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Study on the electrochemical production of hydrogen from bio methanol and renewable energy

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Abstract

One of the most important challenges of the twenty first century is the reduction of greenhouse gas emissions, which are the main cause of climate change. The use of renewable energy sources, such as wind, solar and hydroelectric power, stands as an alternative to the use of fossil fuels that are still widely used to meet the growing demand for energy. The need to meet climate requirements arises in a context in which fossil fuels cannot be completely eliminated yet: firstly, they are widely used today as fuels for the transport sector; on the other hand, the need to constantly feed the electrical grid requires a stable energy source that can cope with the randomness of renewable energy. Among the possible climate-neutral alternatives there is hydrogen: it is an energy carrier that can be used both to produce electricity and as a fuel for the transport sector. Nowadays Hydrogen is mainly produced from fossil fuels such as coal and methane, only less than 1% is produced by electrolysis of water. The latter relies on a type of device, called an electrolyser, that uses electricity to break up the water molecule, producing hydrogen. The major problem of this technology is that it is highly energy intensive. An alternative proposed within this study is aqueous methanol electrolysis. The studies carried out on this topic show that the theoretical operating voltage of methanol electrolysis is 0.02 V compared to the 1.23 V of water electrolysis, so for the same amount of hydrogen produced, the energy consumption is about 60% lower for methanol electrolysis rather for water electrolysis.

Since information in the literature is scarce and often conflicting, this study has the aims to investigate the performance of a PEM-type electrolyser in terms of polarisation curves, trying to find the optimal configuration by varying the operating temperatures and the concentration of methanol in the solution. Finally, the polarisation curve that presents the lowest voltage for the same current density is used to develop a case study where it is supposed to power the cars and buses on the island of San Pietro with the hydrogen produced by the aqueous methanol electrolyser, concluding the analysis by calculating the Levelized Cost Of Hydrogen. The first four chapters illustrate the energy supply problem and how hydrogen and methanol can help in the decarbonization process. Chapter five describes the test bench and the methodology used for the results shown in chapters 6 and 7. Finally, the eighth chapter is dedicated to the description of the case study.

1. Electricity Generation in remote places

It is becoming increasingly evident that the development of society and energy infrastructure are closely related. Humans consume energy in the form of goods and services, which, starting with the use of fossil fuels, has enabled their economic and social expansion. The availability of energy and its use in an increasingly efficient manner has led to increased comfort and length of life, resulting in an increase in the world's population.

In this sense, we can rely on two very significant parameters:

- LEI: Lambert Energy Index, which considers the quality, quantity and distribution of energy;
- HDI: Human Development Index, which is a measure of a nation's longevity, education and income.

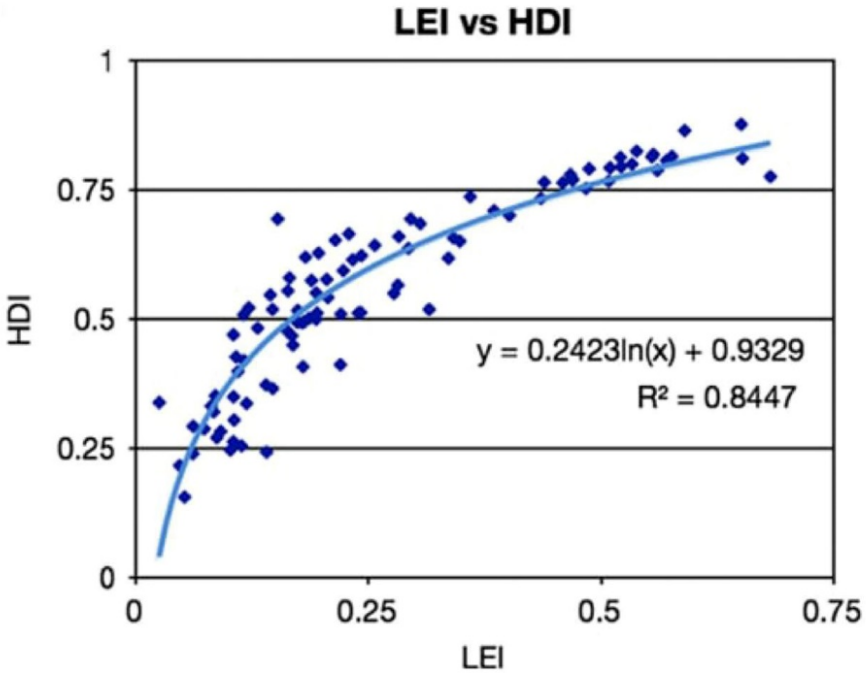

Figure 1:HDI and LEI graphic

As can be seen in Figure 1 (1), in the first part there is an almost linear trend in the HDI index as the LEI increases, corresponding to those countries that are increasing their energy infrastructure and thus begin to benefit from the consequent increase in their living conditions, until an almost constant parameter is reached for LEI values above 0.45, i.e. countries with a solid infrastructure, investment and knowledge on the subject of energy. Once the energy has been produced, it must be distributed to all consumers, which is quite advantageous for large population centres and densely populated areas, as the investment in setting up a branched electricity grid is cost-effective, as the number of people using the service is high. The same cannot be said for remote locations or islands, where the extension of the electricity grid is not always cost-effective (1).

1.1. Energy supply problem

As reported in the world bank data archives, 733 million people live without an access to electricity and 2.4 billion people still use fuels that are dangerous for the environment and for their health (2).

The main problems encountered in these areas are essentially two (3): the first is undoubtedly the lack of qualified personnel for the construction and especially the maintenance of energy production plants, with consequences of low-capacity factor values and high expenses due to damage to the various components; the second is that often the most used and cheapest way to produce electricity is through diesel generators, which however goes against the 2050 decarbonisation targets. It is also important to underline the fact that several countries try to address this problem, for example Colombia created government entities as the institute for Planification and Promotion of Electrical Solutions in Non-Interconnected Zones (3).

Italy in this sense guarantees 100% access to electricity for the entire population (4). Analysing the report on sustainable islands (5), it can be seen that even in a context of full ramification of the national electricity grid, there are places where it is necessary, at the moment, to use local energy production plants for islands that are not interconnected. Furthermore, the local energy needs of these islands not interconnected to the grid are often covered using fossil fuels. In fact, the percentage coverage by renewable energy sources is almost always less than 5% and only in the case of Ustica is 11.99% (5).

1.2. A possible solution: Renewable energy systems and alternative fuels

There is therefore the necessity to find a compromise between the need for electricity for isolated locations and covering this amount exclusively with fossil fuels. A first way forward could be hybridisation, i.e., covering the energy needs by coupling the use of renewable energy and batteries with diesel generators used as a backup source during peak and intermittent periods.

A feasibility study for a remote village on the Himalayan mountains in India (6) shows that a cost of electricity of 0.63 $/kWh was found using a wind-hydro hybrid system with a battery storage and a diesel generator to cover peaks and periods in which renewables energy systems are not able to satisfy the demand and that this system is able to emit 87% less CO_2 with respect to a system that uses only the diesel generator to cover the same demand (6). This combination works both from an economic and environmental point of view, covering the demand without any interruption. Fossil fuels are widely used in the transport sector due to their physical and chemical characteristics, such as very high energy density, ease of transport and storage (7). Introducing a new type of fuel is not easy but will be necessary to reduce CO_2 emissions and all those contaminants that interfere with achieving the 2050 zero-emission targets (8). Among the most promising and under-researched alternatives there is certainly hydrogen, due to resource scarcity and improving environmental quality.

2. Hydrogen

The huge increase in the amount of CO_2 and other Green House Gases (GHGs), from 1970 to 2011, is mainly related to the fossil fuel combustion and industrial processes (9), so, it is necessary to find a sustainable and clean way of generating energy that can also cope with the problem of the randomness of renewable energy sources.

Hydrogen is not a primary source of energy, it is always bound to other elements, such as oxygen to form water, or to carbon to form various hydrocarbons, which means that to have it in the simple H_2 form, it must necessarily be separated from the rest of the compounds in which it is found, and energy is required to do this.

The reasons why hydrogen will play an important role between now and 2050 is due to multiple factors:

- It is possible to use the existing gas grid with a certain amount of hydrogen, currently the research shows that the limit is 15%-20% of hydrogen blending, with more of this, the quality of the gas would be compromised (10);
- In the transport sector, considering trucks, trains buses, ships and cars, hydrogen seems to be the most promising option since, with respect to batteries, the systems that use hydrogen requires lower initial cost and also an advantage in terms of space as hydrogen charging stations would require one-tenth of the space that fast-charging stations would need (11);
- Central role in the transition to renewable energy sources, using electrolysers it is possible to convert electricity into hydrogen that can be used to meet the demand without CO_2 emissions.

Hydrogen is colourless, odourless, not toxic, flammable but, being lighter than air, it dissipates rapidly in case of leak that makes it relatively safer with respect to other type of fuels (12).

Although hydrogen has a very good value in terms of higher heating value (141.8 MJ/kg) (12) and lower heating value (120 MJ/kg) (12) at 298K with respect to gasoline (44 MJ/kg) (12), one of the main problems with hydrogen is his very low-density value. This is a major disadvantage in terms of storage cost due to its low energy density, which is about one fourth of that of gasoline at 20°C and 1 bar (9.9 MJ/l for H_2 and 32 MJ/l for gasoline) (13), meaning that to transport the same amount of energy in the form of hydrogen requires about four more containers than oil (12).

3. Hydrogen production

In 2021 Hydrogen production was roughly 94 Mt, emitting around 900 Mt CO_2 since most of it is produced from fossil fuels (14):

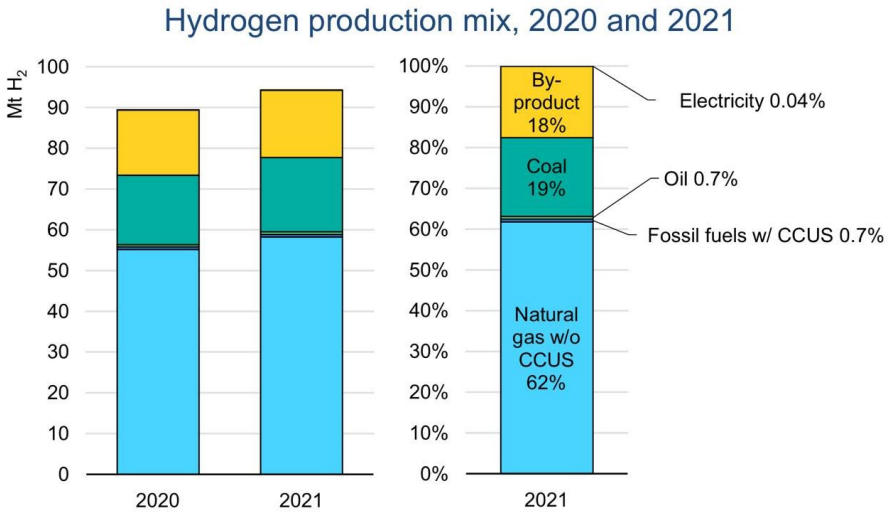

Figure 2: Hydrogen production mix.

Hydrogen, as mentioned above, can be produced from hydrocarbons or water, using energy to separate it from these compounds (14).

This is precisely why it is important to understand where this energy that drives the process comes from; there can be different ways and each of them is usually associated with a 'colour' for the quality of the hydrogen produced (15):

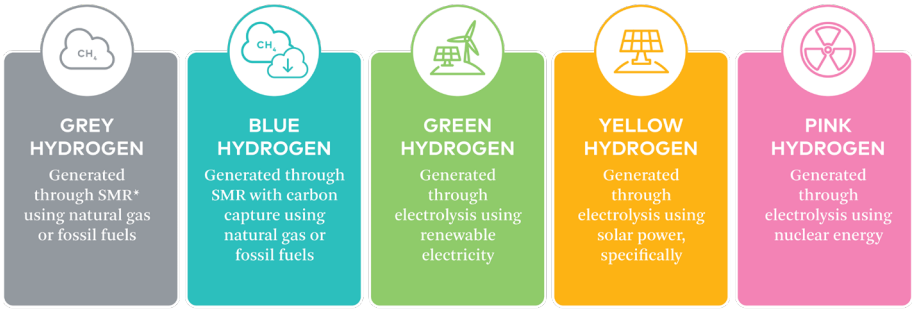

Figure 3: Colours of hydrogen associated to the production method

The steam methane reformirng reaction process consists in two steps, the first one is the reforming of natural gas, where methane reacts with high temperature steams (800°C) to produce a syngas, mainly made of H_2 and CO. The second step is the water gas shift reaction, where is produced H_2 and CO_2 starting from CO and steam (16). The only difference between blue and grey hydrogen is that in the blue one, the CO_2 is captured.

Currently, considering the amount of hydrogen produced from coal (19%, grey hydrogen), from natural gas without CO_2 capture (62%, grey hydrogen), and as a by-product of naphtha reforming at refineries (18%, grey hydrogen), the vast majority of hydrogen produced is grey type (14).

In accordance with the new international energy policies aiming at de-carbonisation (14), it is clear that there will be a change in how hydrogen will be produced in the future, pushing towards the use of green or yellow hydrogen.

For what concern the pink hydrogen, is the one produced using the electricity that comes from nuclear power plants.

The current energy crisis could also lead in the medium to long term to the production of pink hydrogen, as nuclear power is a stable energy source like gas -whose absence and uncertainty for future supplies is now being suffered- but which does not emit climate-altering gases, so it could be a good compromise for an adequate transition to green hydrogen (17).

Furthermore, the impossibility of guaranteeing the production of low-emission hydrogen in all parts of the world with continuity, trying to meet demand, increases the interest of countries where there is an abundance of renewable energy for its production, with the intention of about exporting it. According to the IEA, about 12 Mt/y of green hydrogen can be exported by 2030 (Figure 4) (14)

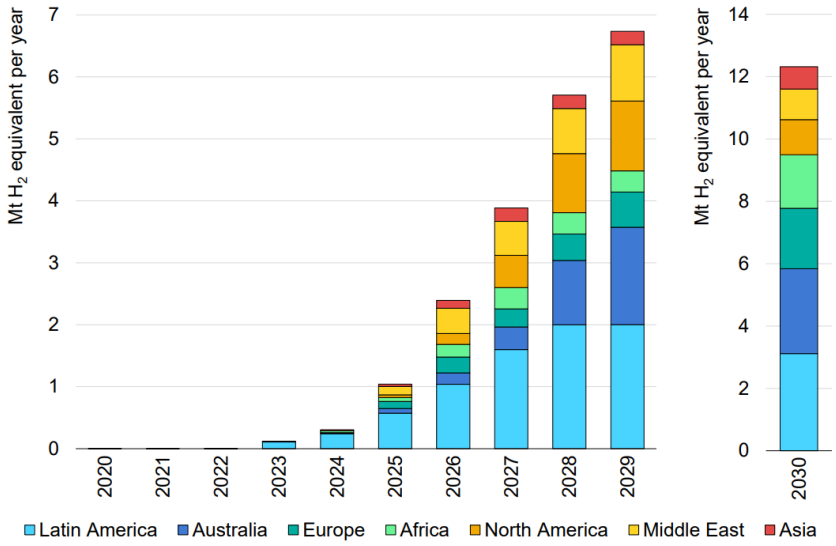

Figure 4:Planned hydrogen exports by region, 2020-2030

Most of the hydrogen that will be exported, will be produced in those countries that, as previously mentioned, have abundant resources to produce electricity from solar, wind and hydroelectric power to feed electrolysers, while only a small part will be blue hydrogen.

As is evident from the graph, hydrogen is currently consumed locally where it is produced, between now and 2030, to allow for the proper export of this energy carrier, solid infrastructures must be developed.

The delivery options for hydrogen can be essentially two (18):

- Liquified H_2 (LH_2): after the production, the hydrogen is first liquified, at temperature less than -252.9 °C, and stored in storage tanks and after, as soon is needed, delivered to the refuelling stations. Before to be used as a fuel in vehicles must be vaporized and compressed at high pressure;
- Gaseous H_2 (GH_2): before being delivered by tube trailers, to increase the energy density, must first be compressed to at least 70 bar and then, in the refuelling stations to over 700 bar.

3.1. Green Hydrogen: Electrolysers

As explained in the previous paragraph, pushing towards a cleaner way to produce hydrogen, electrolysers play a key role to be able to produce massive amounts of low-emission-hydrogen. Thus, a water electrolyser is an electrochemical device that uses electrical energy to break up the water molecule, producing hydrogen. Now, the aim is to arrive at the end of 2022 with 1 GW of installed power for electrolysers however, to reach the NET-Zero emission targets of 2050 using this type of technology, roughly, 720 GW of installed power should be reached in 2030. This would be a huge growth compared to what has been seen in recent years (19). As can be seen in Figure 5, the main players in this rapid growth should be Europe and China. (19)

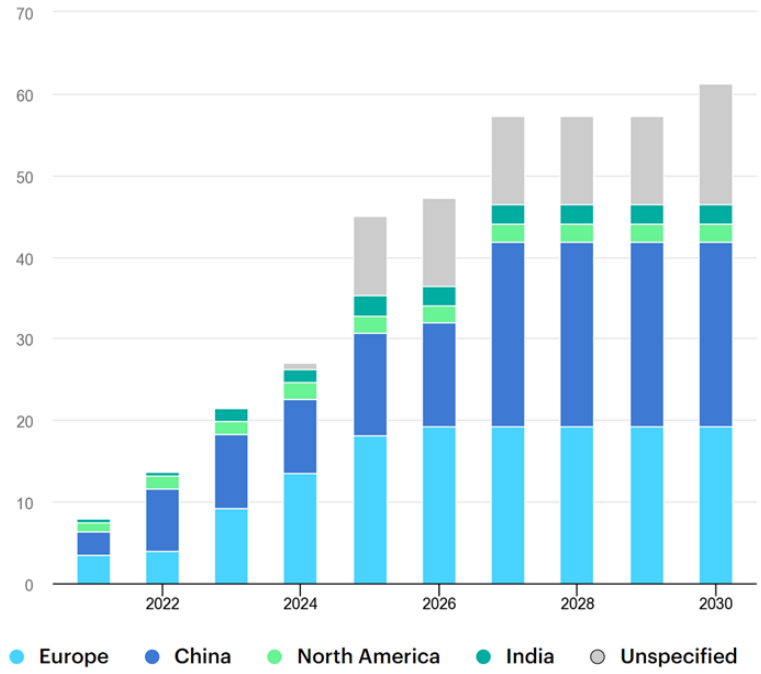

Figure 5: Planned electrolyser manufacturing capacity by region, 2021-2030

The water splitting is a non-spontaneous reaction that therefore requires a driving force, which in this case, as said before, is electrical energy:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \qquad \text{Eq. 1}$$

The most important typologies of electrolysers are (19):

- Alkaline: Technology Readiness Levels (TRL) 9, that is a parameter used to measure the maturity of a technology;
- Proton Exchange Membrane (PEM): TRL 9;
- Solid Oxide Electrolyser Cell (SOEC): TRL 7.

Alkaline and PEM electrolysers are already available on the market but still have very high investment costs so, they require policy support to be competitive on the market with respect to fossil fuel. SOEC electrolysers are not commercially available yet.

An electrolyser is composed of several parts (20):

- Bipolar plates: they are used to supply fuel to the anode and an oxidant to the cathode and they provide electrical conduction between the cells;
- Membrane Electrode Assembly (MEA) composed by:
    - Anode electrode: where the oxidation reaction takes place;
    - Cathode electrode: where the reduction reaction occurs;
    - Electrolyte membrane that can conduct protons or anions;
    - Catalyst: in each electrode, a layer of a material is deposited, touching the membrane, which acts as a catalyst to speed up the reaction, depending on the technology and on the electrode considered his composition could be different.
- Gas Diffusion Layer (GDL): is a very important component which is mainly responsible for the gas and water transport, Carbon-based material are usually used for the construction of the device since has a good electrical conductivity, gas permeability, elasticity and durability (21);
- Interconnectors: the individual cells are connected in series using interconnectors, are made of graphite or low-quality stainless steel, it must be easy to manage, dense and must be a good electronic conductor.

3.2. Alkaline Electrolysers

Currently, this technology is the most used at the market level with almost 52% of installed capacity, roughly 727 MW (19), is considered as low temperature Electrolyser since operating temperature range is $60\ °C - 80\ °C$, with an efficiency between 59% and 70% (22). The Alkaline Electrolyser uses usually as electrolyte a blend of Liquid Potassium Hydroxide and water, (80-60) % H_2O+ (20-40) % KOH (or NaOH) (23). So, the electrolyte is the liquid KOH while H_2O is the split specie already contained by the electrolyte to permit the charge transfer through OH^- ions.

The schematic configuration is shown in Figure 6 (24):

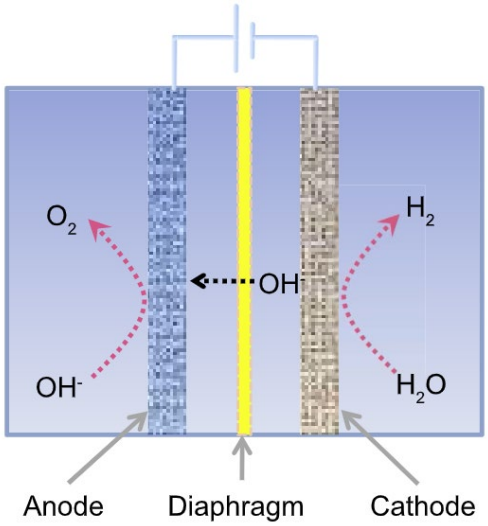

Figure 6: Alkaline water electrolysis scheme

The electrochemical reactions involved in the alkaline electrolyser are shown in Eq. 2, Eq. 3 and Eq. 4 (25):

$$Cathode\ reaction \qquad 2H_2O + 2e^- \rightarrow 2OH^- + H_2 \qquad \text{Eq. 2}$$

$$Anode\ recation \qquad 2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^- \qquad \text{Eq. 3}$$

$$Overall\ reaction \qquad H_2O \rightarrow H_2 + \frac{1}{2}O_2 \qquad \text{Eq. 4}$$

As said before, the charge transfer is performed by the ion OH^-. The H_2 obtained at the Cathode is not dry hydrogen because is present water, thus is not a high pure hydrogen and has to be divided from water.
Using non-precious metal electrocatalysts, Ni/Fe based material (26), with high durability and compatibility with the Alkaline water electrolysers and the easy operation mode makes this technology very competitive. As drawback, low current densities, high ohmic losses through the electrolytes and low operating pressure affect the hydrogen production cost.

3.3. Proton Exchange Membrane electrolyser

On the other hand, the Proton Exchange Membrane electrolyser has several advantages with respect to Alkaline one (27):

- Compact design;
- High current density, which means higher hydrogen production rate;
- Can be used in reverse mode, so as a fuel cell, that is a device that can produce energy starting from a H_2;
- Operating voltage is lower with respect to the alkaline device;

- The H_2 obtained at the cathode is dry, so is a better quality with respect to one produced in the alkaline since at the cathode is not present H_2O.

The schematic configuration is shown in Figure 7 (28):

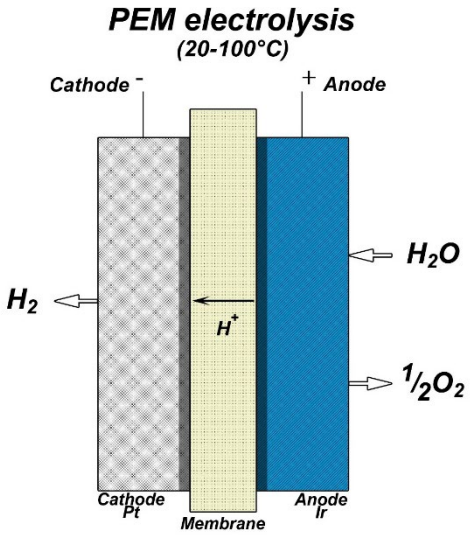

Figure 7: PEM electrolyser configuration

The electrochemical reactions involved in PEM electrolyser are shown in Eq. 5, Eq. 6 and Eq. 7 (29):

$$Cathode\ reaction \qquad 2H^+ + 2e^- \rightarrow H_2 \qquad \text{Eq. 5}$$

$$Anode\ recation \qquad 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad \text{Eq. 6}$$

$$Overall\ reaction \qquad H_2O \rightarrow H_2 + \frac{1}{2}O_2 \qquad \text{Eq. 7}$$

Since the membrane must be hydrate, the operation temperature, at ambient pressure, must be lower than 100 °C, because of this a cooling circuit is necessary in the stack to remove the heat produced and this is made using microchannels. So, since temperature cannot be a relevant parameter for increasing the kinetics of the process, a very good catalyst is needed, this means high cost with respect to Alkaline. The most common catalyst is Platinum, Iridium or Palladium (30).

3.4. Solid Oxide Electrolyser Cell

The third kind of electrolyser is the solid oxide that has several differences with respect to the other two electrolyser's typology. The main difference is the operation temperature in fact are in the range of $[600; 850]°C$ (31), this means that the kinetic of the process is very high due to high temperature involved so, no need of precious catalyst, in fact now is used Nickel as catalyst. The second main difference is the electrolyte that is the key component of the electrolyser: the most used electrolyte material is Yttria-Stabilized-Zirconia (YSZ) that, in this temperature range, exhibits very high conductivity of O^{2-}. A schematic representation of one cell is shown in Figure 8 (32):

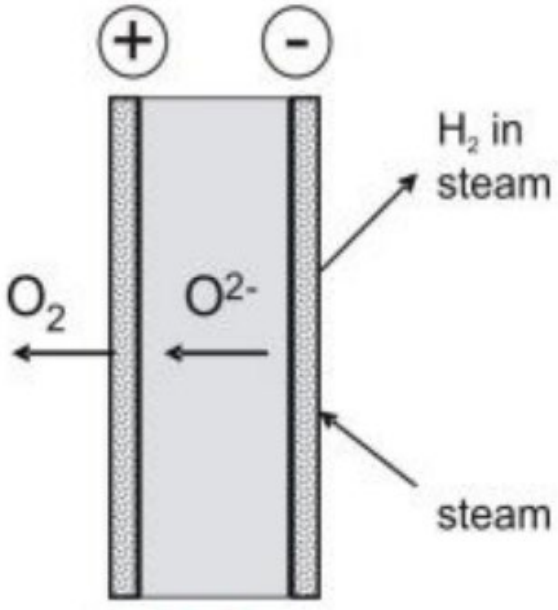

Figure 8: SOEC scheme

The electrochemical reactions involved in the SOEC are Eq. 8, Eq. 9 and Eq. 10 (33):

$$Cathode\ reaction \qquad H_2O + 2e^- \rightarrow O^{2-} + H_2 \qquad \text{Eq. 8}$$

$$Anode\ recation \qquad O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^- \qquad \text{Eq. 9}$$

$$Overall\ reaction \qquad H_2O \rightarrow H_2 + \frac{1}{2}O_2 \qquad \text{Eq. 10}$$

This Type of device is the best in term of specific consumption (see Eq. 11, Eq. 12 and Eq. 13), assuming as hydrogen density $\rho_{H_2} = 0.08988\ \frac{kg}{m^3}$ meaning that less energy is required to produce the same amount of hydrogen (34):

$$ALKALINE \qquad [4.5; 6.6]\frac{kWh}{m^3} \rightarrow [50.1; 73.4]\frac{kWh}{kg} \qquad \text{Eq. 11}$$

$$PEM \qquad [4.2; 6.6]\frac{kWh}{m^3} \rightarrow [46.73; 73.4]\frac{kWh}{kg} \qquad \text{Eq. 12}$$

$$SOEC \qquad [3.7; 3.9]\frac{kWh}{m^3} \rightarrow [41.17; 43.39]\frac{kWh}{kg} \qquad \text{Eq. 13}$$

4. Liquid Organic Hydrogen Carriers: Methanol

In chapter 3.1, it is shown that there are already mature technologies with high TRL that can produce hydrogen quite efficiently, but, with a view to decarbonisation, it is crucial to produce it in a sustainable manner and to strive for so-called 'green hydrogen'.

The problem of the intermittency of renewables, as well as the impossibility of obtaining the same energy from them in all parts of the world makes this challenge rather difficult. Furthermore, producing hydrogen locally only where there is a large supply of renewables, presents problems: once obtained, storage and transport are inconvenient in terms of high costs and inefficiency (35), essentially due to the low energy density with respect to diesel for example.

For these reasons, an alternative solution for long-distance transport is being sought: Liquid Organic Hydrogen Carriers (LOHC) (36). During transport and storage, the hydrogen is covalently bonded with the LOHC, in ambient conditions, is easy and safe to handle and therefore also has advantages in economic terms: the energy density can be increased a lot and, since the LOHC's properties are closer to the crude oil derivative, the same infrastructure could be used. Furthermore, the storage is based on a reversible process of hydrogenation and de-hydrogenation of carbon double bonds, the former being an exothermic process, the latter endothermic where catalysts are used in both processes (36).

Methanol is an alcohol that is already used to produce several industrial and consumers chemicals products, at atmospheric condition is liquid that is a great advantage in terms of transport and storage systems. Can be used also as fuel in Internal Combustion Engines being more environmentally friendly with respect to gasoline, showing 7% lower specific CO_2 emissions, 57% lower carbon content by mass (37) and it is biodegradable.

The world global methanol demand in 2021 was 106 Mt and for the 2022 should be around 111 Mt reaching 500 Mt by 2050 (38). Nowadays, the cheaper way to produce methanol is from fossil fuels -for economic reasons- and China has several coal reserves that make this country the leader in the sector of methanol production with more than the half of the actual world production.

About $\frac{2}{3}$ of the total production is using natural gas reformation and the other part is covered by coal gasification only a very small amount of methanol is covered from renewable sources (38). In the Figure 9 are summarized all the possible pathways to produced methanol (38).

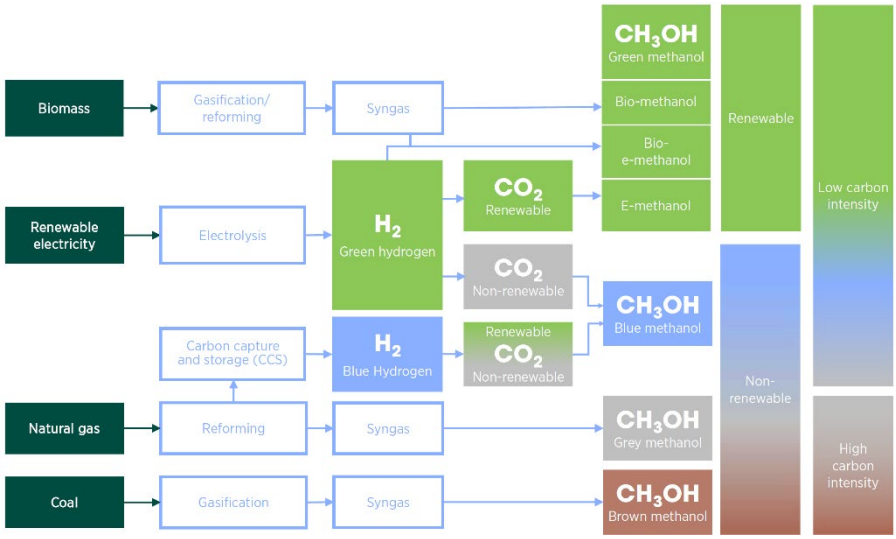

Figure 9: Proposed classification of methanol

Also in this sector, the climate change plays a very important role so, the aim is to produce methanol in a more sustainable way, for this reason the research is increasingly pushing renewable methanol.

Is possible to use several process to obtain renewable methanol:

- Bio-methanol that is produced from biomass, such as agricultural waste, biogas, municipal solid waste and his cost is related to these feedstock cost;
- E-methanol is produced using CO_2 and H_2 and it is called renewable e-methanol, if CO_2 is captured from renewable sources -bioenergy with carbon capture- and green hydrogen is used;

Methanol therefore has several characteristics that makes it a better alternative to other energy carriers: the simplicity with which it can be transported, same transport method of gasoline, and its volumetric energy content are certainly among the most relevant.

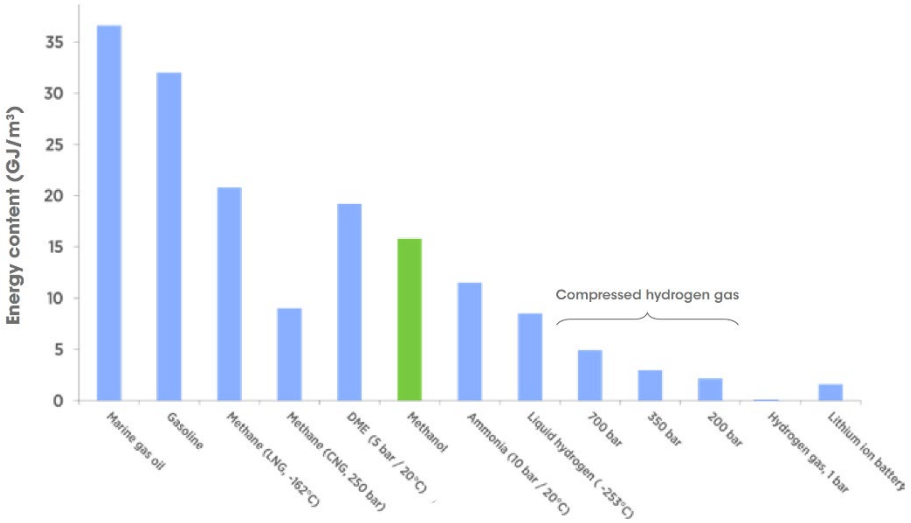

Figure 10: Energy density of various fuels (38)

The possibility of storage and transport methanol at ambient pressure and temperature makes it economically and technologically better than hydrogen. To be transported, as already said, hydrogen must undergo liquefaction (-253°C) or compression processes up to 700 bar that are highly energy intensive.

4.1. Methanol economy

The interest on this type of fuel is mainly due to its wide use in the chemical sector, where the greatest growth is expected in China to produce formaldehyde acetic acid and Methyl tert-butyl ether (MTBE), and for his compatibility with ICEs, making it an alternative with less environmental impact than gasoline and a viable alternative to reduce the emissions in the heavy transport sector, such as the shipping industry (38).

In addition, methanol can be used to produce DME, used in some countries for household heating and cooking, and can be an alternative for both diesel and high temperature fuel cells. DME, having small carbon chains, when used as a fuel, can reduce emissions of particulate matter, NO_x and CO without making major modifications to existing engines (38).

The process to convert Methanol in DME (CH_3OCH_3) is the dehydration, shown in Eq. 14 (39).

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \text{Eq. 14}$$

The growth in the production over the next 30 years will be strong, it is projected to produce 115 Mt of fossil methanol and slightly less than 400 Mt of renewable methanol: 250 Mt of e-methanol using CO_2 and H_2 produced by electrolysers exploiting solar or wind power, 135 Mt of bio-methanol through gasification using about 230 Mt of dry biomass (38). The costs projections based on the Methanol production method is presented in the Figure 11.

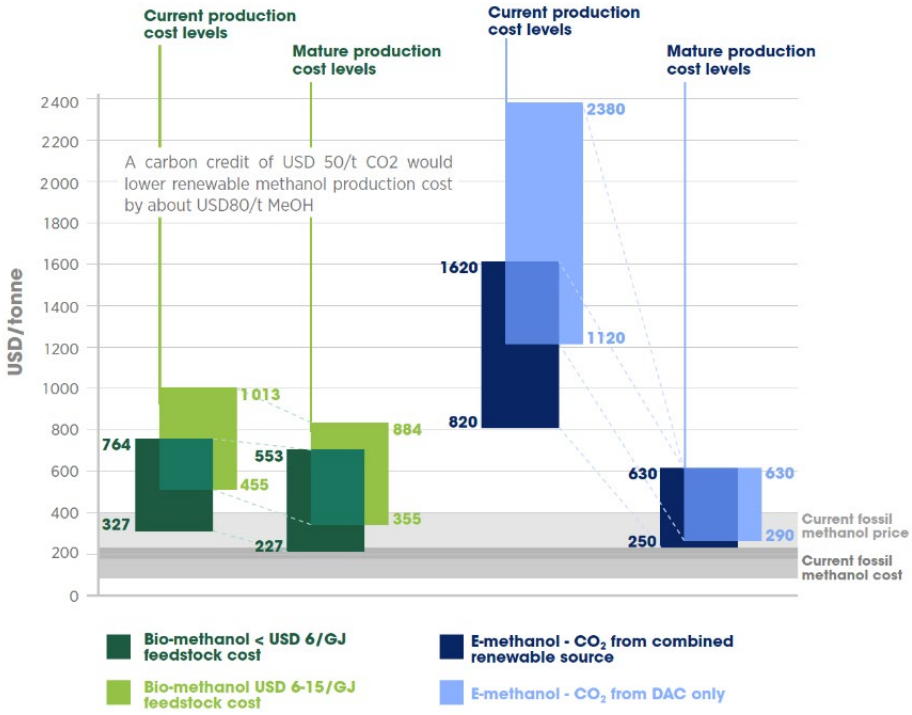

Figure 11: Current and future production costs

4.2. Methanol Electrolysis: State of the art

Nowadays, hydrogen is usually obtained by steam reforming of natural gas being the most economical solution for large-scale production systems (14). Looking towards a possible alternative on small-scale production, the most cost-effective solution for the future seems to be electrolysis of water even though it is a highly energy-intensive method of hydrogen production, therefore, electrolysis of aqueous methanol is gaining increasing interest.

As mentioned earlier, methanol is one of the most promising LOHCs and it is also compatible in PEM electrolysers, in a solution of methanol and water, in a device with a configuration like the one shown in Figure 12 (40).

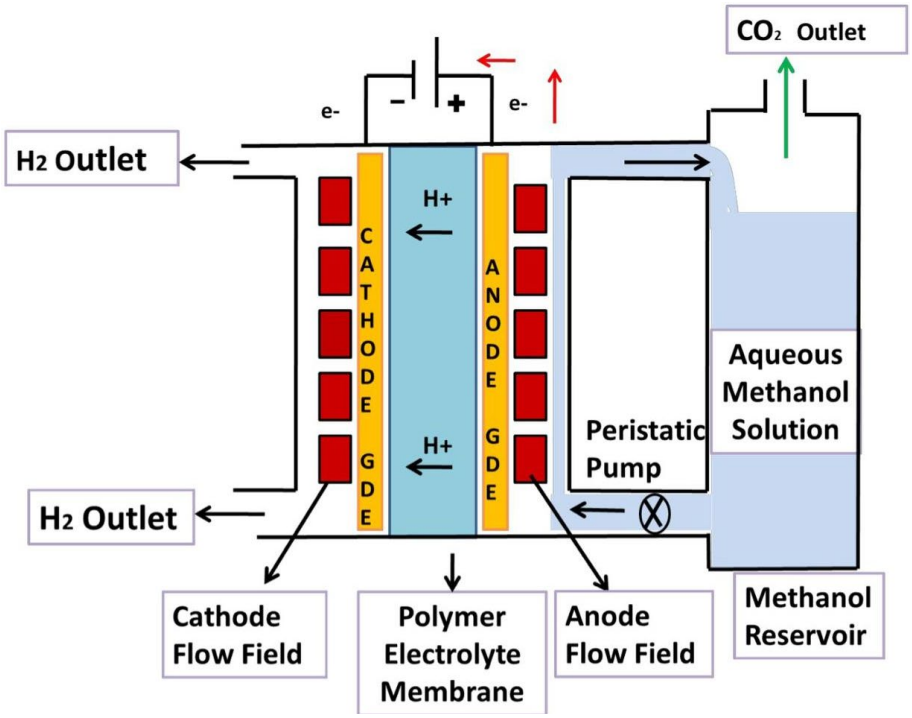

Figure 12: Methanol PEM electrolyser

The electrochemical reactions involved in the PEM methanol electrolyser are the Eq. 15, Eq. 16 and Eq. 17:

$$Cathode\ reaction \qquad 6e^- + 6H^+ \rightarrow 3H_2 \qquad \text{Eq. 15}$$

$$Anode\ recation \qquad CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \qquad \text{Eq. 16}$$

$$Overall\ reaction \qquad CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \qquad \text{Eq. 17}$$

In this process, it can be obtained very high pure hydrogen and, the PEM electrolyser design allows to automatically separates both hydrogen, cathode side, and CO_2, anode side. The main advantage of this technology is the theoretical operating voltage, that is around 0.02V with respect to the 1.23V of the water electrolysis: thus, the theoretical energy consumption for methanol electrolysers compared to water electrolysers is significantly lower.

4.3. Membrane Electrode Assembly

The methanol electrolysis device is quite similar to the one for the water electrolysis, the most relevant change is in the use of some materials for the catalysts and the storing device that must be used to store methanol and that could be used to store CO_2 that, since is toxic, has to be treated with more attention with respect to a water tank. As said before, the core of the electrolyser is the Membrane electrode assembly (MEA). In Table 1 are summarize the main materials used in the literature:

Table 1: Information about the main components of a MEA in the literature

Anode catalyst	Cathode catalyst	Membrane	Reference
40% Pt–Ru/C	20% Pt/C	Nafion117	(40)
PtRu/C	Pt/C	Nafion117	(41)
PtRu/C	Pt/C	Nafion117	(42)
PtRu/C	Pt/C	Nafion117	(43)
Pt–Ru (1:1) black	Pt black	Nafion115	(44)
50% Pt–Ru/C	50% Pt/C	Nafion117	(45)
PtRu/C	Pt/C	Nafion117	(46)

As can be seen from Table 1, the MEA is often constructed in the same way, the membrane is usually Nafion 117, just one case with Nafion 115, while the cathode electrode is predominantly Pt/C while PtRu/C is usually used for the anode.

As alternative Pt/C cathode catalyst, it is been studying the Pt-WC/C one: comparing the performance of the Hydrogen Evolution Reaction (HER), the addition of Tungsten has increased the process. (41)

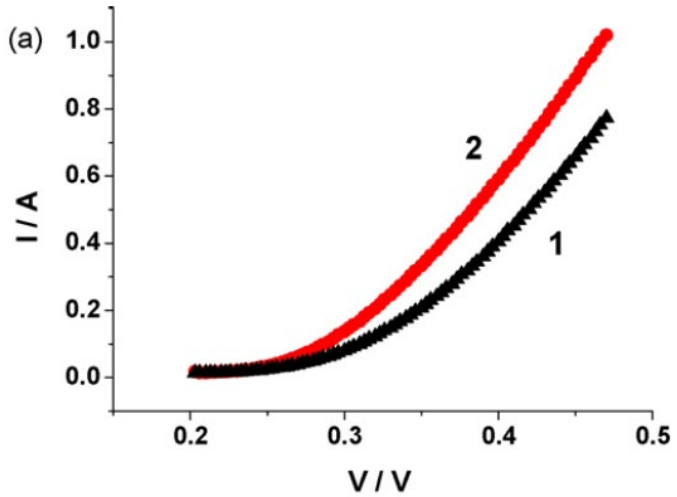

Figure 13: (1) V-I curves of MEAs using Pt/C; (2) V-I curves of MEAs using Pt-WC/C; Temperature=90°C

In the Figure 13, the curve (1) represents the V-I using Pt/C, the other one is for the E-I that uses Pt-WC/C, using temperature equal to 90°C with a 2M methanol concentration as operating condition, the performance of the second configuration shows a slightly better behaviour with respect to the conventional cathode catalyst in Pt/C, lowering a bit the voltage for the same amount of current density.

At the end, is under developing, another solution for both cathode and anode catalyst, Pt nanoparticles deposited over the ZIF-67-derived CoSe/N-doped carbon nanospheres (Pt-CoSe/NC) (47), this solution, as said, could be used as bifunctional catalyst construction for methanol electrolysis resulting first of all convenient for MEA fabrication. Moreover, using this type of catalyst exhibit huge current density with respect to the usual Pt/C catalyst, reaching values 3.1 higher than the common catalyst material.

4.4. Methanol concentration and temperature dependency

Going in depth with research on this new technology was found that methanol electrolysis could depends strongly on two main parameters: methanol concentration, and temperature.

It is shown in Figure 14 that the production of hydrogen increases until the concentration of methanol reaches 6M, even 4M is probably the best value, as the increase is insignificant, furthermore, after the value of 6M, the current density decreases because dissolution of nafion ionomer in the catalyst layer probably occurs (48).

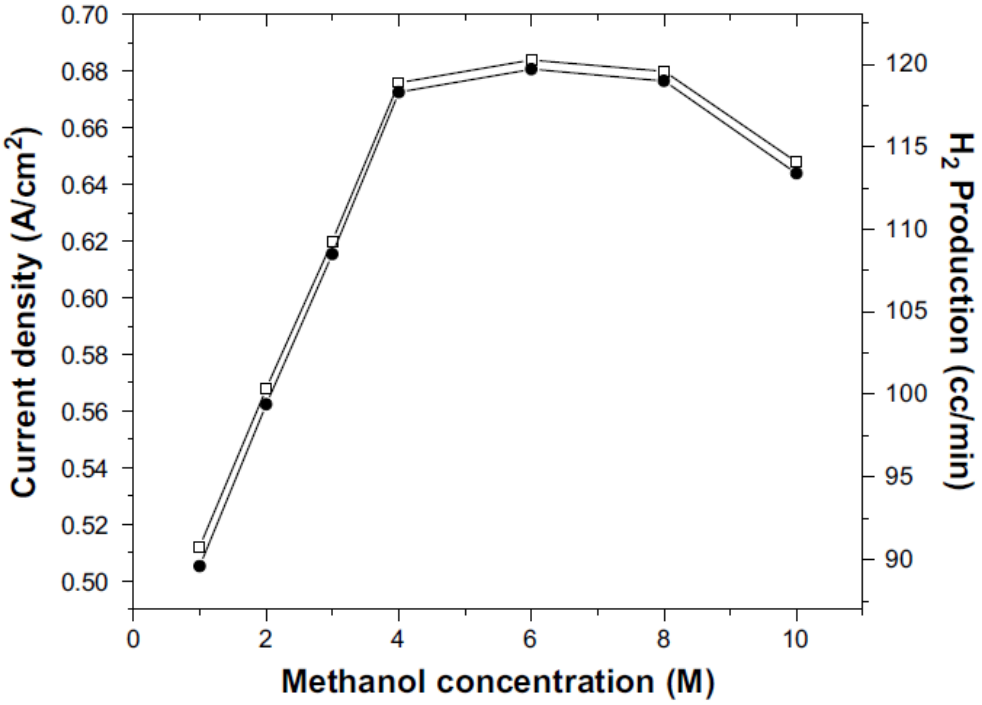

Figure 14: Influence of methanol concentration in the Hydrogen production at 30°C and 1V using nafion 117 membrane

In this case the temperature used to carry out the experiment is equal to 30°C and, as membrane, is used Nafion 117 at a fixed cell voltage of 1V.

Furthermore, if it is considered a certain amount of current density, it's shown in Figure 15 that increasing the concentration of methanol, the cell voltage is lower, that means less energy consumption and the best value is again 4M, using nafion 115 as membrane at Temperature equal to 30°C and ambient pressure (p=1 bar). (49)

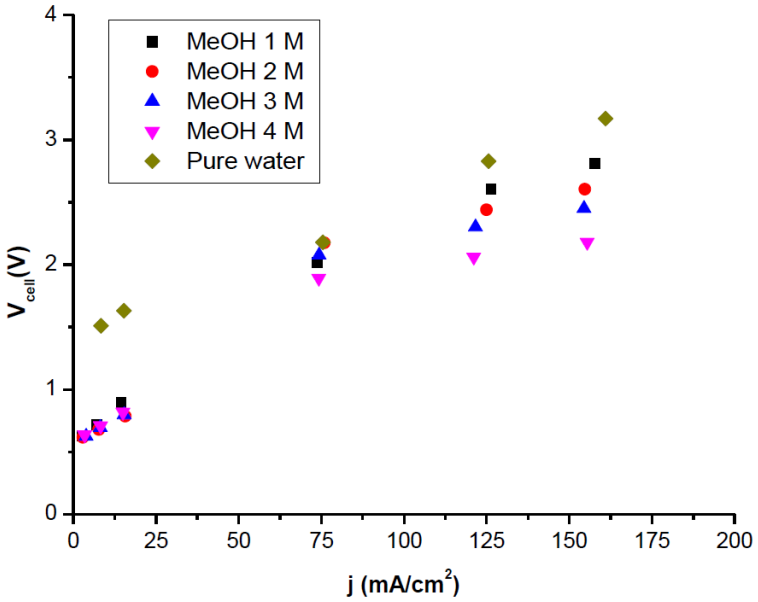

Figure 15:Polarization curve considering 4 methanol concentration at 30°C, 1 bar and using nafion 115 membrane

At the end, another study (41) shows that, at temperature equal to 60°C, the behaviour in terms of voltage of the cell change a lot increasing the methanol concentration from 1M to 2M, and is more or less the same at 2M, 3M and 4M.

The second important role is the effect of the temperature, increasing the temperature value, current density increases and thus, hydrogen production increase too (41) (44).

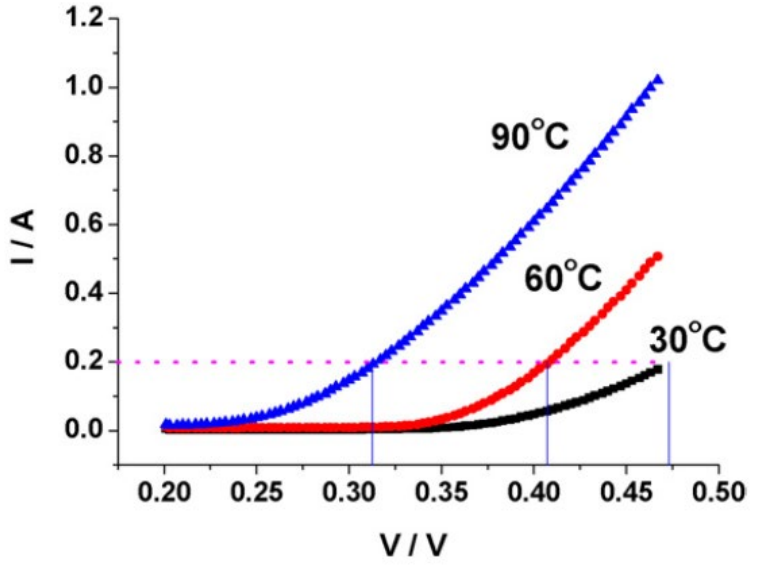

Figure 16: Influence of the temperature in the polarization curve using a methanol concentration of 2M, with a Pt-WC/C cathode electrocatalyst

Finally, in Figure 17, it can be proved that coupling the two effect it is shown a different behaviour (43).

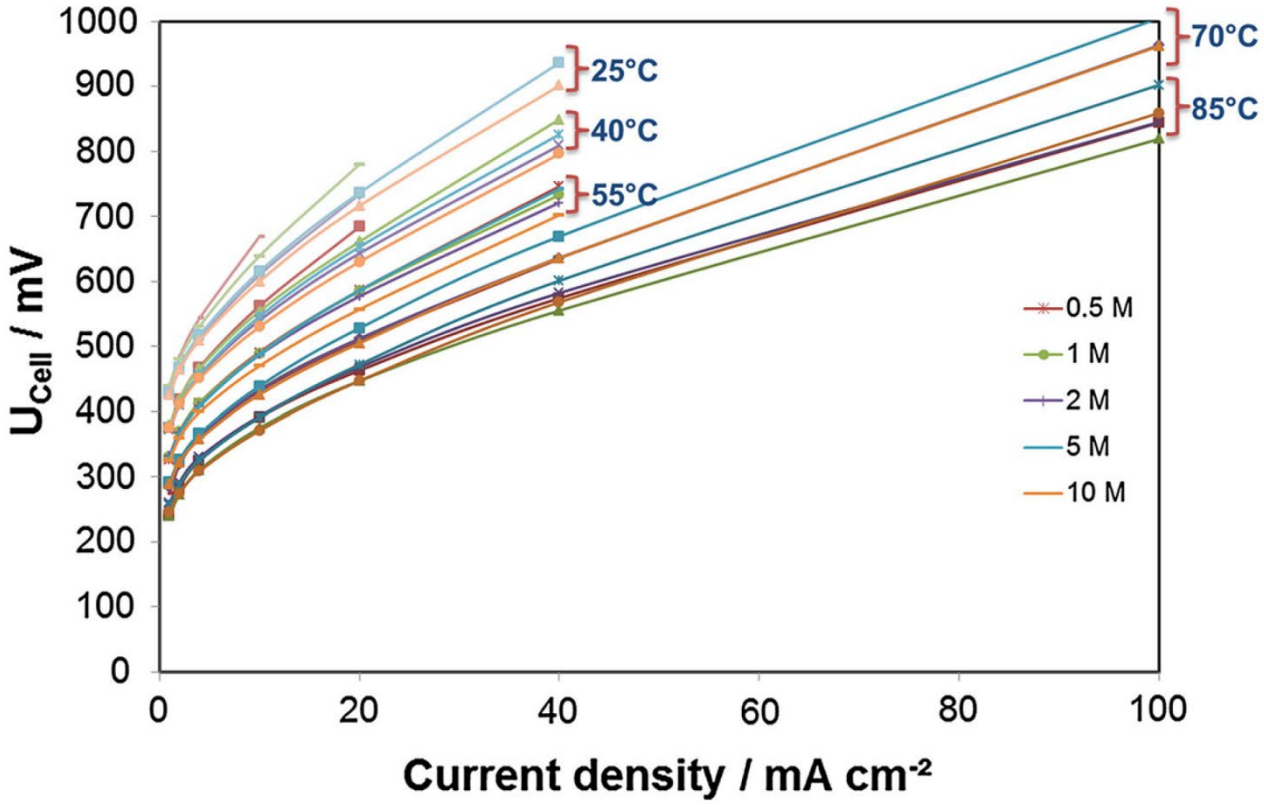

Figure 17: Influence of temperature in the polarization curve using 5 methanol concentration temperature.

In this case (Figure 17), increasing the temperature and methanol concentration it can be seen that, with high temperature, like T= 85°C, the best configuration, so the one that has the lowest value of the U_{CELL} at the same current density, is the one with methanol concentration equal to 1M. At the same time, for lower temperature value, so between 25°C and 55°C, high methanol concentrations are better.

This behaviour could be explained since, at high methanol concentration value, the ion conductivity in the membrane decreases, due to degradation of nafion membrane (48). Moreover, it was observed that in an alkaline methanol electrolyser could involve the problem of methanol crossover (MCO) that is when methanol pass through the membrane and arrives to the cathode side, mainly due to the diffusive mass transport that is proportional to methanol feed concentration, so at higher temperature could be better to lower the methanol concentration (50).

4.5. Renewable energy hybrid systems with methanol electrolysis

Using renewable energy as a driving force for the electrolysis process seems to be the cheapest and fastest way to produce green hydrogen in the coming years (17). This could be even more convenient in the electrolysis of methanol since large amount of energy could be saved, due to the voltage associated with the start of hydrogen production is theoretically much lower than that of water electrolysis (methanol electrolysis 0.02 V and 1.23 V for water electrolysis).

As regards this consideration, it can be considered the using of Photovoltaic energy technology (51), both in on and off grid configuration, one of the best ways to drive the reaction in a very efficient way from the point of view of the utilization area and the correct use of backup systems such as batteries, as this could avoid exceeding safety limits, optimising their lifetime.

It can be useful to analyse the differences between the polarization curve of the water electrolysis and the methanol electrolysis as it is shown in Figure 18, where on the vertical axis there is the cell voltage and on the horizontal one there is the current density (51).

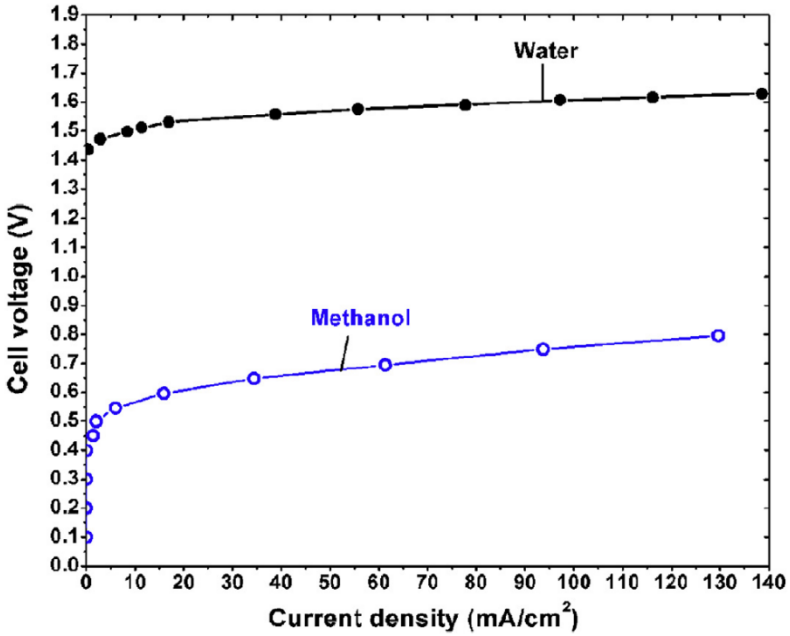

Figure 18: I-V characteristics at 4M and 80 °C

The difference between the hydrogen production starting point for the water electrolysis and the methanol electrolysis is huge: for the first one, operating voltage of 1.45 V is required, for the second only 0.45 V. As said before, this leads a very huge energy savings for the methanol electrolysis device.

5. Methodology

The following conditions are established to study what are the best operating parameters of a methanol electrolyser, to also guarantee the best performance in the further case study:

- Temperature: 40°C, 50°C, 60°C,70°C;
- Molarities: 1M, 4M, expresses the number of moles of solute contained in one litre of solution, in this case the solute is methanol and the solvent is distilled water.

The decision to operate with this temperature range was taken from a review of the literature (41) (43) (44) (48), the parameters of the polarization curve vary significantly as a function of the operating temperature, decreasing the voltage for the same current density as the temperature increases.

Furthermore, from the literature (41) (43) (46) (48) (49), it has been found that a parameter that also affect the electrolyser performance is the molarity of the solution: in most of the cases, the molarity used is between 1M and 4M. Methanol crossover may increase if there are higher concentrations than 4M. However, the benefits of increasing molarity up to 4M has been reported in the literature, improving the methanol electrolyser performance as the molarity increases. Only in one case there is an improvement reported in polarisation curve with a methanol concentration of 16M (46).

To obtain the polarization curves the galvanostat applies a current from 0 to 400 $\frac{mA}{cm^2}$ with a step of 5 $\frac{mA}{cm^2}$ between 0 $\frac{mA}{cm^2}$ and 20 $\frac{mA}{cm^2}$, a step of 10 $\frac{mA}{cm^2}$ between 20 and 100 $\frac{mA}{cm^2}$ and a step of 20 $\frac{mA}{cm^2}$ between 100 and 400 $\frac{mA}{cm^2}$, each step with a constant duration of 3 minutes and each polarization curve is repeated twice.

The decision to use the smallest step for the construction of the first values of the curve is due to the fact that at low current densities, it is necessary to estimate more accurately the voltage at which the reaction begins.

Since a linear trend is shown in the literature, for the second part of the polarisation curve, it was decided to increase the step value.

5.1. Experimental test system

To study the hydrogen production through aqueous methanol electrolysis, the test bench presented in Figure 19 has been used following the PiCoHiMA research group designs and indications (52).

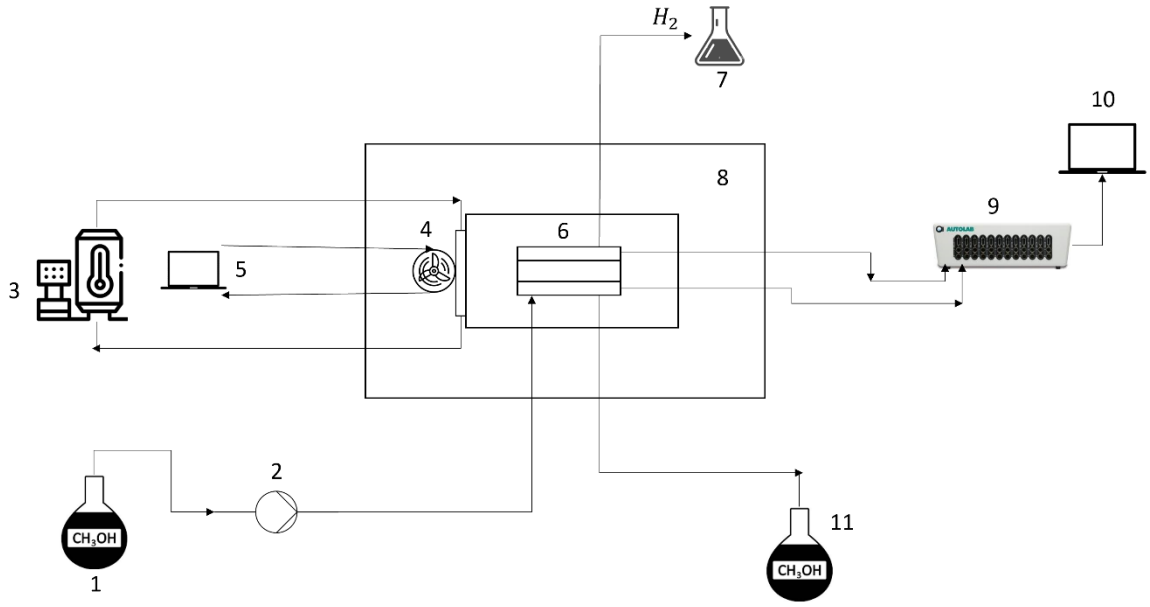

Figure 19: Water-methanol electrolyser test bench

Where:

- (1) Aqueous methanol tank;
- (2) Pump;
- (3) Heating circulator;
- (4) Fan;
- (5) Power source;
- (6) Electrolyser;
- (7) Hydrogen flow indicator;
- (8) Two isolation cases;
- (9) Autolab: galvanostat;
- (10) Computer: to monitor the results;
- (11) Tank for aqueous methanol and CO_2 product;

5.2. Aqueous methanol tank and pump

The aqueous methanol solution is drawn by the pump (2) from a cylindrical glass tank (1) with a capacity of 2 litres (see Figure 20).

This tank has two circular holes at the top that extend a few centimetres:

- The former is used to insert the delivery tube to the pump, which then draws the aqueous methanol solution and sends it to the cell;
- The latter is used to avoid leakage or the contamination of the solution and to introduce the aqueous methanol solution in the tank.

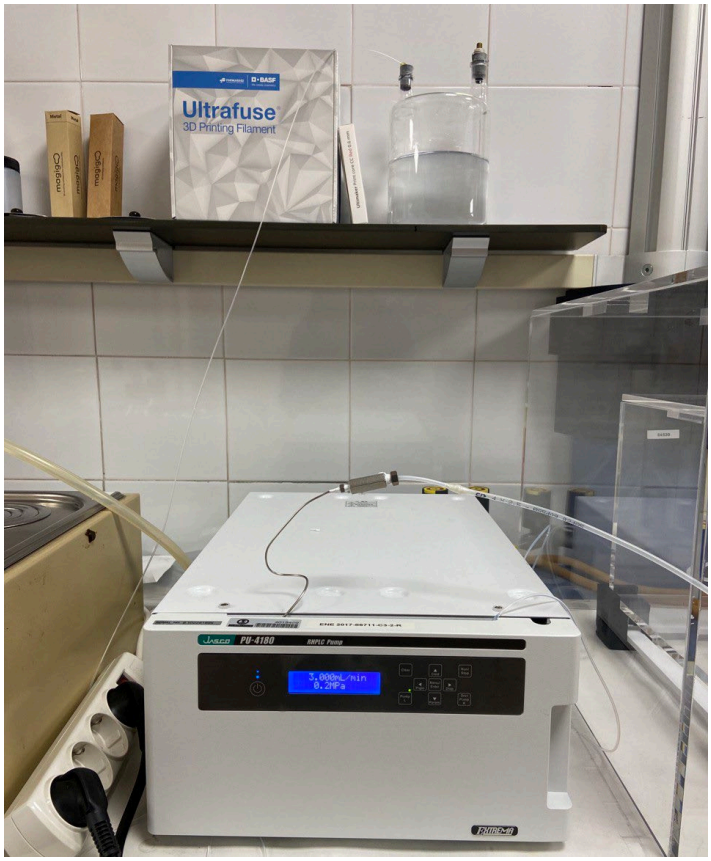

Figure 20: Pump (2) and methanol-water tank (1)

Regarding the pump, the technical specifications are:

- Minimum mass flow rate: 1 $\frac{mL}{min}$;
- Maximum mass flow rate: 10 $\frac{mL}{min}$;
- Mass flow rate used in the experiments: 6 $\frac{mL}{min}$;
- Minimum pressure: 0.1 MPa;
- Maximum pressure: 70 Mpa.

5.3. Insulating chambers

The electrolyser (6) is inside the second insulating chamber (8), where there are two circular holes on the front wall, one on the top and a rectangular one on the side wall where the fan (4) is located, in a perpendicular position with respect to the cell (see Figure 21and Figure 22).

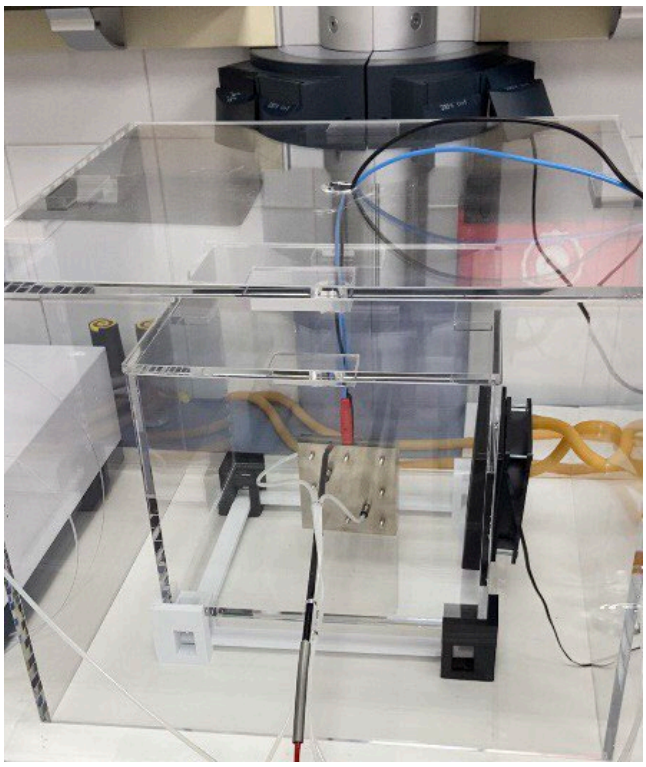

Figure 22:Insulating chambers (8)

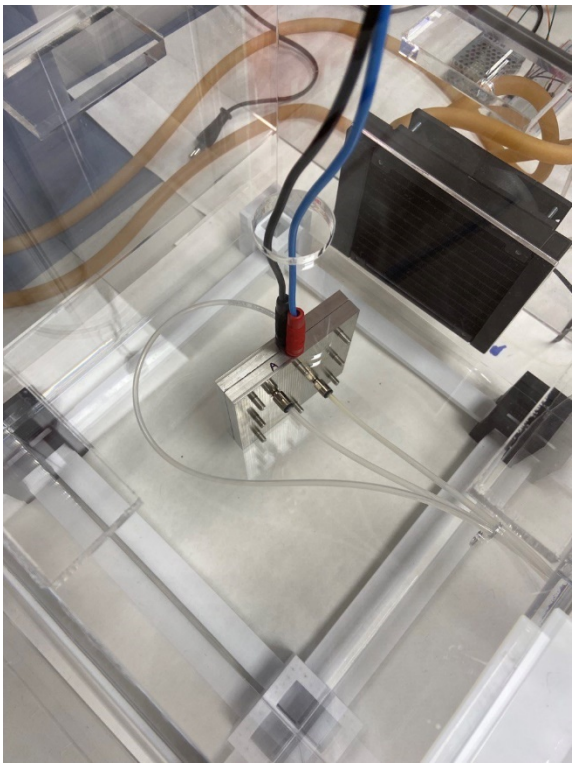

Figure 21: Insulating chambers (8)

Going in order, one of the two front circular holes is used to insert the thermometer shown in Figure 21 that, when is connected to the heating device (3), shown in Figure 23, allows the temperature inside the second chamber to be constant and automatically regulated. This is done to obtain a constant temperature inside the chamber, being able to start the experiment as soon as the desired temperature is reached.

The second of the two front circular holes is used for the pump output cable, which is connected to the anode of the cell, and for the two output tubes for anode and cathode, which contain aqueous methanol solution and CO_2, and hydrogen respectively. The aqueous methanol solution, which is not recirculated, is sent to a second glass tank, the hydrogen, having no device for measuring the flow rate at the cell outlet and since the quantity produced is too small, is discharged into a becker filled with water to observe the bubbles that are produced.

Lastly the fan (4), which is inserted in the rectangular-shaped hole, perpendicular to the cell, and serves to bring the interior of the second chamber to the correct temperature, using hot water that is recirculated and heated by a heating system (3), shown in Figure 23 located below the bench.

Figure 23: Heating systems (3)

5.4. Electrolyser

As far as the electrolyser is concerned, it consists of a single cell: the MEA is positioned in the middle of the two steel plates (see Figure 24) of a square with 100 mm side and 10 mm thickness, Steel 316L was used.

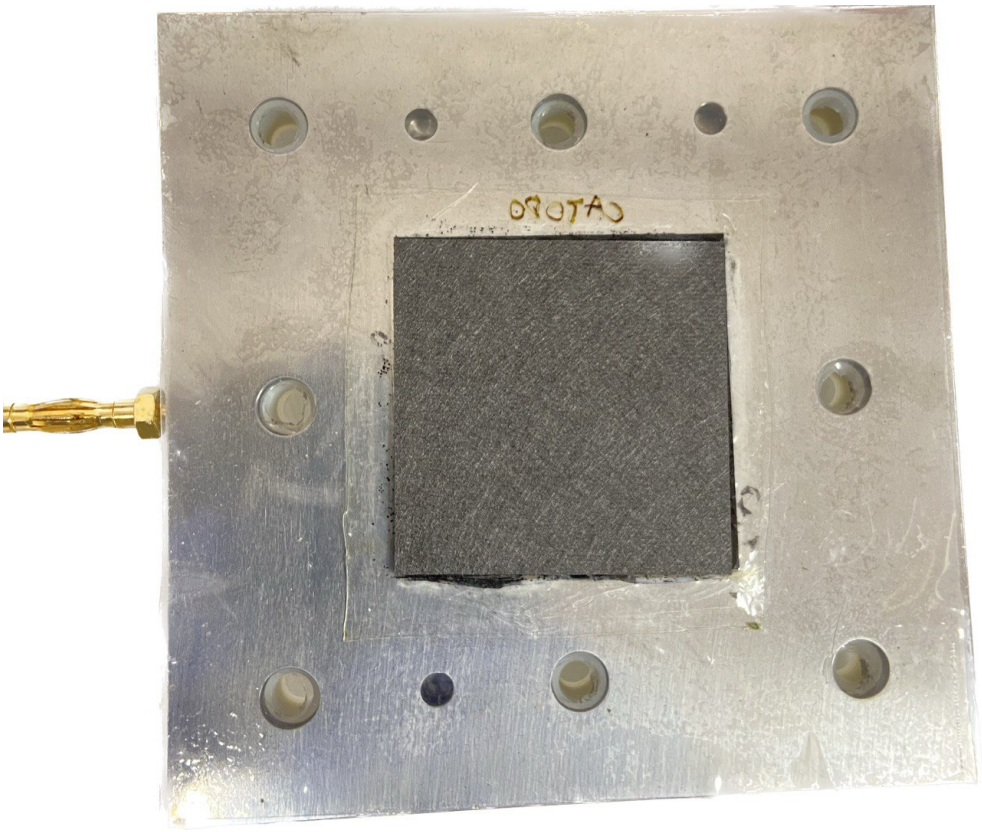

Figure 24: Cell (6)

In the central part of the steel plate, it is positioned the MEA, precisely it is shown in the Figure 24 the layer corresponding to the carbon support of the anode electrode, that is called Gas Diffusion Layer. The active part- the catalyst- faces the Nafion membrane, which will be described later.

The MEA is composed by the two electrodes and the nafion membrane:

- Anode BC-M100-30F (Figure 25):
  - Catalyst load: 3 $mg\ \frac{PtRu}{cm^2}$;
  - Dimension: 16 cm^2;

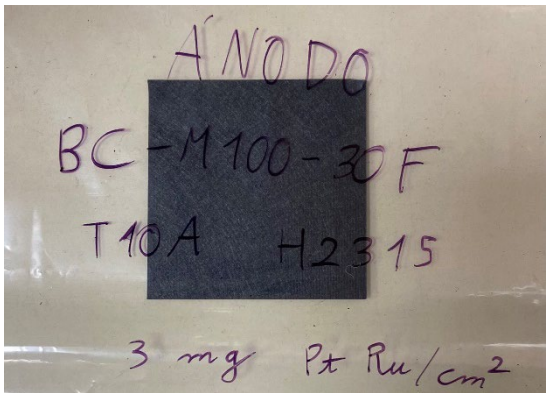

Figure 25: Anode electrode

- Cathode BC-H225-10F (Figure 26):
  - Catalyst load: 1 $mg\frac{Pt}{cm^2}$;
  - Dimension: 16 cm^2;

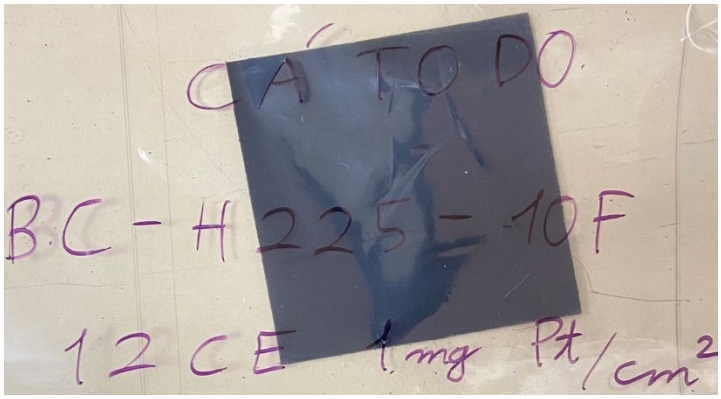

Figure 26: Cathode electrode

- Membrane Electrode Assembly (Figure 27): to create the MEA, the two electrodes and the nafion membrane must be joined. To do this, liquid nafion is smeared on the active part of the catalyst and the electrode is placed on the nafion membrane. The Gas Diffusion Layer faces the two aluminium foils, as they must be pressed together at 60 bar and 130 degrees for 3 minutes.

Figure 27: MEA

5.5. Nafion 117 treatment process

The nafion treatment process consists of several steps. First, the nafion membrane is cut, in this case an area of 25 cm^2 was chosen, for a square-shaped membrane.

Once cut, there are 4 steps, following the PicoHima methodology, that take 1 hour each:

- The nafion membrane is immersed in a 30% solution of hydrogen peroxide (H_2O_2) at 80°C, to remove organic impurities (53);
- After that, it is rinsed lightly with distilled water at room temperature and then immersed in distilled water tank at 80°C to clean it from the previous step;
- As third step, it is again lightly rinsed with distilled water at room temperature and then immersed in a 0.5 M solution of Sulphuric acid (H_2SO_4), to remove metallic impurities and to acidify the sulfonic sites (53) so, to activate the membrane (54);
- The last step is equal to the second one, so again one hour in a distilled water tank at 80°C;

Before the MEA is assembled, the nafion membrane is left to rest for 24 hours.

5.6. Final test bench configuration

The configuration for the methanol electrolyser test bench it is shown in Figure 28 and Figure 29:

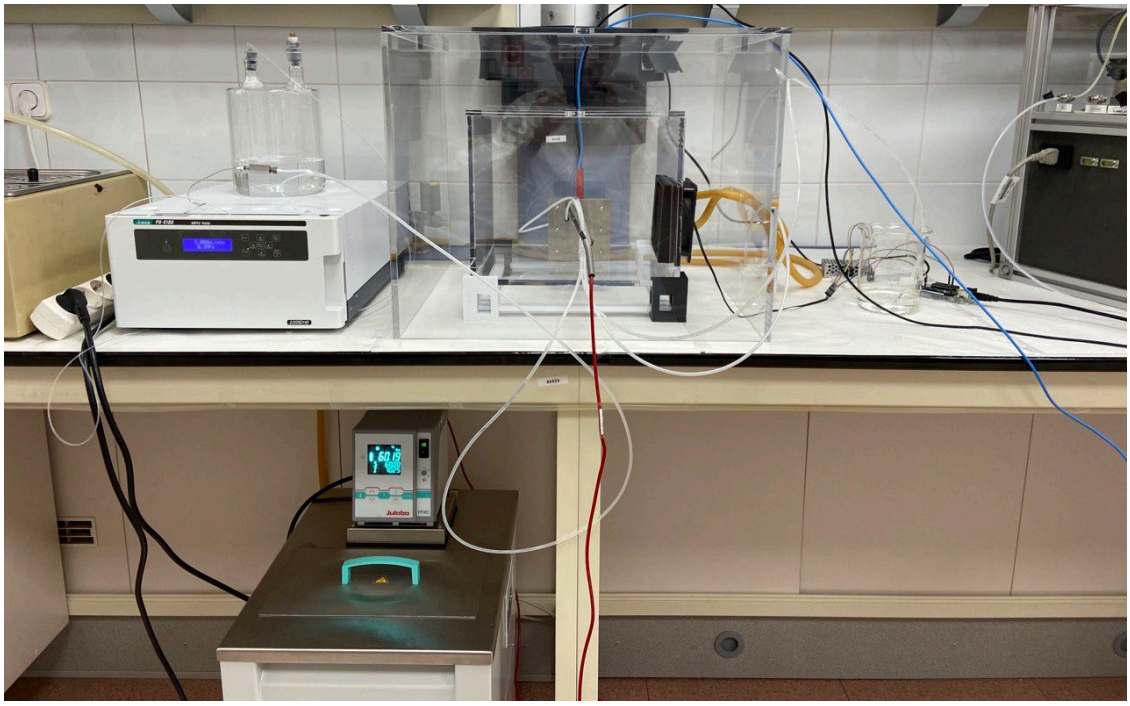

Figure 28: Test bench configuration

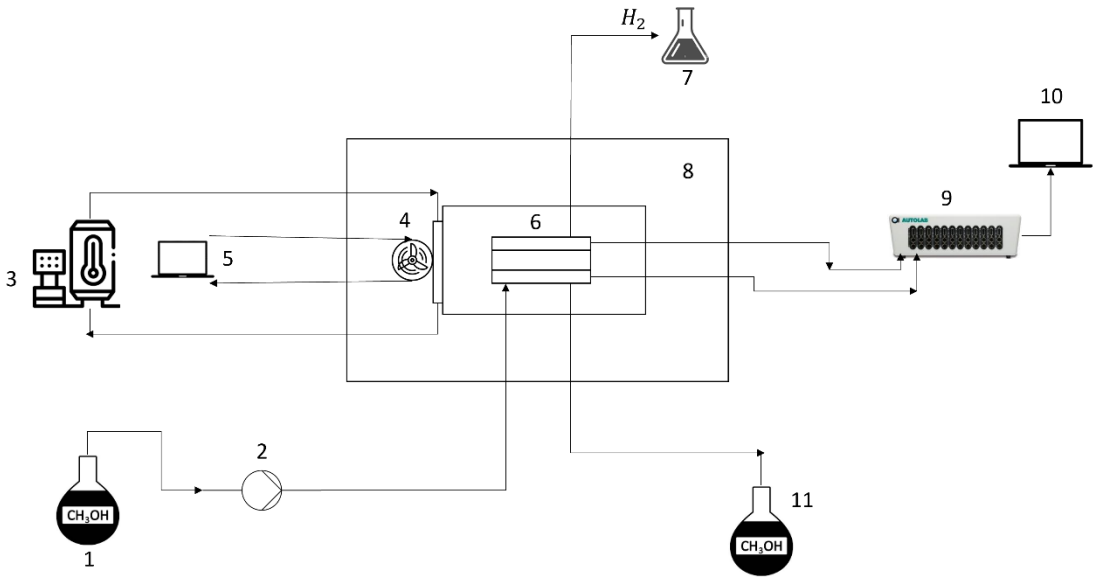

Figure 29: Final test bench configuration scheme

6. Results and discussion

The results are grouped in two graphs in which the methanol concentration is fixed and the polarisation curves at different temperatures are represented (see Figure 30 and Figure 31).

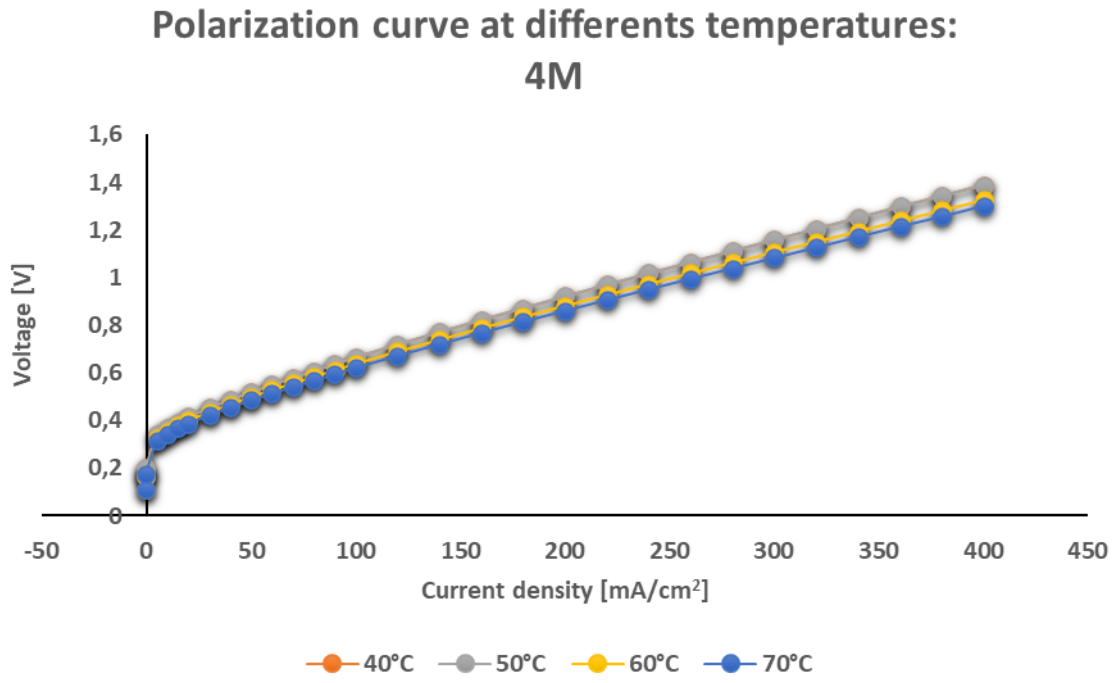

Figure 31: Polarization curve with concentration of methanol equal to 4M and at different temperatures 40°C 50°C 60°C 70°C

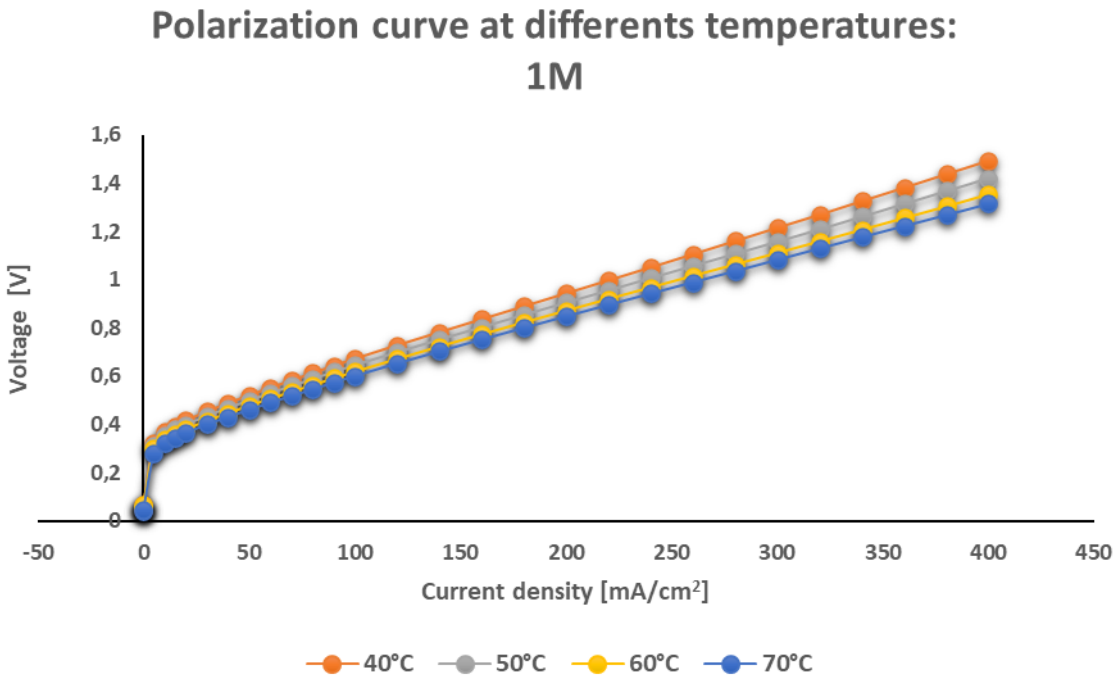

Figure 30: Polarization curve with concentration of methanol equal to 1M and at different temperatures 40°C 50°C 60°C 70°C

Analysing the results, it can be seen, as previously mentioned, that the role of temperature is important: as it is shown in the literature, an increase in temperature shows an improvement in terms of polarisation curves, i.e., for the same current density the voltage decreases, the best curves are at 70 °C in both molarity condition. If are considered the two curves presented in Figure 32, at 40°C it is more evident that below a certain temperature, that is lower than 60°C, as it is shown in Claude Lamy report (43), increasing the molarity improves the polarization curve.

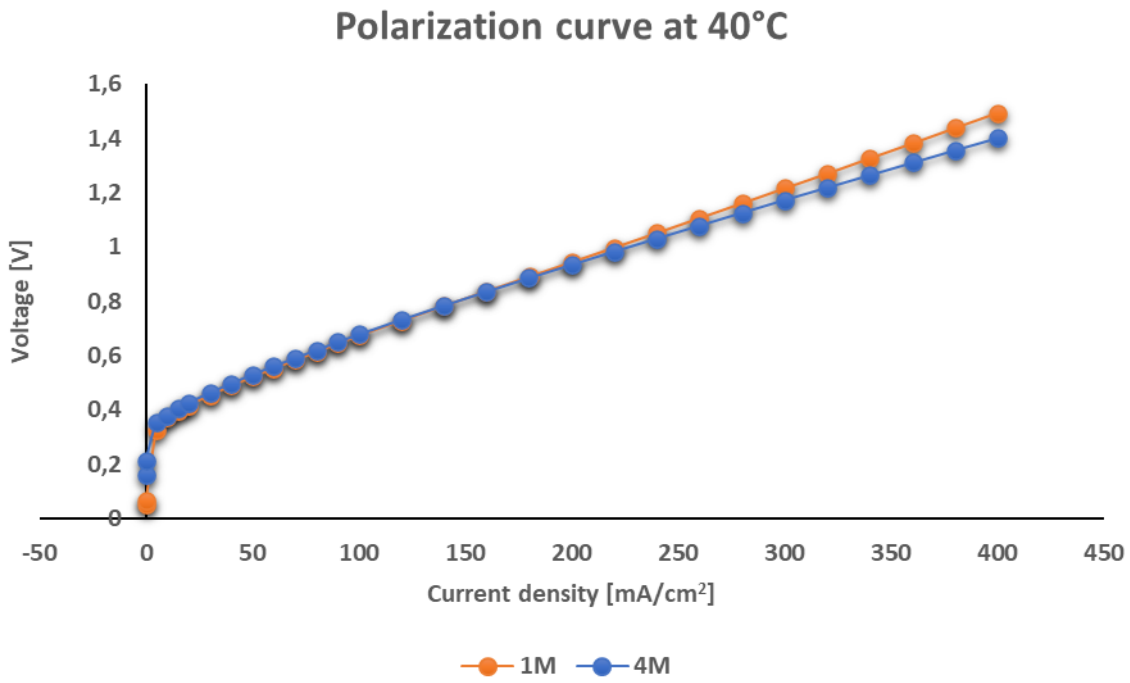

Figure 32: Polarization curve at temperature equal to 40°C and methanol concentration of 1M and 4M

In fact, it can be seen in Figure 32 that, after a current density of 200 $\frac{mA}{cm^2}$ and just in the case of 40°C, a higher molarity value increases the performance of the electrolysis, since a lower value of voltage is obtained. In the other curves the results are or independent from the molarity at each current density, or the differences are negligible.

Even if is less evident with respect to the temperature dependency, the variation in the methanol concentration is important too. In fact, in the case of 4M aqueous methanol concentration (see Figure 31), the curves related to 40°C and 50°C are overlaid, due to the contribution of an higher concentration value, as it is shown in Figure 17 (43).

7. Best results

At the end of the analysis, as previously mentioned, the best result was obtained for both molarities at a temperature of 70°C, the polarization curves obtained are shown in Figure 33:

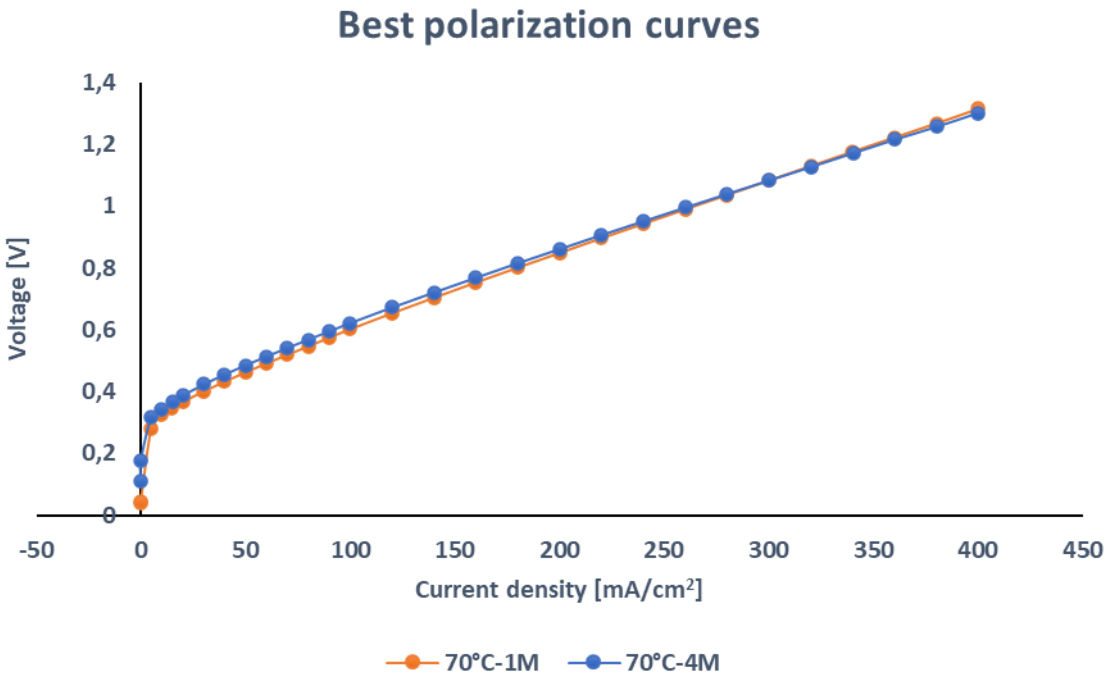

Figure 33: Best polarization curves

The two curves are overlaid, in the first part of the curve, the best one is with 1M, after a current density of 320 mA/cm^2 the best one is 4M, even if in both cases the difference is very low.

The polarisation curves found in the literature have different values; the Table 2 groups together the main characteristics of the various devices and the operating conditions of the cells.

Table 2: Comparison between literature and the results of this work

Ref.	Temp. [°C]	$\dot{V}\left[\frac{mL}{min}\right]$	Molarity [M]	Membrane	Cathode	Cathode $\left[\frac{g}{cm^2}\right]$	Anode	Anode $\left[\frac{g}{cm^2}\right]$	Active area [cm^2]
(41)	90	Not mentioned	1	Nafion 117	Pt/C	1.5	PtRu/C	2.5	6.25
(43)	25-40-55-70-85	Not mentioned	0.5-1-2-5-10	Nafion 117	Pt/C	2	PtRu/C	4	5
(44)	30-50-70	Not mentioned	1	Nafion 115	Pt black/C	3	PtRu/C	3	9
(46)	25	Not mentioned	0-1-2-6-16	Nafion 117	Pt/C	2	PtRu/C	4	2
(48)	30-40-50-60-70-80	Not mentioned	4	Nafion 117	Pt/C	0.5	PtRu/C	3	25
(49)	30	Not mentioned	1-2-3-4	Nafion 115	Pt/C	0.5	IrO_2/C	2	6.25
(51)	30-40-50-60-70	20	1	Nafion 115	Pt/C	2	Pt/C	2	6.25
This work	**70**	**6**	**1**	**Nafion 117**	**Pt/C**	**1**	**PtRu/C**	**3**	**16**

Comparing the results of this work with the ones obtained in the reports citied in the Table 2, it is found a lower voltage value considering the same current density with respect to (43) (44) (49).

The voltage loss associated with the resistance of the electrical cable connecting the galvanostatic with the cell could be the reason why there is a difference in term of polarization curve with respect to the other works (41) (46) (49) (51). So, it was decided to measure the resistance of this cable, which was found to be R=0.2 Ω. An improvement in this sense could lead at better results.

7.1. Further works

Continuing to work with this temperature range and these two molarity values, possible future work could be modifying the following parameters:

- Catalyst: Pt/C and PtRu/C are usually used as cathode and anode catalysts respectively, but often with different catalyst load, and the most recent reports include a new type of catalyst at the anode which is IrO_2/C (49);
- The water-methanol solution flow rate entering in the cell is only specified in a report (51), so, there are no parameters to assess whether the selected flow rate is the best one for the electrolyser.

As mentioned in chapter 7, the high voltage value compared to the above-mentioned documents could be attributed to the voltage losses associated with the length of the cable connecting the galvanostat with the cell: therefore, it was decided to try a new polarization curve by decreasing the original cable length. The new polarisation curve is shown in the Table 3.

Table 3: Polarization curve obtained with a reduction of the distance between the galvanostat and the cell, at T=70°C and 1M

Voltage [V]	Current density $\left[\frac{mA}{cm^2}\right]$
0.293	4.925
0.321	9.981
0.339	14.940
0.355	19.995
0.379	30.014
0.400	39.942
0.419	49.972
0.438	59.986
0.456	70.000
0.473	80.013
0.489	90.029
0.505	100.043
0.534	119.991
0.562	140.018
0.589	160.065
0.617	179.996
0.643	200.062
0.668	220.089
0.695	240.124
0.721	260.068
0.747	280.094
0.774	300.140
0.800	320.244
0.826	340.271
0.852	360.298
0.877	380.325
0.904	400.352

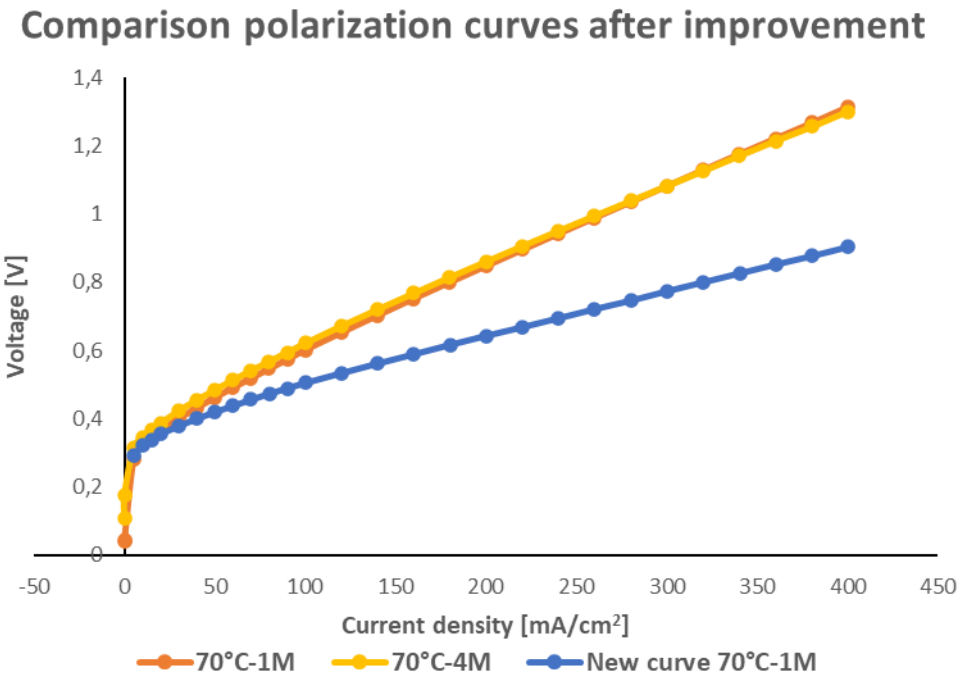

Figure 34: Comparison between polarization curves after the improvement of the test bench

Comparing the results obtained with the new set up of the test bench and shown in Table 3 and in Figure 34, with the best polarization curve obtained with the old configuration (see Figure 33), at $j_c = 400 \frac{mA}{cm^2}$, the new voltage value is $V_{new} = 0.904\,V$ with respect to $V_{old} = 1.314\,V$, so, the 31% less with respect to the first configuration, considering the same temperature of 70°C and concentration of 1M. To be validated, the new polarization curve should be run for 2 weeks consequently, as it was done in the curve shown in Figure 33, but in this case, these values are referred at just one simulation.

8. Use of methanol electrolyser to produce hydrogen as fuel for vehicles in San Pietro island: a case study

Currently there are no plants in operation or under development to produce hydrogen from methanol electrolysis. For this reason, the aim of this case study is to calculate the Levelized Cost Of Hydrogen considering a time span of 20 years for the production of hydrogen from methanol. The configuration of the case study is shown in Figure 35.

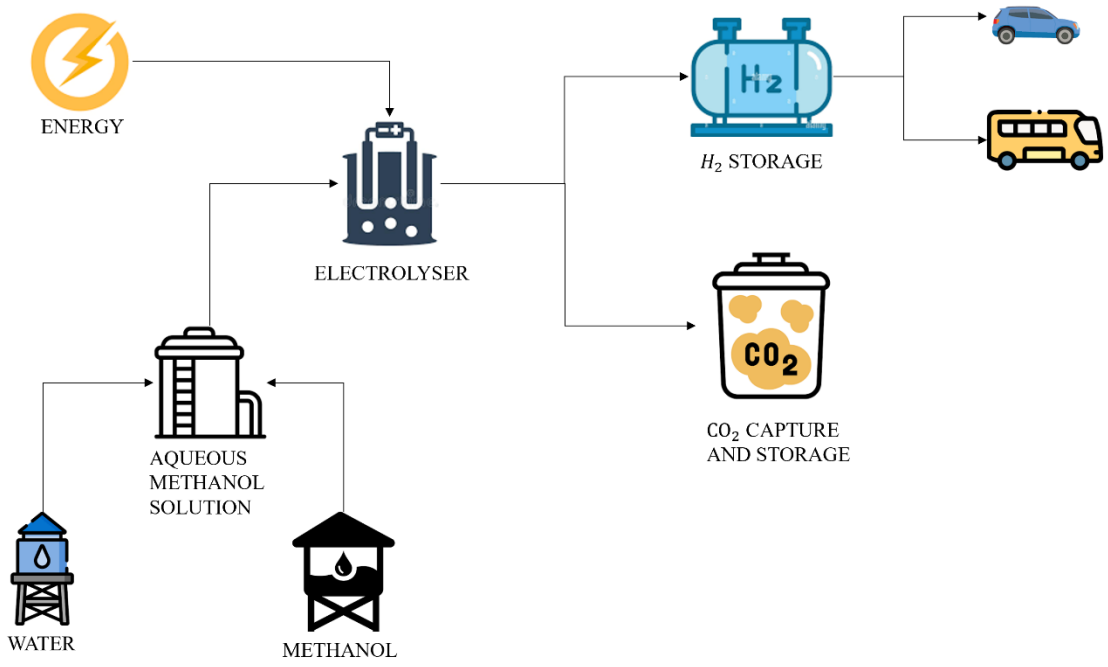

Figure 35: Methanol electrolyser power link scheme

The value of hydrogen needed to power the cars and buses of a small Italian island is taken as input, in this case study the island of San Pietro was chosen. This is due to the relatively small size of the island and the fact that it is connected to the national electricity grid (55). In fact, to ensure constant energy supply to the electrolyser and thus constant hydrogen production, it was assumed that the electrolyser is connected to the national grid and that the required energy load is constant during all operating hours. In the first part, the hydrogen demand is calculated, which will be used to make a suitable sizing of the electrolyser, the key values of it such as efficiency, energy consumption and hydrogen mass flow rate will be reported. Moreover, the sizing of the electrolyser does not follow a demand profile but is based on the total annual hydrogen consumption calculated for the island. The stoichiometric values for water and methanol are calculated to determine the total volume of the solution. As far as the products are concerned, the CO_2 generated is again calculated using the reaction, but there are no uses for CO_2 in this analysis, only the cost relating to capture and storage is reported. The hydrogen produced is stored in tanks, and to avoid oversizing the plant, I assumed a storage capacity of 5 days. Finally, to calculate the Levelized Cost Of Hydrogen, the economic analysis is carried out.

8.1. Hydrogen demand: cars and buses

Going in deep with the case study analysis, the main parameters for the cars are shown in the Table 4.

Table 4:Input values for cars

Cars		
Average car distance per year	11,500	$\frac{\text{km}}{\text{y}}$
Km with full tank capacity	650	km
Number of fill up in one year	18	
Full tank car capacity	5.6	kg
Numbers of cars	3,320	
Total amount of hydrogen per car per year	100.8	$\frac{\text{kg}}{\text{car} \cdot \text{y}}$
Hydrogen cars demand	**334,656**	$\frac{\text{kg}}{\text{y}}$

Starting from the numbers of cars present in the island (55), it has been used as full tank capacity $m_{H_2,car\ tank\ capacity} = 5.6\ kg$, the same of one Toyota Mirai (56) that is fully powered with hydrogen, and with a consumption of 0.8 $\frac{kg}{100\ km}$ (56), it is assumed 650 km as an average consumption with a full tank capacity. The total hydrogen demand for cars is calculated using Eq. 18 and Eq. 20.

$$n_{\frac{fu}{y},\ car} = \frac{L_{avg\ car}}{L_{avg\ car,full\ tank}} \qquad \text{Eq. 18}$$

Where:

- $L_{avg\ car} = 11{,}500\ \frac{km}{y}$ is the average distance covered by one car in one year;
- $L_{avg\ car,full\ tank} = 650\ km$ are the km that the car can do with full tank capacity of 5.6 kg of H_2;
- $N^{\circ}_{Cars} = 3{,}320$, that is the numbers of cars in the island.

So, the number of fill up per year is calculated using Eq. 18:

$$n_{\frac{fu}{y},\ car} = 17.69 \approx 18 \qquad \text{Eq. 19}$$

$$\dot{m}_{H_2 Consumption,car} = n_{\frac{fu}{y},\ car} \cdot \dot{m}_{H_2,car\ tank\ capacity} = 100.8\ \frac{kg}{y \cdot car} \qquad \text{Eq. 20}$$

$$\dot{m}_{H_2\ Total\ consumption,cars} = N^{\circ}_{Cars} \cdot \dot{m}_{H_2 Consumption,\ car} = 334{,}656\ \frac{kg}{y} \qquad \text{Eq. 21}$$

The main parameters for the buses are shown in the Table 5:

Table 5:Input values for buses

BUS		
Average bus distance per year	4,500	$\frac{\text{km}}{\text{y}}$
Km with full tank capacity	500	km
Number of fill up in one year	9	
Full tank bus capacity	45	kg
Numbers of bus	6	
Total amount of hydrogen per bus per year	405	$\frac{\text{kg}}{\text{bus} \cdot \text{y}}$
Hydrogen bus demand	**2,430**	$\frac{\text{kg}}{\text{y}}$

Starting from the numbers of buses present in the island (55), it has been used as full tank capacity $m_{H_2,bus\ tank\ capacity} = 45\ kg$ (57), and with a consumption of 9 $\frac{kg}{100\ km}$ (57), so, it is assumed 500 km as an average consumption with a full tank capacity (57). The total hydrogen demand for buses is calculated using Eq. 22, Eq. 24 and Eq. 25:

$$n_{\frac{fu}{y},\ bus} = \frac{L_{\text{avg bus}}}{L_{avg\ bus,full\ tank}} \qquad \text{Eq. 22}$$

where:

- $L_{\text{avg bus}} = 4{,}500\ \frac{km}{y}$ is the average distance covered by one bus in one year (57);
- $L_{avg\ bus,full\ tank} = 500\ km$ are the km that the bus can do with full tank capacity of 45 kg of H_2;
- $N^{\circ}_{Buses} = 6$, that is the numbers of buses in the island.

So, the number of fill up per year is shown in Eq. 23:

$$n_{\frac{fu}{y},\ bus} = 9 \qquad \text{Eq. 23}$$

$$\dot{m}_{H_2 Consumption,\ bus} = n_{\frac{fu}{y},\ bus} \cdot \dot{m}_{H_2, bus\ tank\ capacity} = 405\ \frac{kg}{y \cdot bus} \quad \text{Eq. 24}$$

$$\dot{m}_{H_2\ Total\ consumption, bus} = N^{\circ}_{Buses} \cdot \dot{m}_{H_2 Consumption,\ bus} = 2{,}430\ \frac{kg}{y} \quad \text{Eq. 25}$$

So, the total amount of hydrogen that the Island needs is obtained considering Eq. 21 and Eq. 25, the result is shown in Eq. 26:

$$\dot{m}_{H_2\ demand} = \dot{m}_{H_2 Consumption,\ car} + \dot{m}_{H_2\ Total\ consumption, bus} = 337{,}086\ \frac{kg}{y} \quad \text{Eq. 26}$$

8.2. Electrolyser

To size the electrolyser, it was chosen to work with the curve that showed the lowest voltage value at a current density equal to $j_c = 160 \frac{mA}{cm^2}$ among those obtained as a result of the experiments (see Chapter 6), so, the one with a 1M concentration and a temperature of 70°C (Figure 33), is presented in the Table 6.

Table 6:Best polarization curve and Power at 70°C 1M

Voltage [V]	Current $\left[\frac{mA}{cm^2}\right]$	Power $\left[\frac{mW}{cm^2}\right]$
0.280	4.904	1.371
0.325	9.959	3.232
0.346	14.917	5.167
0.366	19.973	7.315
0.401	29.991	12.012
0.432	39.921	17.235
0.462	49.934	23.071
0.491	59.967	29.434
0.519	69.977	36.301
0.546	79.992	43.695
0.574	90.008	51.681
0.602	100.021	60.180
0.653	119.953	78.334
0.703	139.999	98.444
0.753	160.027	120.500
0.801	179.966	144.084
0.848	200.024	169.679
0.896	220.051	197.114
0.943	240.093	226.373
0.989	260.043	257.297
1.036	280.060	290.062
1.083	300.102	324.874
1.130	320.180	361.706
1.176	340.226	400.249
1.222	360.298	440.451
1.268	380.325	482.214
1.314	400.162	525.971

Where the *Power* in $\frac{mW}{cm^2}$ is calculated using Eq. 27:

$$Power = I \cdot V \qquad \text{Eq. 27}$$

The efficiency of the device is calculated considering each point of the curve following Eq. 28 (58), and the results are shown in Table 7.

$$\eta = \frac{U_{TN}}{U_{TN} + U_{CELL} - U_{REV}} \qquad \text{Eq. 28}$$

Where:

- U_{TN} is the thermoneutral voltage, calculated using Eq. 29.

$$U_{TN} = \frac{\Delta H(T)}{n \cdot F} = 0.224\, V \qquad \text{Eq. 29}$$

- where $\Delta H(T = 70°C)$ is the enthalpy variation and n is the number of exchanged electrons, that in the case of methanol is calculated using Eq. 30 and Eq. 31 (42).

$$C_x H_y O_k = 4x + y - 2k \qquad \text{Eq. 30}$$

$$CH_3OH = 4 \cdot 1 + 4 - 2 \rightarrow n_{CH_3OH} = 6 \qquad \text{Eq. 31}$$

- Faraday constant: $F = 96485\ \frac{C}{mol}$;
- U_{REV} is the reversible voltage, that is the minimum voltage at which the reaction occurs, calculated using Eq. 32.

$$U_{REV} = -\frac{\Delta G(T)}{n \cdot F} = 0.015\, V \qquad \text{Eq. 32}$$

  where $\Delta G(T = 70°C)$ is then Gibbs free energy variation;

- U_{CELL} is the voltage of the cell [V]: the voltage at each point of the curve (see Table 6).

So, in the Figure 36, is reported the polarization curve and the efficiency calculated with the Eq. 28:

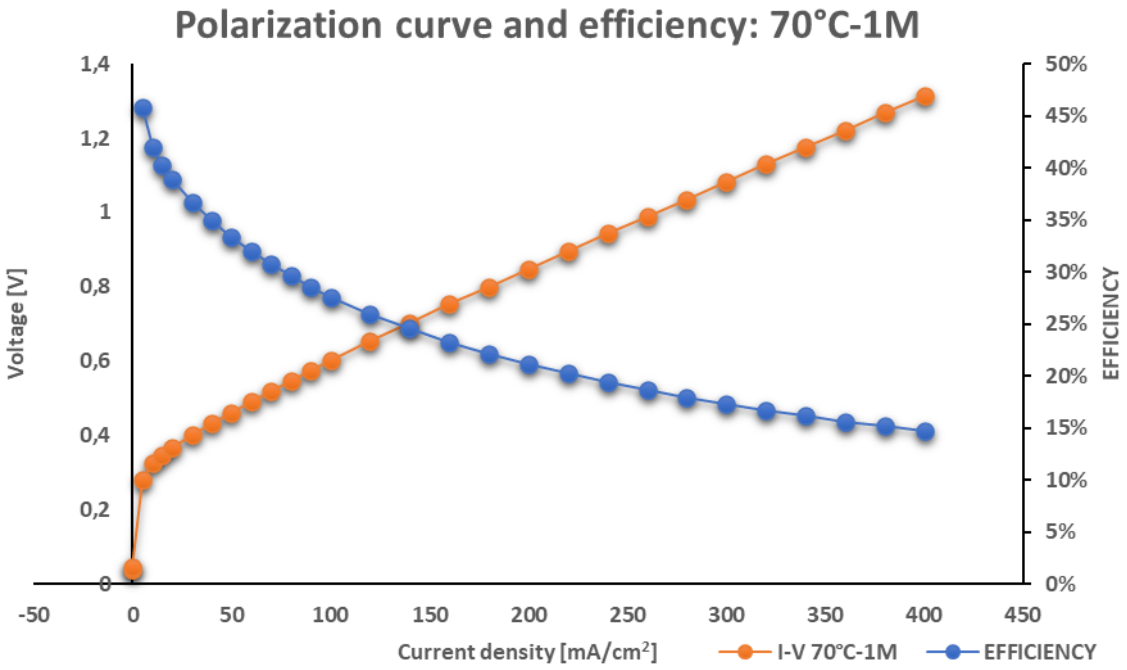

Figure 36: Polarization curve and efficiency at temperature of 70°C and 1M

Table 7: Efficiency of the electrolyser at 70°C and concentration of methanol 1M

Efficiency of the process
0.458
0.420
0.403
0.389
0.367
0.349
0.334
0.320
0.308
0.296
0.286
0.276
0.260
0.245
0.233
0.222
0.212
0.203
0.194
0.187
0.180
0.173
0.167
0.162
0.156
0.152
0.147

Since no flow meters are available to measure the actual hydrogen produced by the cell, the total amount of hydrogen produced is estimated using Faraday's law (see Eq. 33) and considering the following assumptions:

- The number of cells per stack is: n_{cells}= 500 (59);
- The active surface area is: $Area_{active} = 1200\ cm^2$ (59);
- Since it is assumed that the electrolyser operates at nominal load without interruptions during the year, the number of hour of operations are $8760\ \frac{h}{y}$;
- Seconds in one year of operation are: $s = 31{,}536{,}000\ \frac{s}{y}$;
- Faraday efficiency is assumed $\eta_{faraday} = 0.83$ (60);
- $MM_{H_2} = 2\ \frac{g}{mol}$;
- $Z = 2$;
- $F = 96485\ \frac{C}{mol}$;

- Current density: $j_c = 0.160\ \frac{A}{cm^2}$, this value is chosen both to guarantee an adequate efficiency for the device and for the equation that estimates the electrolyser's cost (see Eq. 59);
- Faraday law (61), so, the amount of hydrogen produced is calculated using Eq. 33 expressed in $\frac{g}{y}$ and the total amount of hydrogen produced by the electrolyser is shown in Eq. 41:

$$\dot{m}_{H_2} = \frac{\eta_{faraday} \cdot j_c \cdot n_{cells} \cdot s \cdot Area_{active} \cdot MM_{H_2}}{Z \cdot F} \quad \text{Eq. 33}$$

So, the total amount of hydrogen produced by one stack in one year is calculated in Eq. 35:

$$\dot{m}_{H_2,stack} = 2.97\ \frac{kg}{h \cdot stack} \quad \text{Eq. 34}$$

$$\dot{m}_{H_2,stack} = 26{,}048\ \frac{kg}{y \cdot stack} \quad \text{Eq. 35}$$

The number of stacks, rounded per excess to be sure to satisfy the hydrogen demand, are calculated in Eq. 36, and the hydrogen mass flow rate for the whole electrolyser is shown in Eq. 37.

$$n_{stack} = \frac{\dot{m}_{H_2\ demand}}{\dot{m}_{H_2,stack}} = 12.94 \rightarrow\ n_{stack} = 13 \quad \text{Eq. 36}$$

$$\dot{m}_{H_2,13\ stack} = 38.66\ \frac{kg}{h} \quad \text{Eq. 37}$$

As nominal power, is chosen the one that corresponds to the operational point of the polarization curve (see Table 6), so, at $j_c = 160 \frac{mA}{cm^2}$, and to consider the total power installed this value is multiplied for the number of cells and the number of stacks using Eq. 38 and Eq. 39:

$$P_{Nom,stack} = j_c \cdot V \cdot Area_{active} \cdot n_{cell} = 72.3\ \text{kW} \quad \text{Eq. 38}$$

$$P_{Nom,tot} = P_{Nom,cell} \cdot n_{stack} = 0.94\ \text{MW} \quad \text{Eq. 39}$$

The energy consumed each year to meet the hydrogen demand running the electrolyser at each moment at the nominal load is calculated in Eq. 40.

$$E_{consumed,tot} = E_{tot,EC} = P_{Nom,tot} \cdot h = 8{,}233.5\ \frac{MWh}{y} \quad \text{Eq. 40}$$

So, at the end the total hydrogen produced by this electrolyser is shown in Eq. 41.

$$\dot{m}_{H_2,total\ produced} = 338{,}619.4\ \frac{kg}{y} \quad \text{Eq. 41}$$

$$\dot{m}_{H_2,demand} = 337{,}086\ \frac{kg}{y} \quad \text{Eq. 42}$$

So, the excess of hydrogen is calculated in Eq. 43, considering the amount of hydrogen produced Eq. 41 and the hydrogen demand for the island Eq. 26 (shown in Eq. 42 too):

$$\dot{m}_{H_2,excess} = \dot{m}_{H_2,total\ produced} - \dot{m}_{H_2,demand} = 1{,}533.4\ \frac{kg}{y} \quad \text{Eq. 43}$$

8.3. Methanol, Water and CO_2

Starting from the methanol electrolysis reaction and the amount of hydrogen produced (see Eq. 41), it is calculated the amount of water and methanol needed as input and the amount of CO_2 that is produced.
The reaction is the Eq. 20 and the stoichiometric methanol consumed is calculated using Eq. 44:

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \quad \text{Eq. 20}$$

$$C_{s,CH_3OH} : C_{s,H_2} = \dot{n}_{CH_3OH} : \dot{n}_{H_2} \quad \text{Eq. 44}$$

Where:

- C_s is the stoichiometric coefficient, that indicates in which mole ratios the reactants enter the reaction and products are formed:
  - $C_{s,CH_3OH} = 1$;
  - $C_{s,H_2} = 3$;
- $\dot{n}_{H_2} = \frac{\dot{m}_{H_2,total\ produced}}{MM_{H_2}}$;
- $\dot{m}_{H_2,total\ produced} = 338{,}619{,}400 \frac{g}{y}$;
- $MM_{H_2} = 2\ \frac{g}{mol_{H_2}}$;
- $MM_{CH_3OH} = 32 \frac{g}{mol}$

So, the total amount of methanol is calculated using the numbers of moles calculated in Eq. 45 and the total value it is shown in Eq. 46:

$$\dot{n}_{CH_3OH} = \frac{C_{s,CH_3OH} \cdot \dot{n}_{H_2}}{C_{s,H_2}} = 56{,}437 \frac{kmol}{y} \quad \text{Eq. 45}$$

$$\dot{m}_{CH_3OH,consumed\ tot} = \dot{n}_{CH_3OH} \cdot MM_{CH_3OH} = 1806\ \frac{ton}{y} \quad \text{Eq. 46}$$

Using the same procedure, it is possible to calculate the stoichiometric amount of water consumed using Eq. 47:

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \quad \text{Eq. 17}$$

$$C_{s,H_2O} : C_{s,H_2} = \dot{n}_{H_2O} : \dot{n}_{H_2} \quad \text{Eq. 47}$$

Where:

- $C_{s,H_2O} = 1$;
- $C_{s,H_2} = 3$;
- $MM_{H_2O} = 18 \frac{g}{mol}$

So, using the numbers of mole calculated in Eq. 48, it is shown the stoichiometric of water consumed Eq. 49:

$$\dot{n}_{H_2O} = \frac{C_{s,H_2O} \cdot \dot{n}_{H_2}}{C_{s,H_2}} = 56{,}437 \frac{kmol}{y} \quad \text{Eq. 48}$$

$$\dot{m}_{H_2O,consumed\ tot} = \dot{n}_{H_2O} \cdot MM_{H_2O} = 1016 \frac{ton}{y} \quad \text{Eq. 49}$$

Since in the laboratory was calculated the density of the aqueous methanol solution that is $\rho_{sol} = 988 \frac{kg}{m^3}$, it is possible to know the amount of solution for this case study starting from the molarity $M = \frac{\dot{n}_{solute}}{V_{sol}}$ where:

- $M = 1\ \frac{mol}{L}$, that is the molarity of the solution;
- $\dot{n}_{solute} = \dot{n}_{CH_3OH}$, since the amount of methanol is lower with respect to the amount of water, methanol is the solute of the solution;

So, the volume of the solution is $V_{sol} = 56{,}436{,}570\ L$, using the density is possible establish the actual amount of water used for the entire process:

- $\dot{m}_{sol} = V_{sol} \cdot \rho_{sol} = 55{,}759 \frac{ton}{y}$;
- $\dot{m}_{H_2O} = \dot{m}_{sol} - \dot{m}_{CH_3OH,consumed\ tot} = 53{,}953 \frac{ton}{y}$.

In this study the amount of water consumed is not consider in the economic part, but the value is reported to be thorough. A further work on this case study could be to evaluate a recirculation process, with purification steps in which the outlet solution is purified and just the correct amount of methanol is added to the same purified water content, to reduce the water consumption.

Finally, it is possible to calculate the total amount of CO_2 produced using Eq. 50:

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \quad \text{Eq. 20}$$

$$C_{s,CO_2} : C_{s,H_2} = \dot{n}_{CO_2} : \dot{n}_{H_2} \quad \text{Eq. 50}$$

Where:

- $C_{s,CO_2} = 1$;
- $C_{s,H_2} = 3$;
- $MM_{CO_2} = 44 \frac{g}{mol}$

So, using the numbers of mole calculated in Eq. 51, it is shown in Eq. 52 the stoichiometric amount of CO_2 produced. This value will be used in the economic analysis to assess the annual CO_2 capture and storage cost.

$$\dot{n}_{CO_2} = \frac{C_{s,CO_2} \cdot \dot{n}_{H_2}}{C_{s,H_2}} = 56{,}437 \frac{kmol}{y} \quad \text{Eq. 51}$$

$$\dot{m}_{CO_2,produced\ tot} = \dot{n}_{CO_2} \cdot MM_{CO_2} = 2{,}483 \frac{ton}{y} \quad \text{Eq. 52}$$

To summarize, the main input and output values are shown in Table 8:

Table 8: Input and output values for hydrogen, water, CO_2 and methanol

Main Value		
Hydrogen demand	337,086	$\frac{kg}{y}$
Hydrogen produced	338,619	$\frac{kg}{y}$
Stoichiometric water consumed	1,016	$\frac{ton}{y}$
Stoichiometric CO_2 produced	2,483	$\frac{ton}{y}$
Stoichiometric methanol consumed	1,806	$\frac{ton}{y}$

8.4.Storage: H_2 and CO_2

As products of the methanol electrolysis process, it is produced hydrogen, calculated in chapter 8.2 and CO_2, calculated in chapter 8.3, that are stored, the former to be used as fuel for the island's cars and buses, the latter to avoid environmental impact and his value is just considered as a cost for the economic part.

Table 9: Summarized stored product: hydrogen and CO_2

Stored product		
Hydrogen produced each hour	38.66	$\frac{kg}{h}$
Hydrogen produced each day	928	$\frac{kg}{d}$
Hydrogen produced each 5 days	4,639	$\frac{kg}{5d}$
CO_2 produced	2,483	$\frac{ton}{y}$

In the Table 9, it is reported the amount of hydrogen produced each five days, to avoid oversizing the hydrogen storage facilities it is assumed to store a certain amount of hydrogen since it will be continuously consumed refuelling the vehicles. In fact, the amount of hydrogen I can store in five days is enough to fill up 25% of the cars on the island.

The CO_2 is considered in the case study but just for the economic part -that will discuss later- and an average cost in $\frac{€}{ton_{CO_2}}$ will be considered as a cost that includes capture and storage.

9. Economic analysis

To estimate the Levelized Cost of hydrogen, the following paragraphs show the several costs involved in the case study discussed in chapter 8. Initially, the cost of purchasing methanol and related tanks is discussed. Next, the costs of hydrogen storage, of the compressors installed to ensure that hydrogen is stored under pressure, and a cost for capturing the CO_2 produced are reported. Finally, the costs for the electrolyser and for the electricity consumed are presented.

9.1. Methanol cost

With respect to the water electrolysis, the aqueous-solution is more expensive due to methanol cost. In fact, also for this reason, the concentration of methanol equal to 1M it was chosen as the best option, since with a concentration equal to 4M, the amount of methanol consumed is four times the 1M solution.

Table 10: Methanol cost and values

Methanol		
Methanol consumed each day	6263	$\frac{\text{l}}{\text{d}}$
Methanol density 25 °C	0.79	$\frac{\text{kg}}{\text{dm}^3}$
Methanol consumed	1806	$\frac{\text{ton}}{\text{y}}$
Bio-methanol cost	455	$\frac{€}{\text{ton}}$
Capacity	30	days
Numbers of tanks	13	
Storage tank capacity	195,000	l
Methanol tank cost: 15000L capacity	0.017	M€

Since is known the amount of methanol produced from Eq. 48, is possible to establish the methanol cost, using an average value of $c_{Methanol} = 455 \frac{€}{ton}$ (62). So, the cost related to the annual methanol consumption (Eq. 46) is calculated in Eq. 53.

$$C_{methanol} = c_{methanol} \cdot \dot{m}_{CH_3OH,consumed} = 0.822 \frac{M€}{y} \quad \text{Eq. 53}$$

The methanol transportation cost is not considered in the economic analysis but, as hypothesis, 30 days of methanol storage capacity in continuous hydrogen production at nominal power it is chosen, that correspond to 13 tanks of 15000L, the cost is shown in Eq. 55, considering a methanol tank cost showed in Eq. 54 (63).

$$C_{tank,methanol} = 17{,}000 \frac{€}{tank} \quad \text{Eq. 54}$$

$$C_{methanol\ tank} = 0.222\ M€ \quad \text{Eq. 55}$$

9.2.Storage cost: hydrogen, CO_2 and compressors

The methanol electrolysis reaction produces hydrogen and CO_2 as an output (see Eq. 20), in this case study the costs to store these two products are considered:

- Hydrogen storage cost: considering an average hydrogen storage tank price of $c_{H_2} = 600\ \frac{€}{kg}$ (64), for moderate pressure application $p_{max} = 430\ bar$ (64), with a corresponding tank size of 65 kg (64) and using 5 days of capacity (see Chapter 8.4), the total cost is shown in Eq. 56.

$$C_{H_2\ stored} = c_{H_2} \cdot \dot{m}_{H_2,produced\ in\ 5\ days} = 2.78\ M€ \qquad \text{Eq. 56}$$

- Since hydrogen is stored under pressure, two compressors are installed, one of which is used as a backup (64), the total cost is shown in Eq. 57.
  - $Compressor\ peak\ flow = 100\,\frac{\text{kg}}{\text{h}}$;
  - $Compressor\ specific\ energy$: $E_{compressor} = 2.8\,\frac{\text{kWh}}{\text{kg}}$;
  - $Outlet\ pressure\ capability = 860\ bar$;
  - $Lifetime\ not\ mentioned\ so\ is\ assumed\ 20\ years$;
  - $Capital\ cost = 0.225\,\frac{\text{M€}}{\text{compressor}} \rightarrow C_{Compressors} = 0.45$ M€;
  - $Annual\ maintenaince\ cost = 4\%\ of\ Capital\ cost$;

$$C_{O\&M,compressor} = 0.018\ M€ \qquad \text{Eq. 57}$$

- Carbon dioxide capture and storage cost: based on the CO_2 produced, calculated in Eq. 52, an average carbon dioxide price of $c_{CO_2} = 80\ \frac{€}{ton}$ (65) is considered to estimate the capture and storage cost for all the amount of CO_2 produced, so, the total cost associated to Carbon dioxide is shown in Eq. 58.

$$C_{CO_2\ capture\ and\ stored} = c_{CO_2} \cdot \dot{m}_{CO_2,produced\ tot} = 0.2\,\frac{M€}{y} \qquad \text{Eq. 58}$$

To summarise, the economic parameters related to storage, are presented in Table 11:

Table 11: Storage cost

Storage		
Hydrogen storage tank price	600	$^{€}/_{\text{kg}}$
Total hydrogen storage cost	2.78	M€
One unit compressor cost	0.22	$^{\text{M€}}/_{\text{compressor}}$
Total compressor cost	0.45	M€
Compressor maintenaince	0.02	$^{\text{M€}}/_{\text{y}}$
CO_2 capture and storage price	80	$^{€}/_{\text{ton}}$
Total CO_2 cost	0.2	$^{\text{M€}}/_{\text{y}}$

9.3. Electrolyser cost

As already mentioned, the production of hydrogen from the electrolysis of methanol is not a commercially available technology. Although the design of PEM methanol electrolysis and PEM water electrolysis are very similar, it is not possible to take the cost of a normal water electrolyser as a reference because there are higher costs, e.g., the use of more precious catalysts (66).

So, the Eq. 59 is used to estimate the cost of the device (66), and it is the only one found in the literature:

$$C_{electrolyser} = 663{,}894{,}313 \cdot \frac{\dot{m}_{H_2}^{0.79}}{j^{0.32}} \qquad \text{Eq. 59}$$

Where:

- $\dot{m}_{H_2} = 0.01074\ \frac{kg}{s}$ is the hydrogen mass flow rate considering all stacks;
- $j = 0.160 \frac{\text{A}}{\text{cm}^2}$ is the current density, this value is assumed to guarantee an adequate efficiency of the stack, that is for this point of the polarization curve $\eta_{j=0{,}160\ \frac{\text{A}}{\text{cm}^2}} = 0.233$ (see Table 7);

So, the total cost of the electrolyser is shown in Eq. 60:

$$C_{EC} = 33.2\ M€ \qquad \text{Eq. 60}$$

The Operation and Maintenance (O&M) is calculated using Eq. 61:

$$C_{O\&M,EC} = c_{O\&M} \cdot P_{nom} \qquad \text{Eq. 61}$$

Where:

- $c_{O\&M} = 6\ \frac{€}{kW}$ (66);
- $P_{nom} = 0.94\ M\text{W}$, that is the nominal power of the electrolyser (see Eq. 39);

So, the Operation and Maintenance cost is in Eq. 62:

$$C_{O\&M,EC} = c_{O\&M} \cdot P_{nom} = 0.0056\ \text{M€} \qquad \text{Eq. 62}$$

In the end, the stack substitution cost and the decommissioning cost are considered:

- The stack substitution cost, Eq. 63, is considered since 20 years of operation are assumed, and the lifetime of an electrolyser is between 80.000-100.000 h (66) so, in this case study this cost is related to the 10th year and it is considered equal to the 20% of the total initial cost of a water electrolyser since is not present in the literature a related value for the methanol electrolyser (67):

$$C_{replacement} = 0.2 \cdot C_{electrolyser} = 6.64\ \text{M€} \qquad \text{Eq. 63}$$

- The decommissioning cost is considered as part of the total initial cost too and it is shown in Eq. 64 (66):

$$C_{decommisioning,EC} = 0.1 \cdot C_{electrolyser} = 3.32\ \text{M€} \qquad \text{Eq. 64}$$

9.4. Electricity cost

As an assumption, the electrolyser is connected to the national electric grid to ensure constant operation at rated power:

- The electricity price considered is an average value of $c_{electricity} = 120 \frac{€}{\text{MWh}}$ (66);
- Since the total energy consumption of the electrolyser is $E_{tot,EC} = 8{,}233.5 \frac{\text{MWh}}{\text{y}}$ (Eq. 40), the electricity cost associated to the hydrogen production is calculated using Eq. 65:

$$C_{electricity,EC} = c_{electricity} \cdot E_{tot,EC} = 0.988 \frac{\text{M€}}{\text{y}} \quad \text{Eq. 65}$$

Since hydrogen must be stored in pressure, the energy consumed by the compressor (see 509.2) is considered too, so, the cost of electricity to run the compressor is calculated multiplying the total amount of hydrogen produced (see Eq. 41) and the total cost is shown in Eq. 67.

$$E_{tot,compressor} = E_{compressor} \cdot \dot{m}_{H_2,total\ produced} = 948 \frac{\text{MWh}}{\text{y}} \quad \text{Eq. 66}$$

$$C_{electricity,compressor} = c_{electricity} \cdot E_{tot,compressor} = 0.114 \frac{\text{M€}}{\text{y}} \quad \text{Eq. 67}$$

So, the total electricity cost is considering summing Eq. 65 and Eq. 67, the result is shown in Eq. 68:

$$C_{electricity,tot} = C_{electricity,EC} + C_{electricity,compressor} = 1.1 \frac{\text{M€}}{\text{y}} \quad \text{Eq. 68}$$

9.5. Economic result: LCOH

To summarize, all the costs considered in the case study are shown in the Table 12.

Table 12: Total costs

Total cost		
Methanol storage tank cost	0.22	M€
Methanol cost	0.82	$\frac{M€}{y}$
Hydrogen storage cost	2.78	M€
Compressor cost	0.45	M€
Compressor maintenaince cost	0.02	$\frac{M€}{y}$
CO_2 capture and storage cost	0.2	$\frac{M€}{y}$
Electrolyser cost	33.2	M€
Electrolyser maintenaince cost	0.0056	$\frac{M€}{y}$
Electrolyser decommisioning cost	3.32	M€
Electrolyser substitution cost	6.64	$\frac{M€}{10y}$
Total electricity cost	1.1	$\frac{M€}{y}$

Since 20 years of operation are considered, the Figure 37 shows the cost distribution over the whole lifetime of the plant.

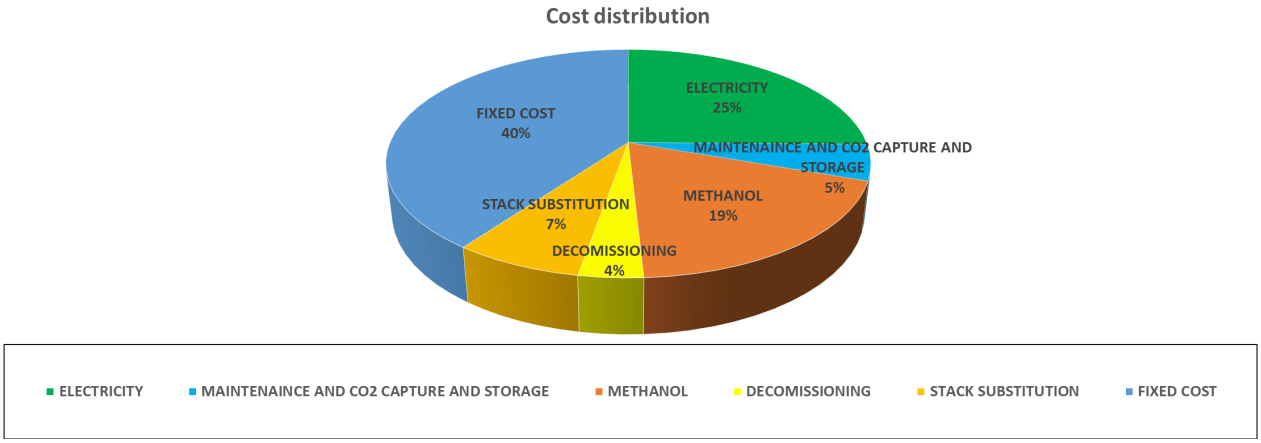

Figure 37: Cost distribution of the plant

Where:

- $Fixed\ cost = C_{methanol\ tank} + C_{H_2\ stored} + C_{compressors} + C_{EC}$ (see Eq. 55, Eq. 56 and Eq. 60);
- $Maintenaince\ and\ CO_2\ capture\ and\ storage = \sum_{i=1}^{N=20} C_{O\&M,compressor,i} + C_{O\&M,EC,i} + C_{CO_2\ capture\ and\ storage}$ (see Eq. 57, Eq. 58 and Eq. 62);

- $Stack\ substitution = C_{replacement}$ (see Eq. 63)
- $Decommisioning = C_{decommisioning}$ (see Eq. 64)
- $Methanol\ cost = \sum_{i=1}^{N=20} C_{methanol}$ (see Eq. 53)
- $Electricity\ cost = \sum_{i=1}^{N=20} C_{electricity,tot}$ (see Eq. 68)

The most important feature of the aqueous methanol electrolysis is the less energy consumption with respect to the water electrolysis:

- PEM water electrolysis (34):

$$PEM: [4{,}2; 6{,}6]\frac{kWh}{m^3} \rightarrow [46{,}73; 73{,}4]\frac{kWh}{kg} \quad \text{Eq. 69}$$

- Energy consumption per kg of hydrogen produced is calculated using Eq. 70 and Eq. 71:

$$E_{EC} = 8{,}233.5\frac{MWh}{y} \quad \text{Eq. 70}$$

$$\dot{m}_{H_2,total\ produced} = 338{,}619.4\frac{kg}{y} \quad \text{Eq. 71}$$

$$E_{spec} = \frac{E_{EC}}{\dot{m}_{H_2,total\ produced}} = 24.31\frac{kWh}{kg} \quad \text{Eq. 72}$$

So, even if the lowest energy consumption for the PEM water electrolysis is considered (see Eq. 69), the energy consumption for the aqueous methanol electrolysis is the half (see Eq. 72), reaching $\frac{1}{3}$ of the energy consumed by water electrolysis if is considered the highest value.

The aim of this case study is to estimate what the Levelized Cost Of Hydrogen might be using this technology since there is no information about it in the literature. This parameter is calculated in three different ways (67), assuming as discount rate a fixed value of $i = 4\%$ (68) and a time span of $N = 20\ years$. The differences between the three LCOH are described below:

- $LCOH_1$ considers as investment expenditure in the first year both decommissioning and stack replacement, and the amount of hydrogen produced is fixed each year;
- $LCOH_2$ decommissioning and stack replacement are no more considered as cost in the first year, so, the $discount\ factor = \frac{1}{(1+i)^N}$ is taken into account, and also to consider the decrease in the hydrogen production during the time is applied the discount factor;
- $LCOH_3$ is equal to $LCOH_2$ for the part related to the cost but, the hydrogen produced each year is kept constant.

To evaluate the cost involved in the process, are introduced these two terms:

- CAPEX: Capital expenditures, is used to evaluate all the installation costs on the first year;
- OPEX: Operating expenses, is used to evaluate all the variable costs that are dealing with the discount factor.

The first way used to calculate the Levelized Cost Of Hydrogen is expressed in the Eq. 73.

$$LCOH_1 = \frac{CAPEX_1 + \sum_{i=1}^{N=20} \frac{OPEX_{1_i}}{(1+i)^N}}{\sum_1^{N=20} m_{H_2,i}} \quad \text{Eq. 73}$$

Capex$_1$ is calculated using Eq. 74.

$$CAPEX_1 = C_{methanol\ tank} + C_{H_2\ storage\ tank} + C_{EC} + C_{decommisioning,EC} + C_{replacement,EC} \quad \text{Eq. 74}$$

$$CAPEX_1 = 46.62\ \text{M€} \quad \text{Eq. 75}$$

Opex$_1$ is calculated using Eq. 76 and it is actualized using Eq. 77.

$$OPEX_1 = \sum_{i=1}^{N=20} C_{methanol,i} + C_{O\&M,compressor,i} + C_{O\&M,EC,i} + (C_{electricity,EC,i} + C_{electricity,compressor,i}) + C_{CO_2\ stored} \quad \text{Eq. 76}$$

$$\sum_{i=1}^{N=20} \frac{OPEX_{1_i}}{(1+i)^N} = 30.1\ M€ \quad \text{Eq. 77}$$

The total amount of hydrogen produced is shown in Eq. 78.

$$m_{H_2,1} = \sum_{i=1}^{N=20} m_{H_2,i} = 7{,}111{,}007\ kg \quad \text{Eq. 78}$$

So, at the end the LCOH$_1$ calculated using Eq. 73, Eq. 75, Eq. 77, Eq. 78, is shown in Eq. 79.

$$LCOH_1 = 10.79 \frac{€}{kg} \quad \text{Eq. 79}$$

The second way to calculate the Levelized Cost Of Hydrogen used is shown in Eq. 80.

$$LCOH_2 = \frac{CAPEX_2 + \sum_{i=1}^{N=20} \frac{OPEX_{2_i}}{(1+i)^N}}{\sum_{i=1}^{N=20} \frac{m_{H_2,i,2}}{(1+i)^N}} \quad \text{Eq. 80}$$

Where:

Capex$_2$ is calculated in Eq. 81.

$$CAPEX_2 = C_{methanol\ tank} + C_{H_2\ stored} + C_{EC} \quad \text{Eq. 81}$$

$$CAPEX_2 = 36.66\ M€ \quad \text{Eq. 82}$$

Opex$_2$ is calculated in Eq. 83 and it is actualized using the Eq. 84.

$$OPEX_2 = \sum_{i=1}^{N=20} C_{methanol,i} + C_{O\&M,compressor,i} + C_{O\&M,EC,i} + C_{electricity,EC,i} + C_{electricity,compressor,i} + C_{CO_2\ stored} + C_{decommisioning,EC} + C_{replacement,EC} \quad \text{Eq. 83}$$

$$\sum_{i=1}^{N=20} \frac{OPEX_{2_i}}{(1+i)^N} = 35.87\ M€ \quad \text{Eq. 84}$$

The total amount of hydrogen produced is shown in Eq. 85.

$$m_{H_2,2} = \sum_{i=1}^{N=20} \frac{m_{H_2,i,2}}{(1+i)^N} = 4{,}750{,}546\ kg \quad \text{Eq. 85}$$

So, at the end the $LCOH_2$, calculated using Eq. 80, Eq. 82, Eq. 84 and Eq. 85, is shown in Eq. 86.

$$LCOH_2 = 15.27\ \frac{€}{kg} \quad \text{Eq. 86}$$

The third way to calculate it is shown in Eq. 87.

$$LCOH_3 = \frac{CAPEX_3 + \sum_{i=1}^{N=20} \frac{OPEX_{3_i}}{(1+i)^N}}{\sum_{i=1}^{N=20} m_{H_2,i,3}} \quad \text{Eq. 87}$$

Where:

$Capex_3$ is calculated using Eq. 88.

$$CAPEX_3 = C_{methanol\ tank} + C_{H_2\ stored} + C_{EC} \quad \text{Eq. 88}$$

$$CAPEX_3 = 36.66\ M€ \quad \text{Eq. 89}$$

$Opex_3$ is calculated using Eq. 90 and it is actualized using Eq. 91.

$$OPEX_3 = \sum_{i=1}^{N=20} C_{methanol,i} + C_{O\&M,compressor,i} + C_{O\&M,EC,i} + C_{electricity,EC,i} + C_{electricity,compressor,i} + C_{CO_2\ stored} + C_{decommisioning,EC} + C_{replacement,EC} \quad \text{Eq. 90}$$

$$\sum_{i=1}^{N=20} \frac{OPEX_{3_i}}{(1+i)^N} = 35.87\ M€ \quad \text{Eq. 91}$$

The total amount of hydrogen produced is calculated in Eq. 92.

$$m_{H_2,3} = \sum_{i=1}^{N=20} m_{H_2,i,3} = 7{,}111{,}007\ kg \quad \text{Eq. 92}$$

So, at the end the $LCOH_3$, calculated using Eq. 87, Eq. 89, Eq. 91 and Eq. 92, is shown in Eq. 93.

$$LCOH_3 = 10.20 \frac{€}{kg} \quad \text{Eq. 93}$$

So, to summarize, the main results are presented in Figure 38.

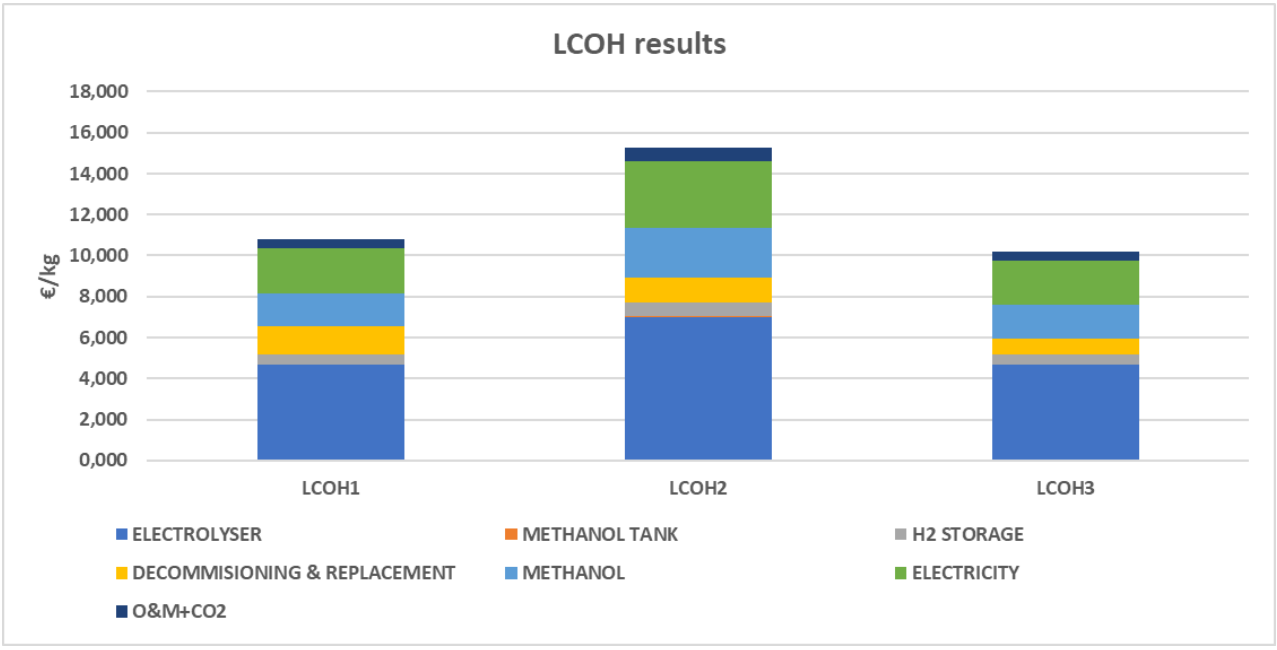

Figure 38: LCOH results using fixed electricity price of 0,12 euro/kg

The LCOH for aqueous methanol electrolysis found in this case study is higher with respect to the one of water electrolysis (see Figure 39) (67).

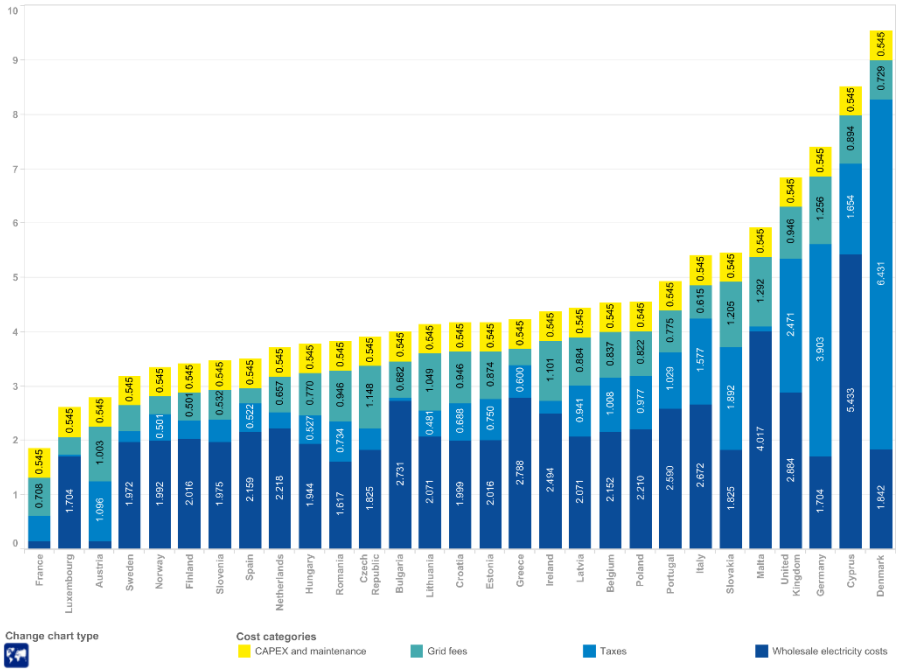

Figure 39: LCOH of grid connected water electrolysis

Even if an higher value was found, the energy consumption for an aqueous methanol electrolysis results much lower than the PEM water electrolysis and since the CAPEX is huge with respect to the same installed power for an existing PEM water electrolyser, in the future, with some improvements in this technology, could be a closer value with the LCOH of an existing electrolyser.

9.6. LCOH sensitivity analysis

As has been shown in the 9.5, the cost of electricity has lower impact on this technology with respect to the water electrolysis one, so the aim is to calculate the LCOH by considering different electricity prices also due to fluctuations of this price last year, due to the fact that in Italy the price reached the maximum value of $654 \frac{€}{MWh}$ (68). The Figure 40 is obtained changing only the price of electricity with respect the case study analysed previously, in which the price was fixed at $120 \frac{€}{MWh}$.

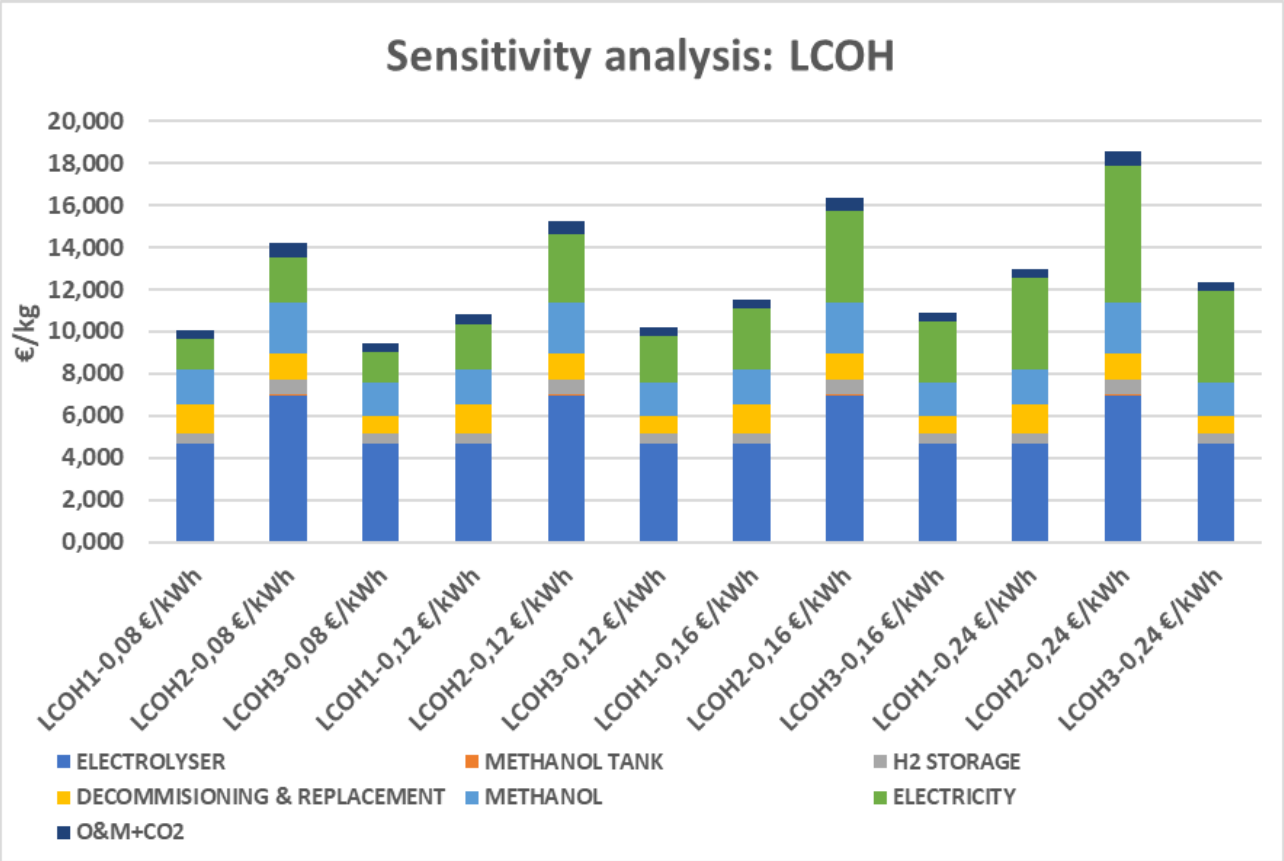

Figure 40: Sensitivity analysis LCOH changing electricity price

In this sensitivity analysis three different electricity prices were chosen:

- $c_{elecricity} = 0.08 \frac{€}{kWh}$, that corresponds to the average price of electricity between 2018 and 2021 in Italy (68) and it is also an average value of the Levelized Cost Of Electricity between off-shore wind, on-shore wind and solar PV (69);
- $c_{elecricity} = 0.12 \frac{€}{kWh}$, that is the price used in the case study and it is related to the average price of electricity during the year 2021 (68);
- $c_{elecricity} = 0.16 \frac{€}{kWh}$, that is the average price of electricity of the current year (2023);

- $c_{elecricity} = 0.24\ \frac{€}{kWh}$, that is the average price between 15th March 2022 and 15th June 2022, interval between two periods in which the price reached the maximum values of $0.588\ \frac{€}{kWh}$ and $0.654\ \frac{€}{kWh}$ respectively.

Even in the case of the electricity price equal to $0.24\ \frac{€}{kWh}$, the highest contribution is still attributed to the cost of the electrolyser. Moreover, if the average electricity price of 2023 is taken as the electricity price ($0.16\ \frac{€}{kWh}$), the LCOH is still very similar to the value chosen for the case study ($0.12\ \frac{€}{kWh}$).

9.7. Economic analysis with the new polarization curve

After a further improvement of the test bench (see Chapter 7.1), a new polarization curve it is obtained in Table 3, since to be considered reliable, the same polarization curve must be obtained several times, how it was done with the previous ones, for the case study described previously it was considered the one shown in Figure 33, with 1M.

At the end of this case study, I would like to see the most important results also for this new polarization curve, that are reported in Table 13 and Figure 41, since at $j_c = 160 \frac{mA}{cm^2}$ the voltage is 22% lower and at $j_c = 400 \frac{mA}{cm^2}$ the voltage is 31% lower(see Chapter 7.1 and Figure 34).

Table 13: Main energetic parameters with the new polarization curve at 70°C-1M

Voltage [V]	Current density $\left[\frac{mA}{cm^2}\right]$	Power $\left[\frac{mW}{cm^2}\right]$	Efficiency of the process
0.293	4.925	1.444	0,446
0.321	9.981	3.208	0,422
0.339	14.940	5.065	0,409
0.355	19.995	7.090	0,397
0.379	30.014	11.370	0,381
0.400	39.942	15.973	0,368
0.419	49.972	20.959	0,356
0.438	59.986	26.246	0,346
0.456	70.000	31.917	0,337
0.473	80.013	37.847	0,328
0.489	90.029	44.051	0,321
0.505	100.043	50.501	0,314
0.534	119.991	64.027	0,301
0.562	140.018	78.682	0,290
0.589	160.065	94.281	0,281
0.617	179.996	110.978	0,271
0.643	200.062	128.680	0,263
0.668	220.089	147.116	0,255
0.695	240.124	166.828	0,248
0.721	260.068	187.589	0,241
0.747	280.094	209.096	0,234
0.774	300.140	232.304	0,228
0.800	320.244	256.267	0,222
0.826	340.271	281.174	0,216
0.852	360.298	307.120	0,211
0.877	380.325	333.618	0,206
0.904	400.352	361.884	0,201

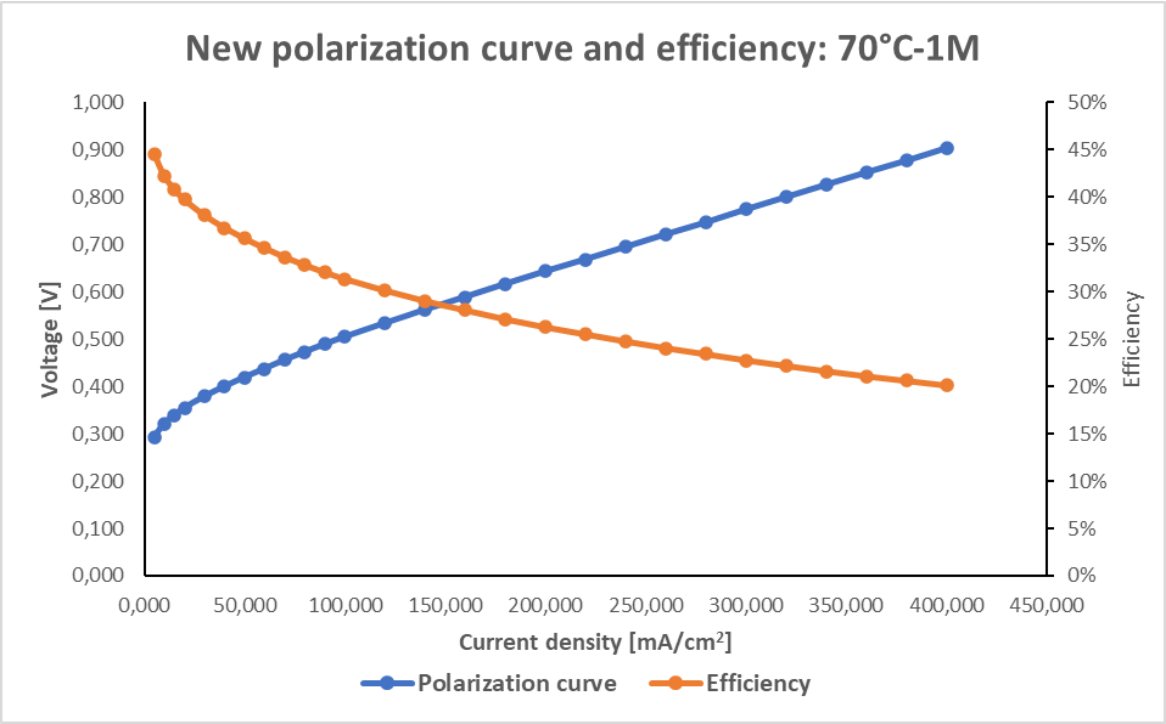

Figure 41: Polarization curve with the improvement of the test bench at 70°C and 1M

Where:

Table 14: Comparison of the old curve with the new one, also analysing the main parameters of the case study with the new configuration

	Voltage [V]	**Current density** $[\frac{mA}{cm^2}]$	**Power** $[\frac{mW}{cm^2}]$	**Efficiency**	**Energy consumed** $[\frac{MWh}{y}]$	P_{nom} $[MW]$
Old curve	0.753	160.06	120	0.233	8,233.5	0.94
New curve	0.589	160.06	94.28	0.27	6,442.1	0.74

So, as did it before in the Eq. 40, the new energy consumption is calculated using Eq. 94 and it is lower with respect to the value associated at the previous curve, since the voltage is 22% lower in the working point of the electrolyser. The energy saved in the case study, thanks to this improvement of the test bench, is calculated in Eq. 95:

$$E_{consumed,new} = P_{nom,new\ curve} \cdot h = 6442.1\ \text{MWh} \quad \text{Eq. 94}$$

$$E_{saving} = E_{consumed,tot} - E_{consumed,new} = 1791.5\ \text{MWh} \quad \text{Eq. 95}$$

The Levelized Cost Of Hydrogen is slightly changing too, and it is shown in Figure 42.

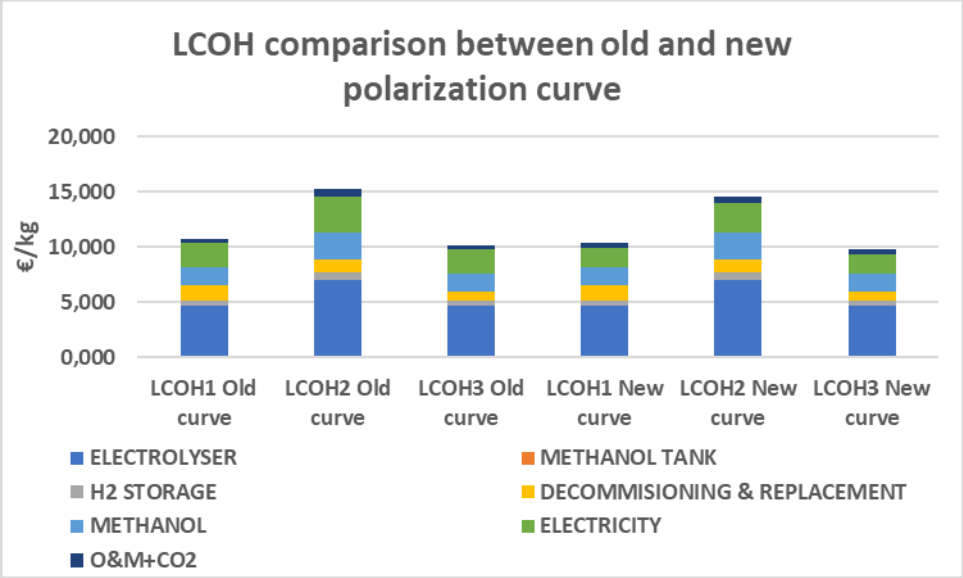

Figure 42: LCOH comparison between the results obtain with the new polarization curve and the old one

Obviously, decreasing the energy consumed by the electrolyser, the electricity cost associated to it will decrease too, this means the at the end of the whole lifetime of the plant there will be a reduction of the Levelized Cost Of Hydrogen. The specific energy consumption is decreasing too, reaching a value of $E_{spec,new\ curve} = 19.02 \frac{kWh}{kg}$ with respect to $E_{spec,old\ curve} = 24.31 \frac{kWh}{kg}$ (see Figure 43), even if in the Figure 42 is not that evident that the electricity contribution is lower with the new configuration.

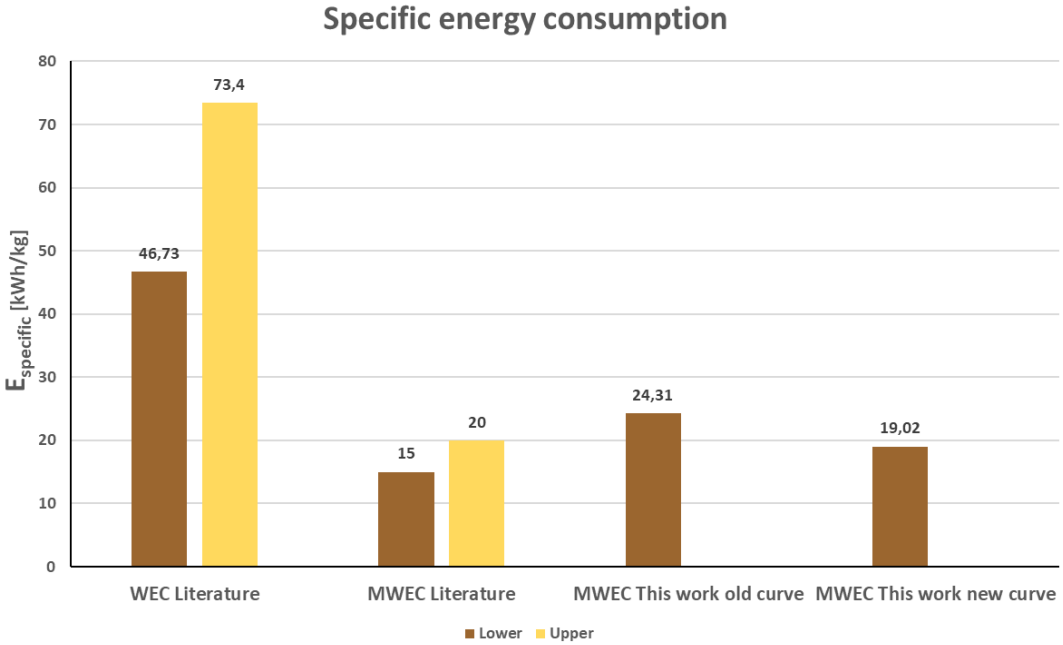

Figure 43: Comparison between PEM Water Electrolysis (WEC) energy consumption, with respect to the Methanol-Water Electrolysis (MWEC) in the literature and in this work

10. Conclusion

Following the experimental activities conducted in this work and the results obtained, the conclusions of the results are presented below.

Firstly, it can be deduced from the literature review that the studies conducted on aqueous methanol electrolysis are not yet sufficient to provide unique results in terms of polarization curve. In fact, the number of publications on this topic are much lower with respect to the water electrolysis and there are no real plants producing hydrogen using this technology. Since the theoretical operating voltage of methanol electrolysis is 0.02 V compared to the 1.23 V of water electrolysis, some studies shown that the electricity consumed could be about a third of that for water electrolysis, so, this technology is attracting particular attention.

The majority of the analyses conducted on aqueous methanol electrolysis uses a PEM methanol electrolyser. The basic structure used to build up the cell in this type of electrolyser is the following: the structure of the MEA consists mainly of a Pt/C cathode, a PtRu/C anode and a nafion 117 membrane, the same configuration is used for the experimental part of this work.

Moreover, even on the best operating conditions, it is possible to find uniform behaviours: analysing the polarisation curve, it can be seen that at the same current density, increasing the temperature up to a maximum of 85°C, in order to avoid problems as membrane degradation, leads to a decrease in cell voltage. In the case of methanol concentration some studies show that increasing this parameter can have benefits in terms of the polarisation curve, showing an optimum value between 1M and 4M with temperatures between 60 °C and 70°C.

On the other hand, there are no information regarding the best flow rate that must be provided to the cell and only one study presents the associated costs of installation, maintenance and decommissioning for the aqueous methanol electrolyser.

From the following information, it was decided to investigate the effect of temperature and methanol concentration on the polarisation curve, to know which is the one showing the best performance of the methanol electrolyser, which is the lowest voltages at the same current density. The optimum result is shown at a temperature of 70°C for both methanol concentrations used (1M and 4M).

Since there are no values in the literature associated with the Levelized Cost Of Hydrogen for this technology, it was decided to carry out a case study in which it is assumed that all the vehicles on the island of San Pietro will be fuelled with hydrogen. The hydrogen requirement necessary to satisfy the demand is calculated, assuming the use of a methanol electrolyser capable of producing the necessary amount of hydrogen, taking as reference the polarization curve at 70°C and 1M. The sizing of the electrolyser does not follow a demand profile but is based on the total annual hydrogen consumption calculated for the island.

The electrolyser used in this case study has a nominal power of 0.94 MW, in which 13 stacks of 500 cell each are considered, consuming 8,233.53 MWh of electrical energy per year, that is supplied by the national electrical grid with a fixed electricity price of $120\frac{€}{\text{MWh}}$, showing a specific energy consumption value of

$E_{spec} = 24.31 \frac{kWh}{kg}$, resulting in about one third of the value present in the literature for a PEM water electrolysers.

The LCOH is calculated using three different methods and the best result is $10.20 \frac{€}{kg}$. Furthermore, a sensitivity analysis was conducted to verify the change in the LCOH value as the electricity price increases.

Finally, it was decided to modify the configuration of the test bench, reducing the length of the cable connecting the cell with the galvanostat to try to decrease the voltage losses: the results obtained show a voltage of $0.904\ V$ at a current density of $j_c = 400 \frac{mA}{cm^2}$ with a reduction of 31% compared to the initial case, maintaining the same conditions of temperature (70 °C), and molarity of the solution (1M).

Since the polarization curve has been reproduced only once, in order to obtain more reliable results, the new configuration will have to be tested more carefully in future works.

Having reached these conclusions, it is appropriate to investigate further on this technology which shows excellent values in terms of polarization curve and consequently of specific energy consumption.

This work stands as a starting point for future studies concerning aqueous methanol electrolysis, both for the experimental part and for the economic analysis conducted in the case study which, limited by the lack of information, can be widely explored.

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