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Review: Biomass-Based Hydrogen Production Technology

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ABSTRACT

One of the most efficient fuels for renewable energy is hydrogen. Currently, fossil fuels and their by-products produce most of the hydrogen with technologies that harm the environment, and fossil sources are rapidly decreasing in quantity. Environmentally friendly and pollution-free alternatives to fossil fuels are interesting to pursue. This paper explores advances in bio-hydrogen technology as an environmentally friendly and sustainable future technology development. Derivatives of crucial products from biomass, such as alcohol and glycerol, and methane-based reforming to produce hydrogen. Biological techniques to produce bio-hydrogen are exciting by fermentative, enzymatic, and biocatalytic methods. Also discussed are genetic engineering components, reactor configuration, and pretreatment. Low hydrogen yield and high cost are the two main problems in bio-hydrogen production. Also discussed are the costs, advantages, and disadvantages of various hydrogen generation methods. This article also discusses the promise of biohydrogen as a clean energy alternative and areas that require further research to realize a viable economic analysis of hydrogen production.

1. Introduction

Biomass is abundant, environmentally friendly and sustainable. Thus, hydrogen production from biomass is an unlimited solution. It is expected that hydrogen derived from biomass will be able to continue to grow and become fuel for a longer period. Biomass, usually in the form of wood, is a basic human energy source. Historically, biomass was produced using direct combustion methods and was highly inefficient. In contrast, the conversion of biomass into gas and oil, coal, sulfur, and hydrogen is an additional effective technique to utilize biomass [1]

Hydrogen is an alternative fuel widely used in petroleum, medicine, vehicles, and the chemical industry. NH_3 and CH_3OH production accounts for more than 40% of the hydrogen used worldwide. In places where helium is unavailable or expensive, H_2 is often used as a lifting gas in meteorological applications. Radio-sound devices are used to observe atmospheric weather. This device floats in the sky using a weather balloon filled with pure, dry hydrogen [2]

Because it is environmentally friendly and can be used in various technologies, such as fuel cells for motor vehicles and aeroplanes, hydrogen has become a better alternative to fossil fuels [3]. Apart from that, hydrogen can also provide electricity for homes and offices. H_2 reduces greenhouse gas emissions from motor vehicle engines as fuel cell generators. Therefore, hydrogen has excellent potential as a fuel that does not produce waste; it is a cost-effective, efficient, and unlimited renewable resource to meet the ever-increasing energy demand. Estimated H_2 production sources for 2050 are depicted in Figure 1.

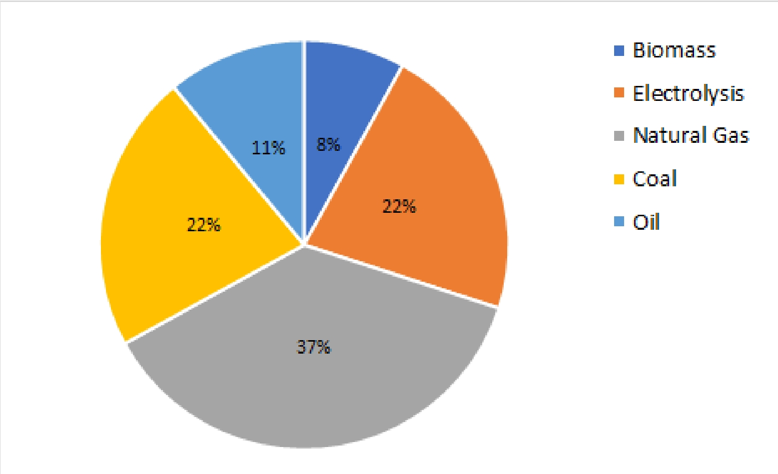

Figure 1. Prediction of hydrogen production sources in 2050 [2]

Hydrogen gas has a very high energy density and does not release carbon dioxide after burning. In addition, biological synthesis can be performed on living things and does not require fossil fuels to continue the process. Hydrogen was previously synthesized using biomass-based fertilizers using thermochemical methods; however, this negatively affected the environment and caused pollution. In this context, discuss biological sources capable of producing hydrogen. This substance can serve as a fertilizing foundation. This hydrogen is known as biohydrogen [3]. This biohydrogen is a by-product of many reactions microorganisms trigger. Due to the use of biomass as a substrate, the production of hydrogen gas is constantly changing, resulting in the formation of biohydrogen [4]

Biohydrogen production from biomass has received greater attention due to its sustainability, low cost and high efficiency to avoid adverse impacts on food products. This process has the potential to be a carbon-neutral process that can be carried out on the surface and in the environment, so it is seen as a more efficient and advantageous process when compared to thermochemical and electrochemical processes [5]. The methods used to produce biohydrogen from biological methods can be classified as dark fermentation, photofermentation, and electro-biohydrogenation, such as microbial biomass fermentation (MFC) or microbial electrolysis (MEC). Each process has unique characteristics and fluctuations in terms of energy efficiency and practicality [6]

The main focus of this paper is on methods for producing BioH2 for use in hydrogen fuel cells, anaerobic fermentation, photo-fermentation of lignocellulosic biomass, generation of BioH2 from green algae and cyanobacteria, biohydrogen fermentation routes, and the design of various bioreactors and factors influencing BioH2 production. However, the most important is research into biomass-derived products for BioH2, direct biomass-based BioH2 generation, or biological techniques.

1. Hydrogen production method from Biomass-derived chemicals

Many materials in the environment contain hydrogen. All carbon dioxide and other contaminants from fossil fuel conversion must be processed by thermal, photonic, electrical, and biochemical energy. Various compounds such as alcohols, hydrocarbons, biofuels, water, biomass, glycerol, and others can be used as raw materials for space shuttles in the United States [7]. Figure 2 shows various biomasses that can be used as raw materials for biological hydrogen production.

Alcohol reform

The conversion of alcohol to hydrogen-enhanced gas can be achieved through various reactions, such as steam reforming and oxidative steam reforming [8], [9].

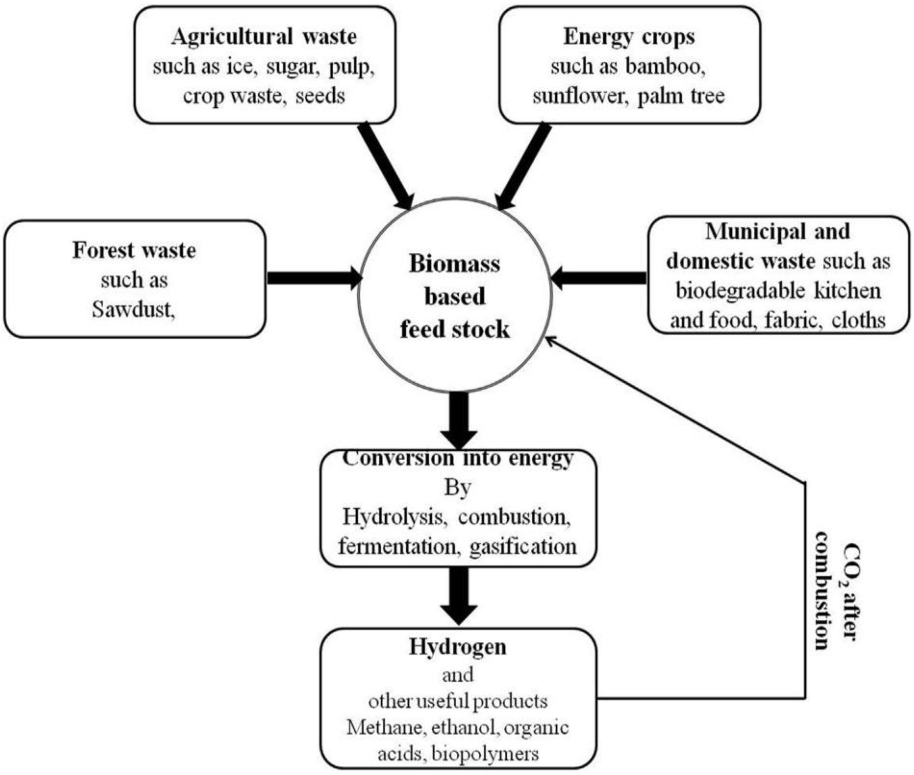

Figure 2. Various sources of Biomass and its conversion to H_2 and other valuable products

[10]

Methanol reforming

Methanol is an ideal H_2 source because it is safe, cheap, and has a higher storage density. In addition, H_2 can come from biomass, a renewable and non-renewable energy source. Steam reforming (SR) can be described in two stages with two pathways. The first stage involves the decay of methanol into carbon monoxide and hydrogen (Equation 1). The second stage consists of the fusion of H2 and carbon monoxide (Equation 2):

First reaction:

$$CH_3OH \rightleftarrows CO + 2H_2 \quad (1)$$

Water–Gas Shift Reaction (WGSR) in Equation (2)

$$CO + H_2O \rightleftarrows CO_2 + H_2,\ \Delta Ho = \pm\ 41.2\ kJ/mol\text{-}1 \quad (2)$$

The second reaction for steam reforming methanol (SRM), which has water and methanol forming CO_2 and H_2 (Equation 3):

$$CH_3OH + H_2O \rightleftarrows CO_2 + 3H_2,\ \Delta Ho = \pm\ 49\ kJmol\text{-}1 \quad (3)$$

Reverse shift reaction (Equation 4):

$$CO_2 + H_2 \rightleftarrows CO + H_2O \quad (4)$$

One of the advantages of the methanol steam reforming procedure is the lower amount of carbon monoxide produced along with carbon dioxide. This is very important because carbon monoxide is toxic to energy fuels. The maximum permitted carbon monoxide concentration ranges between 10 and 100 ppm.

Ethanol reform

The primary way to produce hydrogen commercially is steam reforming (SR) of hydrocarbon fractions. Because it makes more bioethanol, replacing fossil fuels with bioenergy becomes more important for renewable H_2 production. Ethanol conversion is one method that can be used to produce renewable H_2. Bioethanol can be regenerated from various biological resources, such as forest and plant waste [10]. SR, partial oxidation (PO), and autothermal reformation of ethyl alcohol can be demonstrated using equations 5, 6, and 7.

Like the endothermic method, SR requires an input force to start the reaction:

$$C_2H_5OH + 3H_2O \leftrightarrow 2CO_2 + 6H_2,\ \Delta H^\circ = 174\ kJ\ mol\text{-}1 \quad (5)$$

Otherwise, H_2 can be obtained with PO ethyl alcohol at a temperature of around 500°C, according to the following reaction[11]:

$$C_2H_5OH + 1.5O_2 \rightarrow 2CO_2 + 3H_2,\ \Delta H^o = -552\ kJ\ mol\text{-}1 \quad (6)$$

However, automatic thermal reforming can increase H_2 production because the selectivity of H_2 PO ethyl alcohol is usually lower. The overall reaction of auto thermal reforming of ethyl alcohol can be described as[12]:

$$C_2H_5OH + 2.25H_2O + 0.375O_2 \rightarrow 2CO_2 + 5.25H_2,\ \Delta H^o = -30\ kJ\ mol\text{-}1 \quad (7)$$

The above reaction shows that automatic thermal reforming increases H_2 production, with an ethanol conversion rate of 87%.

Glycerol reformation

Generating biodiesel from vegetable oil and bioethanol produces glycerol, a carbohydrate [13]. Glycerol is usually used in medicines, cosmetics, food, and drinks [14] and is available in excessive quantities in the global market. SR from glycerol to syngas is the main component for various petrochemical processing methods; it is a viable alternative.

Glycerol SR can be written as follows (Equation 8)

$$C_3H_8O_3(g) + 3H_2O(g) \leftrightarrow 3CO_{2(g)} + 7H_2(g) \quad (8)$$

It can be seen as a grouping of equations (9) and (10)

$$C_3H_8O_3(g) + \leftrightarrow 3CO_{(g)} + 4H_2(g) \quad (9)$$

$$CO(g) + H_2O(g) \leftrightarrow CO_2 + H_2 \quad (10)$$

Cortright et al. investigated carbohydrates' water phase reformation (APR) to carbon dioxide, carbon monoxide, and hydrogen. This process is usually carried out at high pressure (>2 MPa), with an average system temperature of 503–553 K. Noble metals such as Pt, Rh, Pd, Ru, and Re function as catalysts. In research conducted by Feng et al. [14], the role of Ni-CaO in the glycerin SR reaction was measured between 400 and 800ºC. At 600ºC, Ni-CaO produces maximum H2 output (85.30%) and glycerol conversion (93.71%). The results demonstrate the resistance of this catalyst to carbon deposition, which extends its lifetime. CaO broadens the distribution of Ni species and increases the H2 yield because the water gas transfer process is activated.

2. Hydrogen production through biological processes

Bio-hydrogen is an ideal replacement for the transportation industry due to its many scientific and ecological advantages compared to conservative fossil fuels. The benefits include a reduction in greenhouse gases along with the release of carbon dioxide. This will diversify the energy industry, improve biodegradability sustainability, and increase the market for agricultural products at home and abroad.

Five methods use biological techniques to produce H2 instead of oxygen: direct and indirect bio-photolysis, biological WGSR, photo-fermentation, and shadow fermentation. All these methods are powered by solar power, and certain biological organisms are converted through photosynthesis to produce H2. Photo-biological hydrogen generation is still an attractive option for renewable energy, although several physical and scientific issues must be addressed. Small-level photo-biological hydrogen generation can also help generate renewable energy and protect the atmosphere because it reduces BOD in organically loaded wastewater and reduces economic limitations.

H2 is produced through sunlight, biological components, catalysts, and scientific methods. Physical H2 generation methods are usually carried out at room temperature and pressure, which is less power intensive and yields up to 24% hydrogen as a byproduct. Biohydrogen generation with microorganisms is a relatively new field. It includes direct and indirect biophotolysis of water, photo and shadow fermentation, and bacterial electrolysis by microbes of organic substances. In biophotolysis, certain microorganisms, such as green algae and cyanobacteria, produce H2 using water through the usual metabolic method with sunlight [15]. Different types of biological hydrogen metabolism occur through organisms, algae, and bacteria. Figure 3 shows the effectiveness of a hypothetical sunlight conversion, although this tool is still in the research and development stage.

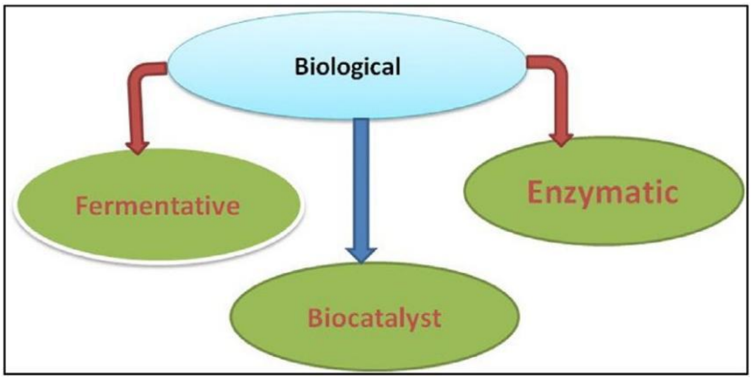

Figure 3. Classification of hydrogen production by biological methods [15]

Fermentation

Living creatures can use the biochemical energy accumulated in organic substances to extract hydrogen gas in conditions of lack or presence of light. Bioreactors do not require solar entry processing for shade fermentation, making it easier and cheaper than photo-fermentation. Figure 4 shows the mechanism of BioH_2 through photofermentation. Shadow fermentation can produce H_2 from organic waste and manage and stabilize biological waste, which has pollution potential.

The dark fermentation mechanism involved in BioH_2 is depicted in Figure 5—a fermentation study. Producing dark fermentative hydrogen from hydrolyzate must be carried out separately. Most of the research on the hydrogen fermentation process of lignocellulosic hydrolysates has been carried out using a batch approach. In support of these findings, the most favourable pH and hydrolyzate composition for hydrogen fermentation of lignocellulosic hydrolyzate was 5.5-7 g L-1, respectively.

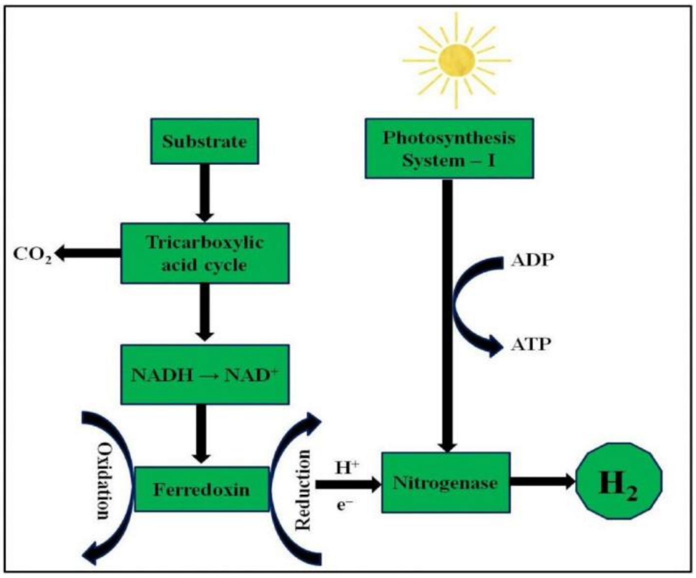

Figure 4. Mechanism of BioH_2 production through photofermentation.

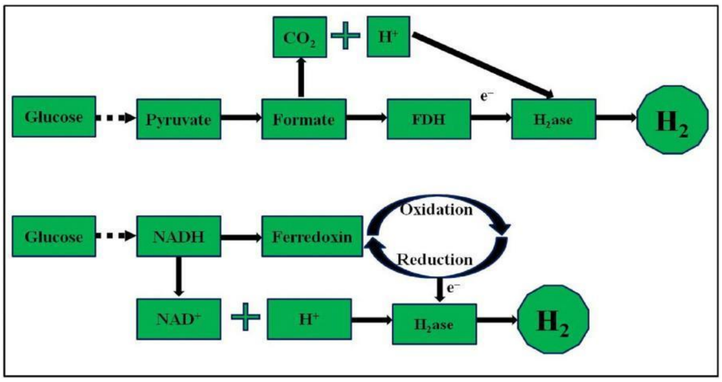

Figure 5. Mechanism of BioH_2 production through dark fermentation.

The study by Zhong and his colleagues [16] showed that using magnetite nanoparticles (Fe_3O_4-NPs) to increase BioH2 production from anaerobic glucose fermentation was practical and profitable. The results showed that the batch trial produced the highest hydrogen level of 12.97 mL H2/g. In addition, the expanded granular waste bed reactor has an H2 production of 4.95 L-H_2/day with an ideal NP dosage. The addition of NPs can increase the accumulation of ethanol and acetic acid. Iron corrosion can increase Fe^{2+} activity. They were adding NPs to granular sludge results in the development of larger electronic conductor chains, which improves the electron transport performance.

Enzymes and biocatalysts

Hydrogenase or nitrogenase is an enzyme that catalyzes hydrogen production in phototrophic organisms. The feasibility of photogenerating hydrogen has long been established with a synthetic strategy consisting of *Clostridium* hydrogenase, chloroplasts, and Fe from spinach. Various aspects of hydrogenase have been thoroughly examined. Hydrogenase is an enzyme that catalyzes the following:

$$2H^{+} + 2e^{-} \leftrightarrow H_2 \quad (12)$$

Nitrogenase is the nitrogen-fixing enzyme limited to prokaryotes. This category includes Purple Non-Sulfur bacteria (PNS), green sulfur bacteria, and several strains of *cyanobacteria*. Nitrogenase, an anticipated byproduct of nitrogen fixation, catalyzes hydrogen synthesis in one way. This is because the reaction is catalyzed by nitrogenase under the most favourable conditions for nitrogen fixation.

Microbial electrolysis cell (MEC)

Electrochemistry drives microbial electrolysis cells. This method is thought to increase the amount of hydrogen released in biological reactions. The mixed microbial consortium, reactor configuration, type of components required for electrodes, and media as experimental conditions are some factors that influence MEC efficiency. Due to their heterogeneous nature, slow kinetics, and high hydrogen consumption, biofilms are considered a problematic bottleneck and raw material. Bio-electro-synthesis is a method to produce hydrogen at an industrial or commercial level.

It was demonstrated that MEC and dark fermentation are effective methods to produce hydrogen from renewable biomass. MEC has many other benefits besides H_2 evolution. Biohythane production (CH_4 + H_2), which reduces microbial electrons, ammonia recovery, and water desalination, is an alternative fuel that can be used to make ethanol. Although this technique is still under development, MEC is a renewable and sustainable source of BioH_2 for new generations. However, improvements are needed to become more efficient and usable. Unlike MEC, electrochemical photobioreactors (EPBR) produce BioH_2 through a double sequestration. While H_2 is made at the cathode, protons are produced at the anode. The system removes oxygen from the cathode compartment, which results in the following reaction:

$$2H^{+} + 2e^{-} \rightarrow H_2 \quad (11)$$

3. Hydrogen production originating from biomass

Due to their ability to produce energy, biomass has four main types of sources that can be used as raw materials. Harvest and livestock residues are the second type of agricultural waste; the third type is forestry waste, which comes from cutting down trees and clearing land; and the fourth type is community and commercial waste. Raw biogas comprises 25% to 55% carbon dioxide and 35% to 75% methane. Other small amounts include H_2S, water vapour, carbon monoxide, ammonia, siloxane, nitrogen, aromatics, oxygen, and particulate hydrogen gas can be produced from biomass via pyrolysis, gasification, and conversion to liquid fuel via hydrolysis, supercritical extraction, and liquefaction [17]. Biomass gasification includes carbon dioxide recycling. Photosynthesis is the process by which plants naturally absorb carbon dioxide from the environment [18]. It produces oxygen from solar energy and stores chemical energy in glucose and sugar. Additionally, during the biomass gasification process, CO_2 is released to make BioH_2, which reduces the net greenhouse gas emissions associated with the carbon dioxide recycling process. Figure 6 shows a flow diagram of the techniques used to extract H_2 from biomass derivatives, and Figure 7 shows the various methods used to produce hydrogen from biomass.

Several charcoals originating from various biomass sources can help catalysts make Ni-based catalysts. Rice charcoal produces 64% H_2 in the gas phase than cotton. Table 2 shows multiple studies on making BioH_2 from biomass.

Pyrolysis

Biomass can produce hydrogen through pyrolysis and gasification processes. The pyrolysis reaction produces gases such as methanol, coke, and others. The gasification mechanism produces 20% hydrogen, 20% carbon monoxide, 10% carbon dioxide, 5% CH_4, and 45% nitrogen. First, this stream can be processed by reacting it with steam, producing more hydrogen than carbon dioxide [19]. High-temperature gasification converts biomaterials into gas, which has hydrogen-rich gas. The hydrogen-rich gas is condensed in the pyrolysis oil and can be followed by steam reforming to produce hydrogen. Between 12 and 7 per cent of the dry basis weight is produced by this process. [20].

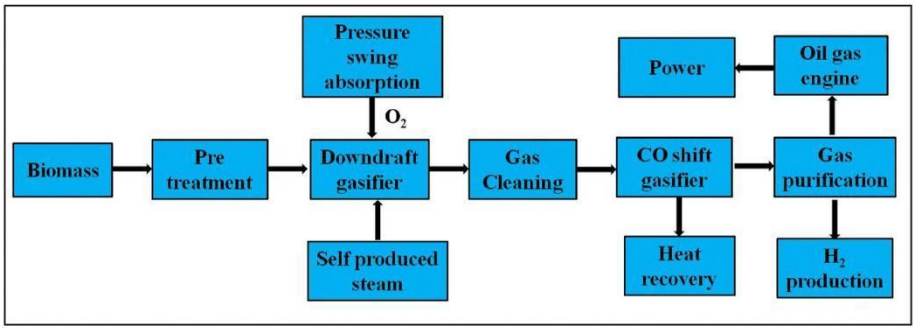

Figure 6. Flow diagram of the biomass hydrogen production process.

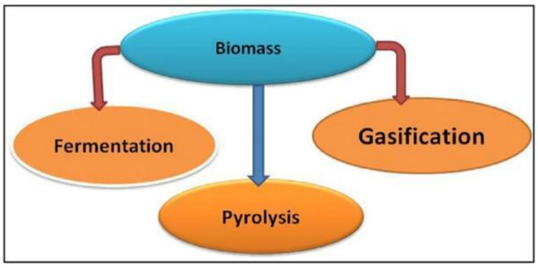

Figure 7. Classification of Hydrogen production using the Biomass method.

Recent studies of wood fuel yield typical weight concentrations of 48% C, 45% O, and 6% H_2, with the balance containing small amounts of N, S, and minerals. Considering the main components, the energy can be described on a basic basis as $CH_{1.5}O_{0.7}$. Solution is:

$$CH_{1.5}O_{0.7} + 0.3H_2O_{(g)} \rightarrow CO + 1.05H_2 \quad (12)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (13)$$

This energy is fully renewable by producing H_2 gas from biological waste used as raw material. Chen et al. convert two-step catalytic steam to produce hydrogen-rich syngas. Bio-oil makes up about 25% by weight and has a superior heating value of about 18 MJ/kg.

Biomass gasification

Various industrial methods use gasification methods, usually used with biomaterials and coal. It is a variation of pyrolysis and relies on the fractional oxidation of substances to the fusion of H_2,

CH_4, CO_2, CO, and N_2. Biomass, animal, and plant waste can be energy sources. Methane gas, generally used for heating and generating power, can also produce synthesis gas through biomass gasification. This method, however, is costly as it requires a lot of energy and results in intrinsic power loss. Producer gas is a mixture of gases that can be heated and compressed. In the gasifier, imperfect biomaterials are burned during the gasification process and react at around 1000 ºC.

Table 2. Biomass is used for BioHydrogen production using various culture media.

No.	**Biomass used for BioHydrogen production**			
	Biomass	***Culture/inoculum used***	***Production/yield H2***	***Reference***
1.	Raw cassava flour	Facultative anaerobic	1.44 mol H_2/ mol-glucose	[21]
		Bacteria	0.52 mol H_2/mol glycerol	
2.	Biodiesel, residue produced from sunflower oil	Anaerobic digester (mixed culture)	48 cm3 H_2/g carbohydrate	[22]
3.	Jatropha curcas residue from the biodiesel industry	Granules and sediment from USAB Reactor (mixed culture)	1.58 mol H_2/mol hexose	
4.	Waste Water (cassava starch)	Mixture		[23]
			0.89 dm3 H_2/dm3	
5.	Palm oil bottle cake with glycerin	Mixture	32 cm3 H_2/g	[24]
6.	Sorghum	Mud	26 cm3 H_2/g	[25]
7.	Corn stove		55 cm3 H_2/g	
			52 cm3 H_2/g	
8.	Rice husks	Cellular	473.1 cm3 H_2/g	
9.	Kitchen waste	Bacteroidetes	6.1 cm3 H_2/g	[26]
10.	Paper waste		0.51 cm3 H_2/g biomass/hour	[27]
11.	Serve food	With Ca & Mg	164.4 ± 2.6 mL H_2.g—1	[28]
		Phosphate-laden biochar	197.15 ± 2.9 mL g—1	[29]
12.	Melon and watermelon residues	Microbial metabolism	395.5 and 62.7 mL H_2/g	
13.	Food waste	*Piggery anaerobic digested residue*	126.50 mL/g	[30]
14.	Tequila vinasse	Lactic acid bacteria	11.7 ± 0.7 L/Ld	[31]
15.	Grape wine	Sludge inoculum	43.25 ± 1.52 mL H_2/g	[32]
16.	Leftovers and thick molasses	Mixed anaerobic microflora	6.17 mol H_2/kg	[33]

Gasification-based bioenergy production still has many benefits, especially on a small scale. Enables increased gasification performance through an endothermic gasification process controlled by concentrated solar heat known as Concentrated Solar Thermochemical Gasification (CSTGB). Biomass gasification is promising to save chemical energy while increasing biomass value [34]. CSTGB can collect solar energy efficiently in gas production, increasing the use of biomass raw materials and total energy effectiveness by 30% and 40% compared to conventional methods. Moreover, it has been shown that the hybrid configuration with partial oxy-combustion of the feedstock and dynamic feed control results in the most stable process operation under variable or sparse solar irradiance while maintaining H_2 and CO formation at night and during cloudy intervals.

4. Bioreactor for BioH2 production

The ability of a biocatalyst to convert substrates and produce $BioH_2$ is strongly influenced by reactor design, process variables, and operating environment. Better bioreactors should have shorter hydraulic retention times and be able to control biomass leaching due to shorter retention times. Bioreactor performance is determined by reforms developed for specific conditions in addition to design. CSTR (Continuous Stirred Tank Reactor) is often used during $BioH_2$ manufacturing. The CSTR mixing pattern ensures that the hydrogen-producing microorganisms are wholly mixed and suspended in the reactor fluid. This flow behavior allows excellent mass transfer and substrate-microbe interactions.

5. Other factors that influence the process

A sustainable and cost-effective method, $BioH_2$ manufacturing requires many optimization steps. So far, it has been shown that various factors, including light intensity [35], stirring mode [36], substrate concentration [37], and pretreatment conditions [38], greatly influence BioH2 production. Batch, continuous, and semi-continuity fermentation modes are also very important. Computing technology will become critical. Further studies should combine all these components to carry out renewable and sustainable $BioH_2$ generation properly.

6. Future aspects of hydrogen and economic outlook

About 80% of energy used in the world is as electricity, with bioenergy and waste (9.7%), nuclear power (4.9%), hydropower (2.5%) and other resources (1.5%) each. Each accounted for 81.4% of the universal power contribution 2018 [39].

Since the share of renewable power requirements is 36% in 2025 and 69% in 2050, the H_2 segment will increase by 11% in 2025 and 34% in 2050. Table 5 shows both the advantages and disadvantages of the available technologies. Biohydrogen technology is a new energy technology that is sustainable and environmentally friendly.

Table 5. Advantages and disadvantages of available H2 production technologies

No.	H_2 Production Technology		
	Production Engineering	***Profit***	***Loss***
1.	Partial Oxidation (PO)	• A complete exothermic process that does not require heat • Save costs	• Hydrogen production is slow
2.	Steam Reform (SK)	• Well-proven technology with thermal efficiency • Ability to produce 99% pure H2	• It requires a lot of energy • High operational costs
3.	Biomass Gasification (BG)	• High productivity • It is beneficial for the environment and financially	• The reactor investment is quite large
4.	Coal Gasification (CG)	• Thermodynamically good • The most environmentally friendly method of producing hydrogen	• Groundwater pollution is a problem

5.	Water Electrolysis	• A completely contamination-free process	• Production costs are high, while efficiency is low • Higher electricity usage
6.	Solar Photocatalyst	• Environmentally friendly	• Lower system efficiency

Conclusion

More and more people are recognizing the importance of hydrogen as a future fuel. This study describes recent biohydrogen generation advances, including alcohol, glycerol, fermentation, biocatalysis, methane-based reforming, and enzyme-based techniques. Hydrogen volumetric production and research output levels have shown significant improvement and progress. It is critical to continue research and innovation to increase the rate of H_2 synthesis and the resulting end product. Due to better designs for bioreactors, faster gas separation and purification, and modification of enzyme pathway genes, biohydrogen systems have much potential. Biomass gasification and solar integration may be viable options for the future.

Reference

[1] D. Prabakar, V. T. Manimudi, S. Sampath, D. M. Mahapatra, K. Rajendran, and A. Pugazhendhi, "Advanced biohydrogen production using pretreated industrial waste: outlook and prospects," *Renewable and Sustainable Energy Reviews*, vol. 96, pp. 306–324, 2018.

[2] M. P. Ramakodi, "Computational biology and genomics tools for biohydrogen research," in *Biohydrogen*, Elsevier, 2019, pp. 435–444.

[3] S. V. Mohan and A. Pandey, "Sustainable hydrogen production: an introduction," in *Biohydrogen*, Elsevier, 2019, pp. 1–23.

[4] G. D. Saratale, R. G. Saratale, Y. Lo, and J. Chang, "Multicomponent cellulase production by Cellulomonas biazotea NCIM-2550 and its applications for cellulosic biohydrogen production," *Biotechnol Prog*, vol. 26, no. 2, pp. 406–416, 2010.

[5] P. Sivagurunathan *et al.*, "Fermentative hydrogen production using lignocellulose biomass: an overview of pre-treatment methods, inhibitor effects and detoxification experiences," *Renewable and Sustainable Energy Reviews*, vol. 77, pp. 28–42, 2017.

[6] M. A. Qyyum *et al.*, "Availability, versatility, and viability of feedstocks for hydrogen production: Product space perspective," *Renewable and Sustainable Energy Reviews*, vol. 145, p. 110843, Jul. 2021, doi: 10.1016/j.rser.2021.110843.

[7] A. Haryanto, S. Fernando, N. Murali, and S. Adhikari, "Current status of hydrogen production techniques by steam reforming of ethanol: A review," *Energy and Fuels*, vol. 19, no. 5. American Chemical Society, pp. 2098–2106, Sep. 2005. doi: 10.1021/ef0500538.

[8] C. Pirez *et al.*, "Steam reforming, partial oxidation and oxidative steam reforming for hydrogen production from ethanol over cerium nickel based oxyhydride catalyst," *Appl Catal A Gen*, vol. 518, pp. 78–86, May 2016, doi: 10.1016/j.apcata.2015.10.035.

[9] A. Haryanto, S. Fernando, N. Murali, and S. Adhikari, "Current status of hydrogen production techniques by steam reforming of ethanol: a review," *Energy & Fuels*, vol. 19, no. 5, pp. 2098–2106, 2005.

[10] J. R. Salge, G. A. Deluga, and L. D. Schmidt, “Catalytic partial oxidation of ethanol over noble metal catalysts,” *J Catal*, vol. 235, no. 1, pp. 69–78, Oct. 2005, doi: 10.1016/j.jcat.2005.07.021.

[11] Z. Al-Hamamre and M. A. Hararah, “Hydrogen production by thermal partial oxidation of ethanol: Thermodynamics and kinetics study,” *Int J Hydrogen Energy*, vol. 35, no. 11, pp. 5367–5377, Jun. 2010, doi: 10.1016/j.ijhydene.2010.03.018.

[12] I. Zahid *et al.*, “Production of Fuel Additive Solketal via Catalytic Conversion of Biodiesel-Derived Glycerol,” *Ind Eng Chem Res*, vol. 59, no. 48, pp. 20961–20978, Dec. 2020, doi: 10.1021/acs.iecr.0c04123.

[13] P. Bondioli, “From Oilseeds to Industrial Products : Present and Near Future of Oleo-,” *Structure*, vol. 1870, no. Figure 2, pp. 129–135, 2003.

[14] P. Bondioli, “From oilseeds to industrial products: present and near future of oleochemistry,” *Ital. J. Agron*, vol. 7, no. 2, pp. 129–135, 2003.

[15] L. Wang, Y. Zhao, and J. Zhang, “Electrospun cerium-based TiO2 nanofibers for photocatalytic oxidation of elemental mercury in coal combustion flue gas,” *Chemosphere*, vol. 185, pp. 690–698, 2017.

[16] A. S. Dounavis, I. Ntaikou, and G. Lyberatos, “Production of biohydrogen from crude glycerol in an upflow column bioreactor,” *Bioresour Technol*, vol. 198, pp. 701–708, 2015.

[17] R. R. Gonzales and S.-H. Kim, “Dark fermentative hydrogen production following the sequential dilute acid pretreatment and enzymatic saccharification of rice husk,” *Int J Hydrogen Energy*, vol. 42, no. 45, pp. 27577–27583, 2017.

[18] R. Slezak, J. Grzelak, L. Krzystek, and S. Ledakowicz, “The effect of initial organic load of the kitchen waste on the production of VFA and H2 in dark fermentation,” *Waste Management*, vol. 68, pp. 610–617, 2017.

[19] S. Eker and M. Sarp, “Hydrogen gas production from waste paper by dark fermentation: effects of initial substrate and biomass concentrations,” *Int J Hydrogen Energy*, vol. 42, no. 4, pp. 2562–2568, 2017.

[20] F. Rezaeitavabe, S. Saadat, N. Talebbeydokhti, M. Sartaj, and M. Tabatabaei, “Enhancing bio-hydrogen production from food waste in single-stage hybrid dark-photo fermentation by addition of two waste materials (exhausted resin and biochar),” *Biomass Bioenergy*, vol. 143, p. 105846, 2020.

[21] L. Wang, Y. Zhao, and J. Zhang, “Electrospun cerium-based TiO2 nanofibers for photocatalytic oxidation of elemental mercury in coal combustion flue gas,” *Chemosphere*, vol. 185, pp. 690–698, Oct. 2017, doi: 10.1016/j.chemosphere.2017.07.049.

[22] A. S. Dounavis, I. Ntaikou, and G. Lyberatos, “Production of biohydrogen from crude glycerol in an upflow column bioreactor,” *Bioresour Technol*, vol. 198, pp. 701–708, Dec. 2015, doi: 10.1016/j.biortech.2015.09.072.

[23] S. Sittijunda and S. Pattra, “Evaluation of different pretreatment methods to prepare an inoculum for bio-hydrogen production from cassava starch wastewater,” *KKU Res. J*, vol. 21, no. 1, pp. 81–92, 2016.

[24] S. Kanchanasuta, K. Kittipongpattana, and N. Pisutpaisal, “Improvement of biohydrogen fermentation by co-digestion of crude glycerol with palm oil decanter cake,” *Chem Eng Trans*, vol. 57, pp. 1963–1968, 2017, doi: 10.3303/CET1757328.

[25] C. Eskicioglu *et al.*, "Assessment of hydrothermal pretreatment of various lignocellulosic biomass with CO2 catalyst for enhanced methane and hydrogen production," *Water Res*, vol. 120, pp. 32–42, Sep. 2017, doi: 10.1016/j.watres.2017.04.068.

[26] R. R. Gonzales and S. H. Kim, "Dark fermentative hydrogen production following the sequential dilute acid pretreatment and enzymatic saccharification of rice husk," *Int J Hydrogen Energy*, vol. 42, no. 45, pp. 27577–27583, Nov. 2017, doi: 10.1016/j.ijhydene.2017.08.185.

[27] R. Slezak, J. Grzelak, L. Krzystek, and S. Ledakowicz, "The effect of initial organic load of the kitchen waste on the production of VFA and H2 in dark fermentation," *Waste Management*, vol. 68, pp. 610–617, Oct. 2017, doi: 10.1016/j.wasman.2017.06.024.

[28] S. Eker and M. Sarp, "Hydrogen gas production from waste paper by dark fermentation: Effects of initial substrate and biomass concentrations," *Int J Hydrogen Energy*, vol. 42, no. 4, pp. 2562–2568, Jan. 2017, doi: 10.1016/j.ijhydene.2016.04.020.

[29] F. Rezaeitavabe, S. Saadat, N. Talebbeydokhti, M. Sartaj, and M. Tabatabaei, "Enhancing bio-hydrogen production from food waste in single-stage hybrid dark-photo fermentation by addition of two waste materials (exhausted resin and biochar)," *Biomass Bioenergy*, vol. 143, p. 105846, Dec. 2020, doi: 10.1016/j.biombioe.2020.105846.

[30] S. Greses, E. Tomás-Pejó, and C. González-Fernández, "Short-chain fatty acids and hydrogen production in one single anaerobic fermentation stage using carbohydrate-rich food waste," *J Clean Prod*, vol. 284, p. 124727, Feb. 2021, doi: 10.1016/j.jclepro.2020.124727.

[31] Y. Wang *et al.*, "Hydrogen production performance from food waste using piggery anaerobic digested residues inoculum in long-term systems," *Int J Hydrogen Energy*, vol. 45, no. 58, pp. 33208–33217, Nov. 2020, doi: 10.1016/j.ijhydene.2020.09.057.

[32] O. García-Depraect, R. Muñoz, E. Rodríguez, E. R. Rene, and E. León-Becerril, "Microbial ecology of a lactate-driven dark fermentation process producing hydrogen under carbohydrate-limiting conditions," *Int J Hydrogen Energy*, vol. 46, no. 20, pp. 11284–11296, Mar. 2021, doi: 10.1016/j.ijhydene.2020.08.209.

[33] M. Tena, B. Luque, M. Perez, and R. Solera, "Enhanced hydrogen production from sewage sludge by cofermentation with wine vinasse," *Int J Hydrogen Energy*, vol. 45, no. 32, pp. 15977–15984, Jun. 2020, doi: 10.1016/j.ijhydene.2020.04.075.

[34] Y. Fang, M. C. Paul, S. Varjani, X. Li, Y.-K. Park, and S. You, "Concentrated solar thermochemical gasification of biomass: Principles, applications, and development," *Renewable and Sustainable Energy Reviews*, vol. 150, p. 111484, 2021.

[35] Z. Zhang *et al.*, "Investigation of the interaction between lighting and mixing applied during the photo-fermentation biohydrogen production process from agricultural waste," *Bioresour Technol*, vol. 312, p. 123570, 2020.

[36] S. Zhu, Z. Zhang, H. Zhang, Y. Jing, Y. Li, and Q. Zhang, "Rheological properties of corn stover hydrolysate and photo-fermentation bio-hydrogen producing capacity under intermittent stirring," *Int J Hydrogen Energy*, vol. 45, no. 6, pp. 3721–3728, 2020.

[37] H. Zhang, J. Li, Q. Zhang, S. Zhu, S. Yang, and Z. Zhang, "Effect of substrate concentration on photo-fermentation bio-hydrogen production process from starch-rich agricultural leftovers under oscillation," *Sustainability*, vol. 12, no. 7, p. 2700, 2020.

[38] T. Zhang *et al.*, “Effects of different pretreatment methods on the structural characteristics, enzymatic saccharification and photo-fermentative bio-hydrogen production performance of corn straw,” *Bioresour Technol*, vol. 304, p. 122999, 2020.

[39] L. C. King, “Biophysical, political and economic challenges to achieving Paris climate targets,” 2020.