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Progress, barriers, and prospects for achieving a “hydrogen society” and opportunities for biochar technology

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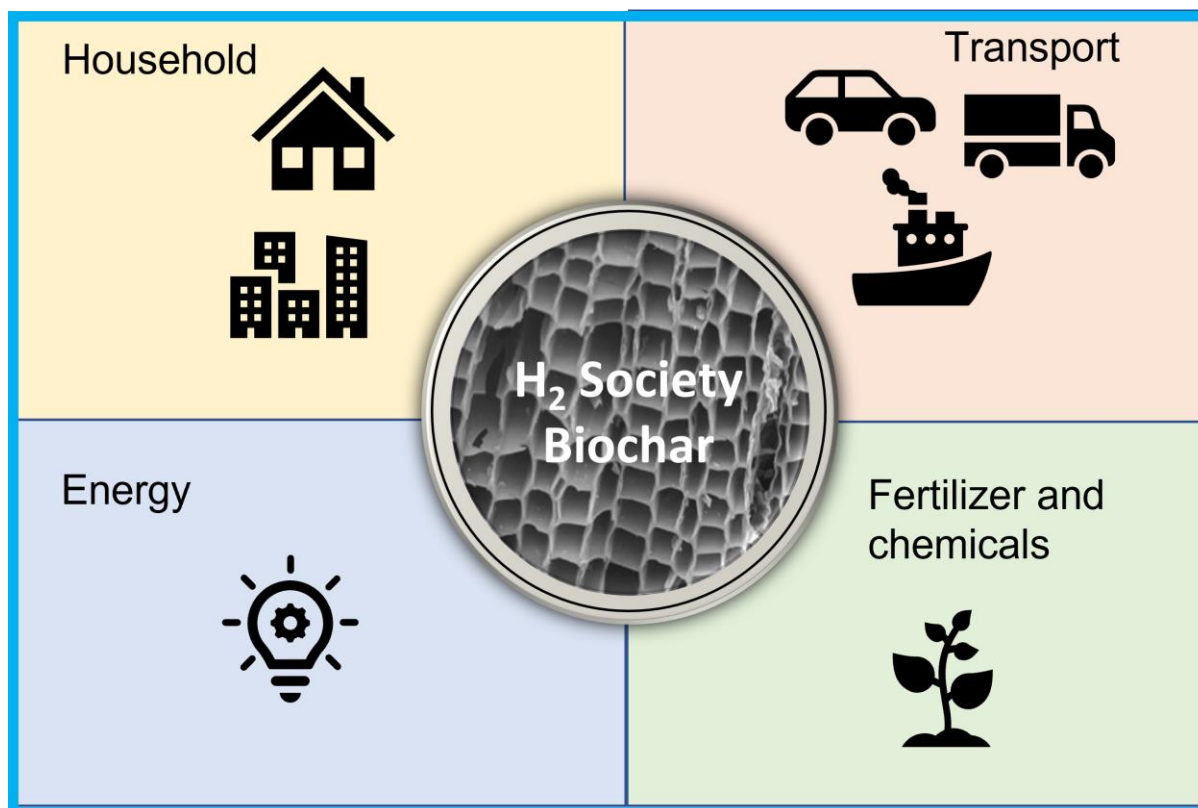
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Abstract

The concept of a “hydrogen (H₂) society” is meant to serve as a greener alternative toward fossil fuel utilization and mitigating the climate crisis. However, major challenges concerning sustainability in the production of H₂ need to be resolved to fulfill the development of a hydrogen society. Climate change cannot be mitigated while fossil fuels remain the primary source of H₂ production. The use of excess renewable energy to produce H₂ can also be economically challenging; moreover, difficulties in storage and transportation could render a hydrogen society infeasible. Biochar, being a renewable low-cost material, could be key toward resolving these challenges, by serving as feedstock for steam gasification, as a catalyst or catalyst support for thermochemical or photochemical processes, or as an additive for biochemical processes. This study examines the plausibility of the concept of an “H₂ society” and the role of biochar in making this a reality. Biochar helps improve H₂ production, being an effective catalyst due to its high surface area, porosity, conductivity, and stability. Its high H₂ storage capacity could facilitate effective stationary storage and transportation. The role of biochar in an H₂ economy is becoming clearer; however, developing effective biochar-based materials for H₂ production and storage is necessary.

Keywords: Biochar; Climate change; Hydrogen society; Renewable energy; Sustainability

Graphic for Table of Contents



1. Introduction

Increased carbon dioxide (CO₂) in Earth's atmosphere is contributing to a change in its climate due to the inexorably increasing anthropogenic consumption of fossil fuels^{1,2}. An increase in the world's population to a predicted 10 billion people by 2050 will lead to a further intensification of cheap fossil fuel consumption, leading to increasing undesirable concentrations of CO₂ in the atmosphere³. The Paris Agreement initiated in 2016 within the United Nations' Framework Convention on Climate Change (UNFCCC) was intended to maintain global warming well below 2 °C^{2,4}. Cutting CO₂ emissions fast enough to limit a global temperature rise of 2 °C is challenging; moreover, the current pace is considerably slow. Wind, solar, water, biomass, and nuclear energy are all part of the portfolio of sustainable energy resources to combat climate change, but have their challenges. For example, wind and solar are intermittent forms of energy. Hydropower is also variable, and, like biomass, water is necessary for sustaining the food supply chain. Use of nuclear energy is contentious due to the high hazard level during accidents; moreover, meticulously storing and processing the spent fuel is essential. Due to these challenges, H₂ is back in the spotlight after a twenty-year hiatus as a carbon-free fuel with similar attributes to traditional fossil fuels. Compared to other energy resources, H₂ is a panacea as it is clean, odorless, and non-toxic; most importantly, abundant sources are available for its production (Figure 1). It has become one of the most prized targets in the global new energy market, being shown to be a cost-effective alternative to bioenergy with carbon capture and storage⁵.

We review the current scenario and prospects of global H₂ production, cost of production, significance of production technologies, possible reduction in CO₂ emissions by using H₂, and the role of biochar technologies in an H₂ society. Extensive adaptation toward being an H₂ society will substantially cut anthropogenic emissions of CO₂; moreover, it could stabilize and reduce climate change more rapidly than is currently expected. The transformation to an H₂ society from conventional carbon societies would be smoothed out by biochar, which has not yet garnered adequate attention. The tunable properties of biochar could play an important and essential role in the next-generation H₂ society by replacing many of the expensive traditional materials in H₂ production and storage. Hence, this study aims to critically examine an H₂ society and the role of biochar. Biochar has been identified as a sustainable precursor for a low carbon society because of its potential to sequester carbon

and its proven qualities to substitute expensive aspects of an H₂ society, such as electrodes, catalysts, and storage devices⁶⁻⁸.

2. Global Production and Usage of H₂

Global H₂ production is currently about 65–100 million metric tonnes, and the value of the H₂ market in 2019 was approximately 117 billion US dollars, which is expected to reach 199 billion US dollars by 2023⁹. The leading suppliers in the global H₂ market are Air Liquide, Air Products and Chemicals, Hydrogenics, Messer Group, and the Linde Group¹⁰. With over 50% of the global supply being produced by these five companies, H₂ production is an oligopoly. In terms of H₂ production sources, half of the supply is delivered by the steam reforming of methane; another 30% is derived from industrial processes or oil refining; and the remaining 20% is sourced from coal gasification, water electrolysis, and other production methods. Globally, 95% of H₂ is produced from fossil fuels¹¹. The annual growth rate in H₂ production from 2018 to 2023⁹ has been forecasted to be at 8%. Currently, the captive use of H₂ accounts for >95% of the global production. Global H₂ consumption is increasing at a rate of 3%–4%¹² per annum; furthermore, it is expected to continue increasing as H₂ utilization penetrates wider energy markets.

H₂ is used in many industrial sectors due to its chemical composition, physical properties, and carbon-free nature. It is mostly used as an industrial feedstock, but is also a by-product of many industrial processes¹³ such as petroleum refinement (e.g. Fischer-Tropsch synfuel production), fertilizer and ammonia synthesis, food preparation, metal refining, and in fuel cells in electric vehicles. In agriculture, H₂ is used to produce ammonia, methanol, and cyclohexane, which are important inputs for agrochemical production. In the energy sector, H₂ is a flexible energy carrier to link different transmission and distribution systems. It can also be transformed into various energy forms such as electricity and heat for diverse applications in other sectors. In the power sector, H₂ is used to generate electricity in both centralized and decentralized systems. Many countries consider the transition from oil to H₂ as inevitable and have invested billions of dollars in H₂ projects¹⁴. The USA, European Union, and Japan have launched roadmaps outlining the role of H₂ in their future energy sectors¹⁵. Moreover, the government of Japan constructed the Olympic Village for the 2020 Tokyo Games as a model of an H₂ Society. Germany, USA, China, and Korea have been developing H₂ storage technologies to buffer wind and solar PV variability; H₂ fuel cells for

applications in road, rail, air, and shipping; and "piggy backing" as a fuel in industry for energy production; and as a feedstock and for building heating and power¹⁶. Since 2003, China has formed several H₂-based industry clusters to promote the development of H₂ fuel cell technology. Many other countries, including the UK and the USA, are also considering utilizing H₂ as a source of green energy in the future. Additionally, H₂ could play a significant role for heating systems in the building sector, consequently helping reduce fossil fuel consumption. The Hydrogen Council estimates that the use of H₂ could help facilitate a reduction of approximately 20% of global CO₂ by 2050¹⁶.

H₂ usage is expected to expand across a wide range of industries with the improvement of existing technologies and development of new technologies. Investment in H₂-based technology balances potential costs and risks with the prospect of achieving sustainable economic growth on the back of an increasing need for highly specific transport, storage, and end-use systems^{17,18}. While H₂ production technologies are evolving, industrial-scale utilization of H₂ is far from being developed¹⁹. If the widespread adoption of H₂ as a long-term sustainable energy solution is to be achieved, research and investment in both production and utilization technologies must be sustained.

3. H₂ Economy

Approximately 95% of H₂ is currently produced by the transformation of fossil fuels, which leads to annual CO₂ emissions of 500 million tons. This represents 2% of global energy-related CO₂ emissions²⁰⁻²². The full realization of H₂ as a clean, versatile, and efficient fuel is, therefore, subject to the sustainable use of resources for its production. An H₂ economy supported by renewable and locally available resources is particularly attractive due to the potential for saving transportation-incurred costs and emissions²³. H₂ production associated with renewable and sustainable energy resources in the form of storage during excess production is considered one of the most promising approaches toward achieving a cleaner environment and a sustainable energy future.

H₂-based energy technologies can serve as a transition mechanism when used in synergy with other renewable energy systems, as H₂ can be transformed into other forms of energy including steam, heat, and electricity. Hybrid systems consisting of renewable electricity generators and water electrolyzers can achieve a higher degree of power stability by using H₂ to store excess electricity and improve the balance between energy generation

and demand. This can mitigate the disadvantage of intermittent power generation from wind and solar energy over diurnal and annual cycles²². Where grid supply is disrupted, hybrid electricity supply systems incorporating H₂ storage and fuel cells are able to maintain both electricity and H₂ supply to essential and critical services²⁴.

4. H₂ -based Transport

The transport sector is one of the biggest consumers of fossil fuels and accounts for around 27% of global greenhouse gas (GHG) emissions²⁵. Moreover, fossil fuel powered transport is a major cause of urban air pollution (e.g., particulate matter (PM), nitrogen oxides (NO_x), sulfur oxides (SO_x), and ozone (O₃)). In 2010, land traffic related PM_{2.5} and O₃ emissions were associated with over 163,000 premature deaths worldwide²⁶. The 2015 United Nations Climate Change Conference (COP21) urged for increased adoption of low carbon technologies in the transport sector to meet the sustainable development goals (SDGs). To address this, the International Energy Agency (IEA) estimated that the transport sector would undergo a transition from oil to alternative energy sources²⁷.

H₂ can be used to power internal combustion engines or fuel cells to enable automotive applications with high energy-conversion efficiencies and pollution-free electricity production²⁸. For example, proton exchange membrane (PEM) fuel cells can achieve efficiencies of 63% and an overall system efficiency of 35%²⁹. The latest H₂ fuel cells are three times more efficient than gasoline engines³⁰. Different types of fuel cells are associated with different efficiencies; the efficiencies of alkaline, phosphoric acid, polymer electrolyte membrane, molten carbonate, and solid oxide fuel cells are known to be 70%, 85%, 60%, 85%, and 85%, respectively³¹. However, despite the gravimetric energy density of H₂ being 2.6 times higher than that of gasoline, the volumetric energy density of H₂ is only quarter that of gasoline. This means that, in comparison to gasoline powered vehicles, considerably large volumes of H₂ are needed over the same driving range for H₂ powered vehicles. Hence, it is necessary to address this technical and economic drawback in transporting and using H₂, which could otherwise undermine the successful transition from a carbon-intensive to a low (or zero) carbon transport sector. Mobile H₂ stations are one of the many potential solutions already implemented in countries such as Japan, UK, and USA³². Hence, having efficient H₂ storage and transport facilities is more essential, for which biochar would be an outstanding candidate.

5. H₂ Costs

Capital cost components of H₂ production include H₂ production equipment, storage tanks, compressors, pipes, pumps, ancillary equipment, dispensers (for refueling stations), and construction. Typical operating costs include those for electricity, staff costs, equipment maintenance, replacement, water, land, and natural gas.

Component sizing is key to determining the economic viability of H₂-based systems. Oversized devices not only lead to excess energy conversion, but also increase the costs of operation, maintenance, and decommissioning; moreover, they have numerous associated life cycle environmental impacts³³. Centralized H₂ production systems are generally more economically viable than smaller, distributed ones. For example, a 2 MW polymer electrolysis-based plant using renewable energy to produce H₂ for distribution by tube trailers could potentially achieve a 9-year pay-back period with a net present value (NPV) of 1.2 million EUR³⁴. In addition to the electrolyzers, such a system involves four 150 m³ containers that can store around 1,800 kg of H₂ at generation pressure, a membrane compressor to increase the H₂ pressure from 10 to 250 bar, and tube trailers with a capacity to transport 367 kg of H₂ each. The estimated NPV considers the filling of the tube trailers but not the transport distance. For centralized H₂ production, H₂ delivery is one of the major contributors to overall costs, energy consumption, and emissions. Alternatively, in distributed H₂ production, transportation costs are reduced by approximately 22–45 EUR/MWh-H₂³⁵. Distributed H₂ production in areas with accessible sources of biomass or suitable industrial by-product streams will reduce energy use, pollutant emissions, and transport costs for the raw materials. The typical H₂ demand of a small industrial process (e.g., food, glass, or metal production) is around 1,000 Nm³/h³⁶. The development of an H₂ economy with a national distribution system is time-consuming; however, relevant development can be initiated by utilizing local, small H₂ generators for both stationary and mobile applications.

The economic feasibility of H₂ production is also contingent upon technology selection. The H₂ production costs of various technologies are shown in Figure 1. With a conversion efficiency of 74%–85%, steam methane (CH₄) reforming is expected to be the most economical method for centralized large-scale H₂ production in the coming decades, with costs closely associated with the availability of natural gas^{22,34,37}. Large-scale H₂ production costs could be <1 USD/kg; however, costs could increase to approximately

8 USD/kg if the scale of production decreases to approximately 300 Nm³/h (Figure 1), which is not economically viable. For a steam reforming system with an H₂ production rate <20,000 Nm³/h, H₂ production costs are higher than that for gasoline, 2.82 USD/kg (cf. dashed line in Figure 1). For example, the cost of producing H₂ of a small-scale steam reforming system with a capacity of 1,000 Nm³/h has been estimated to be 117 EUR/MWh (4.44 USD/kg)³⁸. In this system, natural gas is supplied into a reformer to produce H₂ and CO, and is then passed through a water-gas shift reactor, with a high-temperature shift at 723 K and a low-temperature shift at 493 K, which consumes CO while producing additional H₂. H₂ is subsequently separated from the product gas in a pressure swing adsorption (PSA) unit with a recovery rate of 0.9; thereafter, the remaining PSA off-gas is burned with additional natural gas to supply heat energy to the reformer.

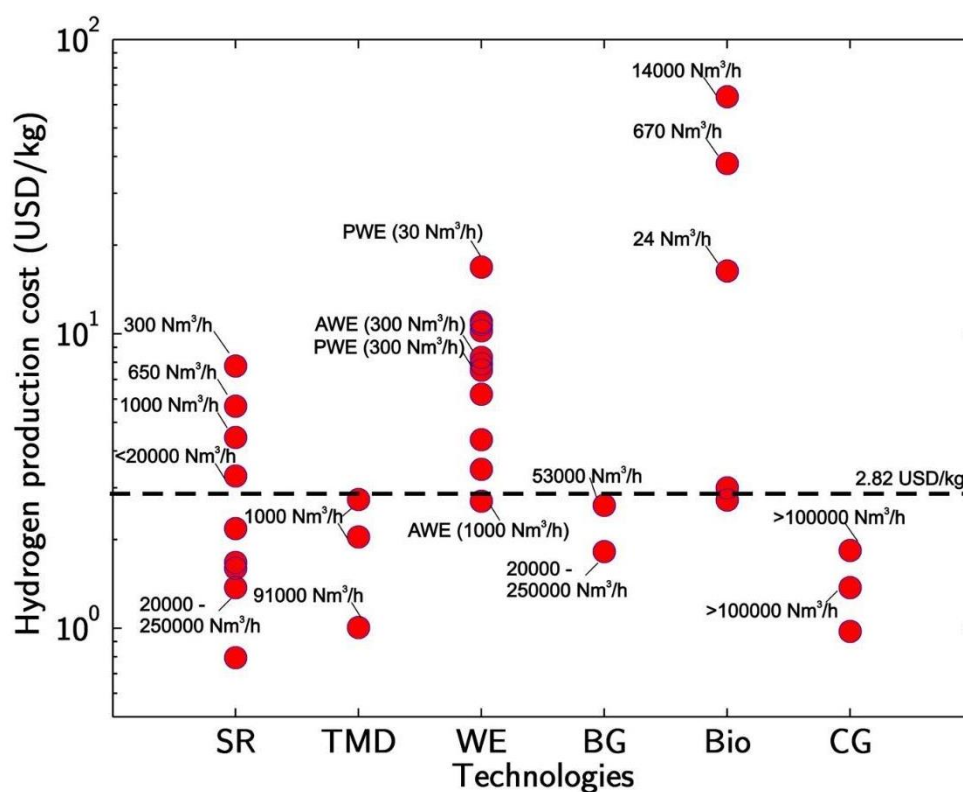


Figure 1. H₂ production costs of various technologies^{13,37,39–49}. All costs were converted to 2018 values considering the inflation rate of the original currency (EUR or USD), and EUR values were converted to USD considering an exchange rate of 1.14. The dashed line denotes the H₂ price calculated based on a gasoline price of 1 USD/kg and an equivalent energy content between H₂ and gasoline. H₂ production capacities are denoted in terms of Nm³/h.

PWE and AWE denote PEM water electrolysis and alkaline water electrolysis, respectively; SR = steam reforming; TMD = thermal CH₄ decomposition; WE = water electrolysis (splitting); BG = biomass gasification; Bio = biochemical methods; and CG = coal gasification.

Thermal methane decomposition is generally more cost effective than steam methane reforming for small or medium scale on-site H₂ production; however, its economic viability depends on the market value of carbon, i.e., it is economically competitive with steam methane reforming if the market value of carbon is higher than 280–310 EUR/tonne³⁷. The cost of H₂ production from thermal methane decomposition has been shown to be comparable to that of large-scale steam methane reforming with a carbon value of 200 USD/tonne and a carbon tax of 78 USD/tonne⁵⁰.

The economics of H₂ production by water electrolysis greatly depends on the cost and availability of electricity^{34,45}. With electricity costs as low as 10 EUR/MWh, water electrolysis is a less expensive method to produce H₂ than steam methane reforming with a natural gas cost >16 EUR/MWh³⁷. The H₂ production from alkaline water electrolysis in systems with production capacities of H₂ >1000 Nm³/h is potentially competitive with gasoline production (Figure 1). For example, the H₂ cost of an alkaline electrolysis-based system with a capacity of 1000 Nm³/h was estimated at 71.1 EUR/MWh (7.2 USD/kg)³⁸. This system was associated with a capital expenditure (CAPEX) of 1000 EUR/kW and an O&M cost of 3% of the CAPEX, as well as an energy consumption rate of 52 kWh/kg-H₂. The unit capital cost of water electrolysis systems will decrease as production volumes increase and as supply chains are developed. A limited supply of low-cost renewable electricity (e.g., 10–30 EUR/MWh) reduces the viability of H₂ production by water electrolysis and, as such, is considered unsuitable for demand-driven H₂ production³⁷.

New strategies have been developed to utilize low-priced curtailed electricity or off-peak electricity from renewable energy sources for more economically viable H₂ production by water electrolysis. The H₂, in this case, serves as an electricity storage method to reduce the peak electric load, stabilize the electricity grid, and raise the grid capacity factor. For example, in China, the life cycle costs of H₂ production by water electrolysis using curtailed electricity are 0.97 USD/kg-H₂ when H₂ is used as a chemical material, 0.1226 USD/kWh

when it is used to power vehicles with a polymer electrolyte membrane fuel cell, and 0.1273 USD/kWh when it used as a fuel for combustion engines⁵¹.

This analysis considered three phases involved in the H₂ supply chain, i.e., H₂ production, storage, and utilization. H₂ was produced by water electrolysis (3 MPa; 353 K) and then compressed (1 kWh/kg-H₂) and stored in a steel composite vessel at 24.82 MPa, followed by final utilization in a chemical plant or gas station. The costs of H₂ production with off-peak electricity ranged from 3 to 3.5 EUR/kg-H₂ for three European countries (i.e., France, Germany, and Spain)⁵². However, if H₂ production solely relies on off-peak electricity that is designated by a threshold price, a larger electrolysis capacity is needed under a lower threshold price to meet a given H₂ demand⁵³.

The economic viability of H₂ production from biomass gasification depends on the price of biomass and CO₂ emission. Assuming a price of 100 USD/tonne of Canadian pine wood, a 630 MW biomass gasification (fluidized bed or entrained flow) plant (with carbon capture and sequestration (CCS)) was shown to be economically competitive with a commercial steam methane reforming plant, assuming that the price of CO₂ was higher than 115 USD/tonne or that the price of natural gas was higher than (with CCS) 5 USD/GJ⁵⁴. In addition to gasification reactors, the plant also involved a tar reformer unit, sulfur recovery technology (LO-CAT and ZnO bed units), a water gas shift reactor to convert CO to H₂, a scrubbing amine unit to remove CO₂, and a PSA H₂ recovery unit. Figure 1 shows that the cost of H₂ production in large-scale biomass gasification is comparable with conventional steam reforming and coal gasification. The gasification of biomass or waste streams is expected to become the cheapest method for renewable H₂ production in the coming decades. Gasification-based H₂ production could achieve further cost reductions with the introduction of new processing routes, especially catalytic ones⁵⁵. Combining catalytic biomass gasification with solid oxide fuel cells in decoupled or direct mode can support particularly high-efficiency (>70%) electricity production⁵⁴.

Biochemical methods (e.g., biophotolysis, dark fermentation, and photo-fermentation) are less energy and investment intensive approaches; however, their viability is contingent upon higher production rates and improved conversion efficiencies²². Unlike other technologies, the production costs of biochemical methods increase as production capacity increases because of substantial additional capital costs (e.g., that for larger tanks).

Biochemical methods may be most suited for small-scale distributed deployment, where biomass and industrial by-product streams are easily accessible.

6. Global Warming Potential (GWP) of H₂ Technologies

The GWP considering the steam reforming of natural gas varies from 8.9 to 12.9 kg CO₂-eq./kg-H₂⁵⁶. Total global CO₂ emissions from natural gas derived H₂ production are strongly affected by CH₄ leakage in the natural gas supply chain (e.g., well site, gas processing, transmission, storage, and distribution). If the leakage rate is assumed to be 7.9%, then the steam reforming of CH₄ for use in an internal combustion engine would lead to a net increase in global CO₂-eq emissions of 19–27%⁵⁷ (cf. Figure 2). The on-site CO₂ emissions from H₂ production by CH₄ thermal decomposition and steam CH₄ reforming with carbon dioxide capture from syngas has been reported to be between 40 kg/MWh-H₂ and 133 kg/MWh-H₂³⁷.

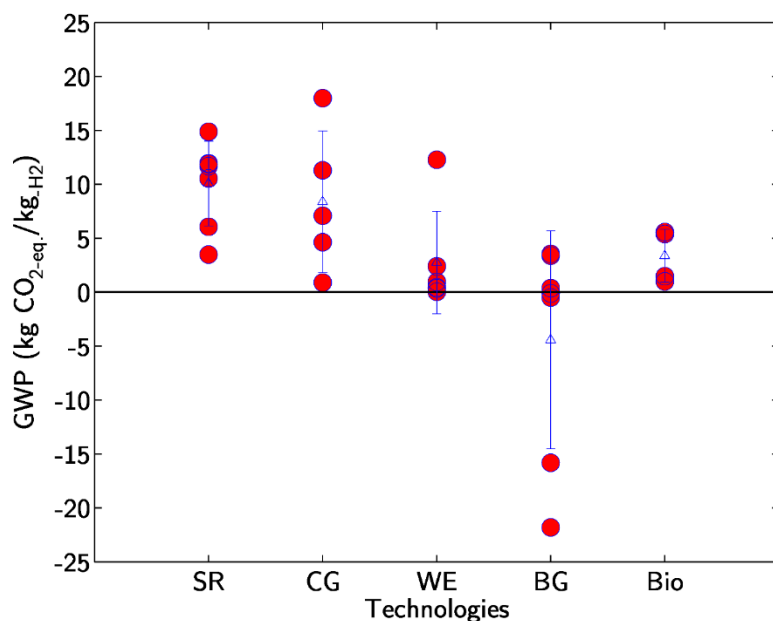


Figure 2. Global warming potential (GWP) of various H₂ production

technologies^{12,38,54,58–67}. SR = steam reforming; CG = coal gasification; WE = water electrolysis (splitting); BG = biomass gasification; and Bio = biochemical methods. The triangles and error bars denote the average values and standard deviations, respectively.

Up to 60% of the overall CO₂ emissions from steam CH₄ reforming can be sequestered when CO₂ is captured from syngas²¹; although, energy consumption while

capturing CO₂ could reduce the energy efficiency somewhat⁶⁸. In comparison, downstream carbon capture can help increase fossil fuel consumption by as much as 39%, reduce the efficiency by 18%, and increase the minimum H₂ selling price by 1.1 USD⁵⁴.

The GWP of water electrolysis based H₂ production depends on the source of electricity and the types of cells. For example, if fossil fuel is burned to produce electricity to power a diaphragm cell, membrane cell, or mercury cell electrolysis, then the associated GWP values are 0.9090, 0.8872, and 1.0510 kg CO_{2-eq}/kg-H₂, respectively⁶¹. Using renewable wind or solar based electricity for mercury cell electrolysis decreases the GWP to 0.032 and 0.37, respectively⁵⁶. Biomass gasification can potentially serve as a carbon-negative solution for H₂ production, given the atmospheric carbon-capturing nature of plants, the co-production of electricity to offset non-renewable grid electricity use, and the use of CCS techniques⁵⁴ that can reduce the GWP by 15–20 kg CO_{2-eq}/kg-H₂. However, CCS could reduce the biomass gasification thermal efficiency by 4%–6%, which could drive the minimum price of H₂ up by 11%⁵⁴. Overall, renewable energy based H₂ production has a lower GWP than conventional fossil fuel based approaches. Biomass gasification offers one of the best solutions for H₂ production considering the economics and carbon emissions. Including CCS in thermochemical and biochemical H₂ production systems can effectively reduce the GWP; however, further research is warranted to mitigate the impacts of CCS on energy efficiency, and thus, determine economic viability.

7. H₂ Production Technologies and Future Prospects

H₂ production technologies with high efficiency, low environmental footprints, and low cost are essential for securing an H₂ economy. Currently, four major production technologies have been developed to varying extents, each with their own pros and cons: (1) thermochemical processes; (2) electrolytic processes; (3) photolytic processes, and (4) biological processes^{69–71}.

First, thermochemical processes refer to the release of H₂ from fuel resources such as coal, natural gas, biomass, and water via thermochemical reactions. Specifically, coal is utilized to produce H₂ through gasification⁷², where a clean coal technology, rather than combustion, is utilized in a conventional coal-fired power plant. Coal gasification typically involves partial oxidation with oxygen (O₂) and steam at high temperature and pressure. This generates synthesis gas (syngas)—a mixture of carbon monoxide (CO), H₂, water vapor, and

CO₂. Syngas further undergoes a water-gas shift reaction ($\text{H}_2\text{O} + \text{CO} \leftrightarrow \text{H}_2 + \text{CO}_2$) to produce more H₂ from CO and steam, followed by high-concentration H₂ recovery via gas separation processes. Owing to the wide availability of coal and coal-processing infrastructure, the cost of generating H₂ from coal is the lowest among the currently available technologies. Consequently, this technology could facilitate and dominate the transition to an H₂ economy. However, for large-scale deployment, further advancements are needed, such as: (1) robust sulfur-tolerant catalysts for water-gas shift reactions⁷³; (2) better gas separation technologies to purify H₂ and capture CO₂ as well as other impurities⁷⁴; and (3) processes that enable combined water-gas shift reactions and H₂ separation process⁷⁵.

Natural gas can also be used to produce hydrogen either via steam reforming ($\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2$), partial oxidation or both in sequence (autothermal reforming), leading to a mixture of CO, CO₂, and unreacted CH₄⁷⁶. A further water-gas shift reaction converts CO and steam into H₂ and CO₂. Separation of H₂ from this gas mixture produces clean H₂. Compared with the coal-based process, the use of natural gas (mainly CH₄) results in much lower CO₂ emissions owing to its higher hydrogen-to-carbon ratio. Moreover, the wide availability and ease of handling natural gas make it viable for distributed H₂ generation (e.g., fueling stations) as well as for centralized generation. Technical and scientific challenges that require further research before scaled-up applications could be realized (given it is currently more expensive than using coal) include developing better gas separation technologies to extract O₂ from air⁷⁷ for partial oxidation, and separating H₂ from nitrogen (N₂).

Through thermal CH₄ decomposition, CH₄ is cracked into carbon and H₂ at temperatures above 700 °C ($\text{CH}_4 \leftrightarrow \text{C} + 2\text{H}_2$)⁷⁸. There is zero direct CO₂ emission from this process, and the carbon produced serves as a valuable co-product that can be used, for example, by the rubber industry, which potentially enhances the economics of H₂ production by such methods. Production of H₂ from biomass can be achieved via gasification or pyrolysis of biomass followed by steam reforming⁷⁹. The biomass itself can be obtained from dedicated bioenergy crops. The significant land area requirements for cultivating biomass feedstocks, and the high price associated with their production, harvest, and transportation, render the cost of H₂ generated from biomass much higher than that derived from coal or natural gas. The additional environmental impacts caused by biomass production are further disadvantageous to its use in H₂ production. An attractive advantage of biomass lies in the net reduction of carbon emissions because the growth of biomass captures atmospheric carbon.

This makes co-firing of biomass with coal a promising technology when combined with coal gasification for H₂ production. Furthermore, the use of agricultural biomass waste, such as food crop residues, could be incorporated into H₂ production, which limits the environmental impacts in using dedicated energy crops⁸⁰. The efficiency of biomass gasification to produce H₂ is only 14%–17%; although, metal catalysts, such as platinum (Pt) and rhodium (Rh), can increase the efficiency by up to 60%⁸¹.

The second main type of H₂ production technology based on electrolytic processes produces H₂ by splitting water into its separate constituents (i.e., O₂ and H₂) using electricity⁸². Depending on the source of electricity, this technology can potentially produce H₂ with zero emissions of greenhouse gases or air pollutants. For example, renewable wind and solar energy can be used to generate clean electricity for water electrolysis. Moreover, given the variable and intermittent nature of wind and solar energy, a more stable energy source could be achieved by incorporating water electrolysis. For example, electrolytic technologies may be appropriate for use in service and fueling stations to facilitate the early stage of fuel requirement, offering clear advantages for distributed production in an H₂ economy⁸³. Water electrolysis itself is a relatively mature technology that has been exploited for decades to meet industrial chemical needs. However, it remains more expensive than the steam reforming of natural gas.

Current electrolysis technologies use either solid oxide electrolyser cells (SOECs) or solid polymers with a PEM or liquid electrolyte, most commonly potassium hydroxide. High temperature electrolysis has garnered much interest in recent years⁸⁴. For example, compared with low temperature PEM and alkaline electrolyzers, high temperature SOECs can produce H₂ with a higher chemical reaction rate with less electrical energy⁸⁵. Lower electrode overpotentials with less power loss is another advantage of this approach. However, despite high temperature SOECs reducing the overall cost of H₂ production, this requires additional capital expenditure and increased heat energy use. The development of electrolysis fueling devices could be improved by developing more efficient systems designed to limit parasitic energy losses. For example, this is achievable by using additional electrolyte in substations and increasing the cell surface area to reduce the current density, or by developing new design concepts, such as the promising electrolysis/oxidation hybrid approach⁸⁶. Moreover, the reducing trend in the cost of electricity generation from wind, nuclear, waste heat, and solar energy is helping increase the environmental sustainability of electrolytic processes.

Along with reducing the economic cost of H₂ production, developing new methods to safely and cost-effectively store H₂ on a small scale are also essential if electrolytic technologies are to be adopted more widely.

The third technology for producing H₂ based on photolytic processes involves using light energy to split water into O₂ and H₂, which is achieved via three processes. (1) Photobiological water splitting: this employs photosynthetic microorganisms, such as green algae and cyanobacteria, that facilitate the direct oxidative cleavage of the water molecule⁸⁷. H₂ production using this approach is in the nascent stages of research, but has great potential as a highly efficient and sustainable emerging technology. (2) Photo(electro)catalytic water splitting: this uses specialized semiconductors that absorb sunlight energy to separate water molecules^{69,88}. This technology is in the early stage of development; however, there is considerable ongoing research effort to develop new, durable, and high-efficiency photo(electro)catalytic semi conductors⁸⁹. (3) High-temperature solar H₂ production: here, solar radiation is focused on a solar receiver, and a temperature above 1500 °C is achieved. The solar heat is utilized to produce H₂ via thermochemical water splitting. Although this technology has been in existence for decades, it continues to face challenges preventing its practical deployment^{84,90-92}. For example, the high thermal flux density and frequent thermal transitions caused by fluctuating insolation render it unsuitable for conventional industrial thermochemical processes. Interruption by cloud cover and the fact that this approach cannot be utilized at night is another important limitation of this technology, meaning that coupling this technology with other types of thermochemical water-splitting may be necessary. Biohydrogen production has also been proposed as a potential route to sustainable H₂ production involving direct photolysis, dark fermentation, and photo-fermentative processes. As per photobiological water splitting, direct photolysis involves photosynthetic reactions wherein solar energy is converted into chemical energy by microorganisms such as green algae and cyanobacteria⁹³. The reaction pathway is $2\text{H}_2\text{O} + \text{light energy} \leftrightarrow \text{H}_2 + \text{O}_2$. In this process, water molecules are split into H₂ ions and O₂ through photosynthesis, and the H₂ ions are converted into H₂ gas by hydrogenase enzymes⁹⁴. The use of water as a primary feed resource is the most remarkable advantage of direct photolysis⁹⁵. However, the O₂ generated can affect O₂ sensitive photosynthetic microorganisms, thus hindering H₂ yields⁹⁶. The removal/separation of O₂ is therefore important for efficient H₂ production. Moreover, safety concerns must be considered because H₂ and O₂ are produced together. Dark-fermentative H₂

production exploits primarily anaerobic bacteria or algae to convert biomass into H₂ under dark conditions^{97,98} at a temperature that could range from room temperature to >80 °C^{99,100}. The H₂ yield depends on the pH, hydraulic retention time (HRT), and gas partial pressure^{93,101}. Biomass feeds should be easily biodegradable, carbohydrate rich, and inexpensive. Industrial wastes and wastewater sludges have been suggested as possible feeds for dark fermentation; however, this requires pre-treatment and multi-step conversion⁹⁶. Photo-fermentative processes exploit the nitrogenase functionality of photosynthetic non-sulfur (PNS) bacteria (e.g., *Rhodobacter sulfidophilus* and *Rhodospseudomonas palustris*)^{99,102}. Here, PNS bacteria convert organic acids, e.g., acetic, lactic, and butyric acids, into H₂ and CO₂ under light irradiation. An advantage is that the reaction does not require spontaneous external energy input, in the form of light, as there is a positive free energy change^{103,104}. The disadvantages include: (1) the high-energy demand of the nitrogenase enzyme; (2) the low efficiency of solar energy conversion; and (3) the limited availability of organic acids. Overall, technical and economic challenges hinder the adoption of biological H₂ production technologies as they remain in the early stage of development for industrial application. The major challenge is the sustainable production from different substrates. Moreover, the technical problems in production systems, such as process inhibition, optimization, and storage are limiting large-scale production, which warrants further exploration¹⁰⁵. Clarifying the best method for H₂ production is challenging, as all have their advantages and shortcomings, and as they need to be established as prominent methods for providing adequate amounts of H₂ for a developing H₂ society⁹⁶.

8. Opportunities for Biochar Technology in H₂ Production

Biochar is a by-product of the thermal decomposition of biomass (e.g., wood waste, crop residues, and bio-wastes) in oxygen-limited environments via different pyrolysis techniques such as slow pyrolysis, fast pyrolysis, or gasification. Slow pyrolysis and gasification provide the highest biochar and syngas yields, respectively. Generally, biochar from plant residues contains over 60% carbon, with more than a 1000 years of potential residence time in the natural environment, contingent on the production conditions such as high temperature. It is the unique and tunable properties of biochar, such as its surface area, pore volume, pore size, pH, cation exchange capacity, electrical conductivity, and surface

functional groups, as well as its comparatively easy production and low cost, which are leading to biochar being exploited across diverse disciplines¹⁰⁶.

Biochar was first used to improve soil quality more than 2000 years ago in the Amazon basin. Presently, biochar is principally used for improving soil fertility; however, we have also discovered new modern applications for biochar, such as for use in carbon sequestration, soil and water remediation, and in building materials. Biochar also presents an alternative to high-cost materials for H₂ production.

H₂ enriched syngas

H₂ is a component of syngas, which can be enhanced by employing biomass gasification, with steam as a gasifying agent¹⁰⁷. Catalytic activity has been reported to increase the H₂ content of syngas by 60%–70% vol. in bench-scale fixed bed and pilot-scale fluidized bed systems^{108,109}. Nickel-based catalysts reduce the production of tar by cracking and reforming, and demonstrate good catalytic activity; moreover, they are associated with low operational costs¹¹⁰. The catalytic activity of lanthanum and cerium-based catalysts can lead to over 82% H₂ production by steam gasification of bio-oil and biochar slurry¹¹¹. Additionally, biochar steam gasification has been reported to produce H₂ rich syngas. Bagasse biochar and commercial biochar steam gasification at 700 °C with a steam flow rate of 1.25 g h⁻¹ g⁻¹ produced 76.2 mol% and 71.1 mol% of H₂ in syngas, respectively¹¹². Water-gas shift reactions at 700–750 °C during steam gasification of biochar maximized H₂ production¹¹³. Alumina (Al₂O₃) can be used as a supporting material for catalysts, mainly due to its physicochemical stability and mechanical properties. Additionally, calcium oxide (CaO), silicon dioxide (SiO₂), magnesium oxide (MgO), ferric oxide (FeO₃), and potassium oxide (K₂O) can also be used as catalyst supports^{110,114,115}. Catalyst supports could possibly be replaced in a metal-based catalyst with biochar, which has relatively high stability compared to the abovementioned compounds¹⁰⁷.

Having a relatively high surface area and porous structure, biochar has been reported as an efficient catalyst in many reactions, including tar cleaning from syngas, conversion of syngas to liquid fuels, gas reforming reactions, transesterification reactions, and oil extraction^{106,116–118}. Biochar-based metal catalysts have also been successfully applied in H₂ production based on steam reforming of bio-oil. Impregnating lignocellulosic biomass with a nickel nitrate (Ni(NO₃)₂) solution reportedly helps increase H₂ yields (57–91%) and decrease

tar production (60–70%)¹¹⁹. These observations represent the simultaneous and *in situ* generation of nickel-biochar nanoparticles, which poses significant catalytic activity for H₂-rich syngas production from biomass gasification and tar reforming. Several biochar-Ni catalysts have also been produced by impregnating wheat straw, rice husk, and cotton stalk biochars with Ni¹²⁰. Using steam reforming, the highest H₂ production rates were obtained using a cotton stalk biochar-Ni catalyst (64 vol.% and 92 mg g⁻¹ of biomass)¹²⁰. The interaction between volatiles and biochar has been shown to enhance the reforming of volatiles during biomass pyrolysis. Moreover, the highest catalytic activity of cotton stalk biochar-Ni resulted from the comparatively high proportion of alkali and alkaline earth metals, which enhanced the interactions with volatiles¹⁰⁷. It has been suggested that the presence of large amounts of alkali and alkaline earth metals is more important than biochar's large surface area for increasing catalytic activity^{121,122}. Moreover, these metals in biochar could enhance gasification by adsorption of water¹²¹. Hence, a complex biochar matrix, comprising multiple inorganic compounds, could further enhance catalytic activity during gasification and CH₄ reforming. Additionally, co-gasification of methane-biomass with catalytic support has led to high H₂ production (63–82 vol.%), with significantly low CO (10–19 vol.%), CO₂ (0.8–5 vol.%), and CH₄ (0.7–4 vol.%) production¹²³. Biochar based metal catalysts are a potentially cheaper alternative to the catalysts traditionally used in co-gasification. Furthermore, biochar has been applied as a catalyst in coal gasification¹²⁴ and in steam reforming of natural gas¹²⁵ (Table 1).

Table 1: Biochar applications in H₂ production and storage

Feedstock	Biochar production methods	Modification	Application	Performance	Reference
Bagasse	Fast pyrolysis	-	Biochar steam gasification	In synthesis gas H ₂ was 71.1-76.2 mol % at 700 °C and steam flow rate of 1.25 g h ⁻¹ g ⁻¹	¹¹²
Wheat straw	Fast pyrolysis at 500 °C	In situ Ni impregnation during biomass gasification	Catalyst/support for biomass gasification	H ₂ yield was 63 vol.%, 41 mg g ⁻¹ biomass	¹⁰⁷
Cotton stalk	Fast pyrolysis at 500 °C	In situ Ni impregnation during biomass gasification	Catalyst/support for biomass gasification	H ₂ yield was 64 vol.%, 92 mg g ⁻¹ biomass	¹⁰⁷
Rice husk	Fast	In situ Ni	Catalyst/support for	H ₂ yield was 39 vol.%, 36	¹⁰⁷

	pyrolysis at 500 °C	impregnation during biomass gasification	biomass gasification	mg g ⁻¹ biomass	
Pinewood	Pyrolysis at 650 °C	-	Two-phase anaerobic digestion of food waste	Cultures statured to produce H ₂ at 35 °C after 12 hr with application of 10 g ⁻¹ biochar and came to plateau on day 3, without biochar it came to plateau on day 7 at 52 °C	¹²⁶
Peanut root nodules	Pyrolysis at 600, 700, 800 and 900 °C	In situ modification with MgCl ₂ , washed with 1 M HCl	Electrocatalytic H ₂ evolution	Best performance Peanut root nodules 800 °C: onset potential -0.027 V, 59.4 mA/cm ² at -0.2 V vs. reversible H ₂ electrode, b=67.8 mV/dec, and better than the metal electrocatalysts	¹²⁷
Sucrose	Pyrolysis at 800 °C	In situ N doping (dicyandiamide)	Electrocatalytic H ₂ evolution	Onset potential of -0.241 V	¹²⁷
Sucrose	Pyrolysis at 800 °C	In situ N and S doping (thiourea)	Electrocatalytic H ₂ evolution	Onset potential of -0.135 V	¹²⁷
Sucrose	Pyrolysis at 800 °C	In situ S doping (S powder)	Electrocatalytic H ₂ evolution	Onset potential of -0.041 V	¹²⁷
Pine needles	Pyrolysis at 600 °C	KOH modification at 700-900 °C	Electrocatalytic H ₂ evolution	Onset potential: 4 mV; Tafel slope: 45.9 mV dec ⁻¹	¹²⁸
Willow catkins	Pyrolysis at 600 °C	Pyrolysis with cobalt(II) acetylacetonate at 700-900 °C	Electrocatalytic H ₂ evolution	Overpotential of 0.21 V for 10 mA cm ⁻²	¹²⁹
Corncob	Pyrolysis at 450 °C	Activated with KOH, K ₂ CO ₃ , or NaOH at 850 °C	H ₂ storage	H ₂ storage capacity: 2.0 wt% at 77 K; 0.6 wt% at 298 K	¹³⁰
Wood	Pyrolysis	In situ modification with H ₃ PO ₄ and after pyrolysis modification with KOH	H ₂ storage	H ₂ storage capacity: 0.8 wt% at 298 K, under 2 MPa	¹³¹
Coffee beans waste	Pyrolysis at 500 °C	KOH modification at 850 °C	H ₂ storage	H ₂ storage capacity: 4.0 wt% at 77 K; 0.6 wt% at 298 K	¹³²

H₂ enriched biogas

Anaerobic digestion of biomass solids using biochar is a promising non-polluting and renewable process, which has been shown to increase H₂ production and generate an H₂-enriched biogas with improved ignition quality. However, its use on a commercial scale

requires further optimization to maximize stability, yield, and the avoidance of H₂ production inhibition¹³³. Biochar use in the anaerobic digestion of organic municipal solid waste was found to increase biofilm formation and colonization by *Enterobacter aerogenes* and *Escherichia coli*, which was associated with enhanced H₂ production¹³⁴. Furthermore, biochar provided growth surfaces for H₂ producing bacteria in the two-phase anaerobic digestion of food waste. This led to the production of H₂ and CH₄ in the first and second phases, respectively, and H₂-enriched biogas¹²⁶. Biochar application shortened the lag time and increased fermentative H₂ production by buffering the pH drop. Biochar produced at a high pyrolysis treatment temperature with characteristic high alkalinity, surface area, and ash content facilitated the greatest improvement in fermentative H₂ production¹³⁵. Biochar also inhibited ammonia emissions via retaining and promoted biofilm formation to increase H₂ production¹³⁶. Moreover, abundant redox active moieties (e.g., quinones and phenazines) on the biochar surface facilitated an increase in the interspecies electron transfer during anaerobic digestion, which revealed a significant role in H₂ production¹³⁷.

Water splitting

Biochar can be used as an electrode material¹³⁸ and electrocatalyst¹³⁹ for water splitting by electrocatalytic methods (Figure 3). Electrocatalysts reduce the overpotential and high catalytic current densities in an H₂ evolution reaction (HER). High performance electrocatalysts for an HER could be created by doping catalytically active elements such as nitrogen and sulfur in biochar¹²⁷. For instance, biochar produced from *Camellia japonica* flowers, which was rich in S, was proved to be a catalyst for water splitting due to its enhanced electron-transfer ability and long-term durability. Furthermore, the biochar-based electrodes were highly stable, and performed both in an HER and O₂ evolution reaction (OER) at 10 mA cm⁻² with overpotentials of 154 and 362 mV, respectively. Additionally, an Ni foam loaded with biochar-based nanocomposite derived from watermelon peels and CoCl₂ at 700 °C revealed high activity for both the HER and OER in a 1 M KOH solution. The water-splitting voltage of biochar-based electrodes was lower (i.e., 1.54 V) than the commercial electrode of RuO₂//Pt/C (i.e., 1.62 V). henceforth, biochar-based electrodes holds good efficiency of electrocatalytic H₂ production¹⁴⁰. However, these technologies remain in their infancy, and further research is warranted to improve the H₂ production efficiency.

Other emerging research has shown that biochar can also be used as a substrate for algae in H₂ production based on photobiological water splitting.

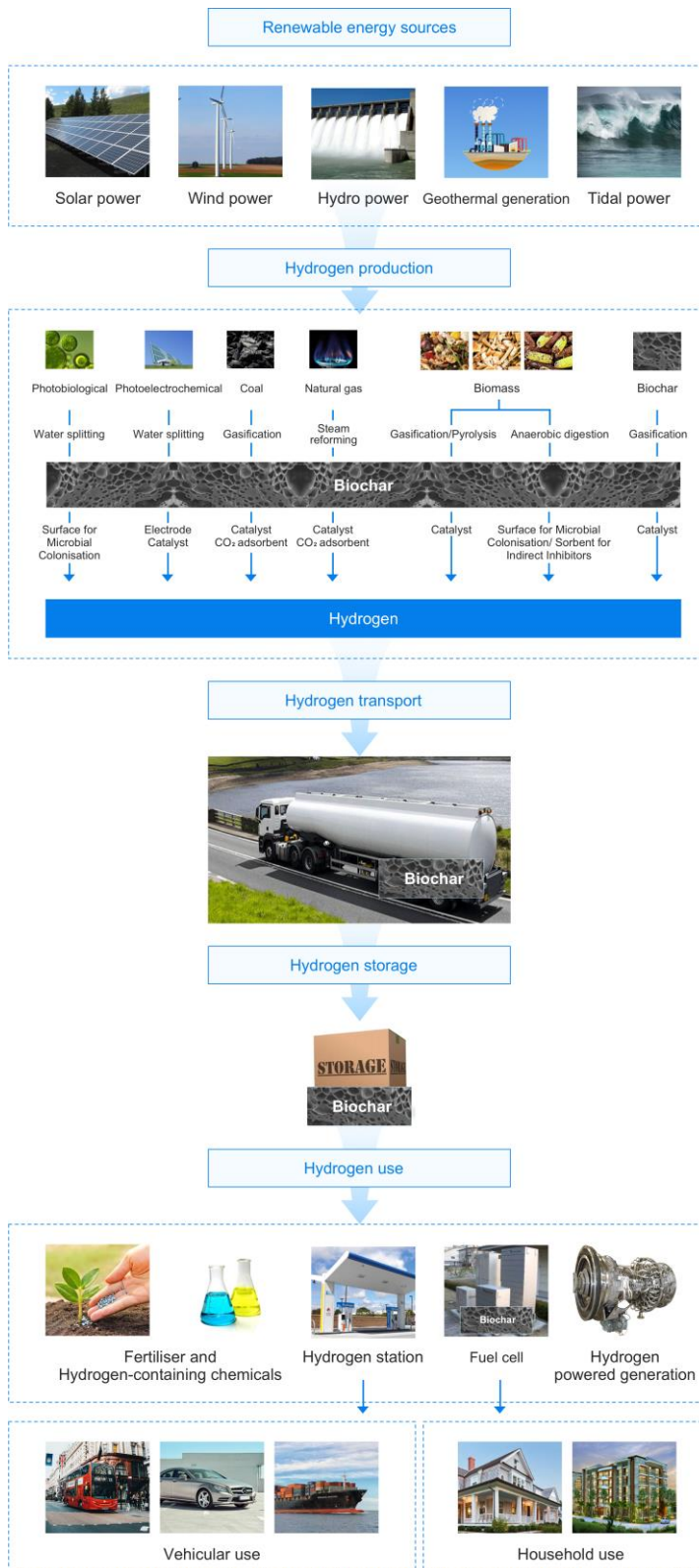


Figure 3: Biochar system in an H₂ Society^{108,109,120,124,125,133,138,139,141–145}

H₂ storage

Considering the urgency of the research, biochar has been among the materials explored for H₂ storage in porous materials¹⁴⁶. H₂ can be stored as a gas or a liquid; however, this requires pressures of approximately 350–700 bar and cryogenic temperatures. Such an approach has safety issues with the added drawback of energy losses and low volumetric energy capacity^{143,147}. Hence, several solid materials have been investigated for surface H₂ storage including metal-organic frameworks¹⁴⁸, covalent organic frameworks¹⁴⁹, zeolite¹⁵⁰, carbon materials¹⁴⁶, and zeolite-like carbon materials¹⁵¹. Porous carbon materials have been evaluated for H₂ storage because of their special features as compared to other materials: they have a tunable high porosity, a high surface-to-volume ratio, an ease of processibility, thermal and chemical stability, and are ultra-light weight and abundant^{143,152}. Furthermore, the porosity and surface area of biochar is tunable by simple modification methods such as steam activation, acid and base activation, and ball milling, as these effectively release the volatile matter filled in porous structures of carbonaceous materials^{153–155}. Chemisorption via strong C-H chemical bonds and physisorption via weak London dispersion forces could be involved in H₂ storage by carbon materials. In contrast to physisorption, the chemisorption of H₂ requires large amounts of energy to detach the H bonds (1.5 eV)¹⁴³. The ability to apply such storage solutions at low pressure, their relatively low material costs, and the simple storage systems involved have been identified as key advantages¹⁵⁶. Chemical (e.g., potassium hydroxide (KOH), zinc chloride (ZnCl₂)) or steam activated biochar has been identified as a promising material to store H₂ via physisorption¹⁴⁴. The micropores in biochar contribute a significant H₂ adsorption capacity by capillary forces¹³⁷. For example, KOH-activated corncob biochar, which has a high density of micropores, showed a substantially high H₂ adsorption capacity of >2.85 wt% at 1.0 bar and -196 °C¹⁵⁷. Previous studies have reported a high H₂ adsorption capacity of materials with micropores of size 0.65–1.5 nm¹⁴⁴. The H₂ storage in biochar-derived carbon materials could be further increased by loading their surfaces with platinum, palladium, nickel, and other transition metals¹⁵⁸. For example, a two-fold increase in H₂ adsorption (1.6 wt%) was observed for KOH-activated and nickel-loaded biochar than for KOH-activated biochar due to the H₂ spillover mechanism¹⁵⁹. Doping with the above transition metals increases H₂ adsorption by biochar at room temperature (25 °C). Furthermore, enhanced H₂ adsorption has been reported on the surfaces of graphene-based materials due to efficient H₂ binding to heteroatoms of alkaline metals, boron, aluminum, silicon, and nitrogen¹⁵⁸. Hence, there is substantial potential to modify biochar-

based carbon materials with these elements to enhance the H₂ storage capacity. The abundant surface moieties, and alkali and alkali earth elements in biochar provide additional support to adsorb H₂ by chemisorption. For instance, K and Na in biochar, could act as alkaline centers to bind H₂¹³⁷. Given these opportunities, an improved understanding of biochar nanostructures should be rigorously pursued to facilitate the production of carbon materials with high H₂-storage capacities¹⁶⁰ (cf. Table 1).

Biochar adsorbent for CO₂ capture in H₂ production

Additionally, biochar could be developed as an effective adsorbent to reduce CO₂ emissions in H₂ production by coal gasification and natural gas reforming¹⁶¹. The tunable microporous nature and surface area of biochar shows high efficacy in capturing CO₂ by physisorption^{145,162}. KOH can be used as a chemical activating agent to increase the microporosity and surface area of biochar, which could lead to a significantly higher CO₂ adsorption capacity¹⁶³. Moreover, high proportions of fixed carbon in biochar are associated with inter-particle force between biochar surfaces and CO₂. Consequently, biochars produced at high pyrolysis treatment temperatures are more effective for CO₂ capture^{163,164}. The presence of heteroatoms such as nitrogen and sulfur can significantly improve biochar's CO₂ adsorption capacity^{165,166}. For example, biochar physically modified by low frequency ultrasound or chemically modified with amines will display an increased adsorption capacity for CO₂, as ultrasound enhances the micro porosity and amine addition increases the abundance of N containing functional groups¹⁴¹. Please see Dissanayake et al.¹⁶⁷ for detailed information.

9. Future Prospects for an H₂ Society

In response to the 2015 Paris Agreement, governments are considering ways to stimulate a low carbon economy. The concept of an H₂ Society is a promising proposal for achieving carbon-neutral development at a global level. An H₂ Society aims to construct a world that utilizes H₂ technology in daily life, in as many sectors as possible. Japan is currently the leader in progressing towards this vision.

Despite the encouraging prospects for the future of H₂ as an energy source, several major challenges must be overcome in the development of an H₂ Society. One of the most challenging issues is high production costs, which hinders H₂ from becoming a widespread

energy carrier in the near future; it must prove cost-competitive to replace existing systems with H₂-based alternatives. The incentive for the transition to H₂ technology is currently low, as doing so increases the costs of both production and consumption. Governments could seek ways to promote the development and deployment of H₂ technology through economic incentives. Technologies devoted to improving the duration and substantially reducing costs will be advantageous. From a management perspective, the challenge of coordinating across various departmental offices is significant, as financial budgets allocated to other energy technologies must be transferred to establish new infrastructure. One of the great challenges is the reluctance of investors to invest hundreds of billion dollars on infrastructure development before society is ready to rely on H₂. For instance, the investment on new nationwide infrastructure to provide access to H₂ for fuel cell vehicles could not be resolved until millions of H₂ vehicles were on the road. Simultaneously, vehicle manufacturers are reluctant to mass produce fuel cell vehicles until nationwide infrastructure is sufficient to persuade customers¹⁶⁸. An integrative system must be initiated to support informed decision-making to deliver on an H₂ Society.

A further issue concerns the system long-time payback. Safety is a major concern when new technology is applied on a larger scale. Therefore, safe and secure infrastructure to provide H₂ both in centralized and decentralized stations must underpin progress towards an H₂ Society. Additionally, gaseous by-products from H₂ production, such as CO₂, have to be captured and stored wherever possible. Currently, over 95% of H₂ production relies on fossil fuels. Efforts to employ H₂ as a means of emissions reduction will be offset by emissions from H₂ production if no reliable capture and storage technology is available.

Public concern is a final hurdle. As the central players in a future H₂ society, the public will have the final say in its success or failure. The rate of cost escalation depends on public acceptance; furthermore, public resistance could raise costs by several orders of magnitude. Appropriate information disclosure and dissemination will be important aspects for policy making. Overall, the requirement of a technological and institutional setting is demanding. Cooperation between industry, energy suppliers, consumers, and governments is critical for the creation of an H₂ Society. If all these issues can be addressed, it is very likely that such a transition will occur over decades.

A possible pivotal breakthrough is biochar, as discussed above and shown in Figure 3. Biochar could potentially mitigate climate change besides having additional, profitable

benefits^{169,170} in an H₂ Society. As an economically feasible and environmentally sustainable material, biochar technology has been proven to enhance H₂ production^{119,134} as well as mitigate ammonia emissions¹³⁶. The cost of H₂ production is expected to fall with the improved production efficiency of various biochar applications¹⁶⁵; moreover, production emissions could be adsorbed using biochar technology¹⁴¹. Therefore, biochar is considered a “green carbon” that could minimize environmental impacts and aid a smooth transition to an H₂ economy¹⁷¹.

What remains are the institutional and political barriers that hamper the development of H₂ infrastructure. Policymakers must provide institutional support to facilitate the technological transition; energy policy and regulations, business practices, and codes and standards are critical elements that must be further developed and adapted for H₂ energy. Establishing communication channels between H₂ supply chain industries and various stakeholders is essential; furthermore, governments must support innovations, act to remove market barriers, and enforce compliance with codes of practice.

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