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Development of an Innovative Hydrogen Production Solution for Use in the Field of Environmental Protection

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Abstract. The European Union has marked out various targets to achieve climate neutrality by 2050, one of which includes reducing CO_2 emissions and the impact of climate change, through a transition to green energy and contributing to the EU targets on the production of an annual hydrogen capacity of 1 million tons by 2025 and 10 million tons by 2030. In this context, the paper analyses the water quality restrictions used for the electrolyser supply, facilitating the placement of a hydrogen installation near any source of water. Renewable energy sources will be used simultaneously to obtain hydrogen production efficiency. The suggested technology offers a decarbonized solution in the protected wetlands regions' naval sector and as natural gas potentially used in the domestic and industrial sectors. Additionally, its potential to be repeatable, resilient, and sustainable makes the developed innovative hydrogen production solution eco-friendly.

1 Introduction

Currently, over 162×10^{12} kWh of energy per year is consumed worldwide in the form of coal, natural gas, and oil, and their by-products act as such or cause the growth of other agents, such as ozone [1, 2]. Hydrogen, a clean and renewable energy source, presents a viable substitute in light of the rising energy demand. It can be produced by fossil energy reforming, from industrial by-product gas, or through water electrolysis. The latter is based on the principle of electrodes splitting water molecules into hydrogen and oxygen using electricity [3, 4]. There are numerous methods for producing hydrogen by electrolyzing water, including alkaline water electrolysis (AWE), proton exchange membrane water electrolysis (PEM), solid polymer anion exchange membrane water electrolysis (AEM), and solid oxide water electrolysis (SOWE), each with its distinct advantages and disadvantages [5].

Water and electricity are the sole resources used in the entire electrolysis process, which produces carbon-free, clean, and non-polluting hydrogen. In this context, the sustainability of hydrogen production at maximum capacity may be uncertain due to a recently observed

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problem, that of water depletion by consumption in electrolysis. Therefore, if all the fossil fuel usage were replaced with green hydrogen, the annual water required for electrolysis would be 8.3 × 10^{13} kg [1]. Although water is an abundant resource, only a finite amount of it is available at any given moment, most of which being affected by anthropogenic activities [6, 7].

Water is seen as required not only as an input for production, but also as a cooling medium with a percentage of withdrawal from 14% to 92%, depending on the technology used for hydrogen production [8]. Thus, hydrogen production will increase the already existing demand for freshwater sources if water-efficient technologies are not adopted [9].

In this context, the present paper will analyse the alternatives in order to remove water quality restrictions used for the electrolyser supply, which along with the use of renewable energy sources will allow the maintaining of hydrogen production efficiency yield. Also, preliminary applications of hydrogen were tested and evaluated. This research resides in the need to obtain hydrogen right where is a demand for it, so that the cost with its management, careful storing and transporting can be reduced. Thus, hydrogen can be used as fuel in protected areas, as it is clean and silent, but also for methane displacing in combustion, to mitigate the pollution.

2 Experimental installation

The installation for hydrogen production uses a hydrogen generator with a PEM stack electrolyser, whose metal plate surface is activated for a proper product discharge by layer deposition, while in the electrolytic space between electrodes, a PEM membrane acts as a source of protons, to ensure ion conduction. Using a PEM membrane means the electrolyser does not require any chemicals as an electrolyte, which could potentially overflow into the environment in case of problems. Process water is introduced into the installation to generate hydrogen at the cathode and oxygen at the anode [10]. Oxygen is initially discharged into the electrolysis tank, for water mist recuperation, and from there into the atmosphere. Hydrogen is obtained in the cathode space of the stack with a proper output pressure, that parameter being controlled by internal automation, to prevent damage by super pressurizing. Subsequently, it is passed through a mist separator, dried, and its oxygen content is reduced by a catalytic mass of palladium on alumina. Finally, the hydrogen flow rate is adjusted from the output flow regulator, from where it enters in the compression unit and is stored in a 300-bar cylinder, as it can be seen in Figure 1a. The compressor is adapted for a relatively small flow of hydrogen, being a hydride type unit with a 14.2 l/min capacity.

The production of hydrogen by electrolysis is powered by electricity, splitting the water according to the following equation:

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

Thus, water flow and green energy are the two main aspects when producing green hydrogen.

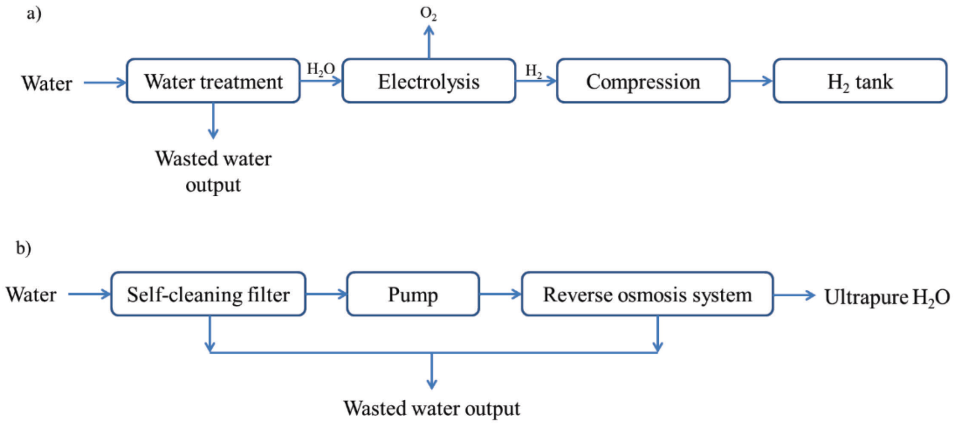

Fig. 1. a) Hydrogen production demonstrator design, b) complex water treatment used to reduce contaminants.

The hydrogen installation obtains purified water through a complex treatment method, which includes a self-cleaning filter, booster pump, and reverse osmosis purification (Figure 1b). Depending on the value of total dissolved solids (TDS), the treating method will be used multiple times until the water used by the electrolyser has an impurities level under 0.5 ppm.

3 Results and discussions

3.1 Analysed water resources for hydrogen production

In order to assess different potential water sources for hydrogen production, the quality of various categories of water that could be used in the processes of obtaining hydrogen by electrolysis was analysed in Table 1.

Table 1. Physical-chemical quality of the analysed water types.

No.	Water type	Source	Treatment at source	Identified pollutants
1	Industrial wastewater	Food industry	No	Suspended matter = 260 mg/L Mineral substances = 370 mg/L Organic substances = 830 mg/L Nutrients ≅ 24 mg/L Metals = absent
2		Beauty industry	Mechanical and chemical treatment	Suspended matter = 120 mg/L Mineral substances ≅ 195 mg/L Organic substances = 400 mg/L Nutrients ≅ 11 mg/L Σ Metals = 0.22 mg/L
3		Pulp and paper industry	Mechanical, chemical and biological treatment	Suspended matter = 68 mg/L Mineral substances = 250 mg/L Organic substances = 70 mg/L Nutrients ≅ 2 mg/L Metals = absent
4		Electrical equipment industry	No	Suspended matter = 50 mg/L Mineral substances = 450 mg/L Organic substances = 60 mg/L Nutrients = 30 mg/L Σ Metals = 1.88 mg/L

5		Automotive parts and accessories industry	Mechanical and chemical treatment	Suspended matter = 155 mg/L Mineral substances > 1000 mg/L Organic substances = 320 mg/L Nutrients ≅ 26 mg/L Σ Metals = 3.5 mg/L
6		Construction materials industry	Mechanical treatment	Suspended matter = 9 mg/L Mineral substances = 405 mg/L Organic substances = 34 mg/L Nutrients < 1 mg/L Σ Metals = 0.1 mg/L
7	Municipal wastewater	Local sewerage system	Mechanical and biological treatment	Suspended matter = 60 mg/L Mineral substances = 1000 mg/L Organic substances = 45 mg/L Nutrients = 25 mg/L Σ Metals = 0.65 mg/L
8	Wastewater from animal husbandry	Animal breeding farms	Mechanical and biological treatment	Suspended matter = 34 mg/L Mineral substances = 12 mg/L Organic substances = 220 mg/L Nutrients < 1 mg/L Σ Metals = 0.2 mg/L
9	Surface wate	River	No	Conductivity = 337 µS/cm Mineral substances = 253 mg/L Organic substances ≅ 10 mg/L Nutrients ≅ 1.5 mg/L Σ Metals ≅ 0.2 mg/L
10		Seawater	No	Conductivity = 50000 µS/cm Suspended matter = 48.2 mg/L Mineral substances = 15.2 mg/L Organic substances ≅ 3 mg/L
11	Groundwater	Phreatic surface (well, H = 18 m)	No	Conductivity =840 µS/cm Mineral substances ≅ 180 mg/L Organic substances = 1.4 mg/L Nutrients ≅ 3 mg/L Metals = absent
12		Aquifer (H = 200 m)	Mechanical treatment and chlorination	Mineral substances = 674 mg/L Organic substances ≅ 1 mg/L Nutrients ≅ 4 mg/L Σ Metals = 0.12 mg/L

The comparative analysis of the quality of various types of water (wastewater, surface water, groundwater), showed that none of the analysed water types can be used as such, without further treatment/purification, for hydrogen production as they do not fulfil the quality requirements of the water used for the electrolysis. For the PEM electrolysis, the water consumed is ultrapure, having a minimum resistivity of 1 MΩ*cm, corresponding to a TDS < 0.5 ppm. Zeng et al. [11] have also stated that contaminants might impact the reaction by depositing in the electrolysers (on the electrode surfaces or in the membrane). To achieve the water requirements for the PEM electrolyser, the various types of water must be subjected to several treatment stages (repetitions of the complex treating method).

Fig. 2 highlights the number of treatment stages for each analysed water type. It could be seen that seawater requires five treatment stages, wastewater has allocated four stages, while for the river and groundwater, the treatment is not so advanced, being needed for only three stages.

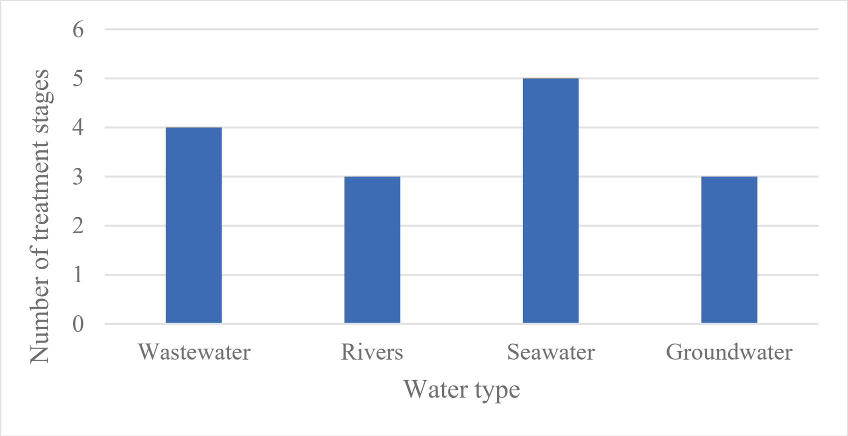

Fig. 2. Number of treatment stages before PEM electrolysis for different water types.

Table 2. Power and water consumption for hydrogen production with different water types.

Level	Efficiency	Power used for water treatment [kW]	Power used for automation [kW]	Power used for electrolysis [kW]	Power used for compression [kW]	Water consumption [L/h]	Water for electrolysis [L/h]	Wasted water from treatment and drier [L/h]	Hydrogen production [m^3/h]
Seawater									
20 kW	50%	0.018	0.400	16.590	1.790	3.207	1.895	1.312	2.358
50 kW	65%	0.059	1.000	40.730	5.712	10.234	6.047	4.186	7.526
100 W	70%	0.132	1.500	85.280	9.091	23.075	13.636	9.440	16.969
1 MW	76%	1.499	10.000	890.100	58.378	261.505	154.530	106.976	192.300
Wastewater									
20 kW	50%	0.012	0.400	16.600	1.790	2.747	1.896	0.851	2.359
50 kW	65%	0.038	1.000	40.750	5.714	8.767	6.050	2.717	7.529
100 W	70%	0.085	1.500	85.320	9.095	19.769	13.643	6.126	16.977
1 MW	76%	0.961	10.000	890.600	58.411	224.050	154.617	69.433	192.410
River and groundwater									
20 kW	50%	0.007	0.400	16.600	1.791	2.556	1.896	0.659	2.360
50 kW	65%	0.023	1.000	40.760	5.716	8.157	6.052	2.105	7.531
100 kW	70%	0.053	1.500	85.350	9.098	18.393	13.647	4.746	16.983
1 MW	76%	0.596	10.000	891.000	58.433	208.462	154.676	53.786	192.490

Table 2 highlights the power and water consumption for hydrogen production, considering the various potential water sources. The water consumption decreases from 1.36 kg/m^3 hydrogen for the 20 kW installation to 1.08 kg/m^3 for the 1 MW installation. The highest losses were determined during water treatment. The irrecoverable water from the electrolysis process is under 5% of total water feeding, being thus only 3-4% of the entire water consumption. The cooling had no water consumption, and the working temperature for the electrolyser was 80 ºC, which ensures a good thermal exchange in the air cooler. The lowest water loss was for river and groundwater with approximately 26% water wasted during three stages of treatment, while wastewater presented around 31% wasted water, needing four stages of treatment. Seawater had the greatest water loss, around 41%, due to the five treatment stages [12]. The power count shows that electrolyser is the main consumer with 88-92% of total consumption, followed by compression with 6.5-10.8 from electrolysis.

It can be noticed that all water sources have the potential to be used in hydrogen production by electrolysis. While river and groundwater have the lowest stages of treatments making them the best solution, their consumption may be limited by other concomitant water uses (i.e. for human consumption, for irrigation). Also, seawater requires complex water treatment and presents a high percentage of water loss during hydrogen production making this option not so feasible. However, wastewater performs well as an electrolysis water source not only because its reuse is encouraged, but also because it does not compete with other water uses and its availability is less susceptible to weather-related disruptions and to the effects of climate change [13, 14].

3.2 Hydrogen applications

Taking into account the possibility of using various water sources for hydrogen production, preliminary tests have been carried out on the use of obtained hydrogen for environmental applications. From the hydrogen produced by the installation, a quantity of 2500 l hydrogen was stored in 50 l cylinders at a pressure of 50 bar for about 60 min. The hydrogen was used to ensure a 1 kWh (3.6 MJ) electricity supply for a boat with a 3 kW electric motor. The transformation of hydrogen into electricity was carried out with a PEM-type fuel cell with computerized control and was assisted by a buffer battery of 50 Ah at 12 V (2.16 MJ) to take over the load peaks (the inertia of the fuel cell being significant during accelerations). The study area was Comana Lake, part of the protected area of Comana Natural Park, as it can be seen in Fig. 3. The results validated the potential use of hydrogen as fuel for boats and it was also observed that the noise of the thermal engines was eliminated. Further development should take into consideration the proper sizing of the hydrogen cylinders in order to increase the boat speed, correlated with the engine power, but also its use in monitoring activities and in situ measurements of water quality and bathymetry [15, 16].

Fig. 3. Testing the use of hydrogen as fuel in a protected area.

Another potential application is the injection of hydrogen into the methane gas supply network. This will produce a reduction in the volumetric calorific value of the mixture, which depends on the volumetric percentage of hydrogen in the mixture. For contents between 0 (pure methane) and 30% H_2 (maximum content considered feasible without structural changes in the distribution network), the calorific value of the mixture decreases from 42 MJ/m^3 to 33 MJ/m^3 (Fig. 4(a)). This decrease in calorific value must be compensated by an increase in the volume of the gas mixture to obtain the same amount of thermal energy through combustion, as it can be seen from Fig. 4(b).

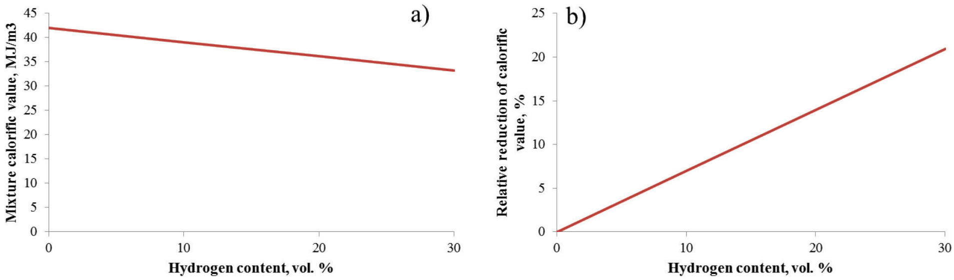

Fig. 4. Content of hydrogen vs a) calorific value of the mixture, b) relative reduction of calorific value.

Replacing a percentage of methane gas with hydrogen will reduce the CO_2 emission, as a result of burning a lesser amount of methane gas. Thus, in the case of domestic consumption, an experimental installation was developed (Fig. 5) to determine the separation time between the two gases and to determine the reduction of CO_2, while maintaining the same calorific value.

Fig. 5. Experimental installation for testing methane displacement by hydrogen.

4 Conclusions

The possibility of producing hydrogen at the site of consumption was examined in this study. Among, the numerous advantages that reside in this approach, it could be mentioned the significant reduction in the costs concerning the converting, storing, and transporting of hydrogen.

The results showed that all the analysed water sources can be used in the electrolyser to produce hydrogen. However, the water loss during the hydrogen production varied from 26% (for rivers and groundwater) to 41% for seawater. If it is available, wastewater presents an optimal alternative as it does not compete with other water uses and it is less vulnerable to extreme weather events. The main energy consumer remains the electrolyser, followed by compression (does not exceed 11% of the energy consumed during electrolysis). Due to the increase in operating temperature, actual electrolysers do not need cooling towers that consume water and do have not an important amount of energy for cell cooling. PEM electrolyser utilisation allows not only a promising way to allow efficient water electrolysis, but also it is safe for the environment due to the absence of chemicals in the electrolyte.

The potential application of hydrogen as a fuel to naval transport in protected areas could be developed as a fair and safe way to environmental protection; its application as a natural gas diluent for domestic consumption was also tested and the preliminary results showed good perspectives for a small amount of hydrogen in the natural gas network, increasing the combustion efficiency in addition to reducing carbon dioxide emissions.

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