggest operating plant is *Sotavento.* It has a rated capacity of 17.56 MW, with 24 wind turbines. It has got an alkaline electrolyzer along with a high-pressure storage tank and an internal combustion engine to produce energy. It was designed to maximize the utilization of the wind power. The H_2 is produced at a rate of 60 Nm^3/h and a pressure of 10 bar [19,20].

Concerning PEM pilot plants there are several aspects to be considered:

- Its operating behaviour is better than alkaline devices. Besides, it has got a wide operational range varying it from 5% to 100% of the nominal power [18].
- The wind energy use should be increased [21].
- The system performance with fluctuating and intermittent power sources is good [22].
- Current PEM electrolyzers provide a high purity hydrogen (99.999%) avoiding the need of further purification steps and equipment [22,23].
- The stack lifetime is too short for long-time operations. That leads to higher costs [22].
- Compared to alkaline electrolyzers, current PEM stacks have an efficiency of 70% but it is expected to increase [24].

Because of its high potential and benefits, PEM electrolyzer have been increasingly installed. Nevertheless, the biggest plants cannot operate with them due to their low power range.

This work aims with a laboratory electrolyzer characterization as a previous step of coupling with a wind turbine and made an estimation of the potential of hydrogen generation at the Atlantic area. This research is part of the Project "HYLANTIC"-EAPA_204/2016 which is co-financed by the European Regional Development Fund in the framework of the Interreg Atlantic programme.

1.6 Objectives.

The main objectives of this Final Degree dissertation are:

1. Technical and economical evaluation of different commercial laboratory electrolyzers and select the most suitable.
2. Install, start-up and complete characterization of the commercial electrolysis setup.

3. Determining the influence and the operating conditions such as current density, temperature and pressure.

2. Materials and methods.

After conducting a market study of the different lab-scale electrolyzer manufacturers, the equipment used for the tests was provided by *Hidrógena S.L,* a company based in Segovia, Spain. This setup was chosen due to its characteristics and prize. It is the low-pressure hydrogen generator *Hart 250*, with a 5-cell stack electrolyzer and multiple regulation. Hydrogen is produced at a low-mid pressure (max 12 bar), and oxygen at ambient pressure. The total exchange surface is 125 cm^2.

The complete electrolysis system is shown in Figure 6. The components are:

- Power source.
- Water pump.
- Electrolyzer stack.
- Phase separator.
- Silica gel tower.
- Multiple regulation system.
- Control display.
- Relief valves.
- Water flow meter (Auxiliary equipment)
- Hydrogen flow meter (Auxiliary equipment)
- Microvalve (Auxiliary equipment)
- Multimeter (Auxiliary equipment)

Figure 6 *Electrolysis system*

Table 2 details the main characteristics and technical specifications of the electrolyzer.

Table 2 *Characteristics and technical specifications of the electrolyzer.*

Max. hydrogen production	500 ml/min
Max. hydrogen pressure	12 bar
Max. current density	0.48 A/cm^2
Hydrogen purity	99.9999%
Operating temperature range	288-333 K
Water volume	1 L
Water type	De-ionized (ASTM Type II)

In Figure 7, a conceptual scheme of the whole hydrogen formation process is shown. The water is pumped from a tank to the electrolyzer. The pump is necessary to assure that the water reaches all the membranes, because they must remain wet. Once it reaches the electrolyzer and the desired intensity is set, water is split. Then, water and hydrogen leave the stack and reach the phase separator while oxygen is driven to the water tank.

To have pure hydrogen, the phase separator is needed to separate hydrogen from water. Water is held into the device while hydrogen leaves at the top. Afterwards, when the water reaches a certain level, it is recirculated to the water tank. This recirculation is controlled by a float valve.

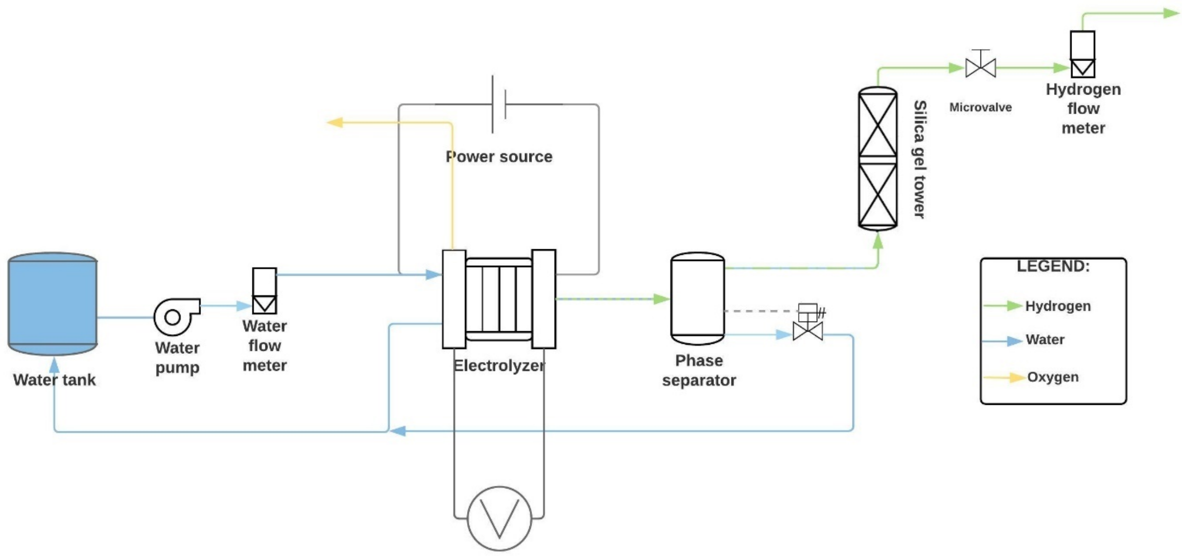

Figure 7 *Conceptual scheme of the electrolysis equipment.*

After that, hydrogen goes through a silica gel tower, the micro valve and the flow meter. The microvalve is essential to maintain the desirable pressure during electrolyzer's operation. Finally, H_2 leaves the system.

The study is focused on the following variables:

- **Pressure** in the range of 0 to 12 bar.
- **Intensity** in the range of 2 to 12 ampere.
- **Temperature** in the range of 10 to 55 º C (283-328 K)

The experiments have been performed by changing the pressure at constant values of intensity and voltage. Pressure was measured using the sensors of the equipment. Both voltage and intensity were controlled by using the equipment sensors as well.

The influence of the temperature was determined by using hot water for electrolysis purposes. This water was previously heated in a furnace to the desired temperature. It was then introduced into the electrolyzer. The electrolyzer worked under different intensity conditions and then, the overall stack voltage was determined by using a multimeter.

Table 3 displays a list of the experiments. In this experiments, the effect of the temperature in hydrogen production and cell voltage was studied. Besides, the influence of the pressure for T=303 K in all the range of intensity was also considered.

Table 3 *List of experiments.*

I (A) / T(K)	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
283	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Exp. 6	Exp. 7	Exp. 8	Exp. 9	Exp. 10	Exp. 11
288	Exp. 12	Exp. 13	Exp. 14	Exp. 15	Exp. 16	Exp. 17	Exp. 18	Exp. 19	Exp. 20	Exp. 21	Exp. 22
293	Exp. 23	Exp. 24	Exp. 25	Exp. 26	Exp. 27	Exp. 28	Exp. 29	Exp. 30	Exp. 31	Exp. 32	Exp. 33
303	**Exp. 34**	**Exp. 35**	**Exp. 36**	**Exp. 37**	**Exp. 38**	**Exp. 39**	**Exp. 40**	**Exp. 41**	**Exp. 42**	**Exp. 43**	**Exp. 44**
303	Exp. 45	Exp. 46	Exp. 47	Exp. 48	Exp. 49	Exp. 50	Exp. 51	Exp. 52	Exp. 53	Exp. 54	Exp. 55
313	Exp. 56	Exp. 57	Exp. 58	Exp. 59	Exp. 60	Exp. 61	Exp. 62	Exp. 63	Exp. 64	Exp. 65	Exp. 66
318	Exp. 67	Exp. 68	Exp. 69	Exp. 70	Exp. 71	Exp. 72	Exp. 73	Exp. 74	Exp. 75	Exp. 76	Exp. 77
328	Exp. 78	Exp. 79	Exp. 80	Exp. 81	Exp. 82	Exp. 83	Exp. 84	Exp. 85	Exp. 86	Exp. 87	Exp. 88

3. Results & discussion.

The main goal is characterizing the experimental equipment to determine hydrogen production as a function of the previously detailed variables.

3.1 Effects of intensity in hydrogen production.

Since hydrogen production is proportional to current density and therefore, to the intensity, this variable was studied within its lower and its higher value. Figure 8 also shows the hydrogen production as function of the intensity. This figure illustrates that the production is directly proportional to the intensity and, therefore, to the current density.

Besides, the higher the intensity, the higher the production.

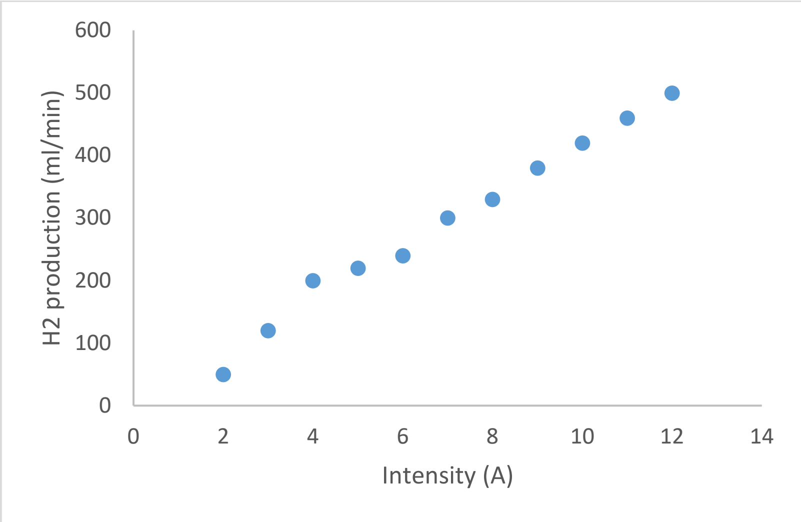

Figure 8 *Hydrogen production as a function of intensity.*

3.2 Effects of temperature in hydrogen production.

The effects of temperature in hydrogen production are shown in Table 4. The results display that there is no influence of the temperature in the production.

Table 4 *Effects of temperature in hydrogen production.*

	H_2 flowrate (ml/min)							
Intensity (A)	T= 283 K	T= 288 K	T= 293 K	T= 303 K	T= 308 K	T= 313 K	T= 318 K	T= 328 K
2	50	50	50	50	50	50	50	50
3	120	120	120	120	120	120	120	120
4	150	150	150	150	150	150	150	150
5	220	220	220	220	220	220	220	200
6	240	240	240	240	240	240	240	240
7	300	300	300	300	300	300	300	300
8	330	330	330	330	330	330	330	330
9	380	380	380	380	380	380	380	380
10	420	420	420	420	420	420	420	420
11	460	460	460	460	460	460	460	460
12	500	500	500	500	500	500	500	500

Then, the influence of the temperature in the cell voltage was studied. The cell voltage is equal to the stack voltage divided by the total number of cells. The polarisation curve (cell voltage - current density curve) is displayed in figure 9.

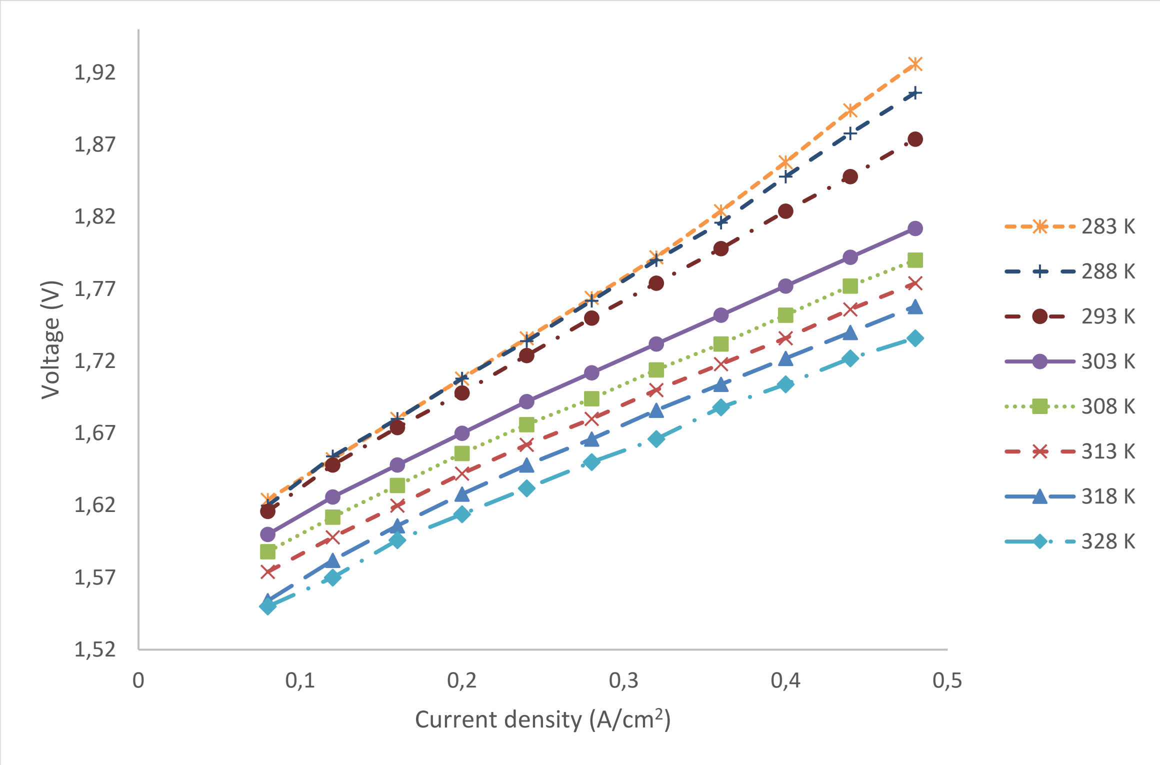

Figure 9 *Polarisation curve at different temperatures.*

The polarisation curve illustrates how the voltage change with the temperature. The higher the temperature, the lower the voltage. It means that, with higher temperatures, the electrolyzer is able to produce the same amount of hydrogen but the overall process requires less energy. At 0.5 A/cm^2 (12 A) the difference between the lowest temperature (10ºC) and the highest (55 ºC) is of 0.2 V per cell. In this particular case, this increase of temperature reduces the voltage in 1 V, resulting in 12 W of power saved. This is an interesting data because in industrial processes, with hundreds of cells, it could save a great amount of energy.

Moreover, for the same intensity, when the temperature rises, the voltage decreases but keeping the hydrogen production constant. Therefore, the process is more efficient.

The next step was obtaining the enthalpy and entropy values for each temperature, following equations 4 and 5. Then, Gibbs' free energy was calculated (eq. 2). Finally, thermoneutral voltage value for each temperature was obtained (eq. 1) and then, the efficiency was determined (eq. 5).

The values of enthalpy, entropy, Gibbs' free energy and thermoneutral voltage for each temperature are shown in Table 5.

__Table 5__ Thermodynamic values of the electrolysis as a function of temperature.

Temperature (K)	**Enthalpy (ΔH) (J/mol)**	**Entropy·T ($T \cdot \Delta S$) (J/(mol))**	**Gibbs' Free Energy (ΔG) (J/mol)**	**Thermoneutral voltage ($E^0_{cell)}$ (V)**
283	284229.45	157.51	284071.94	-1.472
288	284758.28	159.36	284598.92	-1.475
293	285289.78	161.19	285128.59	-1.478
303	286360.75	164.79	286195.96	-1.483
308	286900.24	166.55	286733.69	-1.486
313	287442.38	168.3	287274.08	-1.489
318	287987.19	170.02	287817.17	-1.492
328	289084.79	173.42	288911.37	-1.497

Figure 10 illustrates the efficiency as a function of temperature. It is noticeable that the efficiency improves when the temperature increases. On the other hand, the higher the intensity, the lower the efficiency, since increasing the intensity causes the voltage to increase too, making the process more productive but more inefficient.

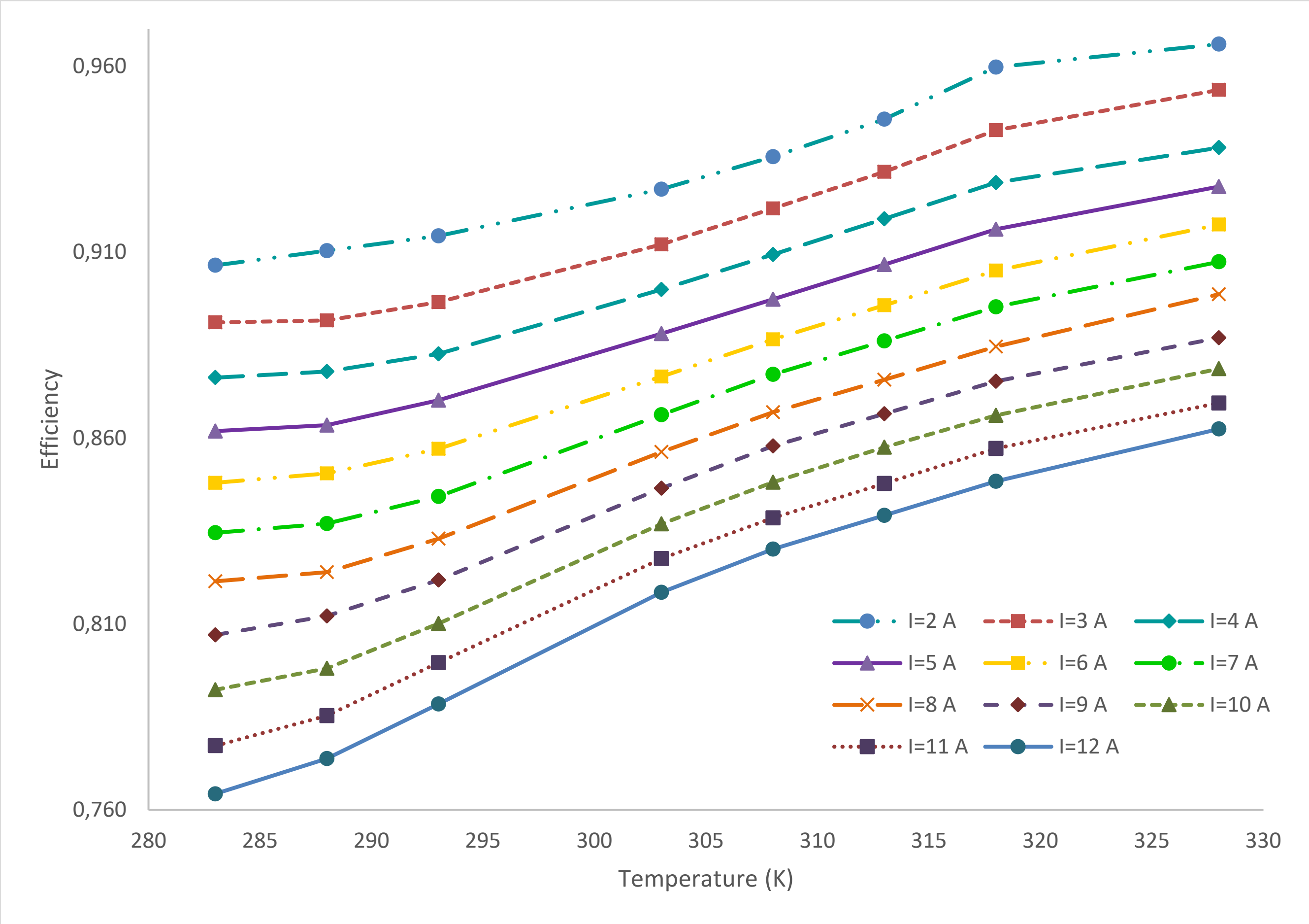

Figure 10 *Efficiency as a function of temperature.*

3.3 Effects of the pressure in hydrogen production.

The influence of the pressure in the H_2 production was studied at 6 A, which is the intensity recommended by the manufacturer. The results are shown in figure 11. It is remarkable that, the higher the pressure, the lower the hydrogen flowrate. At four bar, the hydrogen production falls. The final production at 12 bar is less than the half of the initial.

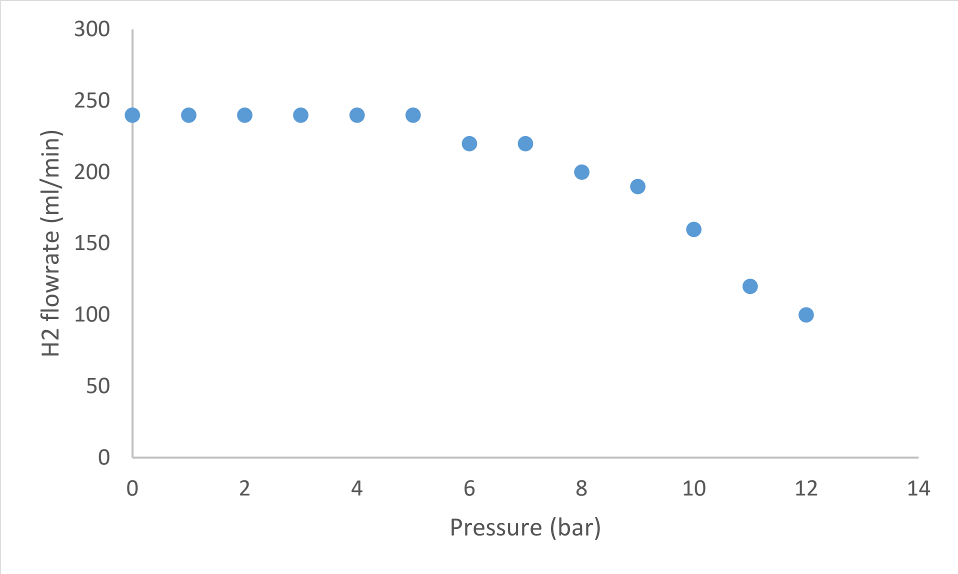

Figure 11 *Hydrogen production as a function of pressure.*

As it is shown, the pressure of the output stream clearly influences the production. This influence causes a flowrate decrease as the pressure increases. The electrolyzer configuration is not able to keep a high pressure and a high flowrate.

In order to have a sufficient hydrogen production alongside with a satisfactory pressure, it is necessary to know the effect of the pressure in production of hydrogen at different intensities.

Because of that, a study of H_2 production in all the intensity range was performed. Results are available in Figure 12. All the productions decrease as the pressure rises. The trend is the same in all the range of intensity.

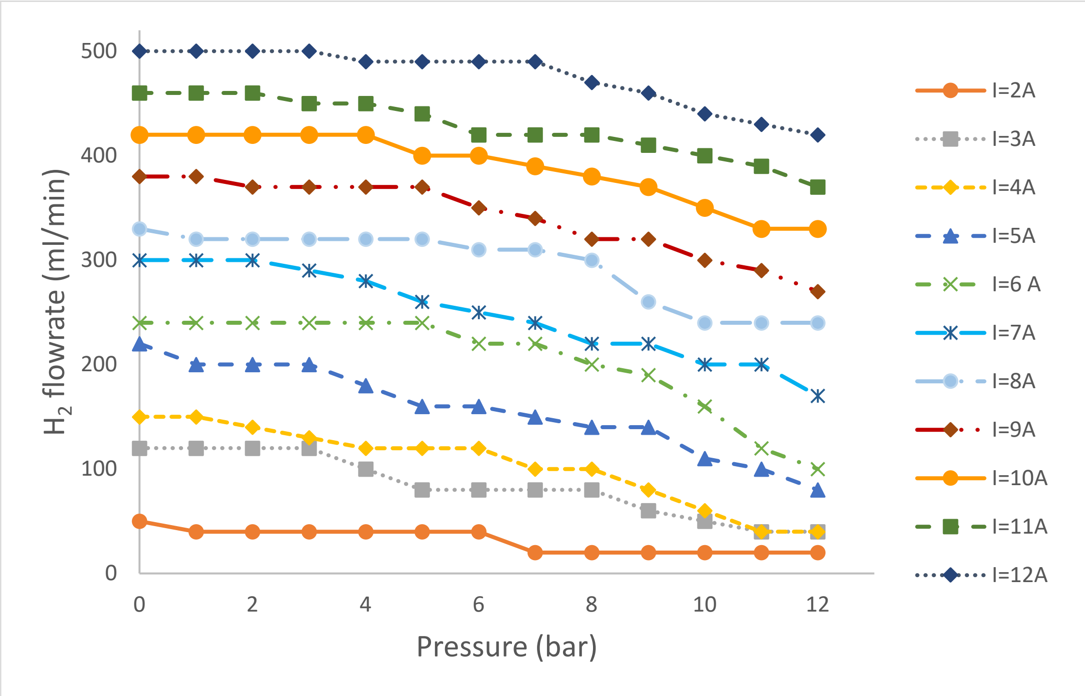

Figure 12 *Hydrogen production as a function of the pressure for different intensities.*

In order to compare the production drop between the productions at different intensities, the production drop percentage was calculated as shown in equation 4.

$$\%\ production\ drop\text{:}\ \frac{Production\ at\ 0\ bar - Production\ at\ 12\ bar}{Production\ at\ 0\ bar} \quad (4)$$

This production drop percentage is shown in table 3.

Table 6 *Production drop percentage.*

Intensity (A)	**% production drop**
2	60
3	66.6
4	73.3
5	63.6
6	50
7	43.3
8	27.3
9	28.9
10	21.4
11	19.6
12	16

As it is shown, at higher intensities, the production drop becomes smaller.

4. Conclusion.

The main conclusions of this study can be summarized as:

Hart 250 setup for electrolysis was chosen. It was the most suitable lab-scale electrolyzer according to economical and technical criteria.

The installation and start-up required auxiliary equipment for the operation and characterization of the setup. The characterization showed that both the intensity and the voltage were important for electrolysis. Intensity was also relevant for hydrogen production, since the higher intensity, the higher production. Pressure affected production too. Increasing pressure caused the production to fall. However, at higher intensities, the production decrease was lower.

Temperature had no influence over hydrogen production. Nevertheless, the voltage was dependant on water temperature. As temperature increased, voltage decreased, which meant that the total power needed for electrolysis was lower. When efficiency was calculated, it turned up that at high temperatures, the process was more efficient. Although, efficiency decreased with intensity.

To conclude, the best operational conditions for high hydrogen production are high temperature and, for high pressures, high intensities even though it is not the most efficient scenario. For the highest efficiency, the best conditions are at low intensities.

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