PRODUCTION, STORAGE AND UTILIZATION OF HYDROGEN IN INDUSTRIAL SECTOR

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ABSTRACT

Hydrogen stands out as a promising alternative energy carrier due to its efficient capacity for electricity and mechanical power production, emitting only water as a by-product. This characteristic makes it a key player in mitigating greenhouse gas emissions and air pollution, underlining its significance in the global transition to clean energy. This paper aims to contribute to the existing literature by providing a brief overview of the current state-of-the-art techniques for the production, storage, and utilization of hydrogen, covering traditional approaches such as steam methane reforming, electrolysis, and biomass gasification. Notably, this examination goes beyond conventional methods to spotlight the emerging potential of producing hydrogen-rich biogas through dark fermentation, an anaerobic fermentation process that occurs in the absence of light. The produced biogas, rich in hydrogen, undergoes a purification system before being utilized for electricity generation within fuel cells.

In this study, as part of the MODSEN project, we will present the initial results obtained from a process of dark fermentation of organic waste, aiming to innovate and enhance the processes of hydrogen production, storage, and utilization through direct, experimental research. This approach aligns with the waste-to-energy paradigm, showcasing a sustainable pathway for simultaneously managing organic waste and generating clean energy. Moreover, the paper presents initial results obtained from a Life Cycle Assessment (LCA) analysis conducted on a green hydrogen production system from photovoltaic-powered electrolysis present in the company's laboratory. Furthermore, the paper explores innovative solid-state storage techniques for hydrogen, highlighting materials like Metal Hydrides, and Metal Organic Frameworks (MOFs). These materials enable safe and compact storage with adsorption and desorption capabilities at moderate temperatures and pressures, suitable for various applications.

1 INTRODUCTION

Hydrogen has gained increasing attention as a potential solution to global energy challenges due to its versatility and potential to be produced from a variety of feedstocks, as a matter of fact, in the pursuit of industrial sustainability, hydrogen has gained unprecedented prominence, driven by a tripling of global demand projected by 2050, with a worldwide production estimated at over 70 million tons annually (European Commission, 2020), (Singh, 2005).

Hydrogen possesses an advantage in its ability to be generated from various sources, including fossil fuels, renewable energy such as wind and solar power and even waste materials. This adaptability makes it an appealing choice for countries seeking to broaden their energy sources while reducing reliance on fuels. In terms of its role as an energy carrier, hydrogen offers versatility in its application, serving as a fuel for power generation, heating, and transportation, among other uses.

Considering current geopolitical uncertainties, countries worldwide have been working together to find fuels that can be used in the transportation industry and decrease its reliance on petroleum. Among the options, hydrogen has emerged as a solution not only because it can be produced from different sources making it a versatile fuel, but also because it has the potential to greatly decrease CO_2 and other impactful emissions generated by transportation systems.

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The European Union aims to produce at least one million tons of renewable hydrogen by 2024 and to have at least 40 GW of renewable hydrogen electrolyzers in operation by 2030 (Osman et al., 2022), (Hydrogen Innovation Report, 2021).
Furthermore, in the heating sector, hydrogen can be used as a replacement for natural gas in industrial and residential applications, blended with natural gas to create a low-carbon fuel that can be used in existing infrastructure, or it can be used in pure form in specially designed hydrogen boilers. Another interesting application of hydrogen lies in its capability to store energy coming from renewable energy sources (RES), offering a solution to mitigate their intermittence. Moreover, hydrogen can be utilized in the synthesis of synthetic fuels such as methanol and ammonia, which hold promise for various industrial applications.
Despite its potential, there are still some significant challenges that must be addressed before hydrogen can become a widely used energy source. Among these factors, the expenses associated with production, storage, and utilization, especially concerning green hydrogen, remain notably high, ranging from $2.5 to $10 per kilogram of produced hydrogen (Hydrogen Innovation Report, 2021).
Nevertheless, a primary challenge impeding the widespread embrace of hydrogen as a fuel remain its storage requirements. Effective storage of hydrogen presents several challenges due to its low energy density, requiring either high-pressure vessels or cryogenic temperatures, alongside safety concerns and material durability issues. Additionally, hydrogen possesses a low boiling point and high diffusivity, making long-term storage without substantial energy input challenging. Thus, the development of cost-effective, safe, and efficient hydrogen storage technologies is critical to the success of hydrogen economy.

2 HYDROGEN PRODUCTION

In 2020 global hydrogen production reached a record of over 70 million tons, marking a substantial stride towards the decarbonization of industrial and energy sectors (Osman et al., 2022). Hydrogen production is a complex and dynamic field, electrolysis, anaerobic fermentation, biomass gasification, and reforming are just a few of the many pathways that have been explored for hydrogen production, each with its own unique set of advantages and challenges. The selection of a particular method depends on a variety of factors, including the availability and cost of feedstocks, the desired purity and volume of the hydrogen produced, and the level of technological sophistication required. In this paragraph, different methods of hydrogen production will be discussed, highlighting the underlying chemistry and engineering principles involved. Currently, around 90 Mt of hydrogen are produced worldwide, but 96% of this quantity is extracted from natural gas, petroleum derivatives, or coal (Ji and Wang, 2021). Of the total, 72 Mt represent pure hydrogen used for petroleum refining and ammonia production, while the remaining 18 Mt indicate hydrogen mixed with other gases to produce methanol and direct reduced iron. Natural gas is currently the most used raw material for hydrogen extraction, and therefore, reforming is the most widespread method. In 2020, 6% of the global natural gas demand was used for the generation of 60% of the extracted hydrogen, while an additional 19% was obtained from 2% of the total coal demand. The use of these fossil sources has led to the development of 900 Mt of CO_2 emissions from hydrogen production in the same year, equivalent to 2.5% of the sum of the energy and industrial sectors (Ji and Wang, 2021). According to the 'Green Hydrogen Strategy' published in 2020 by the European Commission, in order to increase the production of green hydrogen during the next decades, efforts should be made to bring electrolyzer-derived hydrogen to about 5-8 Mt by 2030 and 9 Mt for hydrogen extracted from fossil fuels with simultaneous CCUS (Ji and Wang, 2021) (European Commission, 2020). In the following paragraphs the main methods used nowadays for hydrogen production are discussed.

2.1 Steam methane reforming of natural gas

Steam methane reforming (SMR) currently stands as the predominant method for hydrogen production, accounting for over half of global hydrogen output (Ji and Wang, 2021).
In this initial step, natural gas is combined with high-temperature steam (H_2O) in the presence of a catalyst, to produce H_2 and CO as listed in equation (1):

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$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (1)$$

To remove CO and increase the hydrogen content in the gas mixture, Water-Gas Shift Reaction is employed; in this step, CO reacts with steam to produce CO_2 and additional hydrogen, as listed in equation (2):

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (2)$$

CO_2 is then removed from the products through adsorption systems. The final mixture contains 70-75% hydrogen, while the remaining fraction is composed of CO, CO_2, and CH_4. Since this method involves the conversion of a fossil fuel into hydrogen, the CO_2 emissions during the process are significant, and heat is required to reach the desired temperatures, usually provided by the combustion of a portion of the same natural gas used (Ji and Wang, 2021).

2.2 Coal gasification

Coal gasification (CG) is the process of heating coal in a controlled environment with limited oxygen. The result is a gas mixture known as syngas, which contains hydrogen along with other gases. After cleaning and purifying the syngas, hydrogen can be separated from the mixture and used for various industrial applications. The gasification process can take place on the surface (SCG) or underground (UCG), depending on where the coal is extracted. The first option is currently the most mature: the coal is dried before being fed into the gasifier, where it reacts with oxygen and steam at high temperatures. The products of the reactions are H_2, CO, and CO_2. The reactions with oxygen and steam do not occur simultaneously, but rather in series and cyclically, according to equation (3) and (4):

$$C + O_2 \rightarrow CO_2 \quad (3)$$

$$C + H_2O \rightarrow CO + H_2 \quad (4)$$

At the end of the process, CO_2 is separated from the gas mixture by an adsorption process. Nowadays, coal gasification produces 19% of all hydrogen on a global scale (Ji and Wang, 2021); however, out of all hydrogen production methods, this one has the most significant impact on global warming, releasing from 18 to 20 tons of CO_2 per tons of H_2 produced (Hydrogen Innovation Report, 2021).

2.3 Hydrogen from Biomass

Biomass is defined as: "the biodegradable part of products, waste and residues from agriculture, forestry, as well as the biodegradable part of industrial and urban waste". It is part of renewable energy sources and emissions during conversion processes are considered offset by the CO_2 absorbed during its lifecycle.

Photo-fermentation (PF) and dark-fermentation (DF) are two processes that performs thanks to the activity of microorganisms converting organic substrates into a biogas mainly containing hydrogen and carbon dioxide under anaerobic conditions. DF occurs in the absence of light, whereas PF utilizes a controlled light source. DF is an anaerobic process facilitated primarily by bacteria such as Clostridium, Bacillus, Enterobacter, Klebsiella, and Eubacterium, (Dahiya et al., 2021). It begins with the hydrolysis of complex organic molecules, including proteins, carbohydrates, and lipids, into simpler compounds like amino acids, sugars, and fatty acids, carried out by extracellular enzymes secreted by these bacteria. Subsequently, the fermentative bacteria metabolize hydrolysis products, producing hydrogen gas, carbon dioxide, and organic acids. Maintaining an optimal pH range between 5.5 and 6.5 is critical to prevent the formation of unwanted bioproducts like methane, which occurs at pH levels above 7.0, while temperature control is equally crucial, with the ideal range spanning from 25°C to 55°C, and an optimum temperature of 37°C (Dahiya et al., 2021).

The efficiency of current technologies is low, ranging between 20-40 % in the case of DF and 5-15% for PF and the cost of bioreactors is high, giving a final cost of hydrogen ranging from 1 to 5 dollars per kg of hydrogen in case of DF, and from 3 to 8 dollars per kg of hydrogen in the case of PF (Dahiya et al., 2021).

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This is mainly due to the type of organic waste used, the composition of the waste, the microbial population, and the operating conditions. Moreover, incomplete degradation of organic matter, loss of substrate to secondary reactions, and inhibition of the microbial population by toxic compounds such as ammonia and volatile fatty acids also contributes to low efficiency.
Typically, anaerobic fermentation processes take several days to several weeks to complete and the retention time of the feedstock in the reactor is an essential parameter that affects the process's efficiency. The optimal retention time depends on the feedstock composition and microbial population.

2.4 Hydrogen Production Through Water Electrolysis

Water electrolysis is the electrochemical process in which water molecules are dissociated into hydrogen and oxygen gases via the application of an electric current. The source of the input energy contributes to determining both the costs and emissions of the specific unit of H_2 produced (Nicita et al., 2020). The process takes place in an electrolyzer, a device that facilitates the conversion of electrical energy into chemical energy by splitting water into hydrogen and oxygen gases using two different reactions that occur on the cathode and anode of the system when an electric current is supplied. Several technologies are employed for water electrolysis, including Alkaline Elektrolizers (AEL), Proton-Exchange Membrane (PEM) Electrolyzers and Solid Oxide Electrolizers (SOEL). In 2020, AEL constituted 60% of the nearly 30 MW of installed capacity, with PEM contributing an additional 31% (Nicita et al., 2020). Projections indicate that by 2030, with ongoing projects, installed electrolyzer capacity worldwide could reach 54 GW, predominantly distributed across Europe and Australia. Furthermore, new plants are increasingly larger, with approximately eighty projects surpassing 100 MW and eleven exceeding 1 GW in installed capacity in 2020 (Hydrogen Council, 2017).

3 MODEL OF SAVING ELECTRIC ENERGY FROM ORGANIC WASTE FERMENTATION (MODSEN).

The Green Propulsion Lab is a laboratory located within the testing field in Fusina (VE), created and managed by Veritas, a public company that provides environmental services in the Veneto region. The laboratory's goal is to promote and implement energy efficiency interventions and the use of renewable energy sources in the municipal area through efficient systems. The testing field is divided into four main areas: microbiology, renewable energy, electrochemical storage and sustainable mobility.
The laboratory works primarily focuses on designing and constructing photobioreactors to produce advanced biofuels and bio-based polymers. Additionally, the Power-to-gas (P2G) area is dedicated to testing advanced biological technologies for synthesizing biomethane and biohydrogen.
The Green Propulsion Laboratory is the site where the MODSEN project for the valorisation of organic waste through its conversion into biogas and subsequent implementation into fuel cells for electric generation has been activated.

3.1 The project

The objective of the MODSEN project is the validation of a technology for the energy valorization of wastewater and organic waste through their biological conversion to hydrogen. Recent activities focused on the laboratory-scale study of DF processes able to separate the metabolic phases of acidogenesis and methanogenesis, allowing to produce hydrogen and volatile fatty acids (VFA's) in the first phase, and methane in the second phase.
The project will experimentally develop a two-stage anaerobic digestion process to obtain hydrogen from a mixture of organic waste, then the optimized process will be implemented at the pilot plant level and integrated with a system for separating hydrogen from the produced biogas. At the end the hydrogen will be stored for conversion into electrical energy. The final goal is the optimization of technologies involved to improve the overall process's energy efficiency.
Furthermore, an energy analysis and LCA will be conducted as well as a study to evaluate the replicability of the proposed approach in other multi-service companies. This approach aligns with the concept of the circular economy, aiming to maximize the recovery of both matter and energy from organic waste. This chapter will describe the tests conducted in the preliminary phase of the MODSEN project and present the initial results obtained.

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3.2 Experimental activity

The first months of the project were dedicated to the optimization of the dark fermentation process for hydrogen production through laboratory-scale testing. The primary objective of these experiments is to optimize conditions and assess their impact on the anaerobic fermentation process for hydrogen production, with the ultimate aim of maximizing overall energy efficiency.

After a careful review of the scientific literature to understand the best operational conditions (Cavinato et al., 2012), (Biasiolo Marco et al., 2023) , the study started by using mercatary scraps as substrates for the initial batch tests, mainly composed of fruit and vegetable waste.

Initial tests were conducted in batch with the aim of obtaining suitable conditions to operate in semi-continuous regime. The scraps were blended and homogenized, resulting in a very thick mixture. All tests were conducted in triplicate, with biogas composition measured using gas chromatography (GC). Figure 1 shows the total gas production obtained during the tests conducted at different Organic loads (OLs) using two different mercatary scraps as substrate. The fraction of hydrogen produced, Specific Gas Production (SGP) and Specific Hydrogen Production (SHP) at different OLs is reported in Table 1.

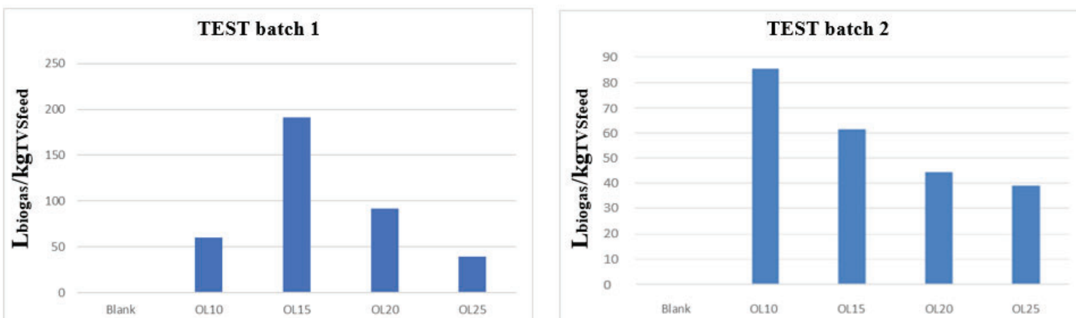

Figure 1: Histogram of total gas production at different OLs using two different mercatary scraps as substrate.

Table 1: Percentage production of hydrogen, SGP and SHP for various OLs.

O.L.	% H2	SGP (NL/kgVS)	SHP (NLH_2/kgVS)
OL10	35	71.92	25.11
OL15	32	65.96	21.75
OL20	30	39.70	12.31
OL25	32	32.44	10.65

At the conclusion of the test, the pH was monitored, falling within the range of 5.6 to 5.8, slightly lower than observed at the beginning of the experiment. This is likely attributable to the enrichment of the mixture in Organic Fatty Acids (OFAs).

It can be clearly seen that the composition of the substrate significantly affects the total biogas production. However, as the OLs varies, the percentage of hydrogen produced does not vary significantly, staying in the range of 32 to 35 percent. Moreover, a decreasing trend as the OLs increases for SGP and SHP is noted (Fig. 2).

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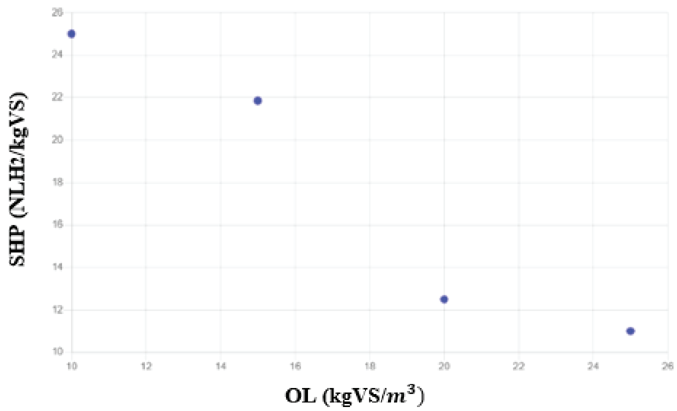

Figure 2: SHP trend graph as a function of OL

From the batch tests results, the optimal OL range in terms of SGP and SHP was determined to be between 10 and 15 kgTVS m^{-3}. This range was used for choosing the Organic Loading Rate (OLR) of the first semi-continuous test, for which the operating parameters are shown in Table 2.

Table 2: Operating parameters for the semi-continuous test

Parameter	Value
Temperature (°C)	39
pH	5.20-5.50
Stirring (rpm)	14 (30s on-30s off)
HRT (days)	3
OLR (kg$_{TVS}$ m^3 d^{-1})	12
Sludge/Mix	80/20
Inoculum	Digestate

Figures 3 and 4 show, respectively, the trend in total gas production over 24 hours and the gas production rate. The production is exhausted after about 12 hours, suggesting that a shorter retention time could lead to an improvement in the yield of the process.

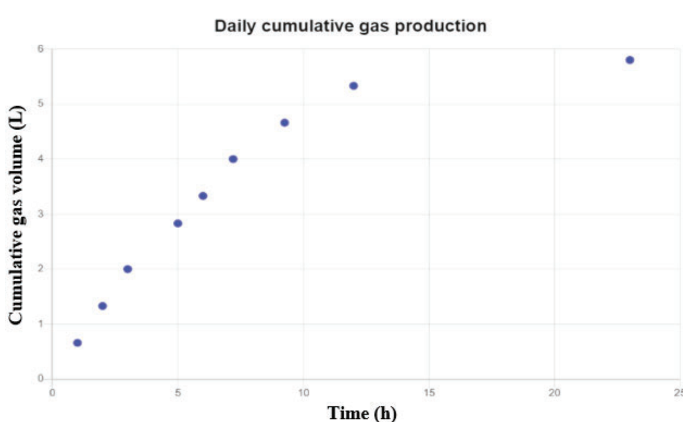

Figure 3: Cumulative gas production over 24 hours, obtained during a middle day of the fourth week of reactor operation, when a steady state had been reached.

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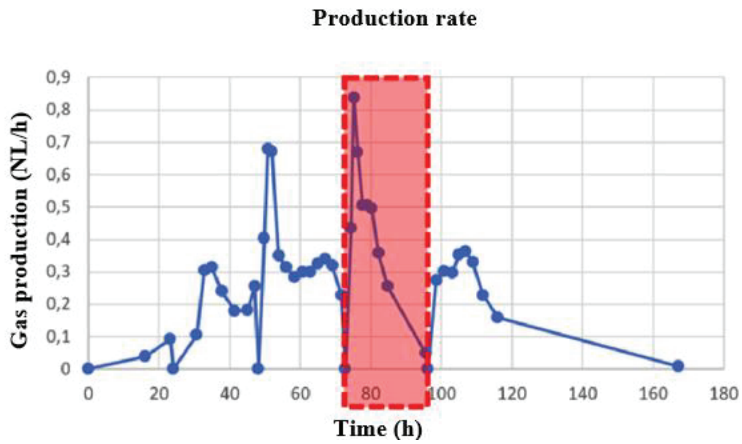

Figure 4: Gas production rate in 24 hours, obtained from semi-continuous testing on the fourth week of reactor operation.

The analysis reveals distinct patterns in gas production dynamics. Firstly, a significant portion of gas generation occurs within the initial 10-hour timeframe of the fermentation process. Notably, during the fourth week of experimentation, peak productivity is observed during the early stages, with gas production rates ranging between 0.85 and 0.51 Nl/h. However, the gas production diminishes considerably after approximately 12 hours, indicating a potential saturation point in the process. This observation suggests that a shorter retention time might lead to a more efficient utilization of substrates and thereby enhance process yields. Furthermore, it is necessary to evaluate whether implementing a continuous feeding schedule, potentially operating seven days a week, could sustain stable long-term gas production rates.

4 LIFE CYCLE ASSESSMENT OF GREEN HYDROGEN PRODUCTION PLANT VIA ELECTROLYSIS

LCA is a systematic method used to evaluate the environmental footprint of products or processes throughout their entire life cycle, encompassing resource extraction, production, use, and disposal stages. In this paragraph, we briefly summarize the preliminary results of an LCA, conducted using the software SimaPro, on a hydrogen production plant utilizing electrolysis powered by RES, with a cradle-to-grave approach. The plant is part of the MODSEN project and will work in parallel with hydrogen production through dark fermentation of organic waste. The plant comprises an Alkaline Elektrolizer (AEL) for hydrogen production and a Proton-Exchange Membrane Fuel cell (PEMFC) for energy generation from hydrogen. The photovoltaic (PV) plant, mounted on a building's roof, consisting of 140 Copper Indium Gallium Selenide (CIGS) panels with a total peak capacity of 49 kWp. As the functional unit, 1 kilowatt-hour (kWh) of produced electricity has been used to ensure consistency in assessing and comparing environmental implications with other options for electricity production. System boundaries encompass the entire life cycle of the production plant, from construction to operation and maintenance, providing a comprehensive understanding of its environmental impact. Within the scope of the study, the balance of the plant, which includes storage tanks, compressors, wires, and other components, is considered.

LCAs focusing on green hydrogen production are relatively scarce in prior research, often examining environmental effects of hydrogen production systems rather than the entire lifespan of green hydrogen, including generation, storage, and conversion. Infrastructure development stages essential for hydrogen processing are frequently overlooked, despite their significant environmental impact potential, impacting the overall sustainability of hydrogen energy systems.

For instance, (Sadeghi et al., 2020) evaluate various hydrogen production techniques, highlighting PV electrolysis with higher levelized costs but lower greenhouse gas emissions (3.08 kg CO_2-eq/kg H_2). (Vilbergsson et al., 2023) compare hydrogen production in Austria, Belgium, and Iceland, noting higher

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Global Warming Potential (GWP) for PV electrolysis due to PV system construction emissions (4.60 kg CO_2-eq/kg H_2). While PV electrolysis demonstrates potential for reducing GWP compared to conventional methods, concerns persist regarding PV system environmental impact, suggesting ongoing research and development for sustainable and efficient photovoltaic electrolysis.

4.1 Results

The LCA analysis presented herein constitutes a preliminary assessment conducted on the photovoltaic-powered electrolysis hydrogen production system previously described. Subsequent integration with data derived from the MODSEN project will encompass the comprehensive lifecycle analysis, incorporating the supply chain for hydrogen produced via dark fermentation of organic waste.
Figures 5 and 6 represent, respectively, the characterization result of the hydrogen production plant and the contribution of each process of the plant to human health, ecosystems, and resource impacts.

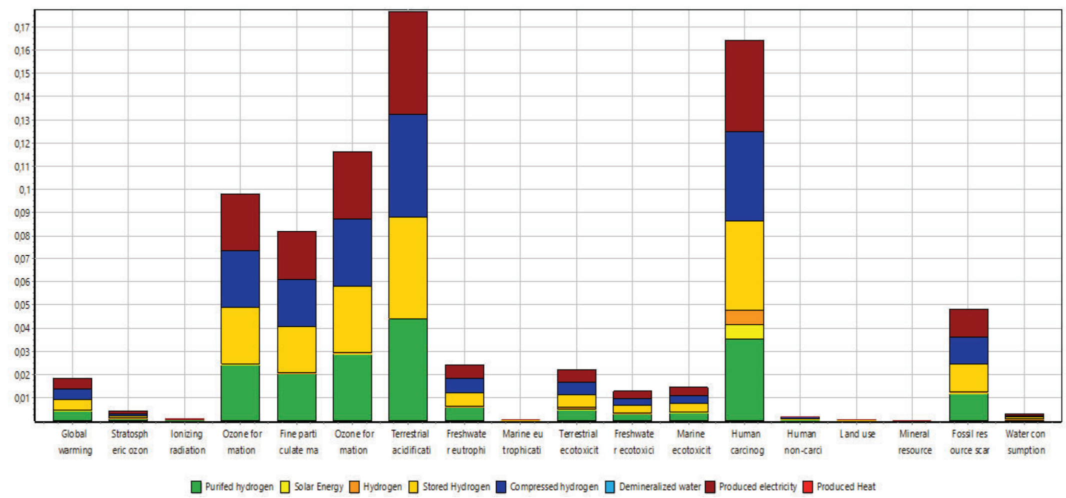

Figure 5: characterization result of the entire production plant obtained from SimaPro, using Method ReCiPe 2016 Midpoint (H) V 1.08

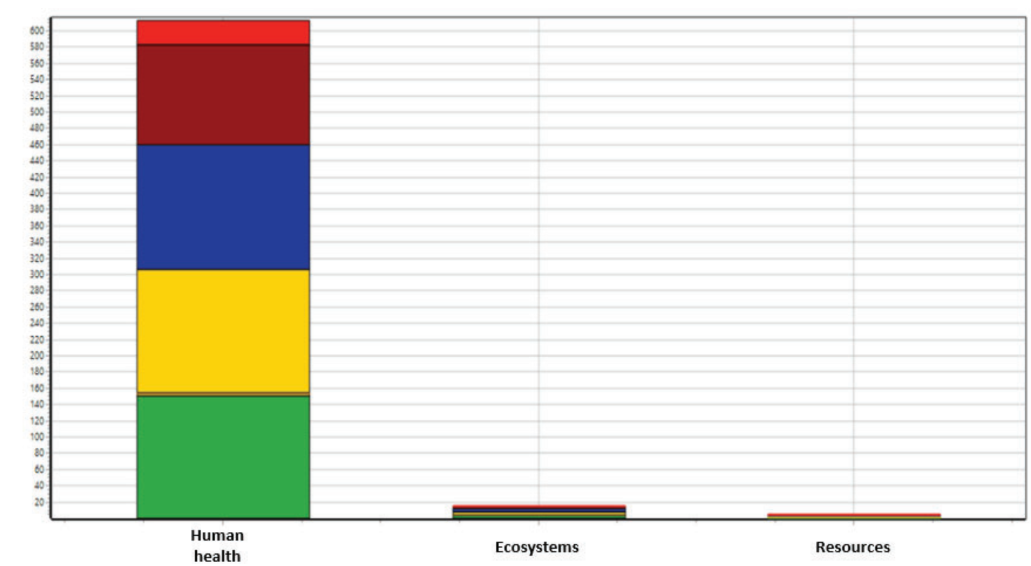

Figure 6: contribution of each process to human health, ecosystems, and resource impacts, using Method ReCiPe 2016 Endpoint (H) V 1.08.

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It is noteworthy that the impact values of each stage underscore varying environmental contributions, with purified, compressed, and stored hydrogen showing high global warming potential (24.19, 24.48, 24.48 $kgCO_2eq/kWh$ respectively), while solar energy and hydrogen production exhibit significantly lower values (1.15 $kgCO_2eq$ and 0.91 $kgCO_2eq$). Fuel cell electricity demonstrates notable impacts on ozone depletion and radiation (25.44% and 25.67% respectively), with similar trends observed for particulate matter, acidification, and ecotoxicity impacts. The purification process emerges as a significant contributor to global warming due to energy-intensive methods like Pressure Swing Adsorption (PSA), this impact is mainly attributed to the use of alumina as the key component for ensuring optimal hydrogen drying. The hydrogen production phase demonstrates a small negative environmental impact, emphasizing the environmental suitability of electrolysis powered by RES. PV panel effects on resources and ecosystems are relatively small, supporting the notion of PV technology's sustainability despite its energy-intensive production process. Overall, this study not only identifies key points in hydrogen production but also demonstrates the potential for green hydrogen to enhance environmental performance in the energy industry, urging technological, policy, and research advancements for sustainable energy transitions. Additional investigations will be conducted to validate the findings of this preliminary analysis, integrating them with the results gathered in the forthcoming months of experimentation within the MODSEN project. This will include an analysis of the environmental impacts by comparing different existing technologies. Furthermore, the economic viability of the proposed technologies will be evaluated, taking into account not only production costs but also potential economic returns and long-term benefits.

5 HYDROGEN STORAGE

Given hydrogen's low density of 0,0899 kg/m^3 at STP, considerable energy is required to compress it into cylinders, and its low boiling point necessitates significant energy expenditure to store it in liquid form. Therefore, the need to develop innovative storage methods becomes evident. Here, some innovative solutions currently under study to overcome the challenges associated with traditional storage methods will be briefly explored. Specifically focus will be placed on metal hydrides and metal organic frameworks (MOFs) as promising alternatives for low-pressure storage, aiming to address concerns regarding energy use and safety. The investigation of low-pressure hydrogen storage systems is a crucial component of the MODSEN project, which primarily aims to optimize energy consumption throughout the hydrogen production, storage and utilization cycle in order to enhance overall efficiency.

5.1 Metal hydrides

Metallic hydrides, compounds formed by the interaction of hydrogen with various metals, exhibit a wide range of structural properties that have attracted significant scientific interest regarding gas absorption applications (Dong et al., 2022). When exposed to hydrogen gas, these materials undergo hydriding reactions, absorbing hydrogen into their lattice structure, causing lattice expansion and releasing heat. Conversely, changing the conditions prompts dehydriding reactions, releasing stored hydrogen gas, causing lattice contraction and absorbing heat. This reversible process not only enables efficient storage, but also allows the utilization of heat generated during fuel cell operation to release hydrogen, providing an auxiliary cooling mechanism for the cell. Commonly used types of metallic hydrides include AB_5 compounds, where A is a rare earth element and B Ni, Co, Al, Mn, St. and AB_2 compounds, where A is Ti or Zr and B is a transition metal. For example, $LaNi_5$ is known for its easy activation and stability over time, with a plateau pressure of 1.8 atm at 25°C. This pressure can be further optimized by substituting Ni atoms with Al, Sn, Mn, or Co and adjusting La with Ce, Y, or Ca (Tarasov et al., 2021). Similarly, AB_2 compounds, featuring metals such as Ti or Zr, offer a wide desorption pressure range with minimal doping. For instance, ZrV_2 exhibits a desorption pressure of $3x10^{-3}$ atm at 227°C, while $TiFe_2$ can reach pressures up to 5000 atm (Tarasov et al., 2021). Despite their advantages, AB_2 compounds can be challenging to activate due to their high melting temperatures and reactivity.

Among the investigated compounds, MgH_2 shows promise, although it requires high activation temperatures (Tarasov et al., 2021). However, this characteristic can be advantageous when used with

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Solid Oxide Fuel Cells (SOFCs). Overall, metallic hydrides present a promising avenue for hydrogen storage, offering a balance between storage capacity, safety, and practicality in various applications.

5.2 Metal-Organic Frameworks (MOFs)

MOFs have recently gained significant attention, finding applications in various fields like gas adsorption and storage, catalysis, and separations. These crystalline materials are composed of organic ligands and metal clusters linked by coordination bonds, offering tunable porous structures and high specific surface areas ideal for gas storage (Chen et al., 2005; Hu and Zhang, 2010; Murray et al., 2009). While previous research has shown efficient adsorption of carbon dioxide and hydrogen on MOFs with large surface areas at different temperatures, many MOFs suffer from low thermal stability, limiting their use in high-temperature applications such as CO_2 separation from flue gas emissions.
Hydrogen molecules mainly interact with two primary sites in MOFs: inorganic metal clusters and organic linker sites. Recent studies using neutron powder diffraction and first-principle calculations have shed light on this process (Chen et al., 2005; Hu and Zhang, 2010; Murray et al., 2009). They show that metal-oxide clusters within MOFs are mainly responsible for hydrogen adsorption, while organic linker sites play a secondary role. Molecular simulations suggest that metal-oxide clusters are preferred adsorption sites, but as pressure increases, the influence of organic linkers becomes more significant. This is because sites on organic linkers have lower binding energies but can accommodate more hydrogen. Additionally, the size of the organic linker affects binding strength, with larger linkers having stronger interactions with H_2 molecules.

5.2.1 Hydrogen Storage in MOFs at Ambient Temperature: While MOFs demonstrate impressive hydrogen uptake at cryogenic temperatures (Chen et al., 2005; Hu and Zhang, 2010), their performance at ambient temperature is significative lower, typically below 2 wt.% at room temperature due to weak binding between hydrogen molecules and the MOF structure. To overcome this limitation, researchers have explored various strategies to enhance the interaction between hydrogen and MOFs. For instance, they have investigated creating bonds between the MOF and a metal capable of reversibly binding H_2, to increase hydrogen overall uptake. In summary, the demand for techniques that boost the bond strength between hydrogen and MOFs opens up exciting possibilities for further investigation in this area.

6 CONCLUSIONS

This study presents the primary methods of hydrogen production, focusing particularly on biological fermentation of biomass with the aim of developing a process for the valorization of organic waste through its conversion to hydrogen. The results obtained will be used to implement the MODSEN project. Through our preliminary laboratory-scale experiments, the OLR of 10-15 kgTVS m^{-3} was found to be optimal. Notably, peak productivity was observed during the early stages of the fourth week, with gas production rates ranging from 0.85 to 0.51 Nl/h. These findings contribute to the advancement of sustainable biorefinery development for renewable energy production and waste management. Moreover, we present the results obtained from an LCA analysis conducted on a green hydrogen production plant using water electrolysis powered by RES, the study identifies key points in hydrogen production but also demonstrates the potential for green hydrogen to enhance environmental performance in the energy industry. Additionally, the article discusses new methods for storing hydrogen in solid form, focusing on materials such as Metal Hydrides and Metal Organic Frameworks. These materials allow for safe and efficient storage, with the ability to absorb and release hydrogen at moderate temperatures and pressures, making them suitable for a range of applications.

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NOMENCLATURE

AEL	Alkaline Electrolyzer
AEM	Anion Exchange Membrane
CCUS	Carbon Capture, Utilization and Storage
F/M	Food-Microorganism ratio
GC	Gas Chromatography
GWP	Global Warming Potential
HRT	Hydraulic Retention Time
LCA	Life Cycle Assessment
MODSEN	Model of Saving Electric Energy from Organic Waste Fermentation
MOFs	Metal Organic Frameworks
OL	Organic Load
OLR	Organic Loading Rate
OFAs	Organic Fatty Acids
PEM	Proton-Exchange membrane
PEMFC	Proton-Exchange membrane Fuel Cell
PSA	Pressure Swing Adsorption
P2G	Power to gas
RES	Renewable Energy Sources
SCG	Surface Coal Gasification
SGP	Specific Gas Production
SHP	Specific Hydrogen Production
SMR	Steam Methane Reforming
SOEL	Solid Oxide Electrolyzer
SOFC	Solid Oxide Fuel Cell
STP	Standard Temperature and Pressure
sCOD	Chemical Oxygen Demand Soluble
TS	Total Solids
TVS	Total Volatile Solids
UCG	Underground Coal Gasification
VFAs	Volatile Fatty Acids

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REFERENCES

Biasiolo Marco, Barchielli Giulio, Tassinato Graziano, Turatello Margherita, Cavinato Cristina, 2023. Coupling Mixed Culture Fermentation and Photo fermentation for Bio H2 Recovery: Preliminary Assessment of the Fermentation Yields and PNSB Growth on Fermentative Broth. Chemical Engineering Transactions 99, 43–48. doi:10.3303/CET2399008

Cavinato, C., Giuliano, A., Bolzonella, D., Pavan, P., Cecchi, F., 2012. Bio-hythane production from food waste by dark fermentation coupled with anaerobic digestion process: A long-term pilot

https://doi.org/10.52202/077185-0112

scale experience. International Journal of Hydrogen Energy 37 15 , 11549–11555. doi:10.1016/j.ijhydene.2012.03.065

Chen, B., Ockwig, N.W., Millward, A.R., Contreras, D.S., Yaghi, O.M., 2005. High H_2 Adsorption in a Microporous Metal–Organic Framework with Open Metal Sites. Angew Chem Int Ed 44 30 , 4745–4749. doi:10.1002/anie.200462787

Dahiya, S., Chatterjee, S., Sarkar, O., Mohan, S.V., 2021. Renewable hydrogen production by dark-fermentation: Current status, challenges and perspectives. Bioresource Technology 321, 124354. doi:10.1016/j.biortech.2020.124354

Dong, Z., Wang, Y., Wu, H., Zhang, X., Sun, Y., Li, Y., Chang, J., He, Z., Hong, J., 2022. A design methodology of large-scale metal hydride reactor based on schematization for hydrogen storage. Journal of Energy Storage 49, 104047. doi:10.1016/j.est.2022.104047

European Commission, 2020, A hydrogen strategy for a climate-neutral Europe

Hu, Y.H., Zhang, L., 2010. Hydrogen Storage in Metal–Organic Frameworks. Advanced Materials 22 20 . doi:10.1002/adma.200902096

Hydrogen Council, 2017, A sustainable pathway for the global energy transition

Politecnico di Milano, 2021, Hydrogen Innovation Report

Ji, M., Wang, J., 2021. Review and comparison of various hydrogen production methods based on costs and life cycle impact assessment indicators. International Journal of Hydrogen Energy 46 78 , 38612–38635. doi:10.1016/j.ijhydene.2021.09.142

Margaret Singh, 2005, Hydrogen Demand, Production, and Cost by Region to 2050

Murray, L.J., Dincă, M., Long, J.R., 2009. Hydrogen storage in metal–organic frameworks. Chem. Soc. Rev. 38 5, 1294–1314. doi:10.1039/B802256A

Nicita, A., Maggio, G., Andaloro, A.P.F., Squadrito, G., 2020. Green hydrogen as feedstock: Financial analysis of a photovoltaic-powered electrolysis plant. International Journal of Hydrogen Energy 45 20 , 11395–11408. doi:10.1016/j.ijhydene.2020.02.062

Osman, A.I., Mehta, N., Elgarahy, A.M., Hefny, M., Al-Hinai, A., Al-Muhtaseb, A.H., Rooney, D.W., 2022. Hydrogen production, storage, utilisation and environmental impacts: a review. Environ Chem Lett 20 1 , 153–188. doi:10.1007/s10311-021-01322-8

Sadeghi, S., Ghandehariun, S., Rosen, M.A., 2020. Comparative economic and life cycle assessment of solar-based hydrogen production for oil and gas industries. Energy 208, 118347. doi:10.1016/j.energy.2020.118347

Tarasov, B.P., Fursikov, P.V., Volodin, A.A., Bocharnikov, M.S., Shimkus, Y.Y., Kashin, A.M., Yartys, V.A., Chidziva, S., Pasupathi, S., Lototskyy, M.V., 2021. Metal hydride hydrogen storage and compression systems for energy storage technologies. International Journal of Hydrogen Energy 46 25 , 13647–13657. doi:10.1016/j.ijhydene.2020.07.085

Vilbergsson, K.V., Dillman, K., Emami, N., Ásbjörnsson, E.J., Heinonen, J., Finger, D.C., 2023. Can remote green hydrogen production play a key role in decarbonizing Europe in the future? A cradle-to-gate LCA of hydrogen production in Austria, Belgium, and Iceland. International Journal of Hydrogen Energy 48 46 , 17711–17728. doi:10.1016/j.ijhydene.2023.01.081

https://doi.org/10.52202/077185-0112