Energy Conversion and Management: X 23 (2024) 100659

Contents lists available at ScienceDirect

Energy Conversion and Management: X

journal homepage: www.sciencedirect.com/journal/energy-conversion-and-management-x

Thermochemical and biological routes for biohydrogen production: A review

Praveen Kumar [a,*], Luca Fiori [a,b]

[a] Department of Civil, Environmental and Mechanical Engineering, University of Trento, Via Mesiano 77, 38123 Trento, Italy
[b] Center Agriculture Food Environment (C3A), University of Trento, San Michele all'Adige, 38010 Trento, Italy

ARTICLE INFO

Keywords:
Biomass
Hydrogen
Renewable energy
Thermochemical
Biological

ABSTRACT

One essential energy vector for building a sustainable bioeconomy is hydrogen, which may be obtained from renewable biomass sources. This study discusses many biological routes used in the conversion of biomass to hydrogen, as well as a variety of thermochemical routes such as pyrolysis and gasification. Thermochemical routes include fast pyrolysis, steam and supercritical water gasification, and related processes; biological routes include photo, dark, and mixed fermentation techniques in addition to bio-photolysis processes. Notwithstanding its promise, improving the reliability and selectivity of hydrogen processing is necessary for economically viable industrial uses in the hydrogen economy. The importance of operating conditions, process parameters, variables influencing hydrogen production, parameters of storage methods, hydrogen transportation, separation, and difficulties in producing hydrogen through thermochemical and biological routes are all covered in this paper. It looks at the problems that come with these procedures, highlighting important knowledge gaps that need for more investigation. Combining biological processes with thermochemical pathways can ensure economic sustainability. Both thermochemical and biological routes can help fulfilling future demand for a hydrogen based society.

1. Introduction

With the world's population growing rapidly, so the energy demand. Currently, fossil fuels are meeting the need of 87 % of global energy usage for various applications [1]. Moreover, growing environmental worries about the exhaustion of fossil resources and substantial harmful gas (CO, CO_2, NO_X, and SO_x) emissions should be addressed by designing and implementing alternative energy sources and vectors [2–4]. Hydrogen fuel seems to be the cleanest alternative energy vector, generating just water as a byproduct of oxidation, providing genuine "environmental friendliness" [5,6]. It is the most abundant chemical element, contributing to around 75 % of all elemental mass on the universe. Since hydrogen gas is less dense than air, it is scarce on earth [7]. H_2 has the most significant energy density of all the biofuels and energy sources. H_2 has a 122 kJ per kilogram energy output, 2.75 times that of conventional hydrocarbon fossil fuels [8–11] Methane steam reforming, electrolysis of water, and steam catalytic conversion of crude oil [10,12–16] are the most common industrial hydrogen generation technologies today [5,17,18]. Fig. 1 illustrates the diverse methods of hydrogen production, each identified by a specific color code. The methods include coal gasification, biomass gasification, steam methane reforming, and electrolysis. Each production technique is associated with different energy sources, highlighting the variety of approaches available for generating hydrogen. Just as an example, the steam catalytic method's conversion of heavy oil to hydrogen is unsustainable.

In contrast, hydrogen generation from biomass is a cost-effective, energy-efficient, and ecologically friendly process of hydrogen generation [19,20]. Biomass is a biological renewable natural resource widely available in various industries, including the agronomic and forest sectors. The primary forms of biomass in significant amounts, which are sustainable feedstock for bio-refineries, include agricultural, forest, fisheries, livestock, and urban waste [21,22]. Biomass is made up of organic components high in carbon, hydrogen, and oxygen elements. The average mass percentage of hydrogen in biomass is 6 %,

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Abbreviations: ADP, Adenosine Diphosphate; ATP, Adenosine Triphosphate; CCS, Carbon Capture and Storage; COD, Chemical Oxygen Demand; CI, Compression Ignition; Di, Inner Diameter; Do, Outer Diameter; Dc, Central Diameter; DF, Dark Fermentation; DOE, Department of Energy; Hc, Height of cylindrical part; Dc, Diameter of cylindrical part; HRT, Hydraulic Retention Time; Ht, Height of thermal reactor; S/B, Steam to Biomass ratio.

* Corresponding author.
E-mail address: praveen.kumar@unitn.it (P. Kumar).

https://doi.org/10.1016/j.ecmx.2024.100659
Received 3 April 2024; Received in revised form 14 June 2024; Accepted 2 July 2024

corresponding to 0.672 m^3 of H_2 produced per kilogram of biomass and accounts for more than 40 % of overall biomass energy [23].

Thermochemical, biological, and electrolytic routes are the most common ways of producing hydrogen from biomass at the current time [25,26]. Biological and electrolytic hydrogen production is challenging and, unfortunately, produces limited amounts of hydrogen, and thermochemical hydrogen generation is gaining popularity [27]. Gasification and pyrolysis are the two most common thermochemical conversion processes for biomass. Thermochemical gasification occurs at temperatures in the range of 700 to 1200 ℃ with no or limited amount of oxygen and generates combustible gas, making efficient syngas production [28–30]. Syngas is a fuel that may be used to heat homes and generate power, as well as synthetic chemicals like ammonia, methanol, and dimethyl ether [31].

Additionally, high-quality hydrogen produced by syngas may be utilized in fuel cells [32,33].

Another method for producing hydrogen from biomass is bioconversion. Bio-photolysis and fermentation are the primary biological mechanisms for generating biomass hydrogen [34,35]. Hydrogen generation by fermentation is an enzymatic process that converts organic material into hydrogen by utilizing a range of bacterial communities. It covers both dark and photoheterotrophic fermentation. Dark fermentation produces hydrogen in the dark using plentiful and low-cost anaerobic microorganisms. Between 30 and 80 °C, hydrogen may be generated from carbohydrate-rich feedstock. Some contaminants, like methane and hydrogen sulphide, are combined with the main product. Developing a safe technique for separating and cleaning hydrogen from gas mixtures is essential to increase practical applicability.

Photo-fermentation differs from the dark fermentation process in that it requires light. Hydrogen may be produced via photosynthetic hydrogen synthesis in aquatic settings at atmospheric temperatures and pressures [36]. However, using light energy to break the bond of water molecules into hydrogen and oxygen is inefficient for microalgae and cyanobacteria [37]. This is one of the most significant roadblocks to the application's success. One of the primary research directions is to increase the rate of hydrogen generation.

Fig. 2 presents a detailed breakdown of global hydrogen consumption by country and region. This includes data from China, the Middle East, the United States, Eastern Europe, Southwest Asia, Western Europe, Africa, Central Europe, Canada, and Japan. The figure highlights the varying levels of hydrogen usage across these diverse regions, providing a comprehensive overview of global consumption patterns, and it can be observed that Asia is the largest consumer of hydrogen. Hydrogen is the primary reactant in the petrochemical industry, and within the next 20 years, it has the potential to be used as a fuel. Fig. 3 highlights the primary applications of hydrogen, with ammonia synthesis being the most significant. Other notable uses include methanol production and hydrogenation/hydrotreatments of in the petrochemical sector (refining) mainly for fuel production.

The uniqueness of the production of hydrogen through

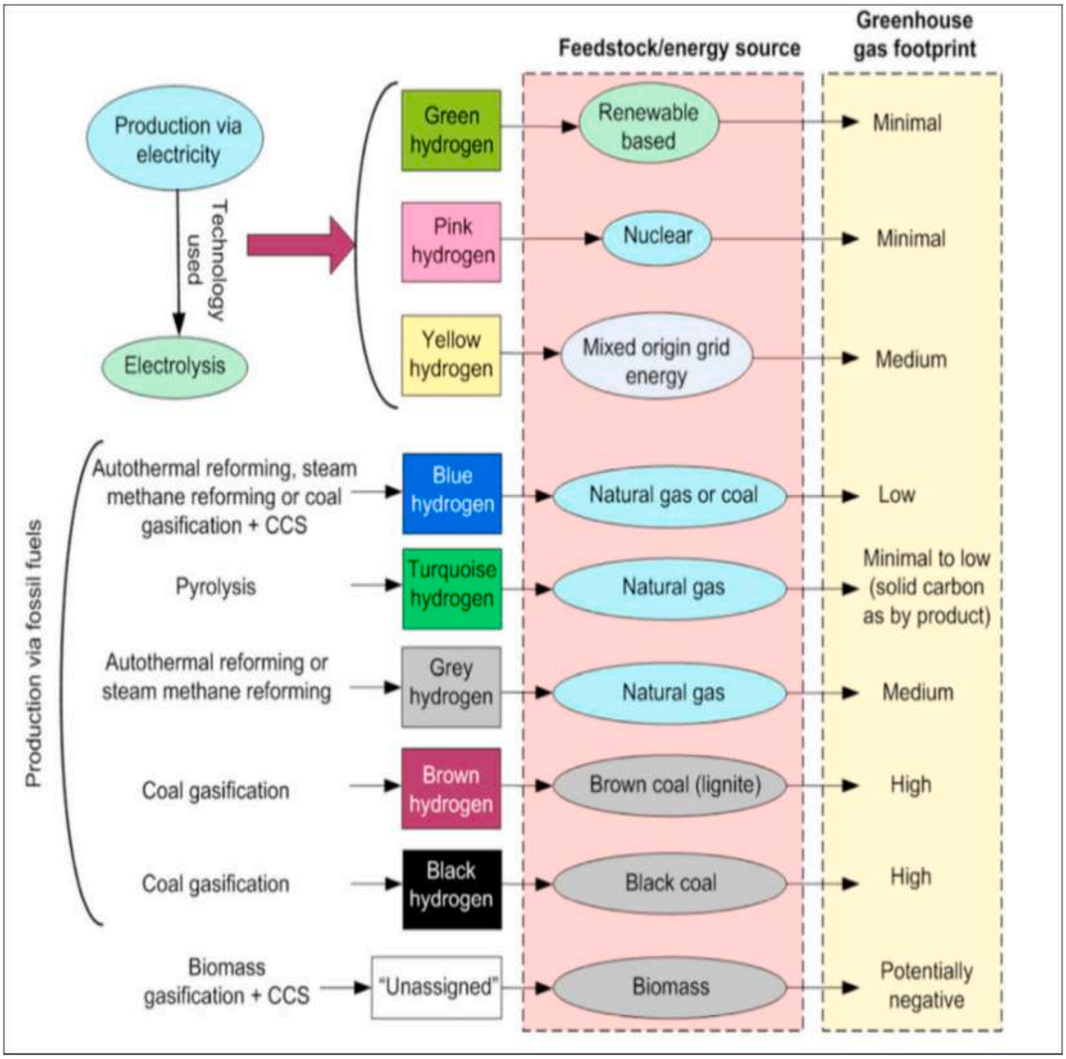


Fig. 1. Diverse methods of hydrogen production with feedstock [24].

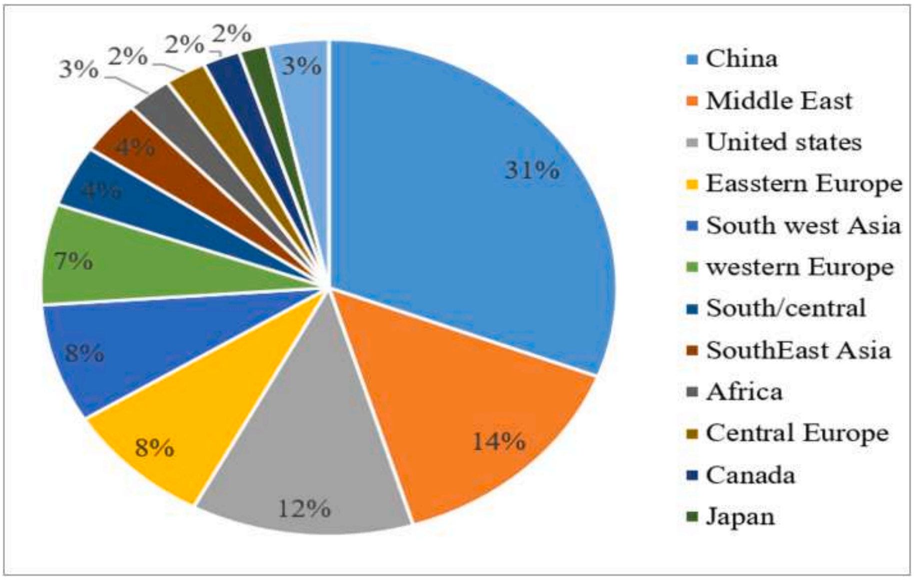


Fig. 2. Global hydrogen consumption by country and region [38,39].

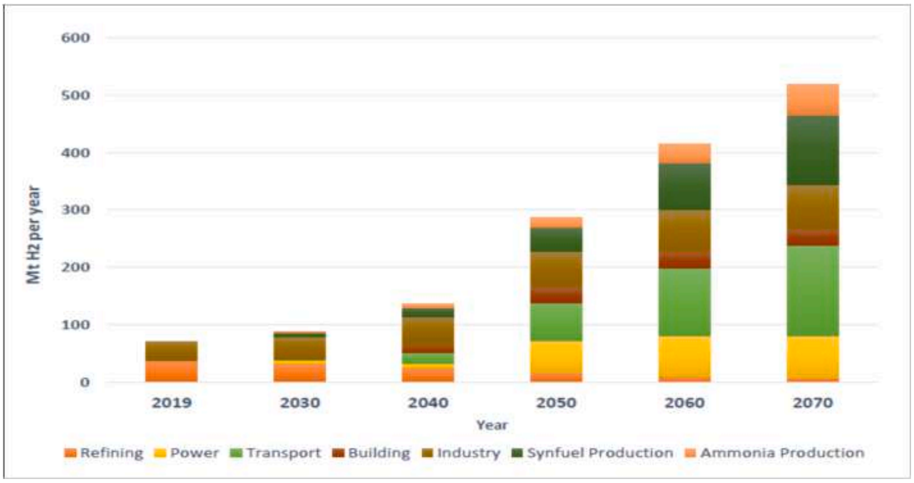


Fig. 3. Global hydrogen demand for various sectors 2019–2070 [40,41].

thermochemical and biological routes is in the innovative methods of producing hydrogen in a sustainable and efficient manner, hence overcoming the constraints of conventional techniques such as steam methane reforming and water electrolysis. Thermochemical methods involve using high temperatures to convert biomass into syngas. This process can be enhanced by using new catalysts and reactor designs to increase the amount and purity of hydrogen produced. Pyrolysis, on the other hand, is a process that breaks down organic materials without oxygen. Innovations in pyrolysis have focused on improving efficiency and managing the by-products generated. Within biological route, specific strains of cyanobacteria generate hydrogen via the process of fermentation and biophotolysis. By employing genetic engineering techniques and optimising growing conditions, the production and stability of hydrogen may be significantly improved. Advanced reactor designs enhance productivity by optimising the distribution of light, supply of nutrients, and exchange of gases. Dark fermentation employs anaerobic microbes to decompose organic materials in the absence of light. This process utilises innovative microbial communities and metabolic pathway manipulation to enhance productivity and expand the range of usable substrates. Integrating dark fermentation with processes such as photo fermentation improves overall efficiency and waste utilisation. The benefits of these approaches encompass the use of sustainable or low-emission energy sources, the capacity to handle a diverse array of raw materials, and the possibility of implementing small-scale, decentralised production systems. Nevertheless, there are still obstacles to overcome, since several procedures are now in the experimental or pilot phases.

These processes necessitate enhanced effectiveness, reduced costs, resilient materials, optimised reactor designs, and the construction of infrastructure for the production, storage, and distribution of hydrogen. This review paper offers an insight into these innovative H_2 production methods and technologies aimed at valorizing biomasses in view of sustainable production through thermochemical and biological routes.

2. Hydrogen production from bioresources

Thermochemical and biological routes have produced hydrogen from various biomass types. They include: almond shell [42], beech wood [43], black liquor [44], cedar wood [45], coir pith [46], coffee husk [47], corn cob [48,49], Food waste [50] hazel nut [51],

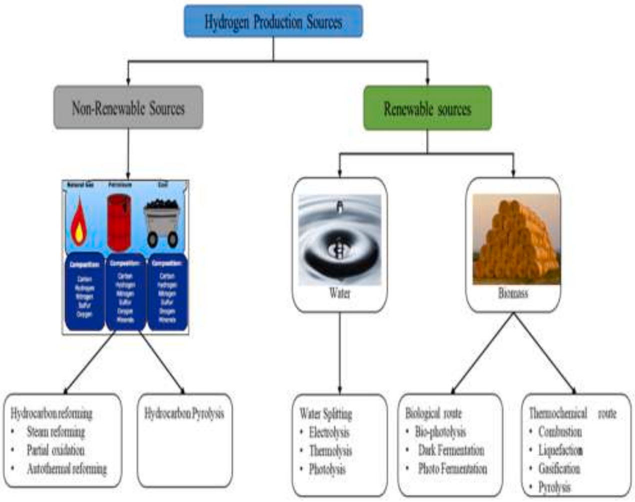


Fig. 4. Hydrogen production source and methods.

Table 1
The diverse thermochemical processes and reactions involved in hydrogen production [72–77].

Name of process	Reaction
Pyrolysis	$\mathrm{Biomass} \rightarrow \mathrm{H_2} + \mathrm{CO_2} + \mathrm{CO} + \mathrm{CH_4} + \mathrm{C_nH_m} + \mathrm{tars} + \mathrm{biochar}; \quad \Delta H > 0\,\mathrm{kJ/mol}$
Combustion	$\mathrm{C} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CO}; \quad \Delta H = -111\,\mathrm{kJ/mol}\mathrm{H_2} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{H_2O}; \quad \Delta H = -242\,\mathrm{kJ/mol}\mathrm{CO} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CO_2}; \quad \Delta H = -254\mathrm{kJ/mol}$
Boudouard	$\mathrm{C} + \mathrm{CO_2} \rightarrow 2\mathrm{CO}; \quad \Delta H = 172\,\mathrm{kJ/mol}$
Methane formation	$\mathrm{C} + 2\mathrm{H_2} \rightarrow \mathrm{CH_4}; \quad \Delta H = -75\,\mathrm{kJ/mol}$
Water gas	$\mathrm{C} + \mathrm{H_2O} \rightarrow \mathrm{CO} + \mathrm{H_2}; \quad \Delta H = 131\,\mathrm{kJ/mol}\mathrm{C} + 2\mathrm{H_2O} \rightarrow \mathrm{CO_2} + 2\mathrm{H_2}; \quad \Delta H = 100\,\mathrm{kJ/mol}$
Steammethane reforming	$\mathrm{CH_4} + \mathrm{H_2O} \rightarrow \mathrm{CO} + 3\mathrm{H_2}; \quad \Delta H = 200\,\mathrm{kJ/mol}\mathrm{CH_4} + 2\mathrm{H_2O} \rightarrow \mathrm{CO_2} + 4\mathrm{H_2}; \quad \Delta H = 165\,\mathrm{kJ/mol}$
CO shift	$\mathrm{CO} + \mathrm{H_2O} \rightarrow \mathrm{CO_2} + \mathrm{H_2}; \quad \Delta H = -41\,\mathrm{kJ/mol}$
General tar cracking	$\mathrm{C_nH_m} + n\mathrm{H_2O} \rightarrow n\mathrm{CO} + \left(n + \frac{1}{2}m\right)\mathrm{H_2}; \quad \Delta H > 0\,\mathrm{kJ/mol}$
Tar cracking	$\mathrm{Tars} + \mathrm{H_2O} \rightarrow \mathrm{CO_2} + \mathrm{H_2} + \mathrm{CO} + \mathrm{lower\,hydrocarbon}; \quad \Delta H > 0\,\mathrm{kJ/mol}$

lignocellulosic char [52], marine algae [53], municipal solid waste [54], paper mill waste [55], pine saw dust [56], palm oil waste [57], saw dust [58], spruce wood [59], tea waste [60], waste water sludge [61], waste wood [62], wheat straw [63], wood saw dust [64], yellow pine woodchips [53,65]. The present study focuses on two primary methods of producing hydrogen from biomass: the thermochemical route and the biological route. The thermochemical methods include gasification [66] and pyrolysis, each employing high-temperature processes to convert biomass into hydrogen. The biological route encompasses biophotolysis, dark fermentation, and photo fermentation, which utilize biological processes and microorganisms to generate hydrogen. These methods are detailed in Fig. 4, providing a comprehensive overview of the diverse approaches to hydrogen production from biomass. Biological processes are more ecologically friendly and energy-efficient since they function under mild operating conditions. Still, they produce modest rates and yields of hydrogen (molH_2/mol feedstock) based on the raw biomass utilized [11]. Thermochemical processes are substantially faster and produce larger hydrogen output, making gasification an economically and environmentally feasible option [67,68].

2.1. *Thermochemical route*

The thermochemical route consists of the conversion of biomass into hydrogen and hydrogen-rich gases by diverse thermochemical process [69,70]. The generation of hydrogen-rich gas from syngas resulting from such procedures is an essential technique for environmental preservation, as it produces minimal greenhouse gases [71].

The thermochemical conversion process is primarily concerned with thermochemical gasification and pyrolysis. Both conversion methods produce gaseous fuel mixtures like hydrogen, methane, and carbon monoxide, which are processed for different hydrogen generations via steam reforming and the water gas shift reaction.

Table 1 outlines the various processes and reactions involved in the thermochemical route for hydrogen production. These include pyrolysis, combustion, the Boudouard reaction, methane formation, the water–gas reaction, steam methane reforming, the CO shift reaction, and tar cracking. Each reaction plays a critical role in converting raw materials into hydrogen, showcasing the complexity and diversity of thermochemical processes used in hydrogen production.

2.1.1. *Fast pyrolysis*

Rapid pyrolysis converts a significant amount of biomass to bio-oil, known as pyrolytic oil. Fast pyrolysis generates liquid material, and a limited quantity of gaseous compounds, including hydrogen, are also produced. Pyrolytic oil can be reformed with steam to extract hydrogen [78,79]. The oil is divided into water-soluble and water-insoluble portions based on its solubility. Hydrogen is generated by steam reforming of the water-soluble fraction. The water-insoluble fraction can be used for making adhesives. The limited effectiveness of this technique and the creation of tar and char are its primary drawbacks. Tar formation causes other unneeded reactions that lower the production of gaseous products. Char interacts with gaseous particles to form undesirable compounds.

2.1.2. *Steam gasification*

The gasifying agent utilized in the procedure is used to classify the gasification process. Steam is used as a gasification agent in the steam gasification operation. A pyrolytic step occurs before gasification because the pyrolysis rate is quicker than gasification. Pyrolysis produces volatiles, generating char (residue), which interacts with steam to produce H_2, CO, and CO_2. Steam gasification produces H_2 and fuel gas for heating [80]. According to estimates, the average steam gasification product gas composition is H_2 (64.40–68.48 %), CO (6.57–5.82 %), CH_4 (0.65–0.83 %), CO_2 (28.20–24.7 %), and CxHy (0.18–0.11 %) [81]. The largest H_2 generation from biomass is reported to be 17 % (on a biomass weight basis) [82]. On a dry basis, the process may create 53–55 % H_2-rich syngas [83].

2.1.3. *Supercritical water gasification*

Supercritical water gasification is a new method of hydrogen production. Water occurs under normal conditions in all three states of matter solid, liquid, and gases (steam) [84]. When subjected to supercritical conditions of 22.1 MPa and 374 °C, water's gas and liquid forms become entirely miscible [85]. Oxygen acts as an oxidant in water under these circumstances. When a carbonaceous substance, such as biomass, reacts with supercritical water, the carbon present in the biomass is oxidized, and CO is released. Then after CO is oxidized and generates CO_2. The hydrogen in the biomass and the water are liberated and, as a result, H_2 is produced. This technique is ideal for biomass with large moisture fraction. Besides, the cost of producing H_2 in this process is much greater than traditional steam methane reforming in refinery, which uses natural gas [86]. The technology is still under research and requires much investigation to be verified. Table 2 provides detailed information on various biomass gasification reactors used for hydrogen production, highlighting the different feedstocks and reactor characteristics. The feedstocks include meat and bone meal, sludge, agricultural waste pellets [87–89] and wood, each chosen for their potential to generate hydrogen. The table also describes the construction details and features of each reactor, such as flow rate, biomass feeding rate, and equivalence ratio. These parameters are crucial for optimizing the gasification process and maximizing hydrogen yield, offering a

Table 2
Different biomass gasification reactors used for hydrogen production

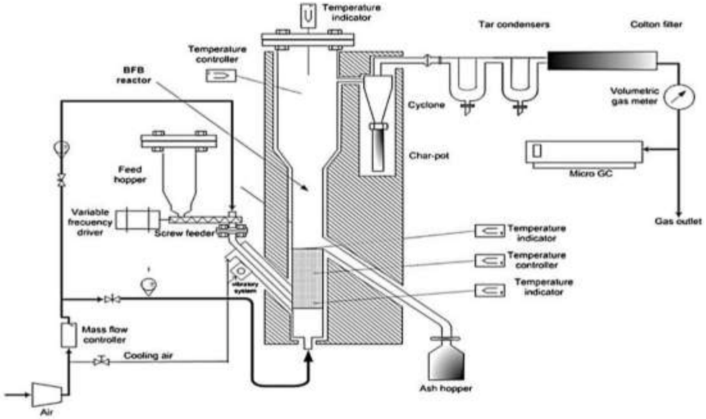
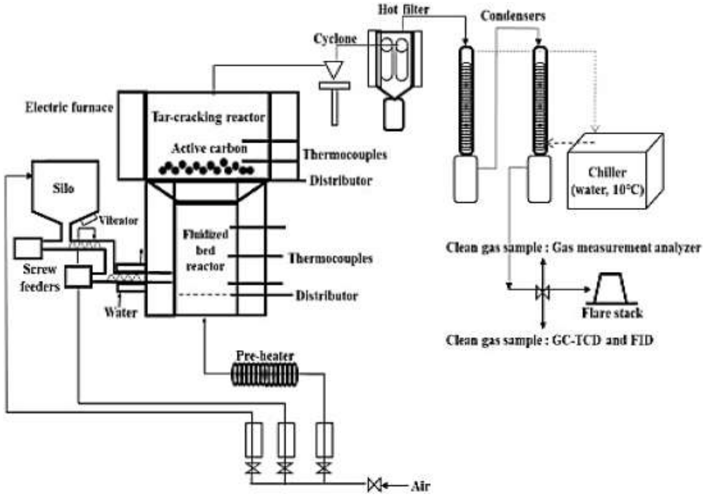
Biomass	Construction detail and effective parameter			Gasifier	
	Feature	Air flow rate H_2 production rate	Feeding rate of biomass	Reactor Equivalence ratio	
 Meat and bone meal Meat and bone meal	- Bed zone, $d_{in} = 40$ mm. free board zone, $d_{in} = 63$ mm. Fluidized bed reactor	- $H_2 = 21.2–22.7$ vol% (100 % coal and 0.5 % meat-99.5 % coal)	1.8 g/min	0.25–0.35	 [90]
 Municipal sewage sludge Municipal sewage sludge	- Silica sand (2.2 kg) with a diameter of between 150–300 mm was used	- Sewage sludge/ coal = 30:70 ProduceH_2 = 26.63 %	13 g/min	0.3	 [91]

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Table 2 (*continued*)

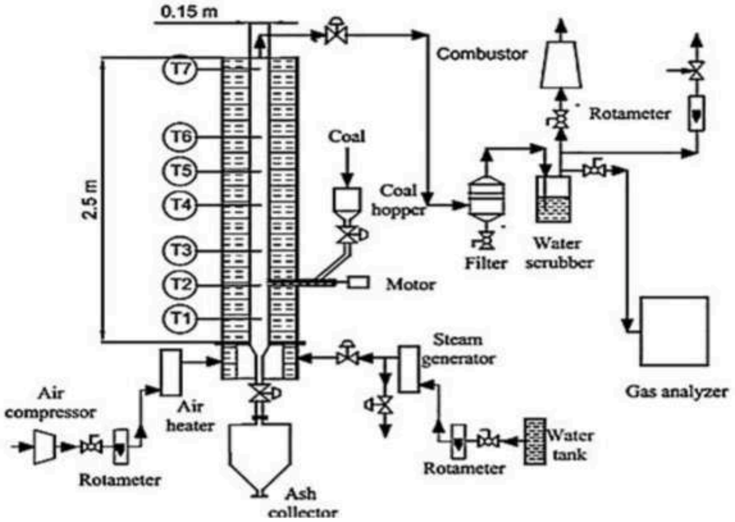
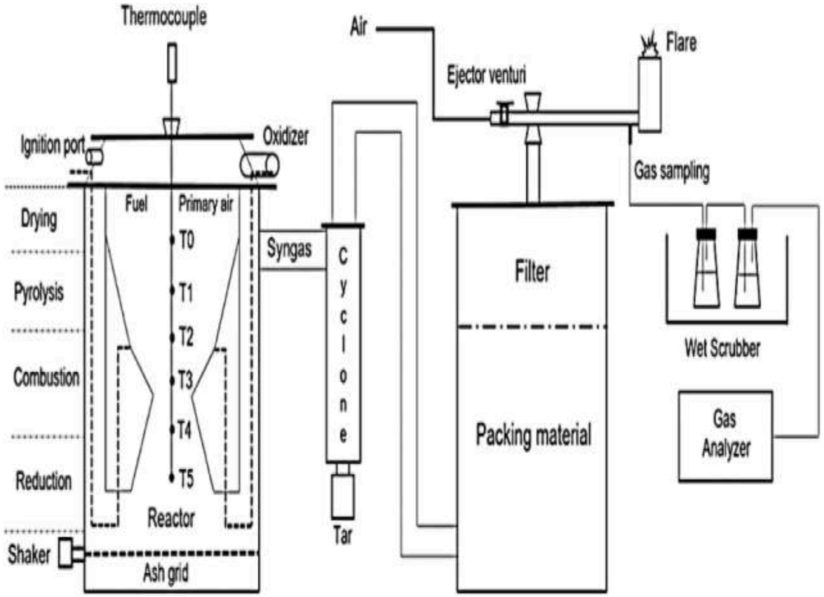
Biomass	Construction detail and effective parameter			Gasifier Reactor	
	Feature	Air flow rate H_2 production rate	Feeding rate of biomass	Equivalence ratio	
 Rice husk	• Air and steam media Bubbling fluidized bed gasification Reactor has been fixed as 40 kW. Diameter 0.15 m with height = 2.5 m.	Air flow rate, 13.92 kg/h	1.0–9.8 kg/h	0.22	 [92]
 Pine pellet	• Diameter (drying zone) = 280 mm Height = 200 mm 10 kWth gasifierAir media	• H_2 molar ratio = 17.28–21.39 % H_2 and CO increased with reactor temperature.	1 kg/h	0.27——0.28	 [93]

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Table 2 (*continued*)

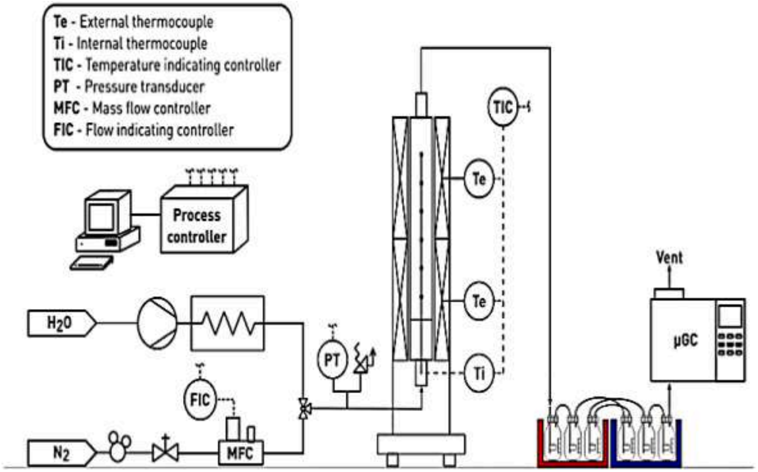
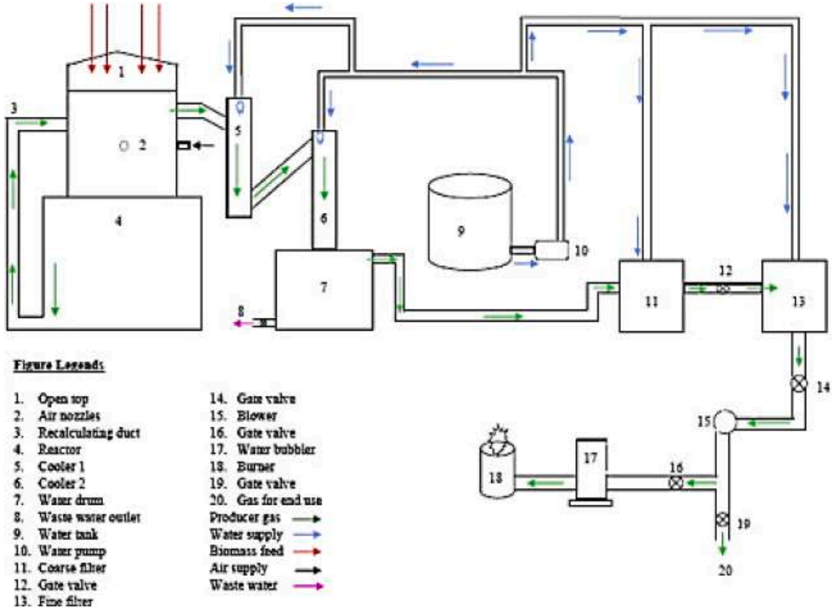
Biomass	Construction detail and effective parameter			Gasifier Reactor	
	Feature	Air flow rate H_2 production rate	Feeding rate of biomass	Equivalence ratio	
 Pruning waste of olive	- Retrofitting small-scale gasifiers Steam media Steam flow rates = 0.04——0.20 g/min	- Optimum H_2 = 70 % at a 800℃ Steam flow rate = 0.04 g/min	214 gm/min	–-	 [94]
 Pine needle pellets and Pongamia pellets	- 20kWeDowndraft gasifier	- H_2 = 7.44 Gas flow rate = 14.10 g/s Efficiency = 65 %	——	0.3	 [95,96]

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Table 2 (*continued*)

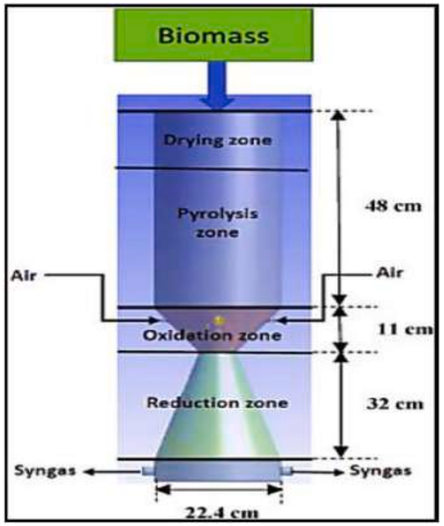
Biomass	Construction detail and effective parameter			Gasifier Reactor	
	Feature	Air flow rate H_2 production rate	Feeding rate of biomass	Equivalence ratio	
 Rubber wood	- Downdraft gasifier Height = 91 cm Diameter = 22.4 cm	- Air flow rate = 1.64 Nm3/hr	3.65 kg/hr	0.30–0.45	 [97]

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Table 2 (*continued*)

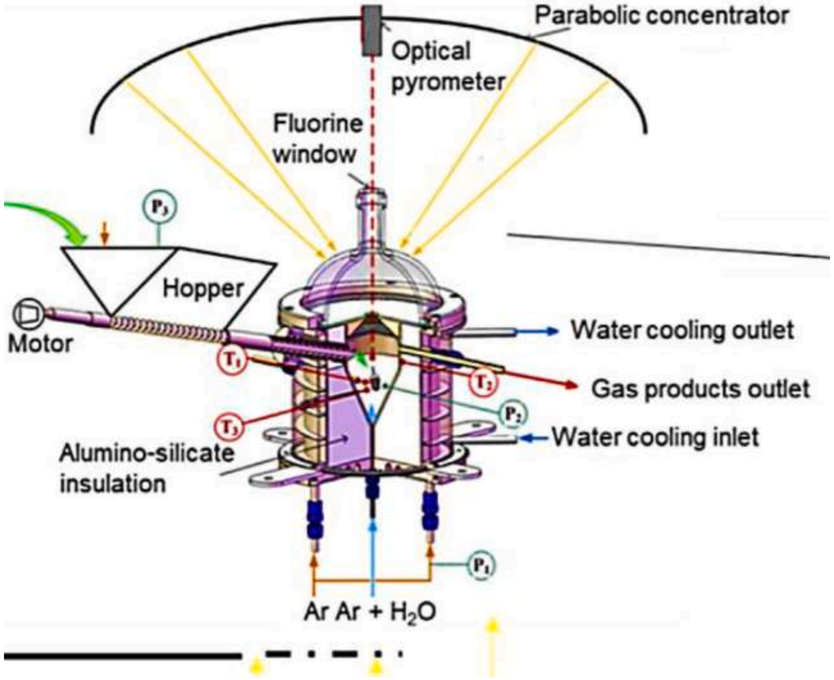
Biomass	Construction detail and effective parameter			Gasifier Reactor
	Feature	Air flow rate H_2 production rate	Feeding rate of biomass	Equivalence ratio
 Beech wood	- Hopper capacity = 1.15 l Air flow = 0.5 NL/minSolar gasification reactor	- H_2 = 1957 k mol CO = 1656kmol Optical mode: H_2 = 71 % Hybrid mode: H_2 = 3349 kmol CO = 3388 kmol	g/min.	 [98]

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Table 2 (*continued*)

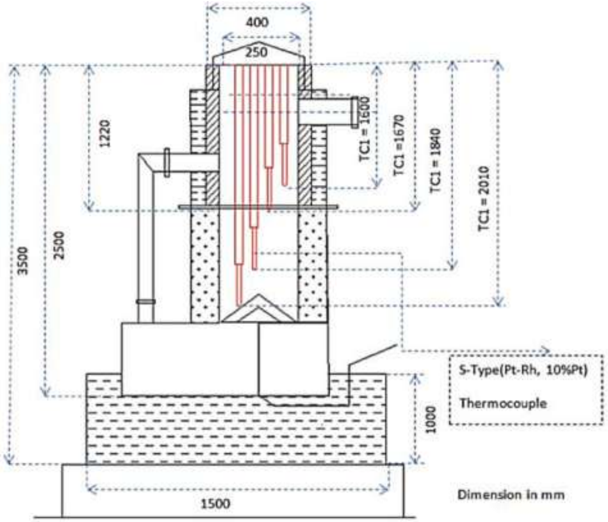
Biomass	Construction detail and effective parameter			Gasifier Reactor	
	Feature	Air flow rate H_2 production rate	Feeding rate of biomass	Equivalence ratio	
 Waste wood	- Height = 3.5 *m* Diameter = 400 mm Gasifier material = Stainless steel Wood shape and size = rectangular shape of 6 cm	- H_2 = 10–15.6 %	2.5 kg/hr	0.30–0.37	 [77]

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Table 2 (*continued*)

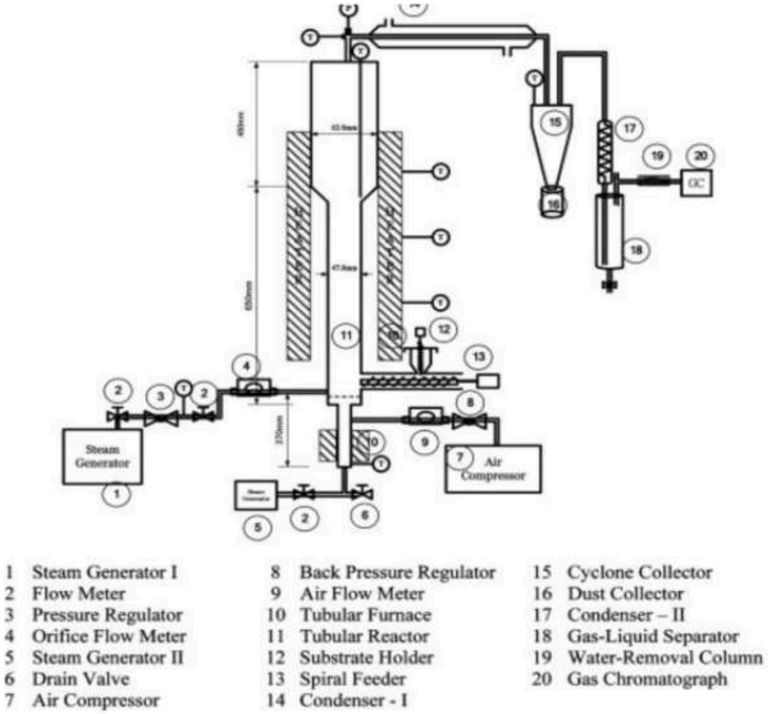
Biomass	Construction detail and effective parameter			Gasifier Reactor	
	Feature	Air flow rate H_2 production rate	Feeding rate of biomass	Equivalence ratio	
 Mushroom waste	- Tubular reactor SS-310 material Freeboard zone inner diameter = 63.9 mm Reactor length = 450 mm	- H_2 = 15–40 vol%	Bach feed.	0.27–0.33	 [99]

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Table 2 (*continued*)

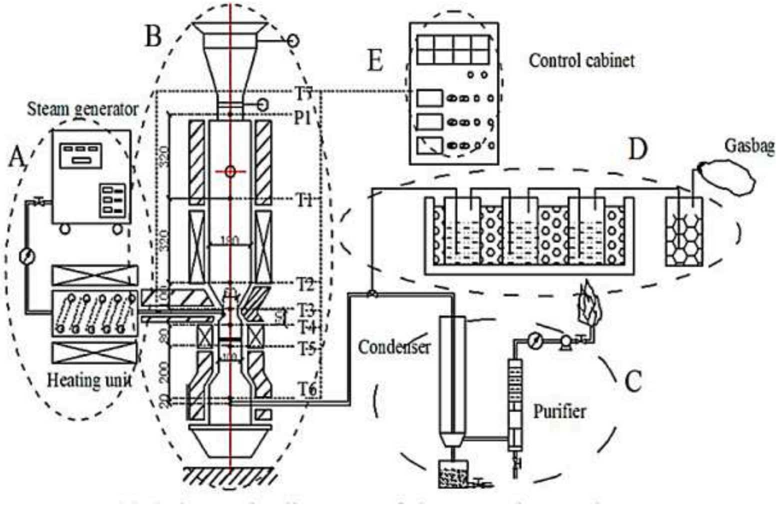
Biomass	Construction detail and effective parameter				Gasifier Reactor
	Feature	Air flow rate H_2 production rate	Feeding rate of biomass	Equivalence ratio	
 Pine wood	- Downdraft gasifier Steam flow = 0.3–0.9 kg/h	- H_2 = 15–105 m^3/kg	Stem to biomass ratio = 0.95	–	 [100]

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Table 2 (*continued*)

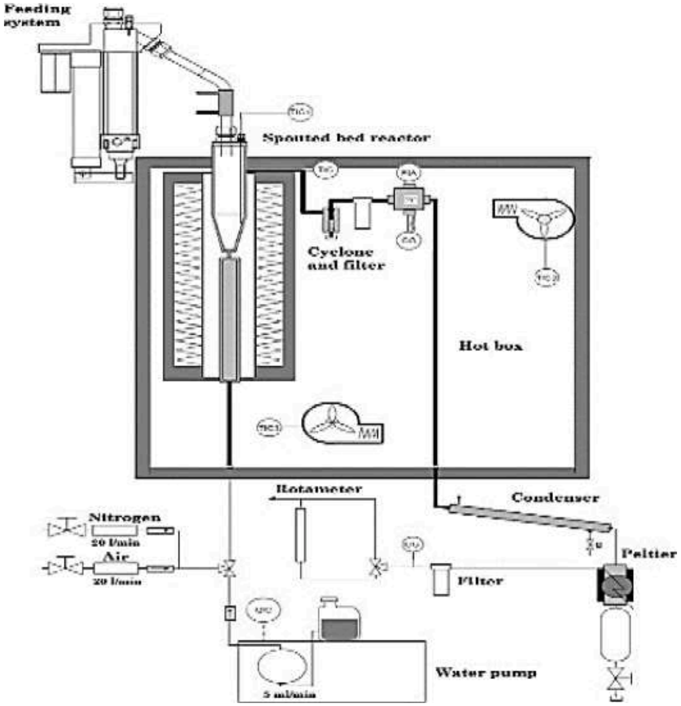
Biomass	Construction detail and effective parameter				Gasifier Reactor
	Feature	Air flow rate H_2 production rate	Feeding rate of biomass	Equivalence ratio	
 Pine saw dust	- Conical spouted bed gasifier Di = 12.5 mm Do = 7.6 mm Dc = 60.3 mm Hc = 73.0 mm Ht = 298.0 mm Steam flow rate = 1.86 l/min	- H_2 = 0–40 %	Saw dust = 0.2 to 3gmin^{-1}		 [101]

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Table 2 (*continued*)

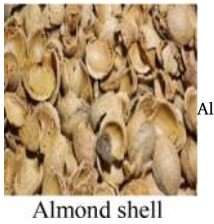
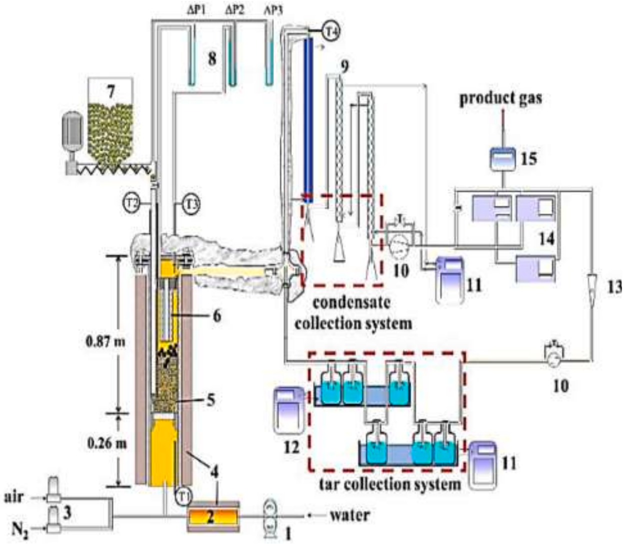
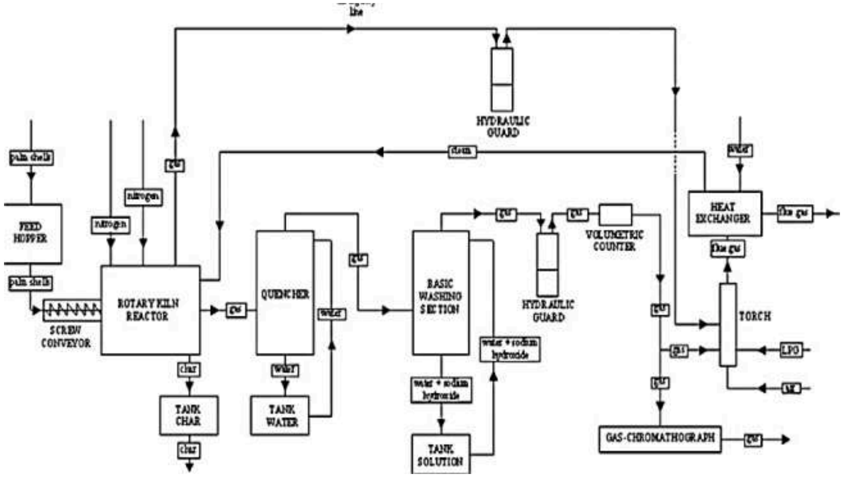
Biomass	Construction detail and effective parameter			Gasifier Reactor	
	Feature	Air flow rate H$_2$ production rate	Feeding rate of biomass	Equivalence ratio	
 Almond shell	- Fluidized bed biomass gasification plant Inner diameter = 100 mmSteam media	- Air flow rate = 10.6 l/min H$_2$ = 31.4–57.5 %	11.6 gm/ min	0.148	 [102]
 Palm shell	- Rotary kiln reactor Diameter = 400 mm Length = 1000 mm	$_2$ = 39.4–52.5 %	5 kg /h	–-	 [103]

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Table 2 (*continued*)

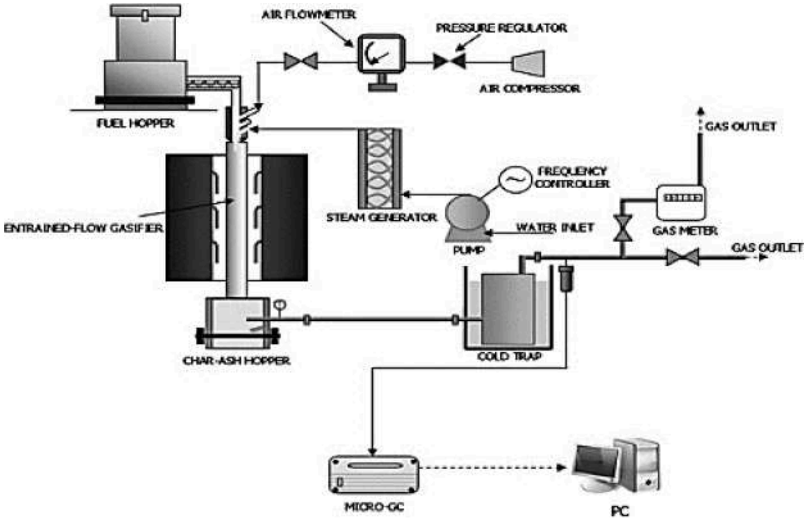
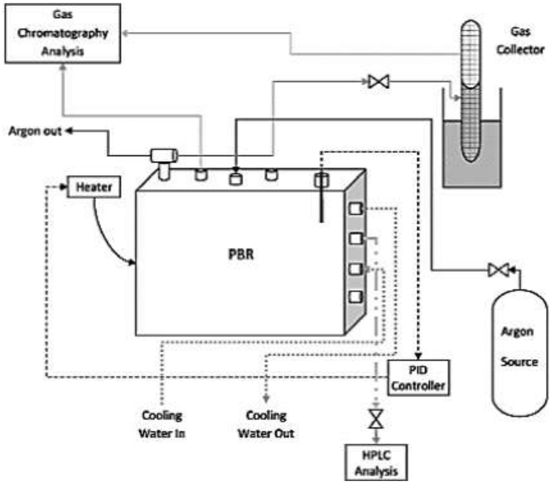
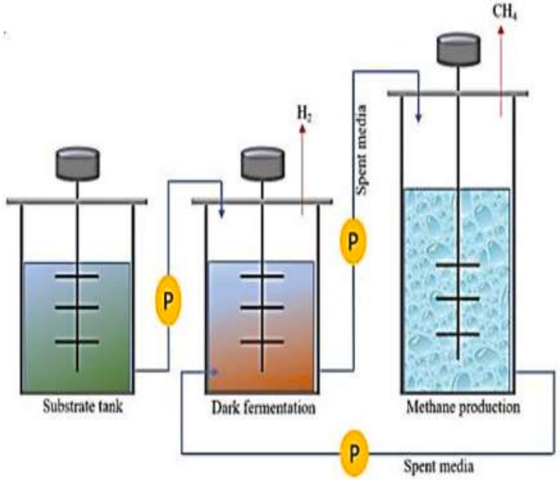
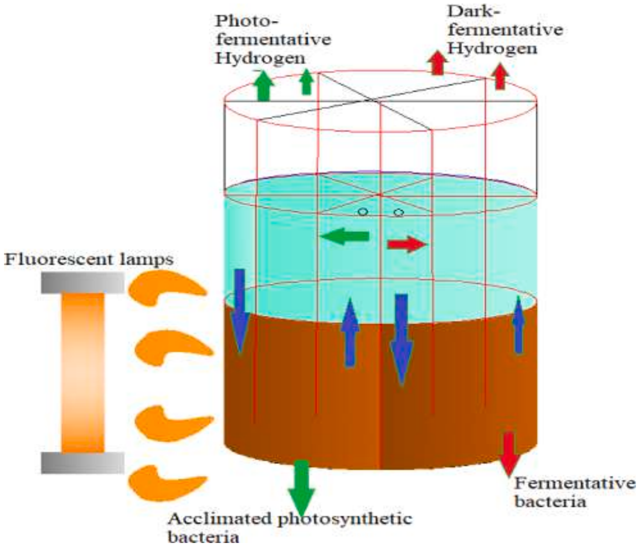
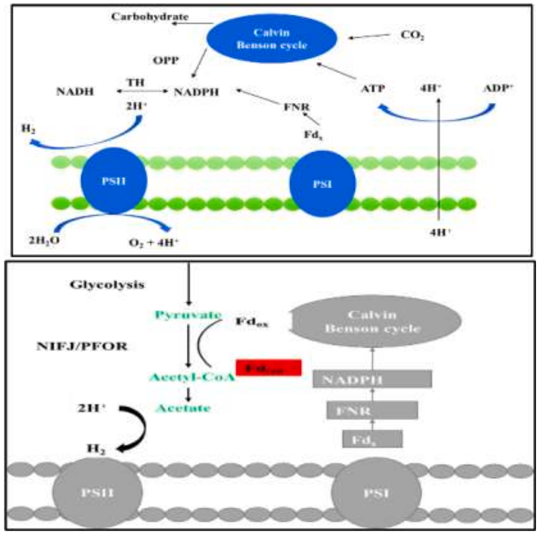
Biomass	Construction detail and effective parameter			Gasifier Reactor	
	Feature	Air flow rate H_2 production rate	Feeding rate of biomass	Equivalence ratio	
 De alcoholised marc of grape	- Entrained-flow gasification pilot plant. Steam flow rate = less than 1.5 kg/h	H_2 = 2.7–5.74 k mol/h	1–2 kg/h	0.2	 [104]

Table 3
Various biological processes used for hydrogen production.

Process	Biomass and substrate	Group of bacteria	Key enzymes	H_2 production	Reactor
fermentation	Molasses,food waste, wastewater	Rhodo bacteria capsulatus,Rhodobium marinum, R.sphaeroides	Nitrogenase,Hydrogenase	H_2 yield rate = 0.01 l/l/h	 [113]
	Pre-treated Water hyacinth, (leaves and stems)	Engineered bacteriaE. cloacae	Hydrogenase	H_2 yield = 74.9 mL/g of total volatile solid	 [114]

(*continued on next page*)

Table 3 (*continued*)

Process	Biomass and substrate	Group of bacteria	Key enzymes	H_2 production	Reactor
	Protein-rich waste water (e.g., gelatin)	RhodospirillaceaeClostridiaceae		H_2 yield = 0.4 l/g COD, at HRT = 24 h and initial pH = 6.5.	 [115]
– photolysis	Water, carbohydrate	Chlamydomonas reinhardtii, Chlorella fusca, Scenedesmus obliquus,Chlorococcum littorale,Nostoc,Anabaena,Calothrix, Oscillatori	Nitrogenaseorhydrogenase	Photoautotrophs aid in the establishment of strains that produce bio hydrogen at appropriate amounts in cyanobacteria	 [116]

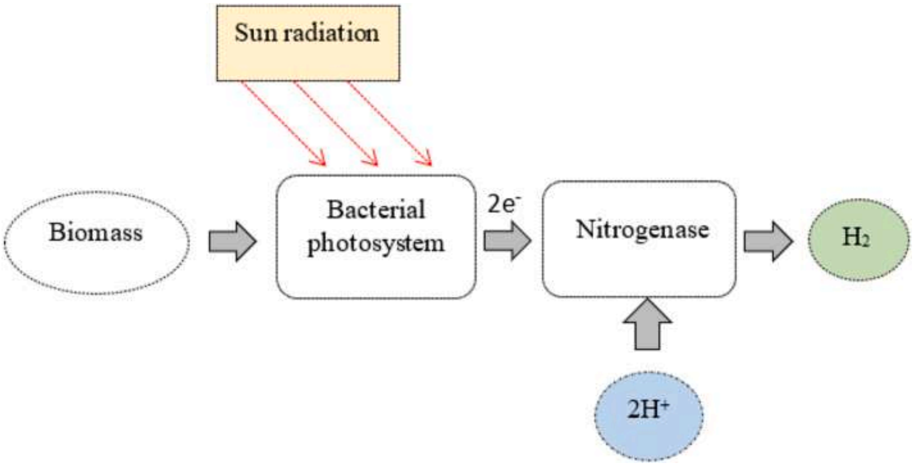


Fig. 5. Schematic flow of photo fermentation process.

comprehensive overview of the technologies and materials employed in biomass gasification for hydrogen production.

2.2. Biological route

Research in hydrogen generation by biological route has risen considerably in the last several years due to a greater focus on environmental sustainability and waste minimization. The majority of biological processes run at atmospheric pressure and temperature. Furthermore, they employ limitless renewable energy resources and help trash recycling since they may use various wastes as feedstock [105,106]. The primary biological methods for hydrogen gas generation are direct and indirect bio-photolysis, photo and dark fermentations, and multistage or sequential dark and photo-fermentation. Table 3 presents an in-depth overview of various biological processes used for hydrogen production, including photo fermentation, dark fermentation, combined photo and dark fermentation, and biophotolysis. The table details the different substrates and groups of bacteria involved in each process and the key enzymes that facilitate hydrogen production.

Additionally, it describes the various reactor types used and their respective hydrogen yields. This comprehensive information highlights the diverse biological methods and their efficiencies in producing hydrogen, showcasing the potential and versatility of biological routes for sustainable hydrogen production. Biomass for fermentative processes, where the carbohydrate-containing materials are changed and transformed into organic acids, which are then converted to hydrogen gas using bioprocessing techniques, produces hydrogen via the hydrogenase or nitrogenase enzyme systems of bacteria and algae [107–112].

2.2.1. Fermentation processes

Fermentation processes are microbial conversions of organic feedstocks that produce modest quantities of alcohols, acetic acid, hydrogen, and carbon dioxide. They may occur with or without the presence of oxygen. These bio-hydrogen production systems are interesting because they utilize waste products and enable low-cost energy generation while simultaneously treating biowaste [117].

2.2.1.1. Photo fermentation process. In photo fermentation, sunlight is used for degrading carbohydrates and organic acids into carbon dioxide and hydrogen. The ability of cyanobacteria to produce hydrogen is widely reported regarding both algae and bacteria [118]. Rhodobacter bacteria are also promising for hydrogen generation via anoxygenic photosynthesis and photo-fermentation [119]. Algae and cyanobacteria may utilize light with a 400–1000 nm wavelength region. *Rhodospirillum* and *Rhodobacter sphaeroides* are photosynthetic bacteria that consume the carbon from the molecule of organic acids [120]. The following equation shows the use of light energy for producing hydrogen.[121].

$$16ATP + N_2 + 16H_2O + 10H^+ + 8e^- + light \rightarrow 16ADP + 2NH_4^+ + 16pi + H_2 \tag{1}$$

Sun energy and organic acids are used to achieve photo-fermentation in nitrogen-deficient environments. While nitrogenase is available, certain photosynthetic bacteria may convert organic acids (butyric, acetic, and lactic) into carbon dioxide and hydrogen [122].

$$CH_3COOH + 2H_2O \rightarrow^{light} 4H_2 + 2CO_2 \tag{2}$$

$$C_3H_6O_2 + 4H_2O \rightarrow^{light} 7H_2 + 3CO_2 \tag{3}$$

$$C_4H_8O_2 + 6H_2O \rightarrow^{light} 10H_2 + 4CO_2 \tag{4}$$

$$C_3H_6O_3 + 3H_2O \rightarrow^{light} 6H_2 + 3CO_2 \tag{5}$$

Light intensification stimulates H_2 output and production rate but has a negative effect on light conversion efficiency. When producing H_2 from industrial wastes, a big issue arises due to the wastewater's color. It might reduce the penetration of light and, in the presence of harmful compounds, such as heavy metal ions, it is necessary a pretreatment before use [123–125]. Low solar energy conversion efficiency and requirement for complex anaerobic photobioreactors require huge areas, despite hydrogen generation under light conditions i generally higher than in the dark [126]. The restricted availability of organic acids is the major obstacle to the proficiency of this approach [127]. A schematic representation of H_2 generation by photosynthetic bacteria is shown in Fig. 5.

2.2.1.2. Dark fermentation process. Dark fermentation eliminates the issue of requiring light as an energy source. Most of the production occurs via the acetate and butyrate paths [128]. Dark fermentation is a type of fermentation that employs anaerobic bacteria to ferment carbohydrate-rich materials in the absence of oxygen. Carbohydrates are used as feedstock for various bacterial strains in the dark fermentation process. H_2 production is measured in terms of the molar quantity of hydrogen produced per mol of substrate. Wastewater treatment sludge [129] has also been used as a substrate for dark fermentation (DF) by Clostridium bifermentans and Pseudomonas sp. GZI. However, the hydrogen yields from this process have been relatively low, producing only 0.9 mmol of H_2 per gram of dried sludge. When considering the molecular formula of activated sludge as approximately $C_5H_7O_2N$, this translates to about 0.1 mol of H_2 per mole of dried sludge [130]. As shown in Eqs. (6), (7), glucose is a model substrate. More than 80 % of

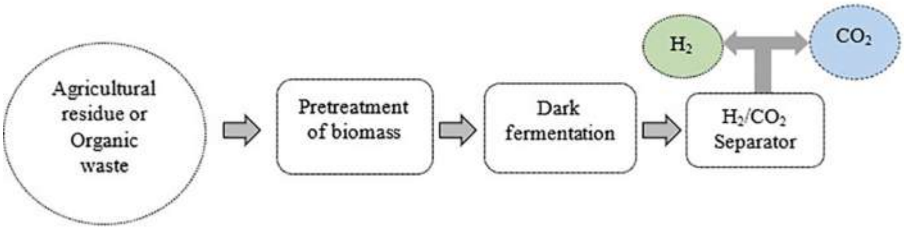


Fig. 6. Schematic flow of dark fermentation process.

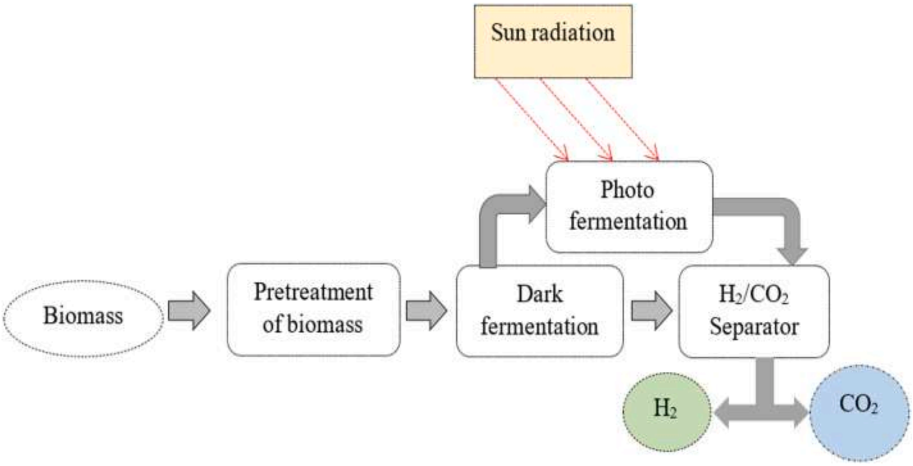


Fig. 7. Schematic flow of combined dark and photo fermentation process.

total end products are acetic and butyric acids. Ideally, acetate fermentation and butyrate fermentation both produce four mol of H_2 per mole of glucose [11].

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2 \quad (6)$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow CH_3CH_2CH_2COOH + 4H_2 + 2CO_2 \quad (7)$$

The primary feedstock for this procedure, glucose, is very costly and not frequently available in large amounts, although agricultural waste may contain it. Alternative materials include starch-containing compounds plentiful in nature and cellulose, the primary component of plant biomass [131]. The pH should be kept between 5 and 6 for better production, as the amount of H_2 produced by this method strongly depends on pH [132]. Another limitation is that the hydrogen must be eliminated from the moment it is produced since H_2 generation tends to decrease as pressure increases [133]. As illustrated in Fig. 6, dark fermentation is a relatively straightforward technique for hydrogen production that operates independently of light sources. This method leverages anaerobic bacteria to break down organic substrates, making it a practical and efficient process for generating hydrogen without complex light-based systems. As a result, a large area of land is not required, and hydrogen may be generated continuously during the day and night from a diverse range of potentially usable substrates, like trash and waste products [134].

2.2.1.3. Combined fermentation. As indicated by its name, the combined process of dark and photo fermentation integrates both dark fermentation and photo fermentation methods, as depicted in Fig. 7. This hybrid approach leverages the advantages of each process, utilizing anaerobic bacteria in dark fermentation to break down substrates without light, followed by photo fermentation which uses light to enhance hydrogen production further. In this process, it can be observed that there is a reduction in the formation of byproducts. This process's economic perspective promises industrial-scale hydrogen production [119,135,136]. As previously discussed, organic acid yield in dark

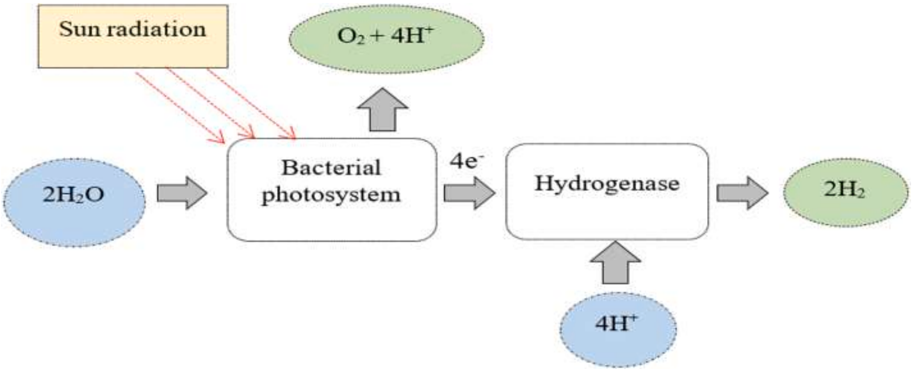


Fig. 8. Schematic flow of the direct bio-photolysis process.

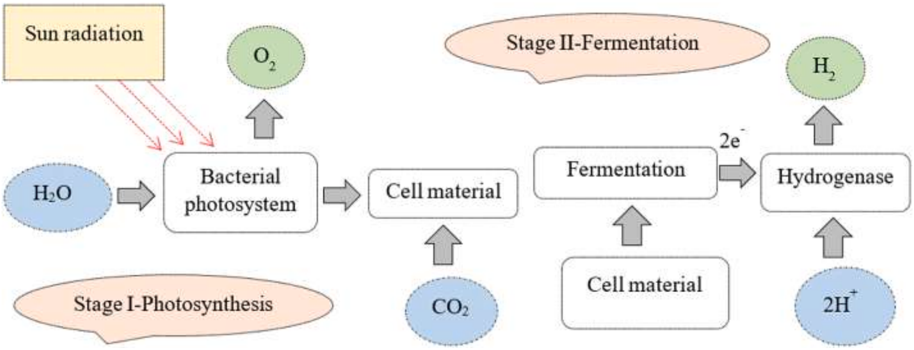


Fig. 9. Schematic flow of the indirect bio-photolysis process.

fermentation can be used in photo fermentation, providing an edge over a single process. Chen et al. [137] observed a reduction in COD and increased hydrogen production in the combined dark and photo fermentation process. This technique eliminated 72 % COD and increased hydrogen production from 3.80 mol H_2 per mol of sucrose to 10.02 mol H_2 per mol of sucrose. Another observation suggests that acetate formation in dark fermentation was used as a carbon source for Rhodopseudomonas palustris in photo fermentation, but inhibition took place when carbon was utilized from butyrate [138]. Chookaew et al. [139] also studied the combined process. Dark fermentation using Klebsiella sp. TR17 was used for the first stage, and Rhodopseudomonas palustris TN1 was used for photo fermentation in the second stage. Hydrogen yield in the first stage was 5.74 mmol H_2/g COD and 0.68 mmol H_2/g COD in the second stage by adding yeast extract (2.3 g/L), NaHCO3 (0.63 g/L), and glutamate (2–8 mmol/L) to the effluent from dark fermentation. Dark fermentation effluent is an excellent photo-fermentation feedstock [140–142].

2.2.2. *Bio-photolysis process*

Bio-photolysis is a biological method that generates hydrogen gas using the same principles as plant and algae photosynthesis. In green plants, H_2 production does not occur because they lack enzymes that catalyze it and the hydrogen ions produced by the first stage of photosynthesis enter the CO_2 reduction reaction carried out by electrons [143]. On the other hand, algae have H_2-producing enzymes that can generate H_2 in specific conditions.

2.2.2.1. Direct bio-photolysis process. In direct bio-photolysis, green algae play a crucial role in splitting water molecules into hydrogen ions and oxygen, a process depicted in Fig. 8.

This method harnesses the photosynthetic capabilities of green algae to produce hydrogen directly from water, making it an efficient and environmentally friendly approach to hydrogen production. The hydrogenase enzyme transforms the produced hydrogen ions into hydrogen gas [144]. Since the hydrogenase enzyme is extremely oxygen-sensitive, the oxygen concentration must be kept below 0.1 percent at all times [145]. At maximal sunlight intensity, however, 90 % of photons received by photosynthesis (chloroplasts and some other pigments) are not used in photosynthesis and instead disintegrate as radiation or fluorescence [146]. To avoid the “light-saturation effect,” microalgae mutants were discovered to have reduced pigment content with fewer amounts of chlorophyll and robust oxygen tolerance, resulting in more hydrogen formation [147]. The following generic reaction can be used to depict green algae’s conversion of water:

$$2H_2O \xrightarrow{light} 2H_2 + O_2 \tag{8}$$

2.2.2.2. Indirect bio-photolysis process. In indirect bio-photolysis, the following processes may represent the fundamental reaction for hydrogen generation from water by cyanobacteria or blue-green algae:

Table 4
Parameters that influence H_2 yield in gasification and biological route.

Parameters	Effects	Ref.
Temperature	Increase in temperature causes complete homogenous reactions that increase the yield of H_2	[153,154]
Residence time	Increase in holding time increases the production of gas	[155]
Biomass particle size	Particle size reduction provides a large surface area, enhancing heat transmission and promoting H_2 production, homogeneity of gasification reactions, and reducing char and tar components.	[99,154]
Biomass characteristics	Biomass with high cellulosic content is gasified within a short holding time. Gaseous products are produced in larger amount when biomass has high lignin and cellulosic content.	[156,157]
Catalysts	Various catalysts such as alkaline metal oxides, dolomites, and olivine can be used for gasification. The usage of catalysts enhances the H_2 and CO content and decreases the tar content. Nickel and Cerium-based catalysts also prevent carbon deposition.	[158,159]
Steam biomass ratio (S/B)	An increase in the value of the S/B ratio increases the H_2 yield. Lowering the ration increases the carbon and methane content. For a better H_2 yield, this ratio must be optimised.	[160,161]

$$6H_2O + 6CO_2 \rightarrow C_6H_{12}O_6 + 6O_2(inlight) \tag{9}$$

$$C_6H_{12}O_6 + 6H_2O \rightarrow 12H_2 + 6CO_2(inlight) \tag{10}$$

where reaction (9) is photosynthesis and reaction (10) is fermentation.

Fig. 9 displays a schematic illustration of the indirect bio-photolysis process. Hydrogenase and nitrogenase enzymes produce hydrogen; the synthesis rate is comparable to green algae’s hydrogenase production [148]. While indirect bio-photolysis methods are already in the conceptual phase, the production cost is estimated at 1.42 $/kg [149] assuming a total capital cost of 135 $/m^2 [149]. Consequently, algal H_2 production might be considered a cost-effective and sustainable method of using water as a sustainable source and CO_2 usage among the airborne pollutants. Furthermore, the critical drawbacks of this bio-hydrogen generating approach are its limited H_2 production capability and the need for a wide surface area to capture adequate light [150,151].

3. Factors affecting hydrogen production

The factors that influence the production of hydrogen include a number of characteristics that have a notable effect on the yield of H_2 in the thermochemical and biological routes. Essential variables in the thermochemical route include residence time, which determines the degree of conversion, and temperature, which impacts reaction rates

Table 5
Different types of membranes for the purification of hydrogen.

Type of membrane	Material of membrane	Temperature (°K)	Stability issue of membrane	Selectivity of H_2 over CO_2
Dense Polymer	Polymers	<373	Compaction, swelling	Low
Microporous ceramic	Silica, alumina, zirconia, titania, zeolites	473–873	Stability towards H_2O	5–139
Dense metallic	Palladium	573–873	Phase taransition	>1000
Porous carbon	carbon	773–1173	Brittle	4–20
Dense ceramic	alumina, titania, silica, zirconia	873–1173	Stability toward CO_2	>1000

and product distribution. The size of biomass particles and their intrinsic properties, such as composition and moisture content, are other important factors in determining how efficiently hydrogen is produced. Moreover, catalysts can improve the selectivity and kinetics of reactions, and the ratio of steam to biomass (S/B) is essential for optimizing the gasification process and creating an atmosphere conducive to hydrogen production. Table 4 presents a detailed overview of the crucial characteristics for determining hydrogen yield in gasification and biological route. It is essential to comprehend these characteristics to optimize hydrogen production and improve the process's overall efficiency. By meticulously considering variables including temperature, pressure, feedstock composition, reactor design [152], and catalysts, scientists and industry professionals may enhance hydrogen production techniques, laying the groundwork for more efficient and sustainable energy solutions.

4. Hydrogen generation using thermochemical and biological routes: separation, storage, transportation with benefits and drawbacks

To achieve the goals of power generation system security, climate safety, and societal economic growth, introducing H_2 generation as an energy and fuel carrier poses numerous challenges in developing the necessary separation, storage, transmission, and utilization technologies. Pressure Swing Adsorption, separation by membrane, and distillation are all feasible methods for the last phase of hydrogen separation. Table 5 provides an overview of different types of membranes utilized for hydrogen purification, including dense polymer, microporous ceramic, dense metallic, porous carbon, and dense ceramic membranes. Each membrane type is associated with specific materials and operating temperature limits. Additionally, the table outlines stability issues associated with each membrane type and their selectivity for hydrogen over carbon dioxide. This information aids in selecting the most suitable membrane for hydrogen purification, considering factors such as efficiency, stability, and selectivity.

H_2 storage is now one of the significant barriers to its widespread usage due to its low density of 0.09 kg/m^3. Hydrogen may be stored securely as a gas or liquid phase, on surfaces or inside solids, using the adsorption and absorption. Standard piston-type compressors are widely used to store gaseous hydrogen up to 77.5 MPa in cylinders [162]. But, the energy needed for compression is more than 2.21 kWh/kg, leading to density of less than 40 kg/m^3 [159]. Cryogenic tanks may store liquid hydrogen by compressing it and then chilling it using a heat exchanger in two steps. Because of its low boiling point of −252.87 °C, the energy needed is estimated to be 15.2 kWh/kg, which results in a volumetric density of 70.8 kg/m^3 at atmospheric pressure.

Table 6
Fundamental approaches for gaseous hydrogen storage processes.

Storage Method	Density (kg/m^3)	Temperature (°C)	Pressure (MPa)
Compression	40	ambient	77
Liquifaction	70.8	−252.87	atm
Adsorption or physisorption	41	−196.15	6
Absorption in metal hydrides	150	ambient	atm
In Complex hydrides	150	>100	atm

Solid-state retention holds large volumes of hydrogen at intermediate temperatures and pressures. A gaseous molecule connects with multiple atoms at the material surface material. On this, it is attached and transiently withdrawn when required in an adsorption process. Table 6 provides a comprehensive overview of the fundamental approaches for gaseous hydrogen storage processes, including compression, liquefaction, adsorption or physisorption, absorption in metal hydrides, and complex hydrides. Each approach is detailed with key aspects such as density, temperature, and pressure values. This information is essential for evaluating and selecting the most suitable method for storing gaseous hydrogen, considering factors like storage capacity, energy requirements, and practical feasibility.

H_2 may be transported and distributed in two ways. The first category covers bulk storage vessels, trucks, rail cars, and shipping containers, whereas the second includes long-distance pipelines [163]. The low density of hydrogen, which is the limitation of transporting H_2 via the traditional first mode, leads to significant shipping costs [162]. The H_2 transportation and distribution in future infrastructure might resemble present natural gas pipes, part of a network system that includes both power and natural gas [164].

H_2 may be utilized in engines, fuel cells, turbines, boilers, and chemical and oil industries [165]. Fuel cells have a lot of appeal regarding power production, heating, and transportation because of their simplicity, modularity, and environmental protection. The two strategies for hydrogen-powered cars are direct, on-board synthesis of H_2 from methanol or direct storage of H_2 delivered via recharging stations [166,167].

The processes of producing hydrogen via thermochemical and biological means are not equivalent and each has a unique set of advantages and disadvantages (see Table 7). Thermochemical procedures are now more scalable and effective than previous methods, making them suitable for large-scale commercial applications. But these procedures also have a significant energy need and produce a lot of CO_2 emissions. While biological techniques provide a more environmentally friendly and sustainable solution, they are not without consistency, scalability, and efficiency challenges. Biophotolysis is an intriguing method for directly using solar energy to make hydrogen, which turns water into hydrogen using photosynthetic organisms. However, longer production durations are typically the result of slower response speeds in biological processes. Numerous biological techniques, such as biophotolysis, are still in the research or early commercial phases and must be improved to compete with well-established thermochemical technology. Future hydrogen generation may use both of these technologies, utilising their respective benefits to meet various energy needs with the least amount of environmental impact.

5. Case studies globally addressing H_2 production

In order to produce hydrogen from organic waste through a variety of biological (Table 8) and thermochemical processes (Table 9), the projects listed in both tables represent a global effort to utilise renewable energy sources and advance hydrogen production technologies. This effort helps to promote waste management and sustainable energy solutions.

Table 7
Advantage and disadvantage of thermochemical and biological route of hydrogen production with hydrogen yield.

Process	Energy efficiency	Advantage	Development stage	Hydrogen cost ($/kg)	Disadvantage	H_2 Yield Ton/Hr.	Ref.
Thermochemical route							
Thermochemical water splitting process	30–50	• CO_2-neutral, plentiful, and inexpensive feedstock.	–	1.0–2.0	• H_2 percentages vary owing to seasonalavailability, feedstock contaminants, and tar production.	0.08–8.1	[168,169]
Fast pyrolysis	56	• H_2 recovery from gaseous and liquid products is oxygen-free and has a relatively high hydrogen concentration.	–	1.25–2.20	• Low efficient, formation of tar and char, and low hydrogen production with high energy usage.	0.11–30.4	[170,171]
Steam gasification		• H_2 generation with high purity and minimal ash output makes it appropriate for commercial scale.	–	1.77–2.20	• Tar formation, high energy input.It is difficult to separate and purify gas products.	–	[172]
Supercritical watergasification	40–50	• Production of H_2 from wet biomass Large conversion and H_2 concentration without tar and pollutants.	–		• High energy input, tar formation not proven, pricy.	–	
Biological route							
Biochemical process							
Photo fermentation process	60–80	• H_2 production from distillery wastewaters sludge. The lack of oxygen minimizes the potential for inhibition, aids in waste recycling, and allows using organic wastes and wastewater.Microbes that can use light radiation of multiple wavelengths.	Lab-scale only	2.8	• It Utilises nitrogenase enzyme, which has a high energy need and poor solar energy conversion efficiency, and it has enormous anaerobic photo bioreactor surface areas.	–	[173–175]
Darkferementation		• Renewable, simultaneous waste treatment and generation of H_2. CO_2-neutral, generates H_2 without sunlight, helps recycle garbage, has no O_2 constraint. H_2 produced without the addition of visible light, the ability to mix and match different carbon sources as a substrate.Produces lactic acid, acetic acid, and butyric acid, all useful byproducts. Anaerobic process	Lab-scale only	2.6	• Low energy conversion efficiency. Separation of fatty acids, limited H_2 rates and yields, poor condensation efficiency, and need for a high reactor space. Poor energy conversion efficiency makes CO_2 removal vital.	–	[169,176–179]
Bio photolyis process							
Direct bio photolysis process		• Direct H_2 production from water utilizing solar energy converts ten times more solar power than trees and crops.	–	2.13	• It needs sunshine, has poor H_2 rates and yields, large reactor capacity required, is sensitive to O_2, and is expensive to produce. Strong hydrogenase enzyme suppression caused by produced oxygen, low 10-fold rise in solar energy H_2 generation, and no waste consumption	–	[172]
Indirect bio photolysis process		• N_2 fixation from the atmosphere H_2 production from water.	–	1.42	• Strong hydrogenase enzyme suppression caused by produced O_2, minimal H_2 generation, and no byproduct consumption	–	[172]

6. Challenges and future Prospects

It is theoretically possible to build pipelines that transport pure hydrogen gas and, in limited amount, they have been operational in several locations, including the United States, Germany, the Netherlands, France, and Belgium. Such pipeline networks are restricted but don't provide enough foundation for rapid hydrogen deployment upscaling. Hydrogen is the most plentiful element in the universe, with the maximum energy density per unit mass and the cleanest combustion, producing only water. This is because hydrogen is considered the strongest contender for replacing fossil fuels as the mobile industry's primary energy source. On the other hand, hydrogen is an energy vector rather than an energy source and is not found in molecular form in nature. It must be created either from water or other chemicals.

Fig. 10 outlines various technical challenges and drawbacks inherent in hydrogen production routes, including both thermochemical and biological methods. Among these challenges, hydrogen storage is the most pressing issue, particularly for mobile applications. Addressing these challenges is crucial for advancing hydrogen's widespread adoption as a clean energy source in mobile applications. Various barriers must be overcome for hydrogen to become a viable energy carrier. The following four essential features of hydrogen utilisation can be addressed:

- Production – It is essential to develop a technique that consume the least amount of energy and enable large-scale hydrogen production since hydrogen must be produced flawlessly by biological and thermochemical routes.

Table 8
Global effort to utilize renewable energy sources and advance hydrogen production using biological technologies.

Project Name	Country	Technology	Details
Europe			
HYVOLUTION	Netherlands	Dark fermentationandphoto-fermentation	Developing sustainable hydrogen production from organic waste using a combination of dark fermentation and photo-fermentation processes.
HYTIME	Denmark	Dark fermentation,photo-fermentation,and biophotolysis	Focuses on maximizing hydrogen yields through an integrated approach, utilizing organic waste as feedstock.
BIO-H2	Spain	Dark fermentationandphoto-fermentation	Research project focused on optimizing hydrogen production from agro-industrial waste through combined dark and photo-fermentation processes.
Asia			
HYFUSEN	India	Dark fermentationandphoto-fermentation	A project aiming to produce hydrogen from organic waste, such as agricultural residues, using a combination of dark and photo-fermentation techniques.
BioHydrogen	China	Dark fermentationAndphoto-fermentation	Investigates the production of biohydrogen from organic waste materials using a combined fermentation approach.
North America			
Bio-H2	USA	Dark fermentationandbiophotolysis	Focuses on the production of hydrogen from organic waste using dark fermentation and biophotolysis, with an emphasis on process integration and optimization.
Africa			
HySA Infrastructure	South Africa	Dark fermentationandphoto-fermentation	Part of South Africa's Hydrogen South Africa (HySA) initiative, this project explores hydrogen production from organic waste using combined dark and photo-fermentation processes.
South America			
Hydrogen Brazil	Brazil	Dark fermentationAndphoto-fermentation	A research initiative aimed at developing sustainable hydrogen production methods from agricultural waste through the integration of dark and photo-fermentation technologies.
Australia			
AUS-BioH2	Australia	Dark fermentation,photo-fermentation, andbiophotolysis	Focuses on the combined use of dark fermentation, photo-fermentation, and biophotolysis for hydrogen production from organic waste, aiming to create a sustainable and efficient production process.

- Storage – fuel must be easily stored for use and transportation, with one of the most essential requirements being easily accessible. This necessitates quick charge/discharge times, exceptional charge/discharge process control, and low energy requirement for charging and discharging operation [180].
- Power generation – As soon as hydrogen is suitable for usage, it must be done in the most efficient manner possible.
- Combined power generation- Hydrogen is utilized as a primary fuel in dual-fuel diesel engines as a viable fuel alternative. At low loads, a heavy-duty hydrogen-diesel dual fuel engine using liquid fuel as the pilot fuel reduces carbon and NOx emissions by over 90 % while reducing soot emissions by 85 %. At a medium load, the critical concern is an increase in NOx emissions [192]. A hydrogen-biodiesel dual fuel CI engine [180]working at full load improves exhaust emissions and exhaust gas opacity. The brake thermal efficiency of the engine also improves when hydrogen-diesel dual fuel is used [193]. Nonetheless, hydrogen and biogas are the best secondary gaseous fuels for dual-fuel mode operating among all gaseous fuels since they are environment friendly, have a high-octane number, and knock resistance capability, apart from being economical and renewable. Hence, hydrogen is very much suitable for combined power generation.
- Safety- Due to the risks associated with hydrogen use and storage, several precautions and safety measures should be taken (flammability).

Table 9
Global effort to utilize renewable energy sources and advance hydrogen production using thermochemical technologies.

Project Name	Country	Technology	Details
Europe			
GoBiGas	Sweden	Steam gasification (fluidized bed)	Located in Gothenburg, this project focused on producing bio-methane and hydrogen from forest residues using fluidized bed steam gasification.
BioEnergy2020+	Austria	Fast pyrolysis and steam gasification	A research initiative aimed at developing advanced bioenergy technologies, including hydrogen production from organic waste through fast pyrolysis and steam gasification.
CHRISGAS	Sweden	Steam gasification (fluidized bed)	The project aimed to produce hydrogen-rich synthesis gas from biomass using fluidized bed steam gasification technology.
North America			
Iowa state university bioeconomy institute	USA	Fast pyrolysis and steam gasification	Research projects focused on hydrogen production from agricultural residues and other biomass through fast pyrolysis and subsequent steam gasification.
University of florida hydrogen production project	USA	Supercritical water gasification	Investigates the use of supercritical water gasification for hydrogen production from wet organic waste, such as agricultural residues and wastewater sludge.
Asia			
Sinopec shanghai research institute of petrochemical technology	China	Steam gasification (fluidized bed)	Focuses on hydrogen production from biomass using fluidized bed steam gasification technology.
Indian institute of science, bangalore	India	Downdraft gasification	Research projects on hydrogen production from agricultural and forestry residues using downdraft gasification technology.
Australia			
ANU Energy Change Institute	Australia	Fast pyrolysis and steam gasification	Research initiative focused on developing hydrogen production technologies from biomass using fast pyrolysis and steam gasification.
South America			
Embrapa Agroenergy	Brazil	Fast pyrolysis	Investigates the production of bio-oil and hydrogen from agricultural waste through fast pyrolysis.
Africa			
Stellenbosch university	South Africa	Fluidized bed gasification	Research on hydrogen production from biomass using fluidized bed gasification technology

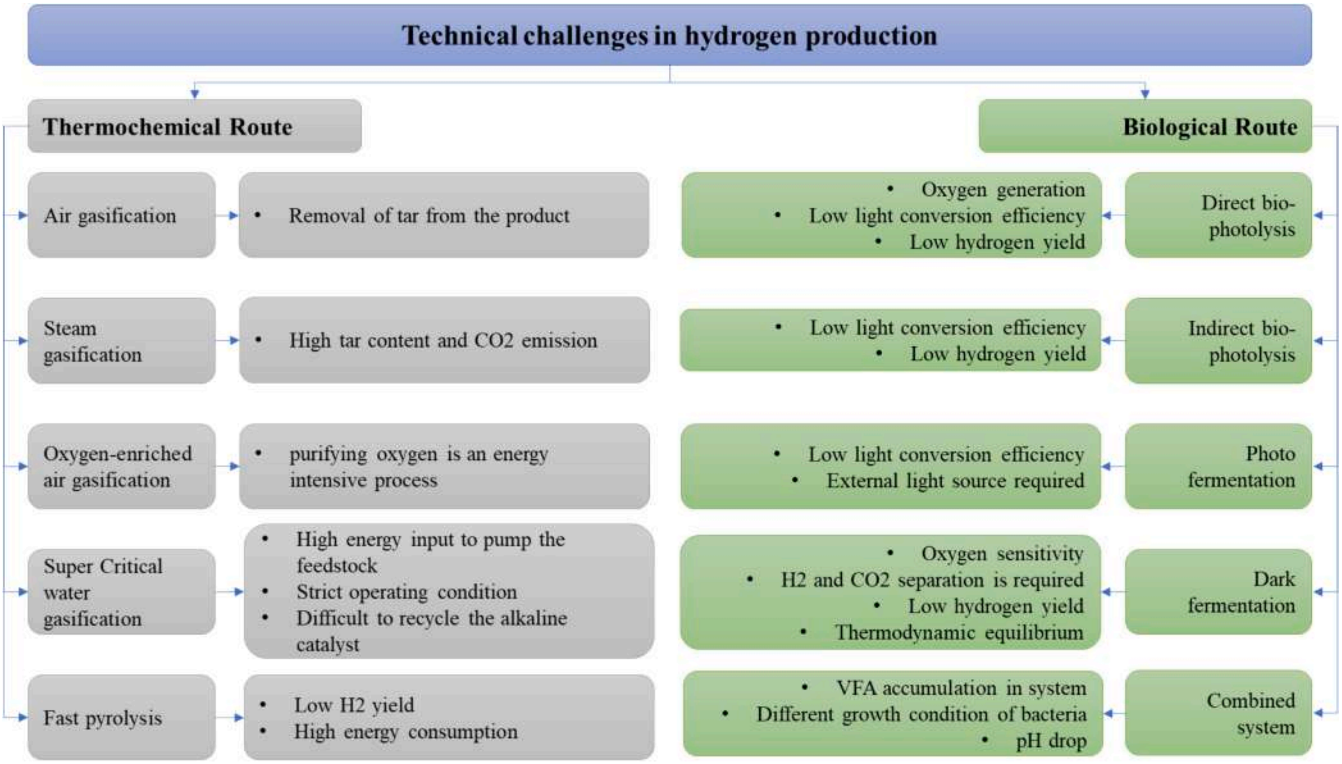


Fig. 10. Challenges and drawbacks in biological and thermochemical routes.

7. Conclusions

Modern bioenergy already today covers over 50 % of renewable energy production and 6 % of the global energy supply [180], and is expected to increase its share in the future. In such energy framework, in view of a progressive shifting from fossil fuels to renewable energy and of the development of a society where H2 would become the energy vector of the future, we can expect a progressive development of technologies for biohydrogen production. Alongside the development of hydrogen production via water electrolysis, other technologies are at different stages of development to produce biohydrogen, i.e. hydrogen from biomass and, in particular, waste biomass. This review covers precisely these technologies, both thermochemical and biochemical: from pyrolysis to gasification to fermentation and bio photolysis processes. The state of the art is highlighted, both in terms of scientific articles and current and past projects, with emphasis on the reactors used, the operating conditions, and the hydrogen yields. The strengths and weaknesses of the various technologies are described. Insights are reported regarding separation technologies, as biohydrogen typically is produced alongside other gases. Finally, mention is made of what is needed for the development of a society in which hydrogen can have an increasingly greater importance, from its storage to its transport.

From the analysis carried out it can be concluded that research and projects to produce biohydrogen are at an advanced stage, with more consolidated but not yet economically competitive technologies and others still in the development phase – typically, biochemical technologies.

Certainly, further efforts are necessary for the engineering and optimization of biohydrogen production processes. If we want to progressively free ourselves from the production of hydrogen from fossil fuels, we must make the production of hydrogen from water electrolysis more efficient and combine this with hydrogen produced from waste biomass. Depending on the type of waste biomass it will be more convenient to resort to thermochemical or rather biochemical technologies, and even within these two macro-categories many different processes can be implemented, as oulined in this review.

CRediT authorship contribution statement

Praveen Kumar: Writing – original draft, Conceptualization. **Luca Fiori:** Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

We acknowledge the financial support from the project “Produrre Idrogeno in Trentino-H2@TN” (PAT-Trento)

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