

Review

From Biomass Waste to Green Fuel: Biochar-Based Catalysts for Hydrogen Production

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Abstract

With the increasing demand for energy given by the effects of extreme weathers in the last years, the need to expand the access to renewable energy such as green hydrogen has become a priority in current research. However, one of the main challenges for hydrogen production is the elevated cost of catalysts due to the consumption and lack of availability of rare metals. To reinforce sustainability, biochar, a carbon-rich material has emerged with huge potential. Its properties such as a high surface area and abundant functional groups facilitate catalyst adsorption and the dispersion of active sites, besides the mineral content and surface chemistry tunability, allow the activation and metal impregnation to improve hydrogen production. Considering these characteristics, this paper will highlight all the potential of biochar as a catalyst and catalyst support, the current advances identifying biochar as catalyst in hydrogen production, and the key characteristics that make it adequate in these applications. Finally, the remaining challenges and limitations are described, providing a perspective on future opportunities and research directions.

Keywords: biochar; catalyst; green hydrogen; biochar properties

1. Introduction

1.1. The Need for Green Hydrogen in the Clean Energy Transition

In 2024, global energy demand grew by 2.2% compared with the steady growth that has been seen since 2013, of 1.3% per year. According to the IEA Global Energy Review 2025, around half of the increase in energy consumption is attributable to the effects of the extreme weather in the summer, when there were a high cooling demand and low winds. To supply this energy demand, coal and natural gas stepped up, which led to a record level of emissions of 37.8 Gt CO₂, and an increase of 3 ppm concentration in the air. Despite the increase in carbon emissions, clean energies have made a difference. They now prevent around 2.6 Gt of annual emissions; it is estimated that, without them, the carbon emissions could have been three times larger in recent years [1].

Green hydrogen is a clean fuel that plays a key role in energy transition. Currently, it is viewed as the potential solution to the dual challenges of energy demands on a growing population and environmental problems caused by the dependence of non-renewable energy systems. The production and use of green hydrogen have several advantages: it can be generated with zero direct carbon emissions, and relies on abundant and renewable



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resources. Moreover, it has a high energy density, making it efficient across many industries such as heat and power generation, and feedstock for industry and transportation [2].

Moreover, green hydrogen has the potential to align with several sustainable development goals (SDGs) established by the United Nations, to achieve a sustainable future. Beyond the immediate energy and environmental impact it generates, it has the potential to address socioeconomic problems, included in the SDGs, like economic growth and job creation (SDG 8), infrastructure development (SDG 9), and sustainable cities and communities (SDG 11). This shows that it is a technology that can be a big driver for innovation [3]. It is imperative to accelerate the hydrogen economy to overcome its current challenges such as storage, expensive production, use of rare elements, intermittency of renewable sources, and lack of infrastructure. Therefore, there should be a big investment in the development of technology and system integration alongside policy frameworks so all populations can benefit from the desired success [4].

1.2. Biomass Waste: An Abundant and Renewable Source

To achieve circular sustainability, the inclusion of other economic sectors is necessary, particularly the ones in waste management and resource recovery. Generally, biomass waste results in landfills, open dumps, and water bodies. As a result, soil degradation and contamination increase the risks to both humans and the environment. With the urgency to mitigate environmental impacts in diverse industries, biomass waste has become increasingly recognized as a valuable and sustainable resource in this transition to low-carbon economies. It is a widely accessible material and considered carbon neutral when it is managed properly, making it an attractive feedstock for energy applications. The thermochemical conversion of biomass enables the production of hydrogen-rich syngas and biochar [5].

Biomass is an organic matrix obtained from plants and animals, and the source-based method is the best way to identify biomass sources. There are five categories: agricultural waste, wood waste, food waste, municipal solid waste, and sewage sludge waste [6]. Due to the complex composition that includes cellulose, hemicellulose, lignin, proteins, lipids, and inorganic materials, especially found in material derived from agricultural and wood waste, they have significant potential for conversion into valued-added products. For example, biomass can be fermented to produce bioethanol or biochemicals and fermentable sugars or be used in thermochemical processes to produce biochar or biofuels [7]; alternative biomass such as medical waste produce high-quality biochar, offering an alternative route to recover this waste [8].

1.3. Emergence of Biochar as a Sustainable Catalyst

Biochar is a carbon-based material that can be produced from the pyrolysis of biomass, under a low or no oxygen condition at temperatures of 350 to 1000 °C [9]. It is considered an economic and viable catalyst to produce biofuels; the functional groups that absorb metals enhances its application to develop biochar-metal-assisted catalysts, as shown in Figure 1. Moreover, it is adaptable for specific uses, changing variables such as feedstock, pyrolysis conditions, and physicochemical modifications that will improve its performance [10]. Nowadays, more than 90% of the chemical processes require a catalyst to improve yield and selectivity. The most commonly used are derived from transition metals such as rhodium, palladium, platinum, ruthenium, iridium, gold, silver, and osmium, among others. The issue with these materials is they are expensive and low in abundance, and most mining techniques are not environmentally friendly. All these problems generate supply fluctuations, reducing its accessibility [11].

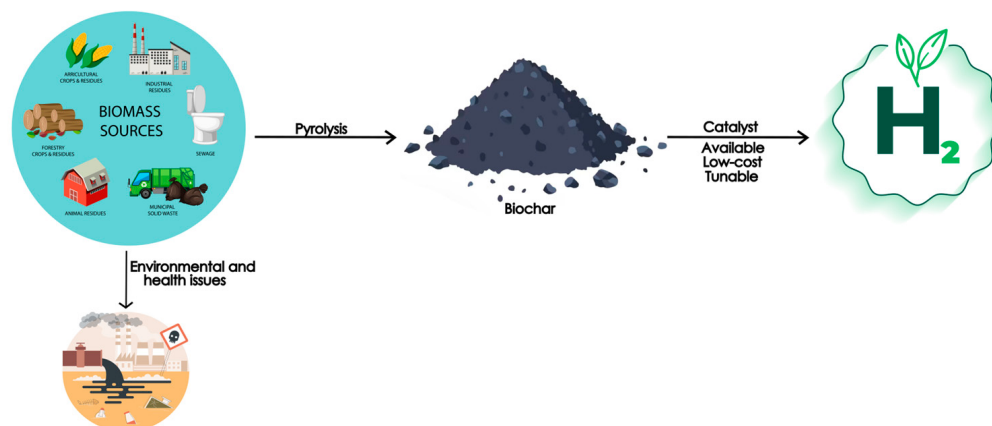


Figure 1. Biochar as a sustainable catalyst giving added value to biomass waste.

In terms of green hydrogen production, metals and minerals are fundamental in the construction of equipment such as fuel cells and catalysts, but it is expected that the demand can surpass the availability of these materials. To improve catalyst sustainability, it is required that we enhance the research into potential materials like polymers, alloys, and carbon materials [12].

1.4. Aims and Structure of the Review

Currently, biochar is an adsorbent that has been showing excellent performance in soil water remediation, and most of the studies presented each year are focused on it. However, biochar is a material that is promising in the field of catalysis, especially in hydrogen applications. For example, in the field of photoelectrochemical water splitting, biochar with metal surface modifications has provided stability and the required bandgap to achieve an enhanced reaction, as pointed out by Jilani et al. [13]. Studies on the current applications of biochar in hydrogen production are available, as Mishra et al. have found [14]. However, biochar as a catalyst is in the early stages of development in the research field. The lack of standardization in its production affects the scalability and reproducibility, reducing the possibility of taking this material to achieve an industrial maturity level.

This review aims to capture the attention of biochar as a catalyst to lead hydrogen technologies to a sustainable path. The present review provides a critical, unified Structure–Property–Function–Performance framework to analyze biochar’s multifaceted roles. We carry out a classification and contrast of these roles, as a catalyst, metal support, adsorbent, electron shuttle, and microbial mediator, and explicitly link these characteristics to pathway-specific hydrogen mechanisms (thermochemical, electrochemical, photocatalytic, and biological). Furthermore, we address the scalability constraints, durability challenges, and industrial feasibility. With the findings, it is possible to offer design rules and prioritized research gaps to guide the field beyond incremental reporting, towards technology maturation.

To achieve the present review article, the literature survey covers publications from 2020 to the present, reflecting the rapid evolution of biochar-based hydrogen research on the last five years. Peer-reviewed articles were primarily identified using major scientific databases, including ScienceDirect, Web of Science, and Google Scholar. The search strategy employed combinations of keywords such as “biochar”, “hydrogen production”, “catalyst”, “catalyst support”, “surface properties”, and “performance” using Boolean operators (AND and OR) to refine the research results and improve the relevance. The selection of articles was carried out in different steps, using the online source CADIMA, and titles and abstracts were screened towards the scope of the review. Then, full-text articles were evaluated through the objectives, methodology, and reported outcomes. Only studies

that provided methodological detail and performance metrics were retained for analysis. Finally, key information from the selected articles was synthesized to identify the trends and structure–performance relationships due to the heterogeneity of the experimental conditions across studies.

2. Hydrogen Production Pathways: An Overview

Hydrogen is a critical part of the energy transition. Its power as an energy carrier and flexibility in being produced from renewable and non-renewable sources make it an attractive choice to pursue development in clean energy. The variety of sources led to the research of a variety of technologies that offer a range of options to create a consistent energy grid. To identify the source and applied technology, a color system was created. Hydrogen derived from natural gas is grey, blue was associated with carbon capture, and turquoise with pyrolysis. It is considered green when the feedstocks are renewable and when renewable energy is applied to electrolysis [15,16]. Figure 2 provides an overview.

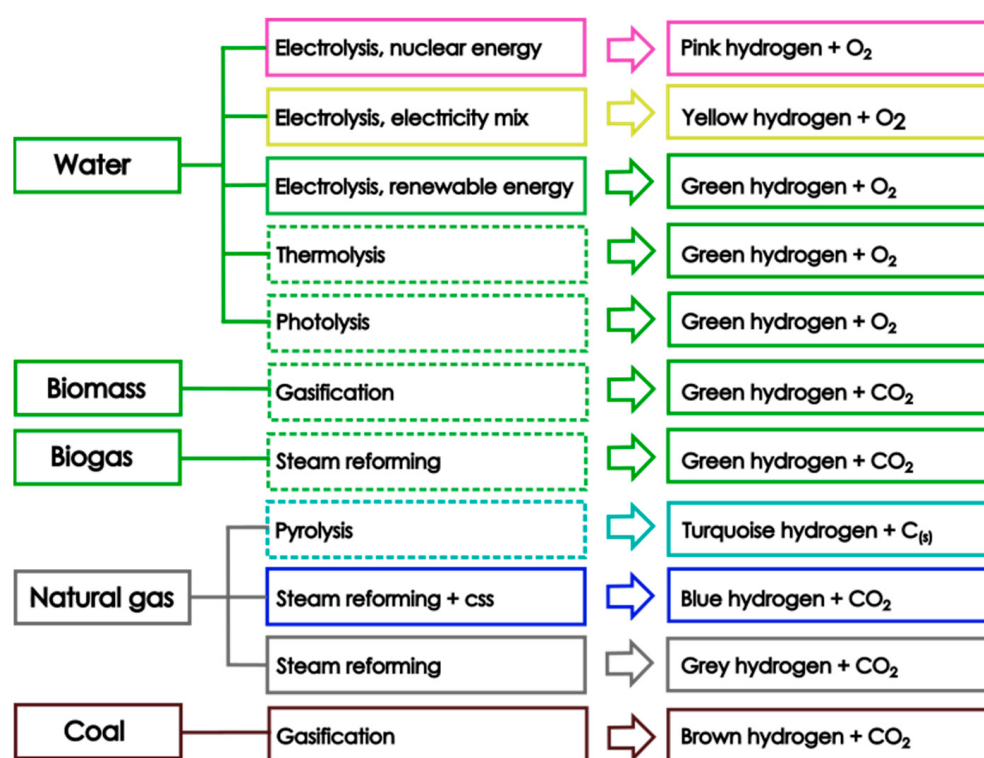


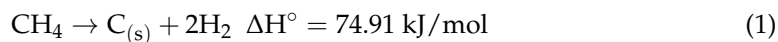
Figure 2. Overview of possible hydrogen production pathways using various technology options and electricity sources. Dashed boxes indicate technologies that are not yet available on an industrial scale. Modified with permission from [17].

2.1. Thermochemical Routes: Pyrolysis, Gasification, and Reforming

2.1.1. Pyrolysis

Pyrolysis is a thermochemical process that involves the thermal decomposition of methane, in the absence of oxygen. It has been proposed as an alternative method for hydrogen production due to its ability to directly generate hydrogen and solid carbon without forming CO₂ during the reaction itself. This method serves as a potential bridge between conventional carbon-based fuels and renewable energy technologies. This process uses endothermic reactions to produce gaseous hydrogen and solid carbon as a byproduct, the one that could be used as raw material contributing on the short or long term to the dioxide carbon inventory. Overall, the process avoids the direct generation of greenhouse gases emissions.

Methane pyrolysis typically requires high operating temperatures, around 1200 °C, to overcome the activation energy barrier of CH bond dissociation. Variables such as methane pressure and the used catalyst have a great impact on the reaction yield. [18] The general reaction equation is



Different reactor configurations for methane decomposition have been studied, as shown in Figure 3. Besides technologies including plasma-assisted pyrolysis, there were also molten metal/melt-based reactor and catalytic pyrolysis. Catalysts are often employed to reduce the required temperature and improve the hydrogen yield to achieve better economic feasibility. Carbon-based catalysts show great stability at high temperatures (800–1000 °C); transition metals, like nickel and iron, are the most common and modifications in their superficies improve the activity and stability. Molten metal alloys and molten salts have shown the best potential by achieving a high yield through lower temperatures [19].

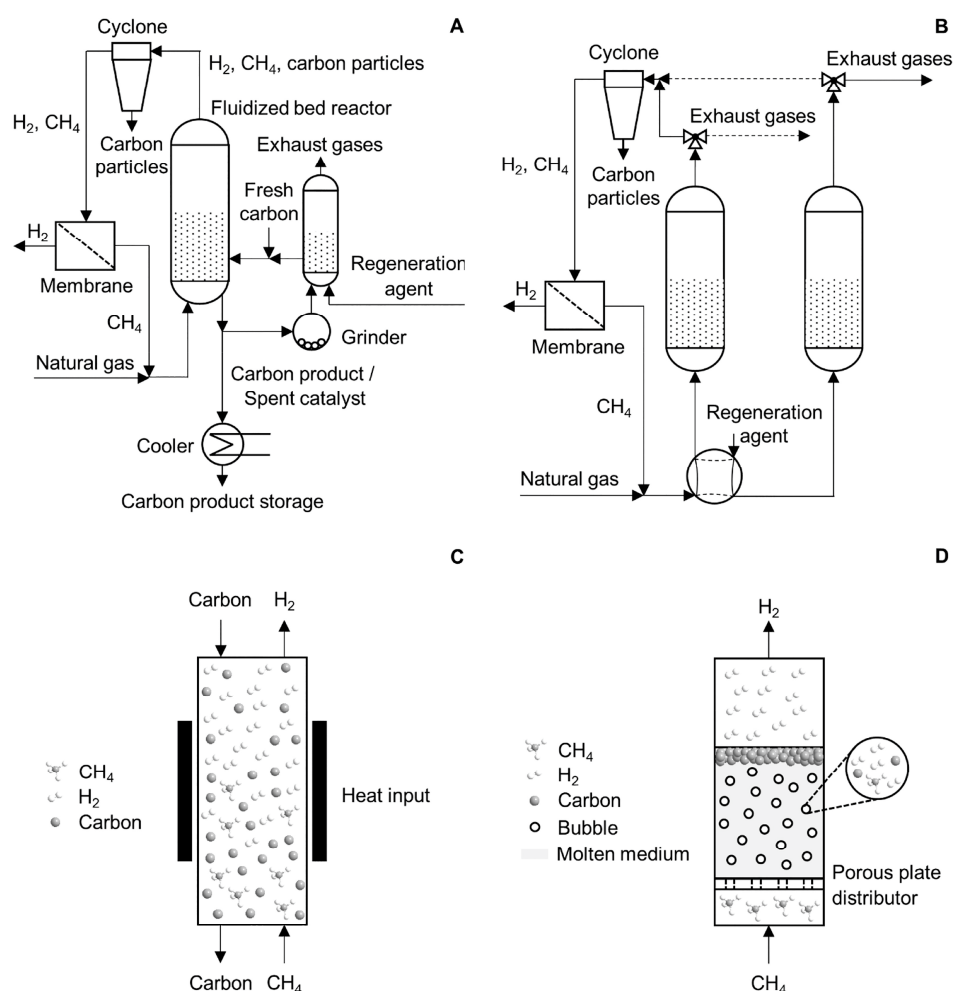


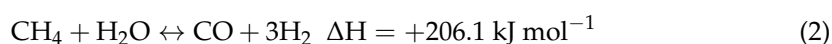
Figure 3. Potential reactor configurations for the industrial implementation of methane pyrolysis. (A) Fluidized-bed reactor with a catalyst regeneration unit. (B) Parallel reactors operating in a cyclic reaction-regeneration mode. (C) Moving-bed reactor. (D) Liquid bubble column reactor. Reprinted with permission of [20].

Moreover, while the process of pyrolysis is low to near zero-emissions, its raw material and its possible byproduct can contribute highly to the greenhouse gas emission total balance and reduce the net environmental advantage of the process. A comprehensive life-cycle assessment is carried out, which includes the methane source, leakage rates, and

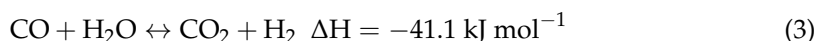
energy input for high-temperature operation, and the long-term handling of solid carbon is essential to accurately evaluate its environmental advantage.

2.1.2. Reforming

Steam gas reforming (SMR) produces grey hydrogen from methane extracted from natural gas. This technology is the most mature in the market; around 75% of global production belongs to SMR. In general, the first process is desulphurization to avoid catalyst deactivation; then, it is sent to the catalytic reforming unit where the following reaction happens:



This reaction is highly endothermic; the temperature is around 800–900 °C to improve the conversion. Moreover, the most common catalyst is metallic nickel with carriers made of magnesia, aluminosilicates, or aluminum oxide. Afterwards, the remaining carbon monoxide has the denominated water–gas shift reaction shown by this reaction:



Finally, the hydrogen is purified with a pressure swing adsorption system (PSA) that is a leading technology in this production route. This typically contains solid absorbents, activated carbon, molecular sieves, alumina, 5A zeolite, and silica gel. Impurities are absorbed at low pressure. The separation and purification step accounts for 50–80% of the total cost production, it is used because it has a low equipment cost and can deliver high-purity hydrogen, around 99.5–99.999% [21].

Although it is the most used technology, the high emissions of pollutants are the reason to search for other technologies and feedstocks. In Figure 4, there is an overview of all the hydrogen colors related to reforming. One of the alternatives to reduce the environmental impact is to use methane from the anaerobic digestion of biomass as the source [22] or the steam reforming of methanol, ethanol, acetic acid, acetone, and bio-oil that has been successful at the laboratory scale [23]. Towards the impact of emissions, carbon capture and storage is a viable option that, currently, is perceived as a mature technology in terms of the individual capture components. It has been implemented in large and semi-large industries around the world. Even though it elevates the cost for hydrogen, it is considered an optimal option because of its integration with hydrogen facilities that are already constructed [24]. Nevertheless, its large-scale development remains limited by a high capital and operating costs, energy penalties, and unresolved concerns regarding CO₂ transports and leakage risks.

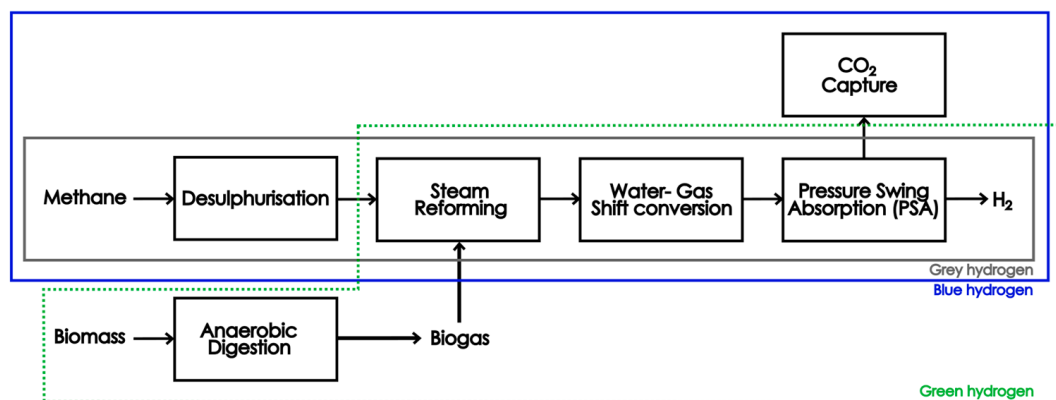


Figure 4. Different pathways for steam reforming. Dashed box is not available on an industrial scale.

2.1.3. Gasification

Most known as brown hydrogen, it is the process of hydrogen production using synthesized gas derived from coal. In general, the process occurs at high temperatures, 800–1300 °C, and high pressure, 30–70 Bar. This process is less efficient than steam methane reformation (SMR) with a conversion of 55%, given the lower H/C ratio in the coal feedstock [25].

The pyrolysis of coal needs steam and oxygen. This one is extracted from air to deliver into the gasifier; the extraction could be made by membrane separation, the cryogenic technique, or pressure swing absorption. After the pyrolysis, the coal is transformed into syngas that goes into a cooling unit. Then, the water–gas shift reaction starts to improve hydrogen production and, finally, goes to the purification process with pressure swing absorption to ensure a high purity [26]. The net reaction of the process is



In terms of steam methane reformation (SMR), this process can be integrated with carbon capture storage in a more efficient way than direct coal combustion because carbon dioxide can be separated in a better proportion. In Figure 5, there is a representation of the process:

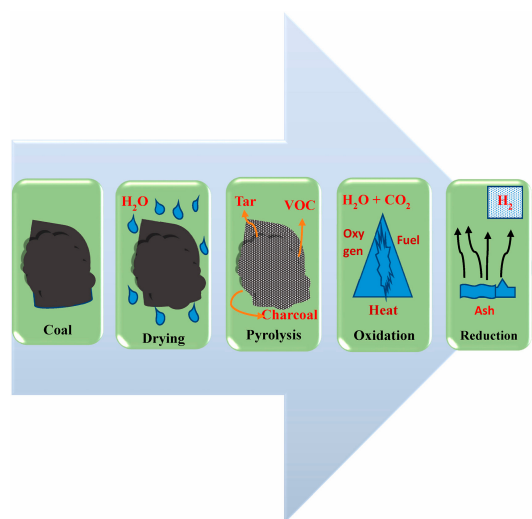


Figure 5. Coal gasification processes for hydrogen production. Reprinted with permission from [27].

Another option for gasification is replacing the use of coal for biomass; these materials, through pyrolysis, can be turned into syngas and cause hydrogen extraction, as explained before. It is a sustainable solution to stop relying on fossil fuels and provide a proper handling of biomass waste [28].

Currently, the thermochemical routes for hydrogen production are leaders. The maturity of the processes and the major industrial scale available make hydrogen affordable. Unfortunately, relying on hydrocarbon sources is not sustainable in the long term but the contribution in the energy grid cannot be denied. That is why it is imperative to keep up the research in alternative feedstock, efficient production process, and carbon capture to improve the sustainability of these processes.

2.2. Electrochemical and Biological Routes

2.2.1. Electrochemical

Electrolysis is the process of using electrical energy to drive a non-spontaneous chemical reaction. Depending on the energy source, a color is assigned. Grid electricity is

identified by a yellow color, and nuclear energy by pink, and, when the source is renewable energy, solar, or wind, it is recognized as green hydrogen. The energy applied decomposes the water, as shown in the following reaction [29]:



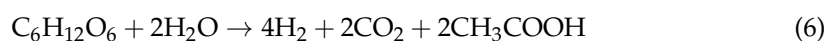
This process comprises two half-cell reactions, the hydrogen evolution reaction (HER) that takes place at the cathode, and oxygen evolution reduction (OER) that takes place at the anode. Currently, there are four primary types of electrolyzers: Alkaline Water (AWE), Solid Oxide (SOE), Alkaline Anion Exchange Membrane (AEM), and Proton Exchange Membrane (PEM) [30]. A quick review of these technologies is presented in Table 1.

Table 1. Available technologies for hydrogen production through electrolysis.

Specification	AWE [31]	SOE [32]	AEM [33]	PEM [34]
Electrolyte	Alkaline electrolyte solution of 20–30%: KOH or NaOH.	Y-doped perovskite oxides	KOH at 30–40% concentration; 1 M KOH aqueous solution 1 wt% K_2CO_3 , and 1 wt% ($\text{K}_2\text{CO}_3 + \text{KHCO}_3$)	Polysulfonated membranes (Nafion [®] , fumapem [®])
Cathode material	Nickel-based alloys	Cermets composed of Ni	Ni-based	Noble metals Pt/Pd
Anode material	Nickel oxides, ferrites, noble metal coatings.	Perovskite and Ruddlesden–Popper oxides	RuO_2	IrO_2 RuO_2
Temperature	60–80 °C	500–1000 °C	50–80 °C	20–80 °C
Pressure	1–3 Bar	Up to 25 Bar	15–30 Bar	Up to 20 Bar
Hydrogen price per kilogram	\$4–\$6	\$1–\$5	\$2.38	\$5–\$7

2.2.2. Dark Fermentation

This is a biochemical fermentation process that occurs in the absence of light and oxygen using strict anaerobes that produce H_2 , VFA (Volatile fatty acids) and CO_2 . The general reaction is given by



The most common bacteria are from *Clostridium* sp., but *Enterobacter* sp. and *Bacillus* sp. are also used. Regarding the conditions for fermentation, the pure carbon source, such as glucose, gives the best results, but it is not economically feasible; that is why biomass waste is the most studied source [35]. It is a robust and stable process that requires a control operation for variables like pH, temperature, retention time, and pressure to avoid inhibition in the bacteria. It is a process that has great potential [36]. However, it is still in the early stages of development, and gives a low and variable hydrogen yield; economically, it requires a high investment cost in reactor design and the treatment of the byproducts and gas separation [37].

2.3. Role of Catalyst in Improving Hydrogen Yield and Selectivity

The largest demand for clean technologies to produce hydrogen has led to a big expansion in developing catalysts. These materials help the overall process to be more

efficient and cost-effective, having a big influence on the kinetics, selectivity, and stability of the reaction [38].

A wide range of materials have been studied for hydrogen applications: noble-metal based ones are used for ammonia borane hydrolysis, non-noble metals are mainly applied in the hydrogen evolution reaction (HER), and metal and metal oxide in photocatalysis and the oxygen evolution reaction (OER), oxide support is applied on steam methane reforming, and carbon-based ones are widely applied electrochemically in fuel cells and are being studied as a support for the catalyst in enhancing stability and activity [39]. In this context, advanced catalyst design becomes a critic bottleneck, directly linked to the relevance of the biochar-based materials discussed in this review. Biochar offers a potential pathway to reducing noble metal loading, improving catalyst dispersion, and enhancing durability, while addressing the material scarcity issues associated with green hydrogen technologies. At the end, catalyst design becomes a strategic approach to overcome key economic and material-related barriers in sustainable hydrogen production.

2.4. Environmental and Economic Challenges of Conventional Methods

While it has been stated that hydrogen is a clean energy carrier, it is important to emphasize that the largest share of current global productions still comes from grey and brown hydrogen routes. These pathways dominate primarily because they are mature technologies allowing the lowest on the market, giving a big advantage towards other production routes. However, the carbon footprint is high, the feedstock relies on natural gas, and the emissions are estimated to be 9–12 kg CO₂ for a kilogram of hydrogen produced. As pointed out before, blue hydrogen is the alternative to reducing these emissions; unfortunately, this is an energy-intensive process, and it is expected to raise the energy consumption between 10–20%, which, depending on the source, can increase the general footprint of the process. Moreover, the design and integration increase the fixed and operational cost, proposing a challenge [40].

On the other hand, green hydrogen offers the lowest environmental footprint, with a clean feedstock, with only oxygen as the byproduct, and, even if it is a high energy process, this comes from renewable energy sources. The main limitation remains in the high capital cost of construction due to the consumption of rare metals [41].

3. Catalysts for Hydrogen Production

To implement a sustainable energy research, catalyst technology is a crucial point. The improvement on these molecules will allow hydrogen technologies to be affordable and scalable, and to achieve the desired environmental outcome. The latest tendencies are applied to novel hydrogen production that involves water splitting; nanomaterials have shown a high performance in terms of activity and stability. Metal oxides, and carbon-based catalysts are pursued due to the economic and availability difficulties that noble metals can offer. As Kumar et al. point out, innovations have been made such as single-atom catalysts, bimetallic catalysts, nanostructures, and MOFs; however, challenges around complex synthesis and corrosion persist [42].

3.1. Metal-Based Catalysts

Rare transition metal materials, such as Pt, Pd, Ru, Rh, Ir, and Au, are leading catalysts for their electronic structure. Between their advantages is the reduction in side reactions; they have a high oxidation resistance and can operate in difficult conditions. One of the main disadvantages is the lack of availability and high cost; this makes it imperative to maximize the catalytic activity per unit mass.

In this context, one of the strategies in aiming for this goal is manipulate the size of the metals. In terms of reducing the particle size, the energy levels are modified, directly influencing the catalytic performance and interaction with their supports as shown in Figure 6. Therefore, noble-metal single-atom catalysts (SACs) have attracted attention towards the design of these materials improving the density of active sites, minimizing metal usage and offering opportunities to enhance the activity with the supports [43].

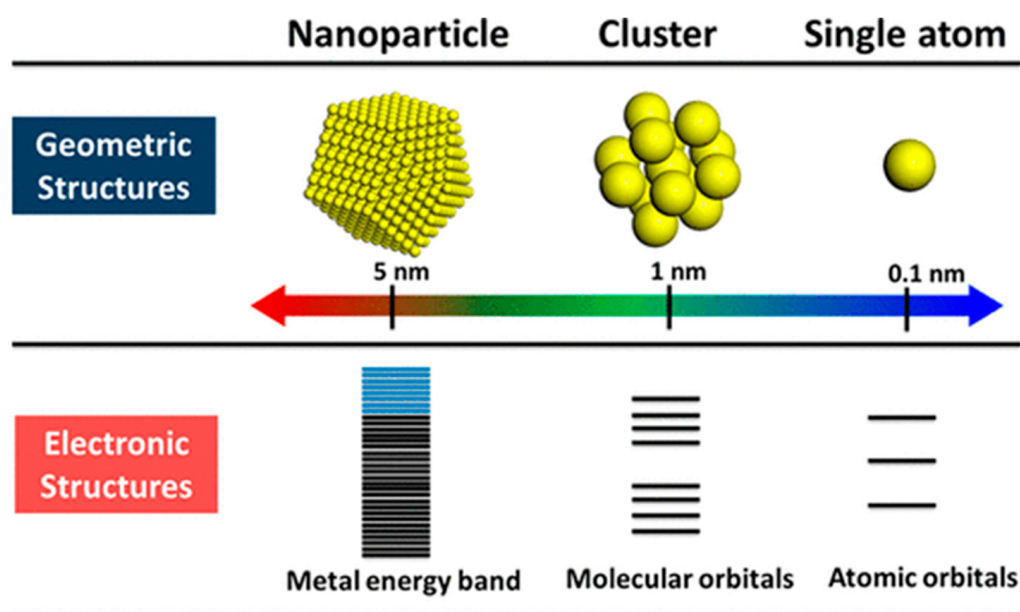


Figure 6. Geometric and electronic structures of single atom, clusters, and nanoparticles. Reprinted with permission from [43].

For example, Pt single atoms and nanoclusters supported on N-doped carbon frameworks have demonstrated substantially reduced overpotentials compared to commercial Pt/C commercial catalysts [44].

Despite these advances, noble-metal systems remain economically restrictive and often rely on complex synthesis routes. As a result, non-noble metals conformed by Ni, Co, Fe, Mg, Ca, Al, and other transition metals are increasingly explored. They have similar properties to noble-metals in their unique electronic configuration that allows intermediate products. As a consequence, they are good catalysts, but they are more abundant and have a reduced price. In terms of electrolysis, there is a trend in developing transition metal phosphides [45], sulfides [46], and dichalcogenides [47]. The approaches that are being proposed involve activity and stability under an industrial current, improving the electron transportation ability, moreover, achieving an optimum hydrogen adsorption by tuning the electronic structure with defect engineering, heteroatom doping, heterostructure, and strain engineering. For instance, Gao et al. reviewed the interaction of single-atom catalysts of non-noble metals supported on carbon. They found that, despite the great achievements across the years, this technology is limited because of the metal agglomeration, changes in the structure in the presence of an electrolyte, and toxic production routes [48]. These limitations underscore the importance of support materials that can enhance metal dispersion, mitigate deactivation, and improve electron transport.

3.2. Metal Oxide Catalysts

This is a wide group of catalysts that involves simple and complex oxides. Among them, there is silica, alumina, zeolites, polyoxometalates (POMs), phosphates, perovskites, and hexa-aluminates. In general, they have different types of defects and vacancies that are

key for catalysis. For hydrogen production, metal oxides are mainly used in electrolysis and photo electrolysis due to the semiconductor properties they exhibit [42]. Hidayatullah et al. provide a comprehensive review of the simple oxides (e.g., TiO_2 , MnO_2 , and Al_2O_3) used in photoelectrochemical water splitting (PEC); this is a promising technology due to the low cost, non-toxicity, and generation of electron–hole pairs to enhance hydrogen production. To overcome the limitations such as light absorption and the rapid recombination of electrons, morphological engineering, doping, and heterostructure design have been studied [49], as can be shown in Figure 7.

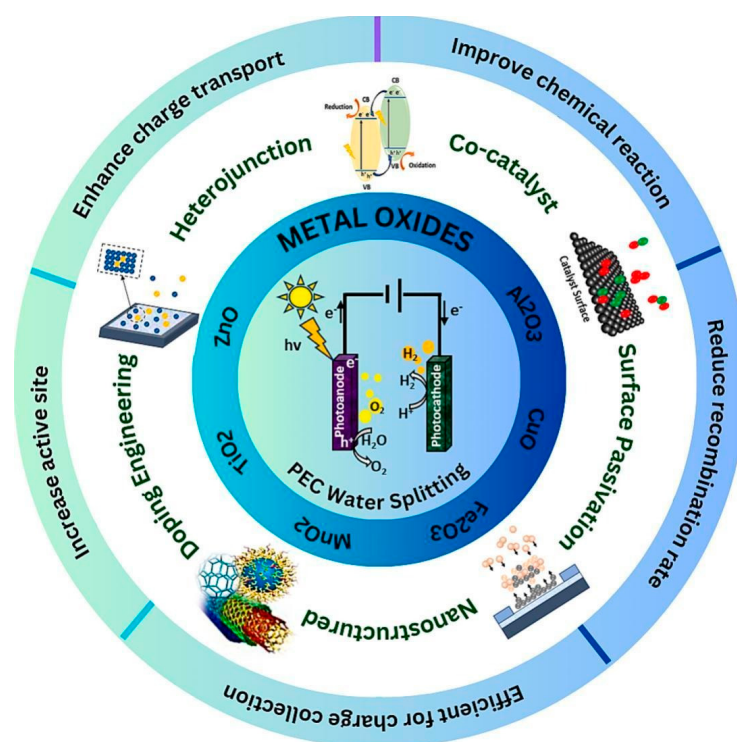


Figure 7. Role of metal oxides and modifications for their use in the photoelectrochemical water splitting systems. Reprinted with permission from [49].

For example, perovskite is an attractive material for hydrogen applications. The main characteristic is the control over band edge positions and catalytic mechanisms on the atomic level that are associated with an improvement in the OER reaction [50]. Ameen et al. emphasize that polyoxometalates have the potential to play a key role in the optimizations of their hydrogen technology, but it is important to overcome limitations such as wide bandgaps and the poor charge mobility, and the fact that it shows instability under certain conditions [51].

These limitations underscore the importance of support materials that can enhance metal dispersion, mitigate deactivation, and improve electron transport.

3.3. Carbon-Based Catalysts

Carbon-based materials have gained recognition due to their high surface area, improved thermal conductivity, and electrical, mechanical, and optical properties [52]. These characteristics make them interesting to be studied as materials for structure support and co-catalysts in metal or metal oxide nanoparticles [53].

Graphene is a carbon allotrope arranged in a hexagonal form, as shown in Figure 8. It has diverse derivatives such as GO, rGO, GNR, GONRs, and fluorographene, among others; they exhibit good electronic properties like high electron mobility, thermal conductivity, and electrical conductivity [54]. For instance, thin reduced graphene oxide (rGO) layers

gave a high conductivity and faster electron transfer, avoided corrosion sites, and, more importantly, facilitated hydrogen adsorption/desorption in a W/WO₂-rGO/NF catalyst. This led to the reduction in overpotential, exhibiting a better performance and resistance than Pt in hydrogen evolution (HER) [55]. Another approach with an electrocatalyst configuration of carbon nanospheres with nickel and cobalt phosphide over N and S co-doped graphene substrate was taken by Zhang et al. They found that the active material used all the carbon structure as a carrier, enhancing the performance, requiring just 144 mV as overpotential, while having a larger current density [56].

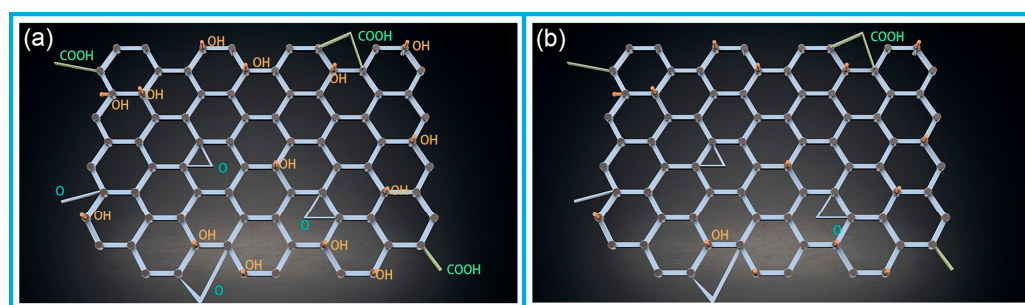


Figure 8. Typical schematic of molecular structures of (a) GO, and (b) rGO. Reprinted with permission from [54].

Carbon nanotubes can be explained as a rolled-up sheet of graphene. Its classification is based on the physical form, such as long or short, the number of layers on its surface, or the crystallographic configuration that is developed. Catalyst structures based on carbon nanotubes can provide an improvement in mass diffusion and electron transport; these properties have been introduced to develop bifunctional catalysts for HER/OER reactions in alkaline media. Xue et al. found that CNTs increased the number of exposed active sites and gave a long-term stability of 350 h for the catalyst NiSe@CNTs, resulting in an outstanding performance for both reactions [57]. Similar results were published by Cai et al. for Co₂P/Co₄N encapsulated by CNTs. The nanocomposites had a better resistance to electrochemical corrosion [58].

On the other hand, carbon nitride in the allotropic form of g-C₃N₄ is a stable material, with a low cost and high availability. Recently, it has gained popularity as a catalyst due to the tunable band gap (2.7 eV) that is useful for photochemical applications [59]. However, it has limitations such as a low surface area, rapid electron recombination, and the costs when it is produced on a big scale. Wei et al. addressed these difficulties doping g-C₃N₄ nanosheets with potassium; the obtained catalyst AKCN improved the migration movement and light utilization, and had a higher surface and narrower band gap, and the mechanism is shown in Figure 9. All these factors led to an increase in hydrogen production of 575 $\mu\text{mol h}^{-1}\text{g}^{-1}$ [60]. In terms of the high costs on a big scale, Wang et al. proposed a successful spillover method to avoid severe agglomeration and give the g-C₃N₄ a sheet shape. This improved the performance in hydrogen production to 1672 $\mu\text{mol h}^{-1}\text{g}^{-1}$, providing new insights into the scalability of carbon nitride materials [61].

Finally, biochar is a material that has shown good properties to be applied to catalytic systems and has been tested for hydrogen applications. In comparison with the mentioned carbon allotropes, characteristics such as a higher surface area, conductivity, inorganic materials, and a structure that has functional groups and aromatic carbon structure make it worthy of research [62]. This carbon structure has been proven to be an effective catalyst in diverse pathways of hydrogen production; its research has used simple biochar, diverse metal doping, and heterojunction. The main hydrogen pathways are dark fermentation [63], water electrolysis [64], photocatalysis [65], and methane pyrolysis [66]. Along the work

of these last years, the use of biochar showed an enhancement in hydrogen production, catalyst stability, and cost-competitive materials for sustainable energy production.

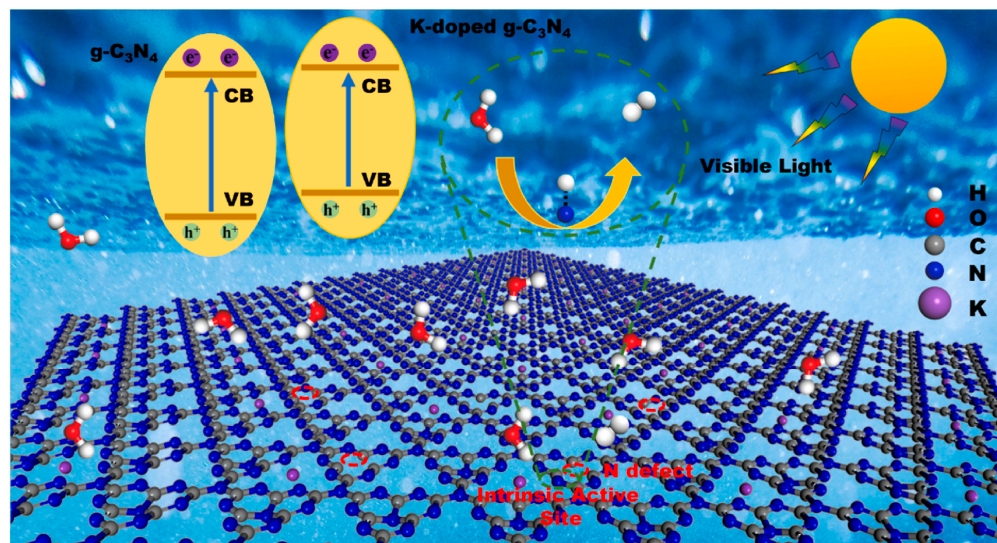


Figure 9. Schematic photocatalytic mechanism for the AKCN under visible light irradiation. Reprinted with permission from [60].

4. Biochar: Characteristics, Preparation, and Functionalization

The formal definition of biochar given by the International Biochar Initiative (IBI) is “a solid material obtained from the thermochemical conversion of biomass in an oxygen limited environment” [67]. Expanding its structure and composition, we have an organic material rich in carbon and containing other elements such as hydrogen, oxygen, nitrogen, and inorganic elements (P, Ca, Al, K, and Si). These elements are randomly organized in groups of alkyl and aromatic structures, creating an amorphous and crystalline phase in the form of condensed polyaromatic sheets.

The manufacture of biochar is defined by two main factors, the biomass feedstock and the thermochemical conditions. The selection of these two variables is going to have a big impact in the quality and performance of the biochar. First, the feedstock is chosen from diverse biomass sources, such as agricultural and forestry residues, animal residues, sewage sludge, and municipal solid waste. Considering its potential to produce biochar, it is important to understand the composition of each type of feedstock. In the chemical characterization of the agriculture and forestry, the main components are cellulose, hemicellulose, and lignin, responsible for providing the abundant carbon in biochar. On the other hand, the other biomass sources have their source of carbon from proteins. All the sources may contain lipids and inorganic substances that contribute to the final characteristics of the biochar [68].

Now, for the thermochemical conversion of the biomass, all of the feedstock has a great influence on its behavior. The kinetics and conversion of these components to biochar have been studied through the years to understand and develop these technologies; Figure 10 shows the reactions around this transformation. Conventional pyrolysis via electrical heating in slow, fast, and flash rates has been used for many years to produce biochar, bio-oil, and pyrolysis gas; however, new technologies have been proposed to improve the physical characteristics of biochar such as the surface area, functional groups, and carbon content. Among these technologies are microwave-assisted, steam-assisted, and solar-assisted pyrolysis, wet pyrolysis, co-pyrolysis, and catalytic pyrolysis, and these have achieved deeper and narrower pores, increasing the surface area and increasing the functional groups on the surface of pyrolysis [69,70].

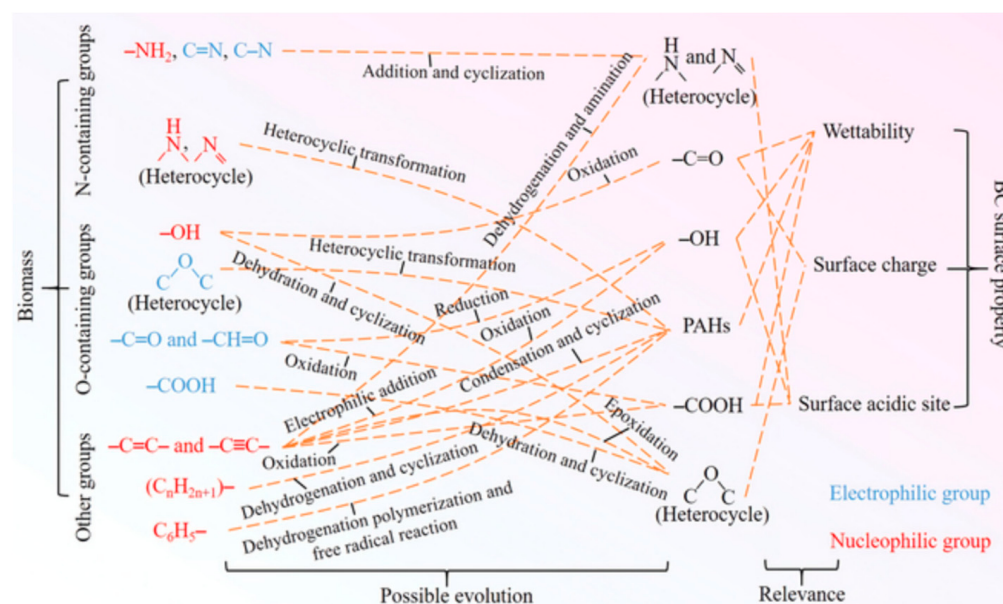


Figure 10. Overview of the reactions in biochar and its outcomes in its characteristics [71].

4.1. Influence of Feedstock and Pyrolysis Conditions on the Physicochemical Properties and Structural Features

4.1.1. Elemental Analysis and Ash Content

The high temperatures at pyrolysis cause the degradation of organic material. It has been observed that higher temperatures favor dehydration and deoxygenation, enhancing the elimination of oxygen and hydrogen, leading to an accumulation of carbon content and a structured aromatic sheet. The reduction in the O/C, H/C, and N/C ratio indicates a reduction in surface functional groups, decreasing the reactivity of biochar [72]. This increase in the aromatic sheet improves the hydrophobic characteristics, given that the aromatic groups are non-polar and there is a lack of surface groups that attract water. However, Mao et al. found that the total organic carbon content was not the main factor contributing to biochar hydrophobicity; it is significantly correlated to the carboxylic groups and biochar surface characteristics that are mainly dependent on the temperature [73].

The influence of the feedstock can be reflected in the content of nitrogen; a high C/N in biomass leads to a high C/N in biochar. Moreover, it has a direct influence on the ash content. It has been observed that, for forestry biochar, the ash content is low compared to agriculture residues and manure biomass due to the absence of these atoms in the original composition [74].

4.1.2. Surface Functional Groups

It has been observed that, between 350–650 °C, the surface functional groups such as carboxyl, lactone, lactol, quinine, chromene, anhydride, ether, pyrone, pyridine, and pyrrole are formed. At 300 °C, the differences between surface groups on the biochar is highly distinctive, but, with the increase in temperature, the number of acidic groups is reduced and there is an increase in the basic functional groups [75].

For the feedstock, the biochar derived from forest and agricultural residues presents a behavior of decreasing surface functional groups while the temperature increases. However, feedstocks that contain a higher content of lignin have the capacity to keep more functional groups at a moderate temperature (500 °C) than a higher temperature where all groups are mostly lost [76]. The effect of the temperature and agriculture feedstock was shown by Muzyka et al. In Figure 11, there is the Fourier-Transform Infrared Spectroscopy (FTIR) for raw wheat straw biomass and biochar obtained at 500 and 700 °C. In the

wavenumber ($1400\text{--}1500\text{ cm}^{-1}$) that belongs to groups CH_2 and CH_3 , and wavenumbers ($3200\text{--}3700\text{ cm}^{-1}$) for the H-bonded hydroxyl groups, there was a significant drop when the temperature increased to $700\text{ }^\circ\text{C}$. However, a rise in aromatic structures (1580 cm^{-1}) was noted with the increase in temperature [77].

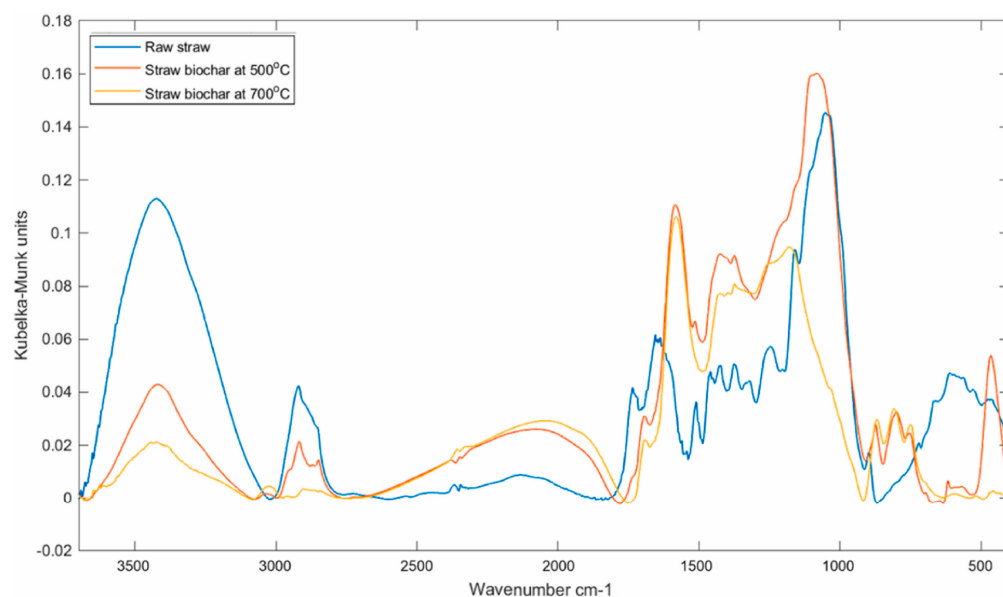


Figure 11. Adsorption bands for raw wheat straw biomass and pyrolysis biochar at 500 and $700\text{ }^\circ\text{C}$. Reprinted with permission from [77].

4.1.3. Surface Area and Pore Size Distribution

In general, the specific surface area of the biochar increases with the temperature; this has been observed in diverse studies. This effect is attributed to the thermal breakdown of organic components as reflected in Figure 2, where the carbon framework is enhanced without blockages. A shorter residence time and high temperature release a large amount of organic matter from the etched pores; this results in the development and expansion of smaller pore structures enhancing the general surface area [78]. The porous structure of the biochar has three main distributions: micropores that are the trapping space for adsorbed substances, mesopores that work as a trapping space, and macropores that allow the diffusion of substances. The formation of the pores is highly influenced by the pyrolysis conditions; a rapid heating rate promotes the evaporation and rapid movement of macromolecules, leaving spaces for deeper micropores and mesopores [71].

Jalali et al. and Ferraro et al. studied the properties of diverse biomass feedstocks, and they found that the biochar derived from manure and sludges are produced with a lower surface area with a low distinct porous structure [79], due to phenomena such as deformation, structural cracking micropore blockage, and the lack of lignin that is associated with increases in surface area and porosity [78]. That explains why the biochar from nut shells, and soft and hard wood is generally the most popular biomass to evaluate its properties and use. Moreover, one of the main conclusions is that feedstock from wood lead to a high surface area and pore volume, given the gas/water volatilization process and the loss of micro-molecule compounds that generate voids in the biochar matrix.

4.2. Surface Modification and Metal Loading on Biochar

Biochar is an adsorbent; its key characteristics such as surface functional groups, surface area and pore volume make it a good candidate in water treatment, catalysis, and energy storage, among others. The controlling of traditional variables is not highly effective and different modifications to the biochar have been studied. Biochar activation and surface

modification are techniques that aim to tailor certain biochar physicochemical properties to increase the activity. However, there is a trade between the surface area and pore volume with the enhancement in the new activities of the modified biochar [80].

The physical activation of biochar is a process that uses steam or carbon dioxide at high temperatures. The general results are a high surface area due to the development of pores.

Bélanger et al. used this technique to evaluate the influence of physical activation in starch-based biochar as filler in rubber. They found that activation had a big impact on the physicochemical properties of biochar: the porosity, carbon content, and ash content. Steam activation produced biochar with a lower carbon content and higher oxygen content than the other methods, and activation with carbon dioxide can produce biochar with a higher ash content [81].

Chemical activation is a process that has a direct influence on the surface area and pore structure of the final biochar. The substances used to carry out this activation are typically acids, strong bases, and chlorides; however, KOH has shown great performance compared with other substances and methods. Sun et al. studied the effects of the feedstock and activation in supercapacitor performance. In this study, there were different feedstocks with a high content in lignocellulosic content and activation methods (steam, carbon dioxide, and KOH). They found a significant increase in the BET surface area of biochar samples, KOH being the one with a surface area increase of more than 85% compared to the pristine biochar. This resulted in an improved performance in the double layer and pseudocapacitive performance, reinforcing the capacity of this sustainable material [82]. Alcazar-Ruiz et al. evaluated steam, carbon dioxide, KOH, and H_3PO_4 with the purpose of enhancing CO_2 adsorption capture; the results showed that the olive biochar activated with KOH has a better development of micropores at low concentrations, allowing a greater volume of gas to be retained [83].

Doping is a strategy to load other functional groups to the biochar. Depending on the atoms that want to be loaded at the surface, the doping can happen in these three scenarios: heteroatom doping, heteroatom co-metal doping, and metal atom doping. In heteroatom doping, the study has been focused on adding atoms of nitrogen, sulphur, phosphorous, and boron; these atoms have the capacity to present stable bonds, increase conductivity, induce defect sites, and increase the electron rate, making them a perfect candidate for sustainable catalysts [84]. Thanh Thuy et al. used phosphorous-modified biochar for the oxidation of vanillyl alcohol to vanillin; the catalyst had an impressive performance compared to other catalysts, achieving a conversion, yield, and selectivity near to 100%, a phenomenon only seen in metal catalysts. The authors found that the doping gave the biochar phosphorus functional groups, porosity, and changes in the electronic structure of the catalyst, showing the advantages of this material [85].

Metal loading in biochar is a technique that has been gaining popularity in the field of adsorption and catalysis. Metals use oxygen functional groups to get into the biochar surface, creating a stable point; moreover, metals can modify the electronegativity, create unique redox properties, and increase stability in acid or basic solutions. Gu et al. recreated the hydrangea (flower) porous structure in a biochar doped with MgO for the capture of heavy metals. The surface area was 2.27 times greater than the pristine biochar; as a result, the modified biochar reduced by almost 50% the concentration of Cd and Pb in the soil. This performance is attributed to the functional groups (C=O) and (Mg-O), along with an increment in electron attraction [86].

Tailoring biochar as a catalyst is one of the main focuses in research; the versatility of raw biochar allows it to be employed across many reactions, with specific modifications thought specifically for the reactant. Across the literature, biochar has demonstrated that it

is an excellent material for achieving strong metal-supported interactions. Currently, the field of catalysis relies on engineered and highly working biochar, with specific surface activations and the design of active sites using different metals to enhance the catalytic performance, and reduce costs and environmental impact, to finally get closer to sustainability and the desired green chemistry.

5. Biochar-Based Catalysts in Hydrogen Production

5.1. Functional Roles of Biochar in Hydrogen Production Systems

Currently, research has been focused on the development of catalysts and catalyst support that can offer a high electron conductivity, resistance to corrosion, and a large surface area to carry out the reaction. Biochar has been reported to enhance hydrogen production across multiple pathways. However, its contribution is not universal and depends strongly on the functional role it plays in a given system. This is shown in Figure 12, where there is a correlation among all the factors that influence the synthesis of biochar and the final use.

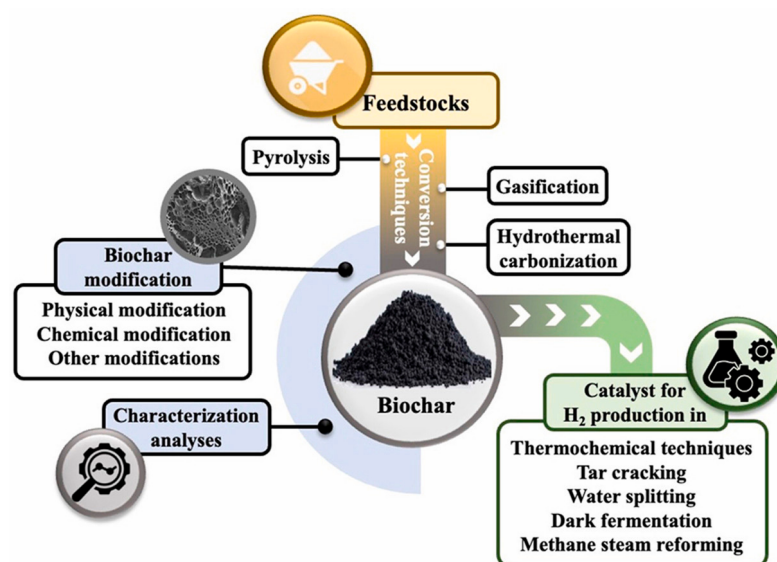


Figure 12. Biochar production and modification routes for catalyst application in hydrogen. Reprinted with permission from [14].

5.1.1. Biochar as a True Catalyst

Biochar exhibits intrinsic catalytic activity without the presence of metal, metal oxide, or non-metal active phases. In these cases, hydrogen formation occurs directly on the biochar surface, and it is attributed to oxygen surface functional groups that promote the involved reactions. For the steam reforming of acetic acid, ethanol, and acetone, biochar showed high activity in C=C and C-O-C species using oxygen-containing groups, promoting the reactions of deoxygenation and dehydrogenation [87]. Eom et al. proved the catalytic activity of the biochar without doping; they used biochar wood pellets in liquefied petroleum gas (LPG). As a result, the concentration of hydrogen increased with the presence of biochar and the gas rate. Due to the catalytic activity, the biochar experimented with changes on its surface oxygen functional groups participating actively in the reaction, although it demonstrated a stable performance over the term compared to other carbon-based catalysts [88].

Despite these observations, biochar acting as a single catalyst generally exhibits lower activity than impregnated biochar and remains highly pathway specific. It has been observed that surface functional groups are progressively lost under a high temperature

operation, leading to quicker deactivation, limiting the application of direct biochar in hydrogen catalysis.

5.1.2. Biochar as a Catalyst Support

As a support catalyst, biochar has shown characteristics of stabilizing and dispersing nanoparticles, being electrically conductive [89]. The doping with nitrogen heteroatoms boosts electrical conductivity and hydrophilicity, facilitating electron charges in enhancing hydrogen production [90]. In addition to those advantages, biochar uses the oxygen functional groups and nitrogen atoms to induce active sites for the reactions. Moreover, the high organization of the biochar matrix promotes enough space for doping metals and facilitates the mass transfer along the surface [89]. Nevertheless, excessive doping or metal loading may lead to pore blockage and the loss of structural integrity. This highlights the importance of the optimization loading strategies and modification rather than a maximal incorporation.

5.1.3. Biochar as an Adsorbent and Sorption-Enhanced Medium

Biochar offers an indirect advantage to hydrogen production through its adsorptive properties. In some studies, it has been proven that, in thermochemical systems, biochar can adsorb intermediates, tar compounds, carbon dioxide, and solid carbon species. Eom et al. found that, besides its catalytic activity, the biochar had the capacity to absorb around 35–60% of the carbon produced in liquefied petroleum gas (LPG). This proposes a solution to the main problem of turquoise hydrogen, which is the management of carbon solid residues [88]. This multifunctionality is advantageous but introduces other challenges related to adsorbent saturation, regeneration, and long-term structural stability, and can accelerate catalyst deactivation by blocking active sites. In conclusion, while adsorption enhances the short-term hydrogen yield, it carries deactivation systems, so it must be considered a secondary, supporting role rather than a catalytic one.

5.1.4. Biochar as an Electron Shuttle and Redox Mediator

The role of biochar as a support has been studied for photocatalysis. It has been proven that biochar can enhance photocatalytic production, and primarily functions as an electron shuttle or redox mediator given its electrochemical properties. It has the function of receiving the generated photoelectrons and inhibiting the rapid recombination; this leads to a wide light absorption band and reducing the band gap, achieving a better hydrogen production [91]. This role depends strongly on biochar conductivity, graphitization degree, and pretreatment. Biochar itself is not the primary active site for hydrogen evolution but acts as a conductive bridge that enhances the performance of coupled catalytic materials.

5.1.5. Biochar as a Microbial and Redox Mediator in Biological Systems

Particularly in dark fermentation, biochar functions as a microbial and redox mediator rather than a chemical catalyst. Biochar enhances the hydrogen yield by microbial growth conditions, buffering the pH and facilitating the hydrogen metabolic rate. Bu et al. found that biochar implemented the selective colonization of functional bacteria and improved the electron transfer efficiency of the fermentation system [92]. Similar results were found by Yang et al., where biochar modified with Fe increased the abundance of the target microbe and reinforced the activity of key enzymes in the process of hydrogen production [93].

However, it is important to reinforce that biochar is system-dependent, and hydrogen production is primarily influenced by biological processes rather than surface catalytic reactions.

Table 2 provides a classification of the functional roles that biochar can play in hydrogen production and highlights the strong dependence of these roles on pathway-specific

requirements. It is evidenced that biochar does not exhibit a universal catalytic behavior, but, instead, contributes through different mechanisms depending on the reaction environment and hydrogen production route. While intrinsic catalytic activity exists in specific reactions, the value of biochar lies in its multifunctionality. Understanding these roles is critical for rational catalyst design, reproducibility, and scalability.

Table 2. Functional roles of biochar in hydrogen production.

Biochar Role	Primary Role	Required Biochar Properties	Dominant Hydrogen Pathways	Typical Evidence	Key Limitations
Catalyst	Directly catalyzes the reaction through surface groups	High surface area, oxygenated functional groups and thermal stability	Pyrolysis, tar cracking, reforming reactions.	Increased H ₂ yield; surface group evolution	Low intrinsic activity; rapid deactivation and poisoning
Catalyst support	Disperses and stabilizes metal active sites	High surface area; mesoporosity; anchoring functional groups	Steam reforming, electrolysis, photocatalysis, gasification	Improved metal dispersion, reduced sintering, enhanced durability	Pore blockage, coke deposition, support degradation
Adsorbent/sorption enhancer	Captures intermediates or inhibitors; shifts equilibrium	High porosity, surface polarity, chemical stability	Reforming, gasification, pyrolysis	CO ₂ /tar adsorption, improved H ₂ selectivity	Saturation, regeneration challenges, structural collapse
Electron shuttle/redox mediator	Facilitates electron transfer between phases	Electrical conductivity, graphitization, heteroatom doping	Electrolysis, photocatalysis	Lower overpotential, reduced recombination, higher current density	Conductivity loss over time, limited role without coupling with metals
Microbial/redox mediator	Enhances microbial metabolism	Moderate surface area, buffering capacity, mineral content	Dark fermentation	Increased H ₂ yield, improved targeted microbial growth	Indirect effect, system specific, biological variability

5.2. Synergistic Effects with Metal Nanoparticles

Given the structure of the biochar, it has a direct influence on the electronic structure and catalytic performance of the doped nanoparticles that are laying in the surface of the final catalyst. Beyond serving as a physical support, biochar actively participates in metal-support interactions offering a strong antioxidative capability and activity; this effect is achieved through the reduction state of the metal forming a surface oxidized metal layer, keeping the catalyst active for a longer time, enhancing its lifespan and activity [94].

Single-metal doping on biochar has been shown to significantly modify the porous matrix, where elements such as Ni, Fe, and Zn are anchored and embedded on the carbon structure, increasing the mesopores, and this leads to a general increase in the surface area, creating more active spots in the reactions. In contrast, an alkaline metal such as Ca has been reported to reduce the amount of mesopore and macropore volumes, causing a decrease in active sites for the performance [95,96].

For bimetallic catalysts, the synergistic effects can arise not only from metal–metal interactions but also from their sequential incorporation into the biochar matrix; Liu et al. found that the order of doping alters the catalytic activity of the general composite. The initial addition of Fe increases the mesoporous structures in biochar, while the addition of K promotes a higher degree of graphitization in the biochar, increasing the π – π interactions. Their interaction promoted oxygen vacancies that could adsorb OH groups, enhancing the activity of the catalyst [97]. Another effect was reported by Di Stasi et al.: the addition of Co in the Ni-biochar catalyst leads to new strong basic sites, a characteristic that reduces the probability of poisoning by coke deposition on the surface [98].

Non-metallic atoms play a key role in the interaction between biochar and metal atoms by influencing coordination environments, electronic conductivity, and active site stability.

Ying et al. noted that the abundance of nitrogen and phosphorous heteroatoms on the surface of biochar favors the bonding of metal ions and carbon to form metal compounds. In the same way, the introduction of iron atoms enhanced the bonding between the other metal, nickel, and the phosphorous. This strong interaction leads to an increase in the electrical conductivity, active groups, and permeation of electrolytes in the OER reaction [99]. Despite these benefits, it also has been found that an excessive quantity of metal or heteroatom loading can cause blocking in the pores, leading to a faster deactivation [66].

The catalytic performance of modified biochar is a delicate balance between the pore architecture, electron structure, and the metal–support interactions. While biochar offers a combination of catalytic activity and support functionality across hydrogen diverse production pathways, a rational catalyst design must prioritize controlled metal dispersion and a mechanistic understanding of the interactions to ensure high activity and sustained stability.

5.3. Applications in Steam Reforming, Pyrolysis, Gasification, and Photocatalysis

Being in this stage of research, biochar still presents a complex parameter in which the feedstock selection, pyrolysis conditions, activation methods, and post-modification strategies collectively impact the catalytic behaviour. To fully unlock the biochar potential, it is necessary to achieve a systematic understanding of these independent variables rather than isolated performance demonstrations. Key trends emerge from the use of biochar in hydrogen production. First of all, pristine biochar exhibits intrinsic catalytic activity, but it lacks robust activity to carry out the hydrogen reaction due to the energy demands it requires. As a result, the main use of biochar is located as a support; the metal doping increases the catalytic activity due to the synergistic interactions between both materials. As a consequence, the tailoring and engineering design of the catalyst becomes one of the most important variables with which to achieve a comparative performance compared to the usual catalysts on the market. Feedstock selection, pyrolysis conditions, activation methods, and post-modification strategies collectively influence its behavior. It is important to remember that these parameters do not affect all hydrogen pathways equally, as discussed in Table 2, underscoring the need for pathway-specific interpretation rather than isolated performance demonstrations.

Thermochemical routes for hydrogen production, which include steam reforming, pyrolysis, and gasification, are processes that, in principle, use hydrocarbon material to carry out the reaction; however, recent studies have used biogas and biomass feedstocks to improve sustainability. In these environments, the requirements for catalysts are thermal stability and resistance to coke formation. In high-temperatures environments, biochar as a catalyst support exhibits a behavior as an adsorbent of reaction intermediates, CO₂, or solid carbon species, becoming a sorption-enhanced reaction. While this multifunctionality is conceptually advantageous, it also carries difficulties in catalyst durability and structural stability [100]. This effect was reflected in the study by Di Stasi et al., where the steam reforming only took place on the surface of metal nanoparticles and the main causes for catalyst deactivation are the high deposition rates and heavy byproducts adsorbed in catalytic sites [98]. This supposes a challenge for the use of biochar as a support catalyst; although it can enhance metal dispersion and provide an adsorption capacity, it does not mitigate the fundamental deactivation mechanisms associated with this production route.

In pyrolysis, Fang et al. studied the implementation of a loop where the byproduct given by the pyrolysis of the biomass is the main component to synthesize new catalysts and the hydrogen is extracted from the volatile matter released from the reaction [94]. In the case of gasification, the research has been focusing on obtaining a hydrogen-rich syngas using the same biomass as a precursor for the reaction and the biochar catalyst. Kong

et al. compared diverse biomass performances: wheat straw, *Chlorella pyrenoidosa*, sewage sludge, and cow manure. Wheat straw showed the best performance, and hydrogen formed almost 50% of the gas produced with a yield of 46.39 mmol/g and the lowest formation of CO₂ [95].

In the case of electrolysis, biochar-assisted water electrolysis and photocatalytic hydrogen generation using biochar are massive; in contrast with thermochemical routes, the governing mechanisms are electron transfer kinetics, charge transport, and interfacial electronic interactions. In this case, biochar serves as a conductive support and electronic mediator. Among the principal characteristics is the enhancing of the metal utilization efficiency and electron transport. For photocatalysis, this offers improved visible light absorption, low band gaps, excellent charge diffusion, and a reduction in the rapid recombination of charged particles. In general, the improvement in hydrogen production is enhanced three to five times using biochar; this is achieved through the improvement in the photostability of the catalysts [91,101].

Even in dark fermentation, biochar shows an improvement in hydrogen production. Although the mechanism is dominated by microbial metabolism rather than surface catalytic reactions, biochar is required for redox mediation, having a direct impact on the selectivity of the microbes. In a study conducted by Zhao et al., there was an increase of 2.533 times, with the use of biochar derived from rice straw achieving a yield of 2.08 mol-H₂/mol-xylose. The role of biochar in this interaction was the improvement in bacterial growth, pH regulation, and modulator in redox reactions, and it increased the electroconductivity in the mixture to degrade over 90% of xylose [102]. Table 3 provides an overview of the hydrogen production routes, showing the diversity of parameters for each pathway.

Table 3. Results of hydrogen productions through different production pathways and catalysts.

Biochar Feedstock	Biochar Production Conditions	Used Catalyst	Hydrogen Feedstock	Reaction Conditions	Hydrogen Production	Reference
Steam Reforming						
Wheat straw	Temperature: 500 °C HR: 5 °C/min Time: 1 h	15 wt% Ni/WS-C	Low density polyethylene pellets (LDPE) and wheat straw in a ratio 5:5	Mass ratio material/catalyst: 1:0.8 Pyrolysis temperature: 600 °C Reforming temperature: 800 °C Steam flow rate: 0.2 g/min	77.5 mmol/g	[89]
Rice husk	Temperature: 800 °C HR: 10 °C/min Time: 1 h	RHC@Fe/K	Rice husk	Mass ratio material/catalyst: 1:0.4 Pyrolysis temperature: 550 °C Reforming temperature: 800 °C	23.78 mmol/g _{biomass}	[97]
Pyrolysis						
Wood pellets	Temperature: 950 °C Time: 0.5 h	Biochar wood pellet	Liquefied Petroleum Gas (LPG)	Temperature: 950 °C Gas flow rate: 1 L/min	35% mol H ₂	[88]
Gasification						
Chinese herb residue	Temperature: 700 °C HR: 10 °C/min	HPF (doped with Fe and K)	Chinese herb residue	Gas Hourly Space Velocity: 16,700 h ⁻¹ Temperature: 667 °C Steam Content: 14.5% vol Time: 92 min	140.25 mol/kg	[103]

Table 3. Cont.

Biochar Feedstock	Biochar Production Conditions	Used Catalyst	Hydrogen Feedstock	Reaction Conditions	Hydrogen Production	Reference
Photocatalytic						
Sunflower stalk	Temperature: 450 °C HR: 7 °C/min Time: 2 h	ZnCdS/CoMoO ₄ – 8/5% NC	10% (v/v) lactic acid aqueous solution	Visible light LED: $\lambda \geq 420$ nm, 10 W output Agitation: 800 rpm Temperature: 25 °C	701 μmol in 5 h	[90]
Orange peel	Not specified	CdS-60C	Water	Visible light Time: 4 h	7.8 $\text{mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	[91]
Sewage sludge	Temperature: 800 °C HR: 15 °C/min Time: 1 h	BC/TiO ₂	5% (p/p) glycerol aqueous solution	Xenon lamp: $\lambda \geq 420$ nm	2523 $\mu\text{mol g}^{-1} \text{h}^{-1}$	[101]
Dark fermentation						
Rice straw	Temperature: 500 °C Time: 8 h	Rice straw biochar	10 g/L of xylose in water	Temperature: 60 °C Agitation: 170 rpm pH: 7.00 Biochar: 7 g/L	2.08 $\text{mol-H}_2/\text{mol-xylose}$	[102]

6. Key Factors Affecting Catalytic Hydrogen Production

6.1. Surface Area, Porosity, and Functional Groups

Across the studies of biochar as a catalyst, there has been more understanding in the properties that have a direct effect on hydrogen production. Surface area and porosity are crucial to the catalytic performance of biochar.

Santos et al. found that a meso-macroporous surface can influence the behavior of biochar-based catalysts in steam reforming, in their results, the increment in the porous structure leads to an increase in hydrogen production. In microporous char structures, the molecules of palladium get stuck there and minimize interaction with the reactant. As a consequence, the major activity inside the biochar is inside the meso-macroporous sites; they increase the mass transfer from the bulk to the active site of the metal [104]. Additionally, in rice husk steam reforming, the mesoporous structure had a highly ordered structure that was favorable to the contact of active centers during catalytic reactions [97]. In contrast, Hu et al. found that, for biochar-assisted water electrolysis, the improvement in micropores enhanced the oxidation reaction because the active sites are located in the micropore and the mesoporous structures work as channels to increment ion transportation during the reaction [105].

On the side of surface functional groups, it has been evidenced that basic biochar improves the catalytic performance in methane pyrolysis due to the increment in oxygen surface functional groups [66]. A similar effect is noted in steam reforming where functional groups such as -OH and C=O enhance the oxidation reduction reaction [105]. These groups are also highly important in electrochemistry; they have the capacity to deprotonate in aqueous environments to induce charged sites, and this leads the biochar to be a better electron donor to improve the general reaction [106].

6.2. Reaction Conditions: Temperature, Pressure, and Time

In thermochemical hydrogen production, temperature is one of the most important variables. Due to the endothermic nature of the methane decomposition reaction, the increase in the temperature gives a better performance [66]. In the case of ethanol steam reforming, something similar happens: the increase in the temperature showed an improvement in the dehydration reaction. In the same study, the increase in the partial pressure of steam had a direct negative impact on the hydrogen yield, lowering the quantity. The amount of steam caused an improvement in the water gas shift (WGS) reaction, increas-

ing the yield of carbon-based products; this left a lower surface area in the catalyst for dehydration and decomposition reactions [107].

Yu et al. studied the optimization of variables in biomass gasification. They found that the order of influence of the hydrogen yield is Gas Hourly Space Velocity > Temperature > Steam Content > Time. Using Chinese herb residues, they found that the optimal parameters to carry out this reaction are $16,700 \text{ h}^{-1}$, 667°C , 14.5% vol, and 92 min, respectively [103].

6.3. Feedstock Composition and Pretreatment

Across the literature, different feedstocks and pretreatment are applied to biochar to pursue certain characteristics that can enhance the performance of the general reaction. Part of the tailoring and engineering of the biochar involves choosing an adequate biomass, pyrolysis conditions, and physical or chemical activation, given that each decision will impact the interaction of the biochar with the doping metal and reactant, key characteristics are listed in Table 4.

Faster heating rates promote a sharper, narrower peak, and the particles are uniform and monodispersed in nature; this creates an effect of a uniform particle distribution and, as a consequence, surface charge stabilization, which prevents agglomeration and, as a consequence, enhances the electrical conductivity. Moreover, there is an enhancement in oxygen surface functional groups deprotonating in aqueous environments, inducing charges in the biochar, developing electron-donating properties. These properties are critical for surface interactions, as catalysts for active surfaces and electrodes result in an improved charge mobility and ion diffusion [108].

Sun et al. evaluated the effects of elution treatment in the performance of pristine biochar derived from mixtures of cellulose and lignin in biochar-assisted water electrolysis. Three wash solutions were studied: KOH 1M, HCl 1M, and deionized water. In general, the treatment reduced the ash content and soluble substances from the pores. This exposed oxidizable functional groups (C-OH and COOH) and the surface that favoured the oxidation during electrolysis, facilitating ion diffusion at the anode–electrolyte, enhancing electron transfer. However, the best performance was given by the deionized water treatment: this one only removed the ash content and did not make any changes on the surface functional groups, as it happened with the chemical treatment, with the use of acid deactivated basic groups and the use of base deactivated acid groups leading to a lower kinetic reaction and current density performance [109]. However, keeping the high ash content from sewage sludge in photocatalytic hydrogen production, the charge recombination through redox reactions over the biochar matrix improves its general performance [101]. In dark fermentation, the ash content supplied the required nutrients in the medium, enhancing the general production [110].

Techniques such as doping with nitrogen was studied by Ying et al. They used pine needle biochar doped with nitrogen to enhance activity in the oxygen evolution reaction. This pretreatment caused an increase in graphite nitrogen that leads to a higher conductivity, wettability, and adsorption of intermediates in the electrochemical reaction. The nitrogen heteroatoms altered the electronic structure of the carbon matrix, leading to a charge distribution, leading to better results in the water electrolysis results [99]. Doping with sulfur in camelia flower for hydrogen water splitting was studied by Xia et al.; the atoms of sulfur were induced into the biochar framework, generating polarized surfaces with an increased charge transfer from the electrolyte to electrode. Compared to commercial carbon materials, it showed a better performance for HER and OER reactions, showing potential as a dual electrode for hydrogen production [111].

The feedstock composition can have a big impact on the performance of biochar. For biochar-assisted water electrolysis, biochar derived from cow manure is the one that presented the highest C/O ratio, smallest particle size, and most negative zeta potential; these properties lead this biochar to exhibit a better performance in oxidation efficiency. It is suggested by the behavior of the catalysts that an increase in the C/O ratio enhances the proton–electron transfer kinetics [106].

Table 4. Key factors affecting catalytic hydrogen production using biochar.

Biochar Feedstock	Modification	Modified Characteristic	Hydrogen Route Production	Key Finding	Reference
Residual vine shoot	Chemical activation: ZnCl_2	Pore structure	Formic acid steam reforming	Mesoporous biochar enhances hydrogen production in steam reforming.	[104]
Wheat straw	Chemical activation: KOH	Pore structure	Biochar-assisted water electrolysis	Microporous structure is favorable and the abundant -OH and C=O functional groups increase the oxidation current.	[105]
Cellulose and lignin mixture	Chemical activation: KOH and HCl. Wash with deionized water.	Surface groups	Biochar-assisted water electrolysis	The treatment reduces ash content, exposing functional groups. The chemical activation neutralized functional groups reducing catalytic activity.	[109]
Pine needle	Nitrogen heteroatom doping	Biochar structure	Water electrolysis	The nitrogen atoms induce charge distribution, that improves conductivity.	[99]
Camelia flower	Sulphur heteroatom doping	Biochar structure	Water electrolysis	Induce polarized surfaces, increasing charge transfer. Feasible for dual catalyst.	[111]

6.4. Catalyst Stability and Regeneration Potential

To be considered effective as a catalyst, it has to present a high stability over time to ensure a long lifespan; regeneration allows us to restore the catalyst performance. Currently, achieving both functionalities remains a problem in the industry for heterogeneous catalysts. Biochar as a catalyst is a material that still remains under study. Studies across the literature confirm that the use of biochar as support improves the general catalyst stability; however, its use in thermochemical conversion methods has evidenced problems in deactivation for coke deposition on the surface and a reduction in the surface functional groups.

Buentello-Montoya et al. found a correlation in the porous structure with the deactivation of the catalyst. A mesoporous biochar is less probable to suffer deactivation than a microporous one. The coke deposition can be gasified at high temperatures, allowing the conservation of the surface area. In the case of microporous biochar, the active sites were blocked, reducing the general efficiency of the process [112]. The interaction is shown in Figure 13.

In another study, using Ni/Ca@KWBC (potassium-activated sewage sludge biochar) for biomass pyrolysis, the homogeneous dispersion of metals in the carbon matrix was key to achieve long-term stability. They used the catalyst for five cycles and showed good reusability and less accumulation. Ni/Ca@KWBC (potassium-activated sewage sludge biochar) remained intact, with an anti-coke formation, and can be restored with NaOH and ultrasonic vibration. The improved stability was attributed to the alternating reaction between CaO and CaCO_3 in the catalyst [113].

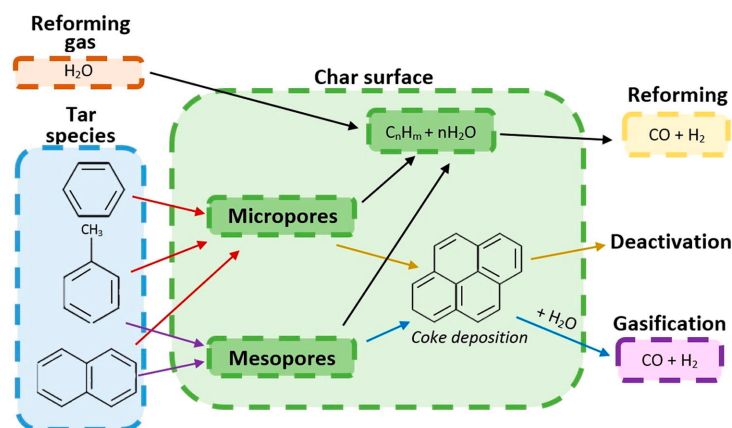


Figure 13. Deactivation mechanism of biochar regarding its pore structure in tar reforming [112].

For electrochemical water splitting, Ertaş et al. found an improved stability for the Biochar/ZnCoNi electrode; it was able to maintain a stable activity for over 1000 cycles and a high current density for 12 h [114]. For photocatalysis, biochar layers are not affected by the long exposure under light radiations [101]. Moreover, the synergistic interaction between biochar and the TiO₂ anatase and rutile phases generates a stable catalyst. During 30 h and 5 cycles, the activity was stable, demonstrating an enhanced lifespan for the catalyst [115].

Long-term stability remains one of the issues for biochar-based catalysts. As can be observed, studies focus on the short-term performance with a limited evaluation of the durability over extended operational cycles, expressing a huge potential for long-term stability, but this still remains unexplored. Furthermore, regeneration strategies for spent biochar are limited and their feasibility remains uncertain. It is imperative to understand the deactivation pathways and develop effective regeneration protocols to assess industrial viability.

6.5. Conceptual Framework for Biochar

As has been explored through the present document, biochar does not enhance hydrogen production by virtue of a single attribute. The effectiveness arises from how intrinsic structural features translate into physicochemical properties that enable specific catalytic roles for different hydrogen production mechanisms.

From the structure, biochar is defined by its degree of aromaticity, porosity, graphitization, defect density, and present minerals, which are determined by the feedstock selection, thermochemical processing conditions. All the characteristics included in Table 4 affect the behavior of biochar. Highly aromatic structures promote electrical conductivity and thermal stability, while porous structures and structural defects increase the amount of exposure of the active sites and increase the surface area. Surface functional groups and inorganic species introduce redox-active centers. These attributes govern the physicochemical properties of biochar, as it has been evidenced that heteroatom doping enhances electron mobility, whereas oxygen functional groups regulate adsorption strength and acid–base behavior.

The combination of these physicochemical properties determines the functional catalytic role that biochar can assume. A porous and chemically active biochar functions as a metal stabilizer, enhancing the dispersion of active phases and the surface area for the reaction to take place; at the same time, it can capture reaction intermediates, with coke precursors increasing the yield and selectivity of the reaction.

Finally, the observed performance characteristics, such as increased hydrogen production rates, enhanced stability, reduced overpotential, or improved selectivity, are emergent

outcomes of this multilevel coupling rather than the isolated material properties. The variability in the reported performance across studies can therefore be rationalized in the biochar structure and the specific pathway—depending on the role it is playing in the system. Biochar performance cannot be generalized across systems. Instead, rational design and comparison require an explicit alignment between the biochar structure, targeted physicochemical properties, intended catalytic role, and hydrogen production mechanism.

7. Challenges and Limitations for Biochar

7.1. Variability in Biochar Quality and Composition

One of the main limitations of the use of biochar is the variability in its physicochemical properties. Each decision in production will impact in a severe form the performance of the material. As has been discussed, the biomass feedstock, pyrolysis temperature, heating rate, and physical or chemical activation will have a direct impact on key catalytic properties such as the surface area, porosity, surface functional groups, heteroatoms, ash content, and synergistic interaction with metals or oxides. This variability complicates cross-study comparisons and prevents the establishment of generalized performance trends, even when identical hydrogen production pathways are employed. As a result, biochar performance remains highly system-specific, limiting predictive design and scalability.

7.2. Scalability, Standardization, and Reproducibility

Biochar is a promising material on the laboratory scale; the performance in different reactions is impressive and that explains why it has been a research focus through the years. However, translating biochar-based systems to an industrial scale still seems far away. Minor variations in the feedstock origin or processing conditions can result in substantial deviations in catalytic behavior. The lack of standardized production protocols and quality metrics for catalytic-grade biochar makes this issue greater. Without clear correlations among production variables and functional performance, it is difficult to ensure a reproducibility and consistent material properties at scale on industrial applications.

7.3. Environmental and Lifecycle Considerations

To be considered a true environmental remedy to sustainability, it is necessary to consider all the environmental impacts that the use of biochar brings. The life cycle of the biochar includes steps that require massive amounts of energy for production; the activation and doping use chemicals that might create toxic effluents. At the end of its productivity lifespan, there is no plan on how to treat the remaining material; due to its self-degradation capacity, the secondary materials pose a threat to environment. Furthermore, life-cycle analysis still is limited, and does not allow us to quantify the true impact in sustainable hydrogen production, as expected.

8. Future Perspectives and Opportunities

8.1. Engineered Biochar for Targeted Hydrogen Applications

The future of biochar relies on the engineering design of catalysts. This material has a huge ability to be tailored to match the necessities of the reactions. A deeper understanding of the patterns in the behavior of biochar could allow computational tools and simulation methods to explore diverse case scenarios to identify key configurations in the biochar–metal surfaces. This will generate biochar composites that have increased activity and stability.

8.2. Hybrid Systems and Integration with Renewable Technologies

The highest compatibility of biochar with renewable technologies is one of the main advantages of biochar. It has been proven to have a compatibility with electrochemical systems, solar-driven energy, and the use of biomass. Biochar offers an opportunity to build new technologies of hydrogen production with a low environmental impact, and a reduction in general costs to make abundant and low-cost energy; this will increase the accessibility and achieve the hydrogen society we are looking for.

8.3. Policy, Investment, and Industrial Scaling

Biochar lacks standardization for catalysis, grade quality, material classification, minimum requirements, and properties; the implementation of regulations for biochar might be the first step to support circular systems at an industrial level. Regulations must be implemented to ensure safety and quality, and reduce the environmental impacts on the production and use of biochar. Government investment in the research, development, and policy framework is necessary in order to strengthen emerging technologies. The appropriate divulgation of information is essential to increase the acceptance of new forms of energy production among the population, policies that look for the evolution of energy but, at the same time, protect all the diverse life forms that live on our planet. Addressing all these issues will promote the energy transition sooner than expected.

Despite promising laboratory-scale results, the translation of biochar-based systems to industrial reactors remains limited. Biochar has demonstrated a compatibility with electrochemical systems. The research and development have achieved the use of metal oxides for doping that are accessible and low-cost to improve catalytic activity; however, their performance under industrial current densities, temperatures, and electrolyte conditions remains unexplored. Other variables such as mechanical stability or pressure drop are rarely addressed. Understanding biochar in these conditions will allow us to test biochar composites in a reactor-level demonstration to prove the real industry capacity.

It is important to highlight that it is necessary that we explore the economic competitiveness. Biochar production involves energy-intensive pyrolysis processes, and activation processes require chemical treatments that elevate the costs. A standardization of the production route could reduce the process complexity, but the framework is lacking. Without scalable, low-energy, and environmentally friendly production pathways, the industrial competitiveness of biochar-based catalysts remains uncertain.

8.4. Research Priorities and Innovation Roadmap

To achieve the full potential of biochar in hydrogen applications, several priorities must be addressed:

1. Critical knowledge gaps: It is urgent that we find behavior patterns in biochar production and hydrogen catalysis. This is to improve the activity, reproducibility, stability, and predictive design of engineered catalysts.
2. Stability and regeneration: For industrial feasibility, it is imperative to understand and improve the biochar stability, longer term cycles, coke deposition, deactivation, and loss of surface functional groups, along with prediction and how biochar would work on a big scale and if regeneration is possible in order to achieve the best performance.
3. Supply chain: A reliable supply chain for the current biomass.
4. Sustainable production routes: Research in low-energy pyrolysis, the reduction in effluents, and low-pollutant chemical routes of production is necessary in order to address the green potential of biochar.
5. System level integration: The evaluation of biochar catalytic performance in a whole functioning plant is necessary; techno-economical studies, a life-cycle assessment, and

compatibility with existing hydrogen technologies are important in order to accelerate the maturity of biochar in the global hydrogen production.

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Abbreviations

The following abbreviations are used in this manuscript:

IEA	International Energy Agency
SDGs	Sustainable Development Goals
SMR	Steam Methane Reformation
AWE	Alkaline Water Electrolyzer
SOE	Solid Oxide Electrolyzer
AEM	Alkaline Anion Exchange Membrane
PEM	Proton Exchange Membrane
HER	Hydrogen Evolution Reaction
OER	Oxygen Evolution Reaction

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