Chemical Engineering Journal Advances 12 (2022) 100410

Contents lists available at ScienceDirect

Chemical Engineering Journal Advances

journal homepage: www.sciencedirect.com/journal/chemical-engineering-journal-advances

Biomass-to-sustainable biohydrogen: Insights into the production routes, and technical challenges

M.G. Eloffy [a], Ahmed M. Elgarahy [b,c,*], Ayman N. Saber [d], Ahmed Hammad [e], Dina M. El-Sherif [a], Moustafa Shehata [f], Ahmed Mohsen [g], Khalid Z. Elwakeel [b,h,*]

[a] National Institute of Oceanography and Fisheries (NIOF), Cairo, Egypt
[b] Environmental Chemistry Division, Environmental Science Department, Faculty of Science, Port Said University, Port Said, Egypt
[c] Egyptian Propylene and Polypropylene Company (EPPC), Port Said, Egypt
[d] Pesticide Residues and Environmental Pollution Department, Central Agricultural pesticide Laboratory, Agricultural Research Center, Dokki, Giza, 12618, Egypt
[e] Chemical Engineering Department, Faculty of Engineering, Port Said University, Port Said, Egypt
[f] Mechanical Power Engineering Department, Faculty of Engineering, Port Said University, Port Said, Egypt
[g] United Gas Derivatives Company (UGDC), Port Said, Egypt
[h] University of Jeddah, College of Science, Department of Chemistry, Jeddah, Saudi Arabia

ARTICLE INFO

Keywords:
Renewable energy
Biomass conversion
Production pathways
Sustainable hydrogen
Circular economy

ABSTRACT

Hydrogen is regarded as one of the utmost competent alternative fuels in the transition to net-zero emissions for the future. Nowadays, it is still majorly derived from non-renewable energy resources (i.e., fossil fuels). Regrettably, a key issue for the reliance on these depleted resources is the extremely negative impacts on our milieu. The emergence of envisioned biomass-to-sustainable H_2 strategy is viewed as an appealing opportunity to generate a sustainable strategic H_2. This review article summarizes the patented approaches (thermochemical, biological, and electrochemical) for H_2 production from an enticing raw material of biomass. The optimization of different prominent parameters to achieve the eventual easiest way for H_2 production was additionally discussed. The advancement in different operational parameters, technical challenges, and scalable improvement of each pathway was briefly addressed. Moreover, the contemporary economic viewpoints on the bankable biomass-to-H_2 processes flow diagrams in terms of the circular economy were additionally highlighted in order to effectively value the biomass supply chains to produce H_2. Hopefully, this work presents a more favorable theoretical in-depth mechanistic understanding of the bio-sourced hydrogen's different production pathways.

1. Introduction

Green energy has increased steadily in recent decades to respond to the global energy demand as modern civilization has developed in conjunction with the rapid growth of the global population [1]. Therefore, there is a strong international interest to discover new energy management and environmental conservation solutions due to the shortage of non-renewable energy sources (NRES) such as fossil fuels (i. e. coal, oil, and natural gas) supplies to meet the energy requirements and other problems impacting the world's population [2]. Global energy consumption is projected to rise by 50% over the current scenario [3]. Thus, various contaminants may be produced throughout the conventional fuel-producing processes; these poisons and wastes have negative environmental consequences if not addressed. Furthermore, treatment methods increase energy requirements and consequently greenhouse gas (GHG) rate emissions [4]. (i.e. especially CO_2 emissions will increase by 6% from 33.0 Gt in 2015 to 35.0 Gt in 2050 under current and planned policies [5]. The GHG emissions harm the planet's natural climatic conditions, such as precipitation and temperature levels, which have a lot of disadvantages [3,6]. The global levels of GHG emissions in 2018 were as follows: 331.1 ppb, 407.8 ppm, and 1869.0 ppb for N_2O, CO_2, and CH_4, respectively [7].

Today, clean energy technologies have steadily increased to minimize the dependency on the NRES, and hence solve a wide shortage of energy requirements for environmental sustainability [8,9]. Alternative renewable energy sources (RES) such as hydropower, biomass energy, geothermal power, wind energy, and solar energy are also regarded as affordable and environmentally friendly alternatives to improve energy security [10–12]. Despite the pandemic, the growth rate in the world's

---

* Corresponding authors at: Environmental Chemistry Division, Environmental Science Department, Faculty of Science, Port Said University, Port Said, Egypt.
E-mail address: khalid_elwakeel@sci.psu.edu.eg (K.Z. Elwakeel).

https://doi.org/10.1016/j.ceja.2022.100410

Nomenclature

NRES	Non renewable energy sources
GHG	Greenhouse gases
RES	Renewable energy sources
SMR	Steam methane reforming
CAPEX	Capital expenditures
OPEX	Operating expenses
WGS	Water gas shift
PSA	Pressure swings adsorbed system
SR	Steam reforming
PO	Partial oxidation
ScWG	Supercritical water gasification
CSCWG	Catalytic Supercritical Water Gasification
BTX	Benzene, toluene and xylenes
RDF	Refuse derived fuel
DF	Dark fermentation
PF	Photo-fermentation
AD	Anaerobic digestion
MECs	Microbial electrolysis cells
VFAs	Volatile fatty acids
HRT	Hydraulic retention time
OLR	Organic loading rate
MFCs	Microbial fuel cells
CCS	Carbon capture and storage
WEO	World Energy Outlook
FCEVs	Fuel cell electric vehicles
IRENA	International Renewable Energy Agency
FEED	Front-end engineering and design
CEC	California Energy Commission CEC
ARB	Air resources Board
FCVs	Fuel cell vehicles
POME	Palm oil mill effluent
CHP	Combined Heat and Power
AI	Artificial intelligence
PEM	proton exchange membrane
PEMECs	Proton Exchange Membrane Electrolysis Cells
EAB	An electrochemically active bacterium
HER	Hydrogen evolution reaction
AEM	Anion-exchange membranes
CEM	cation-exchange membranes

renewable energy capacity jumped 45% in 2020. It's the largest annual rate of increase since 1999 [13]. Extensive efforts have been employed to explore renewable energy to overcome the dearth of non-renewable fossil fuel resources. Among the present initiatives to mitigate global warming, the prominence of H_2 as future fuel has been figured out to preserve our planet, attributed to its zero emissions and high energy content. Interestingly, the H_2 originating from the multifarious biomass resources could replace the current classical scenarios to meet the global need. Biomass and organic solid waste are seen as very promising future alternative energy sources, having the potential to lead to a CO_2-free energy system [14,15]. Biomass is an effective carbon management feedstock for carbon neutrality, with significant potential for sustainability, natural availability, bio-renewability, and recyclability [16]. Economic, social, and cultural factors can influence the optimal technical uses of various types of organic wastes found in various components of the environment, and these are dependent on the availability of resources generated from food preparation and energy synthesis, and thus their waste products are disposed of into water sources [17]. Biomass is made up of all living materials and is classified as lignocellulosic biomass or non-lignocellulosic biomass [16]. These materials are mostly composed of cellulose, hemicellulose, lignin, different extractives, and ash [18,19], and comprise forest woody biomass, and agricultural and industrial waste. In contrast, micro and macro algae contain significant amounts of protein, lipids, saccharides, and inorganics, in addition to lignin and cellulose [20]. Biomass is predicted to account for about two-thirds of total direct renewable energy use in 2050 [5]. Biomass valorization benefits bio-energy generation industries by lowering costs and providing a commercially viable process. This process, however, necessitates several steps and challenges to be successfully implemented. It is critical to develop low-cost processes through research into new technologies such as the use of high-quality raw materials, low-cost manufacturing methods, and new product validation procedures [21]. To create a novel flow process by combining various sequences of unit operations for efficient biomass conversion to a secondary energy source [22]. As a result, it's vital to find economically feasible processes to convert biomass and organic solid waste into a secondary energy source [14]. Hydrogen energy has become one of the most promising secondary energy sources for accomplishing a low-carbon transition in the New Era due to its green, clean, renewable, and widely available properties [14,23]. Hydrogen is thus valuable over other fuels as the combustion products of water can be easily portable, storable, and regenerative [24]. Hydrogen separation via a membrane separation approach was researched by Singla et al. [24]. The membrane allows hydrogen-sized molecules to selectively pass through while leaving the retentate behind on the other side. For later usage and transportation, hydrogen must be stored after separation using an appropriate manner. Hydrogen production is expected to increase by 5.0–10.0% every year, reaching 82.0 Mt by 2050 [14]. Both chemical and biological processes can be used to create hydrogen. Chemical procedures include partial oxidation, catalytic cracking, coal gasification, and steam reforming. Since biological processes require less energy and can operate at low temperatures and pressures, they are efficient and cost-effective. Examples include dark fermentation and photosynthetic activities [25]. The main criteria of the present review aim to focus on H_2-production pathways from biomass and are formated under a single source so that the potential and aspects are recognized as follows. A summary of thermochemical, biological, and electrochemical H_2 production approaches is reviewed as well as their conversion potential mechanisms. Their performance, advantages, drawbacks, H_2 production yields, and recently proposed process optimization are additionally discussed. Moreover, the major technical issues through the various H_2 production processes have been included. Moreover, the bio-circular economy and future prospective considering the advances of produced H_2 derived from biomass are highlighted.

1.1. Hydrogen as a sustainable energy future

Hydrogen (H_2) is the most common in nature, but due to its high reactivity, it does not detect in its molecular form (H_2). It is employed as fuel in the 21st century in various sectors. Although hydrogen is a colorless gas in its natural state, it can be distinguished by one of nine different colors. The sources or methods utilised to create hydrogen are indicated by the color codes for hydrogen. These codes are: green, blue, gray, brown or black, turquoise, purple, pink, red, and white (Fig. 1). Remarkably, H_2 is regarded as a promising alternative to fossil fuels in terms of the green economy, attributed to its merits, such as availability, renewability, and high energy content (i.e. 142.3 MJ/kg approximately three times higher than gasoline) [26], and non-polluting combustion (carbon free-emissions) [27]. Moreover, it can be stored/transported in different valuable forms as; (i) solid by either absorbing or reacting with metals or chemical compounds or storing in an alternative chemical form, (ii) liquid in dewars or tanks (stored at -253 °C), and (iii)

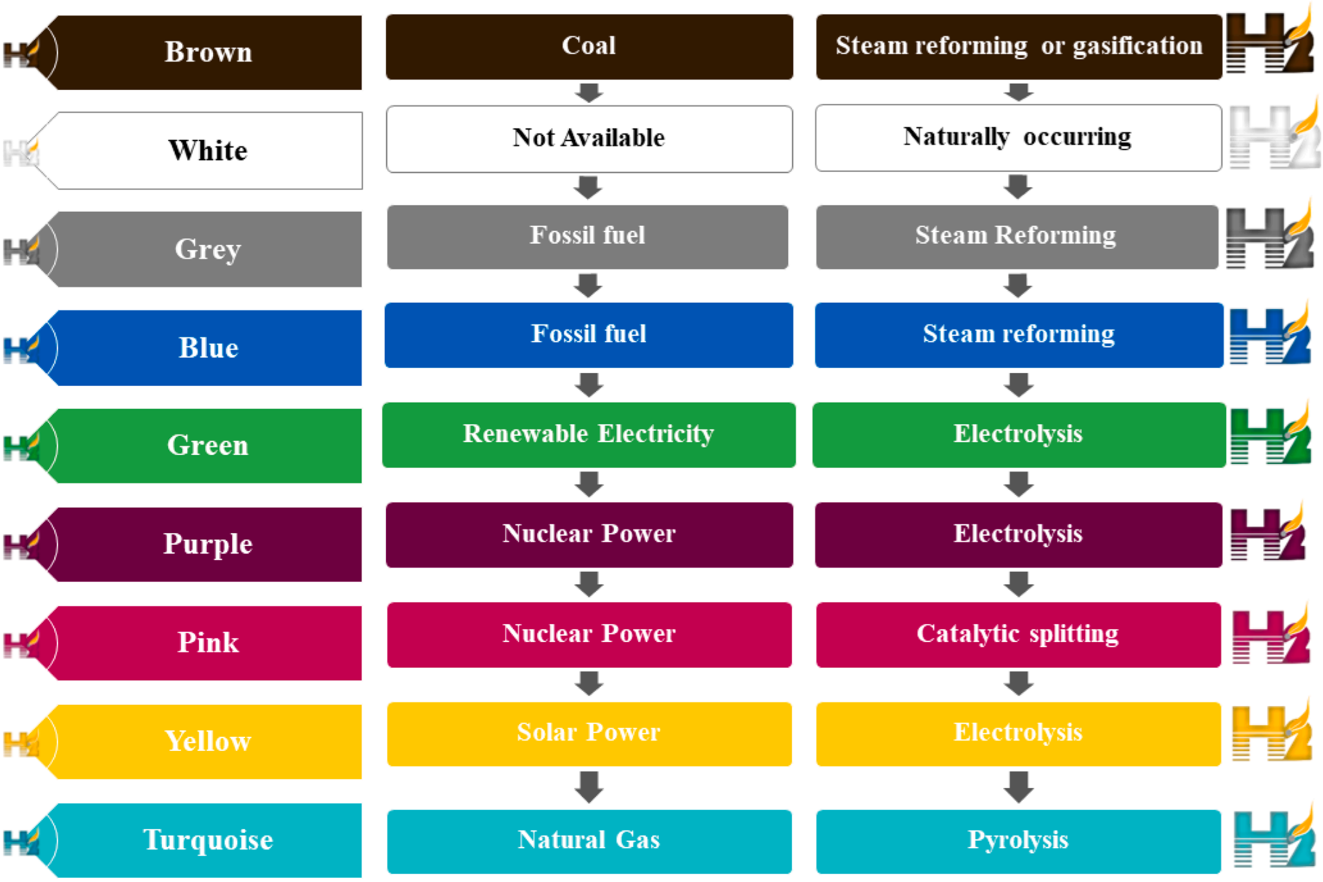

Fig. 1. The main hydrogen color codes, considering the type of energy and/or technology operated for its production process.

compressed gas in high-pressure tanks [28,29]. Nowadays, 98% of the worldwide H_2 used is obtained from fossil fuels, with steam methane reforming (SMR) serving as the primary production mechanism. Various conventional pathways such as steam reforming (SR), auto-thermal reforming, aqueous phase reforming, partial oxidation (PO), and dry reforming are used to produce H_2 [30]. However, different operational obstacles associated with each technology were observed. Thence, innumerable studies have been performed globally, to improve the

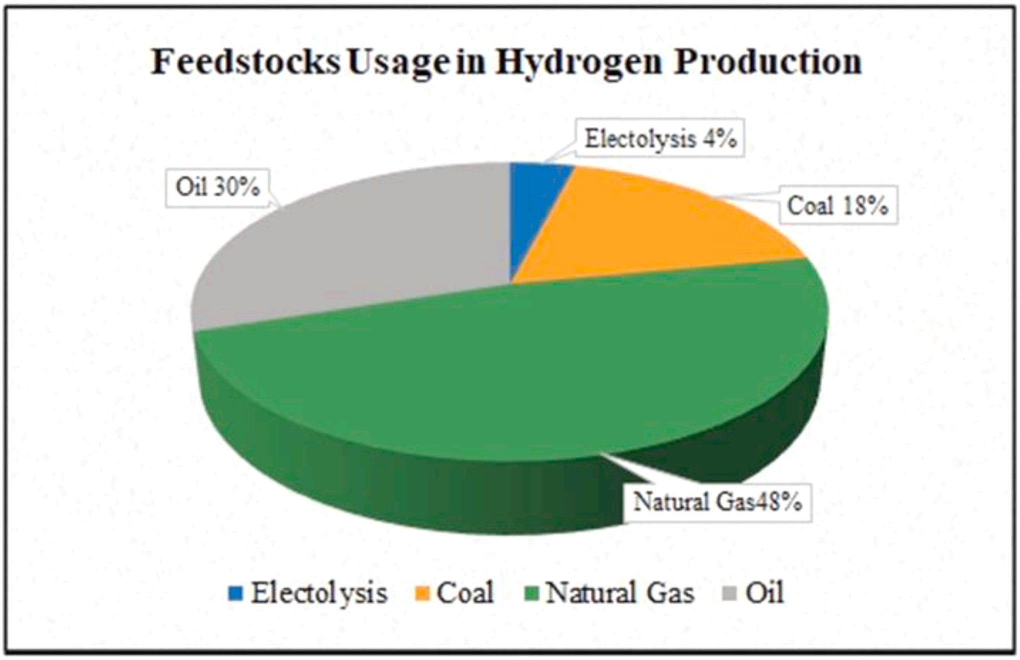

Fig. 2. The global feedstock usage in hydrogen production.

process performance, and reduce both capital expenditures (CAPEX), and operating expenses (OPEX) [31]. Simply, the chemical energy of H_2 (i.e. fuel) can be converted into electricity in the presence of oxygen (i.e. oxidizing agent) via many electrochemical reactions through scalable fuel cells, which is more environmentally than conventional methods for energy production [32]. Several renewable-energy-based possibilities, such as water splitting and H_2-generation from biomass, are now in pilot-scale demonstrations or at the commercial stage [33]. Attractively, they have grown in popularity in recent years due to their environmental sustainability and economic viability [27].

1.2. *Hydrogen production from biomass*

The different feedstocks used in hydrogen production are shown in Fig. 2, It is mainly produced from natural gas 48%, oil 30%, and coal 18%. Biomass is a biologically derived renewable natural resource that may be acquired from several sources. Straw, rice husk, cellulose, sawdust, and animal dung are examples of biomass in large quantities that are emerging as viable biorefinery feedstock [34,35]. These biomasses are made up of carbon, oxygen, and hydrogen-rich organic components. By 2050, biomass is expected to account for almost two-thirds of total direct renewable energy use, including use as liquid biofuels and biomass-based heating [5].

According to a UNEP report, 140.0 billion tonnes of biomass are produced annually throughout the world, with the following components making up the majority of these materials: wood wastes, agricultural wastes, and residual wastes [36]. Wooden wastes, also known as lignocellulosic biomass, are carbon-rich byproducts of wood production [37]. Because of the low ash and sulfur contents in these samples, efforts have been made to use them for carbon capture and storage as fascinating precursors for post-combustion research and biogas upgrading [37]. Wooden shells are another type of waste; while their capacity is less than that of wood processing residues, they are nevertheless a valuable renewable carbon source, making them acceptable raw materials for activated carbons. Some of the most popular sources of wooden shells include almond shells, pine cones, coconut shells, peanut shells, rice husks, and palm kernel shells (PKSs) [36,38]. Coconut shells, for example, have high purity and a regular porous structure as dust-free wooden shells, and about 577,000 tonnes of these waste samples are generated annually in Malaysia [39]. On the other hand, corncob is an appealing agricultural waste that has emerged as a promising precursor for carbon-based sorbents [40], with a total output of more than 20 million tonnes per year in China. Also, Wood ash (WA) is a possible hazard to the environment that results from the combustion of biomass resources, and Germany is the main source in the European Union, generating more than 12 million tonnes yearly [41]. The waste products described are examples of the vast potential of the world's wood and agricultural industries, which may be regarded as outstanding and cost-effective sources [41]. Table 1 provides an overview of the production capacities of several large biomass samples from throughout the world. It was estimated that by integrating landfill gas as a possible energy source alongside biomass and waste, the percentage of potential agricultural waste, MSW, and woody biomass is around 5.0%, 24.0%, and 64.0%, respectively [42]. Furthermore, non-lignocellulosic biomass, which includes micro and macroalgae, is seen as a viable energy source because of its inherent capacity to fix CO_2 from the atmosphere through photosynthesis, resulting in fast growth and high area productivity [43].

Table 2 presents different examples of biomass, and its energy content. The mass% of H_2 in biomass is 6%, equating to 0.672 m^3 gaseous H_2 generated per kg of biomass, accounting for more than 40% of the total energy of biomass [44]. Thermochemical, biological, and electrolytic processes are the most common ways of producing H_2 from biomass at the moment (Fig. 3). While biological and electrolytic H_2 production is difficult to scale up and provides limited amounts of H_2 [45], thermochemical H_2 generation is gaining popularity [46].

Table 1
A summary of the global capacity for some major biomass production.

Sample type	Production capacity	Year	Country	References
Almond	2002,742	2020	USA	[225]
Olive	6559,884	2020	Spain	[226]
Bagasse	306,000,000	2020	India	[227]
Bagasse	758,000,000	2020	Brazil	[228]
Peanut	16,685,915	2020	China	[229]
Rice	148,500,000	2020	China	[230]
Oat	4761,365	2020	Russian Federation	[231]
Wood pellet	52,700,000	2020	Global	[232]
Whitewood	11,800,000 m3/ year	2019	Finland	[233]
Lignin	100,000,000	2019	Global	[234]
Coconut	17,130,000	2019	Indonesia	[235]
Pine sawdust	280,000	2019	Mexico	[236]
Oil tea	56,250,000	2018	China	[237]
Animal waste (manure)	26,361,000	2017	Vietnam	[238]

Table 2
The energy content in different biomasses.

Biomass	Energy content (MJ/kg)	Biomass	Energy content (MJ/kg)
Fresh Grass	4.0	Rice hulls	15.5
Green wood, with 60% moisture	6.0	Commercial wastes	16.0
Air-dried wood, with 20% moisture	15.0	Dried dung	16.0
Oven-dried wood, with 0% moisture	18.0	Groundnut shells	20.0
Domestic refuse	9.0	Paper, newspaper	17.0
Coconut husks	10.0	Olive cake	21.57
Coconut shells	18.0	Olive husk	21.80
Coffee husks	16.0	Olive pits	22.00
Rice straw	15	Olive refuse	15.77
Wheat straw	19.0	Corn cob	17.99
Sugar cane residues	17.0	Maize cobs	19.0
Cotton stalks	17.5	Peat	14.5
Cotton hulls	19.5	Straw, harvested, baled	15.0
Maize stalks	18.0	Wood Bark	20.3
Soybean stalks	19.0	Manure	8.650

2. The main pathways for H_2 production based on biomass

2.1. *Thermochemical production pathways*

Thermochemical conversion is the most sophisticated method of producing H_2 from biomass. While, in terms of commercialization, these procedures face several challenges. The technology was developed based on comparable approaches used for biofuels such as bio-methane and SMR [47]. Gasification, pyrolysis, and aqueous phase reforming are the three basic thermochemical methods.

2.1.1. *Gasification*

Gasification is a thermochemical process that transforms biomass into gaseous fuels through a set of partial oxidation and reduction reactions at high temperatures and can occur with or without the presence of a catalyst. Fig. 4 shows a schematic diagram for the gasification process. The product gases are known as syngas, composed of H_2, N_2, CO, CH_4, and CO_2. The process output is not just the syngas, but there are other combustible gases, inert components, tar, char, dust, and other impurities. The energy inherent in the biomass is not immediately released in this process, but rather transferred into the bond energies of lighter fuels rather than the perceptible heat of combustion products. Among the different thermochemical processes, biomass gasification is

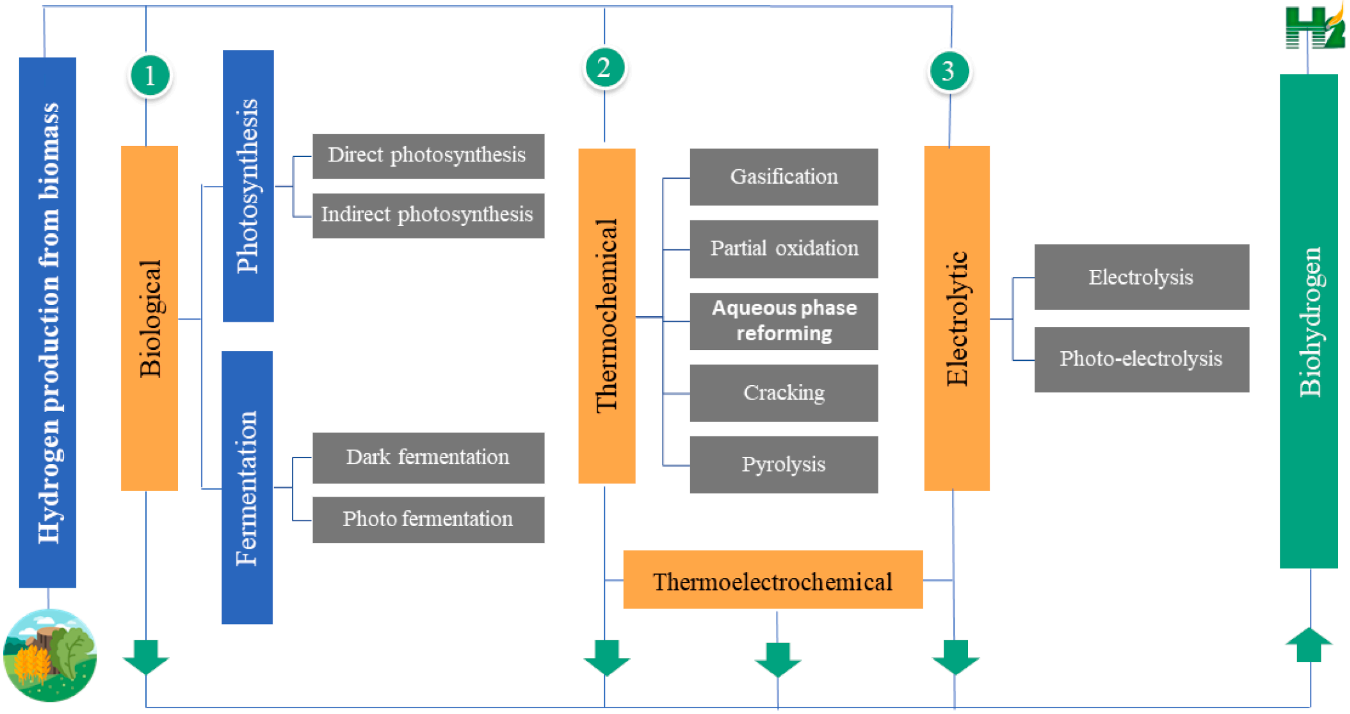

Fig. 3. The main pathways for H_2 production based on biomass.

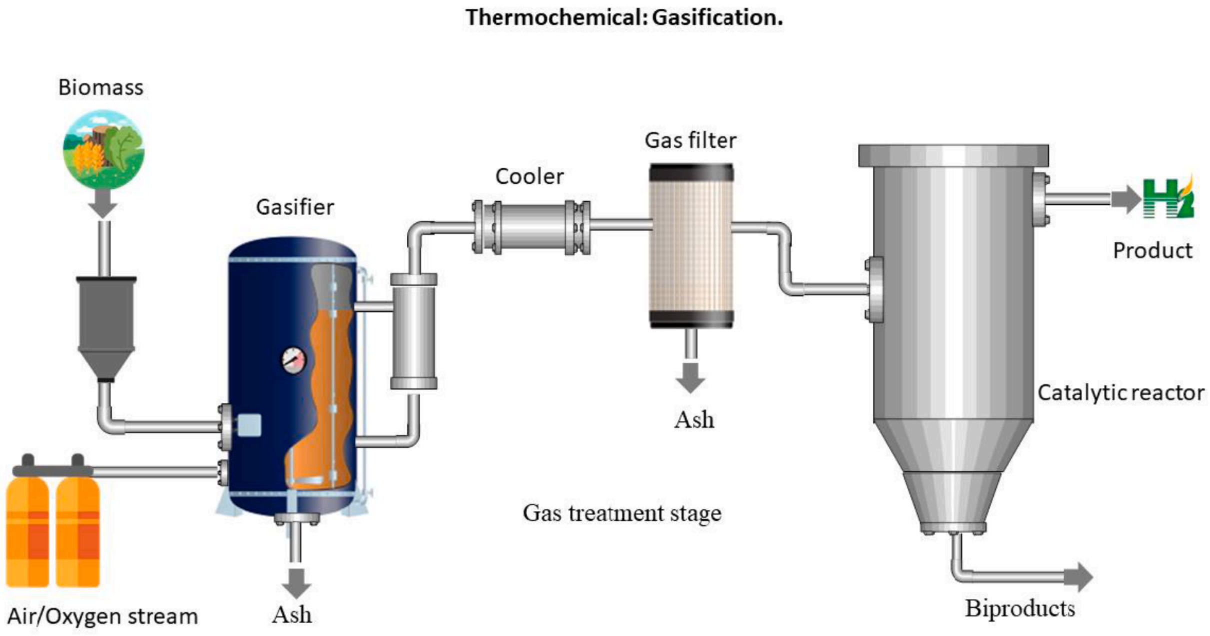

Fig. 4. Schematic diagram for thermochemical (gasification) process.

favored for its operation resilience to produce gases with disparate qualities to suit different applications such as direct combustion, heat generation, boilers, electric power generation by engines, and liquid biofuels through the Fischer-Tropsch process, and fuel cells. The process can be classified into; (i) air gasification, (ii) oxygen gasification, and (iii) steam gasification depending on the oxidizing agent used [48]. The potential of different gasification methods of producing H_2 to demonstrate abundance, relatively inexpensive, and wide applicability in a variety of sectors for biomass conversion should be stressed. Several review articles on biomass gasification have recently been published, although few of them focused on general flaws and process intensification performance [33]. A typical route for biomass gasification and SR reforming and/or water gas shift (WGS) with a pressure swing adsorbed system (PSA) is estimated to require 2.4 TJ of primary energy input per TJ of H_2, and for a plant with an expected H_2 output of 139 700 kg/day and a biomass cost of $46–80 / dry-ton, the H_2 production cost is expected to be $1.77–2.05 / kg. The biomass gasification process involves a cumbersome set of chemical reactions occurring in sequence and at the same time. Some of the reactions are exothermic releasing heat whilst progressing, and many reactions are endothermic demanding heat to proceed. Moreover, the reactions are classified as either homogeneous reactions or heterogeneous reactions. The pyrolysis reaction happens after the drying stage [49–55], and the biomass is transformed into a gas-rich in CH_4, LHC (C_2H_4), CO, CO_2, C, and tar (primary). Primary tar is a complex, condensed combination of polycyclic aromatic hydrocarbons and oxygenated molecules, such as alcohols, phenols, and furans [56]. Homogeneous processes, such as cracking and SR, occur at the temperature conditions of steam gasification (700–1000 °C) and modify the structure of these oxygenated molecules. SR strategy is an attractive complementary technology that may be incorporated with current operations to minimize the amounts of tar and char. For better H_2 generation, the released syngas from the gasifier should have a high H_2 concentration and a low tar yield. Several parameters including temperature, gas velocity, pressure, residence duration, equivalency ratio, biomass properties, and gasifier design can directly affect the quality of gas produced by biomass gasification. Only syngas with a low H_2 level and low heating is produced by air gasification of biomass. Steam gasification produces significantly more H_2 than pyrolysis or air gasification, and the overall conversion efficiency of thermal energy-to-H_2 can reach up to 52%. Table 3 summarizes a comparison of the various gasification techniques. Based on the H_2% in the gas (40%), greater H_2/CO ratio (1.6), and lower contaminants compared to air gasification, steam gasification looks to be the best approach for producing H_2. In terms of feedstock, steam gasification is viable for wet biomass (moisture content ranging from 5 to 35 wt%), but air gasification needs a dry raw material [57]. Biomass oxygen-rich air gasification is one successful technique for producing medium heating value gas, but it requires a significant investment for O_2 generation, which limits its popularity. Experiments published in the literature show that steam-gasification routes based on the fluidized-bed reactor without or with added O_2 are proficient in producing MHV of 10–16 MJ N^{-1} m^3 gas with 30–60 vol% H_2 content. This is owing to the absence of nitrogen from air gasification in the products, as well as the possibility of a homogenous WGS reaction in the early stages of the gasification process to boost H_2 generation. However, this method necessitates a steam temperature of more than 700 °C, and there is an additional expense for high-performance steam generators. Table 4 presents the H_2 production from different biomass feedstocks under various operational parameters.

SR process is a simultaneous purifying procedure that lowers the C-to-H_2 mass ratio (C/H) of syngas during steam gasification [58]. By optimizing the operational parameters of SR, the number of light hydrocarbons and tar responsible for pipe corrosion and clogging due to polymerization and condensation has been minimized [59].

PO scenario is a different method from SR process. The reaction pathway is identical to that of SR, except that H_2O is substituted with O_2 [60]. One feature is that reactions with O_2 are exothermic, which eliminates the requirement for an external energy source or the usage of smaller reactors. Depending on the O_2 content in the reactor, different reactions occur. PO is well-documented for ethanol, the most extensively characterized feedstock in the literature. Since H_2 is generated with carbon monoxide (CO) as a byproduct of ethanol and low O_2 levels, the reaction is endothermic and becomes exergonic as the proportion of O_2 within the reactor grows. The PO reaction is auto-thermal in this case, and carbon dioxide (CO_2) is generated. PO is performed at lower temperatures due to the extremely exothermic process [61,62]. In the presence of less O_2, WGS processes may increase the H_2 output of PO with steam. This is a mildly exothermic reaction, and the water introduced to the system prevents catalyst deactivation by reducing coke production, like in SR [63,64]. Catalysts are likewise required in PO, as in SR, except that there is no external heat source in PO.

Supercritical water gasification (ScWG) is an alternative thermochemical technique that has been designed to be more resilient for the biomass type, including wet biomass (moisture > 35%), such as carbohydrates and wood. To create a supercritical fluid, water must be heated beyond 374 °C and pressurized over 221.2 bars. Water's dielectric constant and the number of H_2 bonds both drop at these conditions. At high temperatures, organic molecules and gases are miscible in supercritical water, accelerating their conversion. The whole process is endothermic and analogous to aqueous-phase reforming. When compared to other gasification processes, residence periods can be very short (2–6 s), and the reaction can be carried out at a lower temperature (600–650 °C) [65]. However, to sustain these conditions, large energy levels are required, which raises the expenses and limits its scalability [66]. As a result, no industrial-scale system has been created since the high pressure required necessitates significant capital and operational expenses [67]. Certain technical challenges (reactor design standardization, waste neutralization, and understanding of chemical dynamics) must be addressed to produce commercially viable ScWG systems [68]. ScWG systems have two temperature regions: high temperatures, generally in the 500–700 °C range, and low temperatures, often in the 374–500 °C range. Pyrolysis processes occur before gasification at high temperatures, splitting the fuel without the need for a catalyst. However, alkali catalysts can be used to boost H_2 production by increasing WGS processes. Hydrolyzed chemicals are gasified and reduced at low temperatures (374–500 °C) by alkali-based catalysts, transition metals, and

Table 3
Comparison of gasification procedures based on the employed oxidizing agent (oxygen, air, or steam).

	Oxygen gasification	Air gasification	Steam gasification
Products[a]	CO, H_2, LHC (CH_4, C_2H_4), CO_2	N_2, CO, H_2, CO_2, LHC (CH_4, C_2H_4), H_2O	H_2, CO, CO_2, LHC (CH_4, C_2H_4)
Tar (g/kg)	2.2–46[b]	3.7–61.9	60–95
Average H_2 composition	40%	15%	40%
H_2/CO ratio	1	0.75	1.6
Heating Value (MJ/Nm^3)	12–28	4–7	10–18
Pros	– Exothermic Oxidation generates the gasification necessary heat – Higher syn gas quality – Higher heating value – Higher Cold-Gas-Efficiency – Less tar and char	– Simple – Available – Least cost – Exothermic Oxidation generates the gasification necessary heat – Less tar and char	– Higher syn gas quality – Higher heating value – Higher Cold-Gas-Efficiency – Higher H_2 content – Less CO_2
Cons	– High capital and operating cost for air separation unit – Energy demand for air separation unit – High CO_2 generation	– High nitrogen content – Gas dilution with nitrogen – Lowest syn gas quality – Lowest heating value – Lowest Cold-Gas-Efficiency – Inappropriate to some applications – High CO_2 generation	– External heat supply is needed to maintain the temperature – Relatively higher tar and char – Energy and cost of steam generation – Excess steam is favorable but decreases reactor operating temperature – Cost of dual separate reactors

[a] Molecules are listed in order of decreasing presence in the gaseous product.

[b] Steam-O_2 mixture.

Table 4
Hydrogen production from different biomass feedstocks via gasification under various operational parameters.

Biomass	Biomass flow	Reactor	Gasifying Agent	Gas Agent Flow	Temperature	Pressure	Gas Agent to Biomass Ratio	Syngas results	References
Rice straw	0.74 kg/h	Bench-scale atmospheric fluidized bed	Pure oxygen; oxygen-enriched air 50%, and air)	NA	900 – 1200 °C	1.05 bar	Steam/ biomass ratio range 0.0–0.6–0.8	H_2 25 - 35%range, CO 26 - 38% range, LHV range 4 - 12 MJ/Nm^3, CCE range 60.3 - 77.3%, and CGE range 48.3 - 68.5%	[52]
Almond shells	120 and 150 kg/h. dry up to 170	Auto-thermal bubbling fluidized bed reactor of 1000 kW nominal thermal input	Steam/oxygen	O_2(kg/h) 44–46 / 58–61 Steam (kg/ h) 48–50 / 70–80	780 – 850 °C	atm	0.4–0.5 Steam/ Biomass	GY of 1.2 Nm^3/kg 27–33%v, H_2, 23–29%v, CO, 31–36%v, CO_2, 9–11% v, CH_4, and light hydrocarbons lower than 1%v, LHV) of 10.3–10.9 MJ/ Nm^3, and CGE up to 75%	[239]
Wood	25 Kg/h	Dual fired downdraft (DFD) gasifier	Air-steam	Air 50 Kg/h steam 5 Kg/ h	900 – 1200 °C	NA	0.1 - 0.39	A maximum of 27.24% H_2 at equivalence number of 1.54 Max HHV6.33 MJ /Nm^3, and CGE 86–87%.	[49]
Sawdust	50 kg/h	Novel pilot-scale bubbling fluidized bed	Air gasification was used as control, and oxygen-enriched air, air-steam, oxygen-steam	NA	500 °C	atm	0.8 - 2.9	Max H_2/CO ratio 1.44 by using air-steam and oxygen-steam at the ER of 0.30, Max H_2 ~ 33%, Max CO ~43%, Max GY about 2.4, Max, LHV 12.2 MJ/m^3 , Max CCE 90%, and Max CGE 90%	[55]
Hazelnut shells	180 kg/h	circulating bubbling fluidized bed gasifier	0.5 kg/h of oxygen and 70.0 kg/h of steam at 150 oC and 1.0 bar.	50 kg/h of oxygen and 70 kg/h of steam at 150 °C and 1 bar.	800 °C	1 bar	0.4 - 0.5	Max H_2 31.3–47.5 mol% (WG, and CO 22 - 31%	[240]
Rice husks	NA	circulating fluidized bed (CFB)	Air	NA	720 – 840 °C	NA	NA	The maximum calorific value and the maximum gasification efficiency of gas was 5751 kJ/Nm3 and 73.41%, respectively, at 789 °C and 814 °C.	[241]

activated carbon catalysts, which are required for high biomass-to-gas conversion [69,70]. Furthermore, methanation happens at low temperatures and consumes the H_2 generated to make CH_4, necessitating the use of charcoal or another carbon-based catalyst to resolve this issue.

Catalytic Supercritical Water Gasification (CSCWG) is also identified as low-temperature catalytic gasification, Because of its low temperature working ranges, 350–600 °C. The catalyst, in conjunction with the lower reaction temperature, decreases the development of char and tar. Resende et al. [71] investigated and reported on the utilization of metal catalysts for the ScWG of cellulose and lignin. Several researchers conducted laboratory-scale tests, which created the groundwork for the concept's application on the pilot and commercial scales. Jesus et al. and Rauzan et al. [72–74] developed the first CSCWG pilot plant in San Diego at the General Atomics site to investigate the earlier results of laboratory-scale studies. It was discovered that the H_2 production was equivalent to the findings of laboratory trials, with 10 g of H_2 generated per 100 g of feed [75]. Catalysts are quite beneficial in the water gasification process, which boosts H_2 generation [76,77]. Watanabe et al. [78] discovered that when CSCWG was used, the quantity of H_2 generated was doubled when compared to non-catalytic supercritical gasification. For aromatic compounds, Park et al. [79] utilized RuO_2. This analysis indicated that RuO_2 supplied the whole activity mechanism for the K_2CO_3 catalyst. K_2CO_3 was more active than $Ca(OH)_2$ in the gasification of cellulose in CSCWG, although it did not collect CO_2 [80]. Metallic nickel catalysts have been utilized for many years in traditional fossil fuel gasification and are currently employed in biomass catalytic supercritical gasification [81]. The cost of H_2 generation is critical for the development of technology; a thorough analysis was conducted that took into account all factors, and the cost of H_2 was 3.4 $/kg for the hydrogasification of biomass wastes [82]. Zhang et al. [83] reviewed the literature on the energy efficiencies of the SCWG process and found values ranging from 0.04 to 42.05%. The H_2 generation from different biomass feedstock via CSCWG is summarized as shown in Table 5.

2.1.2. *Pyrolysis*

Pyrolysis is another thermochemical conversion of biomass to produce H_2 (Fig. 5). It is similar to gasification, but it may be operated at lower temperatures and without the need for an oxidizing agent [84]. Table 6 reports the hydrogen production from different biomass feedstocks via pyrolysis under various operational parameters. To enhance heat production, a tiny quantity of an oxidizing agent might be applied in some circumstances [85]. Pyrolysis normally occurs at temperatures ranging from 400 to 800 °C and pressures of up to 5 bar. Although the main objective of the pyrolysis process is to create bio-oil, it may also result in the creation of H_2 by flashing or rapid pyrolysis at high temperatures and appropriate residence time [86]. Pyrolysis is classified into three types based on the working temperature: conventional (or slow) pyrolysis, rapid pyrolysis, and flash pyrolysis. Conventional pyrolysis is performed at temperatures lower than 450 °C, resulting in a significant charcoal content. Fast pyrolysis yields up to 75 wt% bio-oil at medium temperatures (450–600 °C), a high heating rate (about 300 °C /min), and a short residence period [87]. Flash pyrolysis is similar to rapid pyrolysis, but it is performed at higher temperatures (above 600 °C) and greater heating rates (>1000 °C /s), with a shorter residence period (below 1 s) to maximize gas output [88]. However, the gas yields from rapid and flash pyrolysis are reduced when compared to

Table 5
Hydrogen production through supercritical biomass gasification from various biomasses.

Feed	Catalyst	Reactor type and operating conditions	H_2 production yield	References
Olive mill wastewater	–	The coiled tubular reactor, 25 MPa, 600 °C	10.79 mol%	[242]
Glucose	Ni/activated charcoal	Packed-bed reactor, 28 MPa, 650 °C	15.6 mmol/g	[243]
Bark	Ni/hydrotalcite	Batch reactor, 380 °C, 23 MPa	2.05 mmol/g	[244]
Maize silage hydrochar	K_2CO_3	Micro-autoclaves, 400 °C, 30 MPa	8.9 mol%	[245]
Switchgrass biocrude	Ni/ZrO_2	Packed-bed reactor, 600 °C, 25 MPa	81.67 mol/g carbon reacted	[88]
Sewage sludge	KOH	Fluidized bed reactor, 540 °C, 30 MPa	15.49 mmol/g	[56]
Fruit pulp	RU/activated charcoal	The batch reactor, 600 °C, 25 MPa	54.8 mmol/g	[246]
Microalgae (Cenedesmus quadricauda)	Nickel/α-Al2O_3	The batch reactor, 385 °C, 26 MPa.	4 mmol/g	[247]
Coconut shell	K_2CO_3	Tubular batch reactor, 600 °C, 23–25 MPa	4.8 mmol/g	[248]
Sewage sludge	–	Continuous reactor, 600 °C, 25 MPa	40 vol%	[249]
Microalgae Enteromorpha intestinalis	Fe-Ni-Ru/ γ-Al2O3	Batch microreactor, 440 °C, 25 MPa	12.28 mmol/g	[244]

gasification, owing to the lower working temperatures [89,90]. After pyrolysis, oxygenated molecules (ketones, phenolic compounds, aldehydes, alcohols, and carboxylic acids), water, and ash are condensed to create a complex liquid fraction similar to tar known as "bio-oil." There are two types of bio-oils: water-insoluble fractions and water-soluble fractions. The insoluble portion can be broken down into platform molecules like benzene, toluene, and xylenes (BTX) or olefins and employed in adhesive applications [91]. To boost the H_2 production yield from the soluble fraction, a steam gasification device can be added to the process. The production of H_2 from biomass pyrolysis is highly dependent on the catalyst type, process temperature, feedstock type, and residence time [92].

H_2 production yield is particularly promoted by pyrolysis temperature increase and further improves by high heating rate and longer residence time, and at high temperature, it is higher by fast pyrolysis relative to slow pyrolysis [93]. As explained before, lignin is the most stable fraction that decomposes at high temperatures relative to the cellulose, which decomposes at 310 to 400 °C, and hemicellulose (mainly: xylan) decomposes at 220 to 350 °C range [94]. In pyrolysis experiments on pine, cottonwood, and rice straw, the H_2 initial emission was observed to start at 400 °C for all species, and the rate culminated at the range of 650 to 750 °C, but with differences relevant to the biomass composition rendered the release rate of the rice straw outweighed the rate from pine and the least rate from cottonwood [94]. Solar pyrolysis can provide a very high temperature of up to 2000 °C, which was found to promote the gas yield [95]. Moreover, hot radiofrequency plasma pyrolysis research succeeded to investigate a temperature range of 900–2000 °C and achieved high syn gas productivity [95]. Full decomposition of unstable compounds can be noted beyond 700 °C pyrolysis temperature with the promotion of phenolic compounds [96]. Phuet Prasertcharoensuk et al. [97] observed insignificant yield changes by rising the pyrolysis temperature from 600 to 700 °C but rather recorded a 23% gas yield increase as the temperature rises to 800 °C. They attributed that trend to the complete release of the volatiles above 700 °C range and their cracking and dry reforming with higher temperatures. They generally observed an obvious rising trend of CO and H_2/CO ratio and a declining trend for CO_2 content and justified that by the continuous consumption of the released CO_2 in the Boudouard reaction promoted above 700 °C and the dry reforming of light hydrocarbons promoted above 640 °C to produce more H_2 and CO. [97]. The H_2 and CO content rose from 48.8 to 67.2 mol% and 4.5 to 8.8 mol% respectively at pyrolysis temperature rise from 600 to 900 °C and generally, the gas yield increased from 77.8 to 95.8 wt%, while the solid residues and ash decreased from 16.3 to 0.4 wt%. At all temperatures, the liquids have the main content of aromatics, phenolics, and furans that indicate the high-temperature insufficiency to decompose them [97]. At sugarcane slow pyrolysis by Al Arni et al., syngas yield increased and H_2 particularly increased from 7 to 28.8% along with temperature rise from 773 to 953 K by the promotion of tar cracking reactions, so the gases increased at the expense of heavier hydrocarbons. Notably, CO and CO_2 gases were dominated earlier by the easier hemicellulose and cellulose decomposition, then decreased beyond 400 °C, whereby the slow decomposition of lignin started to give rise to the H_2 and methane release [98]. The same was also experienced, where H_2 content increased significantly from 1.13 to 16.5 vol% by increasing the pyrolysis temperature of palm kernel cake from 500 to 700 °C, and from 2.03 to 20.36 vol% for cassava pulp residue [93]. A significant increase in Syngas yield was also reported to be from 26 to 46% by temperature rise from 300 to 700 °C for the slow pyrolysis of *Salsola collina* Pall. [99] The same trend was recorded also for pine wood and corn stalk pyrolysis [99]. Cheng S, et al. [100] reported a decrease in bio-oil yield and an increase in gas yield beyond the 600 °C during the pyrolysis of Crofton weed. Syngas and H_2 content were also promoted by increasing temperature from 350 to 800 °C during the pyrolysis of Alcell lignin, where H_2 content reached 31.5 mol%. The same was experienced with coconut shells from 500 to 900 °C, where the gas yield increased significantly from 36.59 to 64.47 wt% and H_2 increased from 3.56 to 15.04 vol% at 800 °C and reached 33.49 vol% at 900 °C. During inline pyrolysis-catalytic SR of pyrolysates for sawdust utilizing 10 wt% Ni/Al_2O_3, the gases and H_2 yield increased with temperature rise and maximum H_2 content was reported between 600 and 700 °C [93]. Generally, the heating rate defines the pyrolysis category and affects the yield of all products and may be significant regarding the gases yield. At high heating rate, the gas yield would increase on the expense of the oil and char yield by faster depolymerization of the complex structures to primary volatile matter and vapors, which are subjected to secondary cracking and decomposition at that high heating rate. On the other hand, lower heating rate would not promote the dehydrogenation and the secondary reactions and lead to higher oil and char yield. However, some studies showed that narrow range of examined heating rate, from 5 to 20 °C/min, had insignificant effect on the gas yield, but a higher rate $>$ 30 °C/min would affect notably. At an investigation for refuse derived fuel (RDF) pyrolysis, it was reported that the gas yield increased from 14 to 47% by increasing the heating rate from 5 to 350 °C/min along with considerable decline in bio-oil from 55 to 23% and a slower decrease in solid content. This trend was justified by the cracking and gasification of both oil and solid matter [93]. According to Safdari M-S et al. [101], it is not an absolute trend where they reported that rising the rate from 30 to 1000 °C/min at a constant temperature of 765 °C led to a decline in char and light gases yields whilst increasing the tar content 49–60%. Regarding the residence time, a very short pyrolysis time is insufficient for the decomposition and will not avail enough heat for the reactions to proceed and the pyrolysis would not be completed. Generally, high operating temperature along with a high heating rate and sufficient residence time drive the process kinetics towards a higher gas yield [93]. In slow pyrolysis and very long residence time, re-polymerization is allowed leading to char formation, whilst allowing liquids/tar conversions to higher gas yield. In another investigation by pyrolysis of palm

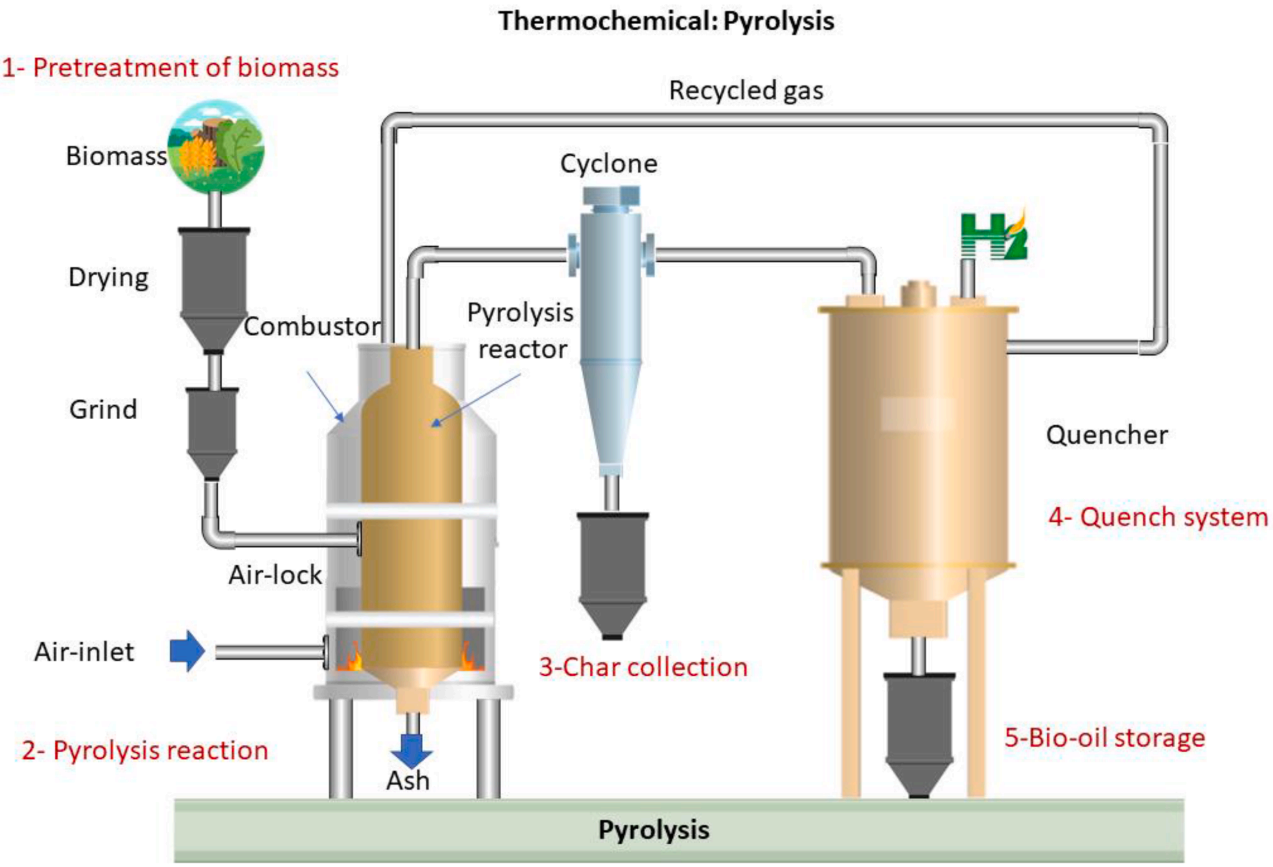

Fig. 5. Schematic diagram for thermochemical (pyrolysis) process.

Table 6
Hydrogen production from different biomass feedstocks via pyrolysis under various operational parameters.

Biomass	Biomass Flow	Reactor Type	Temperature	Heating rate	Gas Flow	Syn Gas	References
pine, cottonwood, and rice straw, representing softwood, hardwood, and grass,	5 g	Vertical quartz tubular reactor - fixed bed reactor	900 °C	10 °C /min	N_2 90 mL/min	Total hydrogen yield at the temperature range of 400–900 °C is 117.76 mL/g for rice straw, 98.95 ml/g for pine, and 76.99 mL/g for cotton wood, respectively.	[94]
Rice husk, coconut shell, sugarcane bagasse, palm kernel shell, cotton stalk, and wheat straw	2 g	Two-stage fixed bed reactor	550 °C	20 °C /min	N_2 carrier gas 200 mL /min and Steam 5.7 g/ h	GY from 37.85 wt% to 43.31 wt% without catalyst and from 50.64 to 69.76 wt% with catalyst/steam, Max H2 59.23 wt% from sugarcane/catalyzed Max H_2 25.35 mmol/g from Palm kernel shell/catalyzed	[250]
Waste wood	25 ± 0.1 g	33.0 mm diameter and 830.0 mm long Inconel 600.0 fixed bed	600 – 900 °C	20 °C /min	5.7 steam to carbon in biomass (S/C) molar ratio 30 or 120 mL/min Nitrogen	H_2 content in the gas phase increased to 67 mol% from 49 mol%, and the aromatic compounds in the gas stream decreased up to 50.6%.	[97]
Modified Water Hyacinth (Eichhornia Crassipes) biomass	500 G	Stainless steel reactor equipped with an electric heater (Parr)	540 °C	NA	35 mL/min N_2 flow	280 0.0 mL of total gas production (42% of hydrogen included, 23% of carbon dioxide, 22% of carbon monoxide and 7% of methane)	[251]

oil wastes in the absence of a catalyst, the total gas yield increases first with increasing residence time and reaches the maximum value at about 14 s then decreases slightly with further increase in the residence time. In more detail, increase of the residence time led to early sudden decline in the H_2 yield, while further increase of the residence time led to higher H_2 yield. However, too much increase in residence time leads to the reduction of H_2 production despite the fact that lengthening the residence time drives toward thermal cracking of heavier hydrocarbons and accordingly higher gas release rate, but it leads to some consumption of the H_2 in reactions and the production of other gaseous components such as carbon oxides and methane [102].

Pyrolysis–steam reforming is a recent two-stage thermochemical method that has received a lot of attention [103]. The catalysts utilized are the same as those used in gasification’s cracking phases, and they are likewise inactivated by carbon deposition (coke). A catalyst regeneration phase allows coke to be converted into CO_2 by burning, hence unblocking the active sites [104]. Global H_2 yields are similar to those obtained from SR by gasification, ranging between 70% and 80% [105].

Separating the reactors in the pyrolysis-steam reforming process prevents coke deposits from inhibiting the reforming catalyst [106]. The technique is simple to scale up and may be used instead of direct gasification and bio-oil reformation [107].

2.1.3. Aqueous phase reforming (APR)

Aqueous phase reforming is the third thermochemical method for producing H_2 from biomass (Fig. 6). APR primarily transforms oxygenated chemicals into H_2. During the aqueous phase, feedstock molecules are dissolved and react with water molecules at low temperatures (270 ºC) and high pressures (up to 50 bar) [108,109]. APR methods are appropriate for biomass-derived oxygenated hydrocarbons with a C/O ratio of 1:1 and that are miscible in water, such as methanol, ethanol, ethylene glycol, glycerol, glucose, or even polyols like sorbitol [110]. The main disadvantage is the limited spectrum of efficiently soluble compounds transformed in the process. However, following a pre-treatment phase, APR may be used to convert pure cellulose and woody biomass [109]. This entails hydrolyzing cellulose and hemicellulose to produce monomers that may be utilized as feedstock [111]. The mechanism of the reaction is similar to that of SR, and it depends on C–C bond cleavage to create H_2. When ethylene glycol comes into contact with the surface of a catalyst, the C–C bonds are broken, releasing CO. The catalyst also enhances the WGS process, leaving just 300 ppm of CO in the gas stream. Other reaction intermediates are available, favoring C–O bond cleavage and resulting in the generation of alkanes (CH_4, C_2H_6) and a reduced H_2 production yield [112].

Choosing a metal (M)-based catalyst is heavily influenced by the stability of the M–C bond (which improves the C–C cleavage route) and the M–O bond (which improves the C–O cleavage pathway). The cost of metal catalysts, on the other hand, is too expensive for large-scale development. Furthermore, the assistance of catalysts must be considered. Because their selectivity for H_2 is higher and lower for alkanes, respectively, basic and neutral supports are chosen as over-acidic supports. Indeed, alkanes are formed in acidic circumstances as a result of dehydrogenation, therefore it is crucial to pick a catalyst that is non-selective to alkanes while operating at a reasonable pH [108]. The selectivity of APR is also influenced by the feedstock biomass and the process parameters [112,113]. Converting complex oxygenated compounds, such as carbohydrates, is difficult because they produce less H_2 [114]. The thermal homogenous destruction of carbohydrates produces a substantial quantity of coke, which deactivates the catalyst and competes with the reforming reactions.

2.2. Biological production pathways

H_2 generation from biological biomass conversion is another critical component of future bio-refinery systems. Levin et al. [115] explored the use of biological processes to produce H_2. It rose to popularity in the mid-1970s, when oil problems rattled the global economy. Biological H_2 generation techniques are thought to be infinite and environmentally beneficial. It enables the generation of renewable and carbon-neutral H_2. Many biological techniques for H_2 generation were invented and used throughout that decade. This section discusses biological H_2 generation by fermentation, biophotolysis, enzymatic processes, and microbial electrolysis. Fermentation to produce H_2 or H_2-rich gases can be divided into two types based on the necessity for light during the conversion; (i) dark fermentation (light-independent) and (ii) photo-fermentation (light-dependent). In the photofermentation process, photosynthetic bacteria employ solar energy to produce H_2 from organic substrates. Furthermore, biophotolysis can be further subdivided into; (i) direct and (ii) indirect biophotolysis.

2.2.1. Fermentation

Fermentation is commonly defined as a chemical process in which the organic substrates are decomposed by the activity of microorganisms (Fig. 7). Based on the necessity for light during the conversion for H_2 and H_2-rich biogas generation, it may be divided into two types; (i) dark fermentation (DF) and (ii) photo-fermentation (PF). Anaerobic bacteria aid in the conversion of biomass into H_2 via a biochemical mechanism in the DF process. H_2 is produced as the primary substrate through a series of biological events. Among biological transformations, this approach is thought to be the most well-understood and promising [14,116]. Despite its relatively modest yields (maximum of 4mol-H_2/mol-glucose and 6 mol-H_2/mol-sucrose, respectively), DF needs simple reactor designs, making it appealing for H_2 generation. Furthermore, much research has been undertaken to boost H_2 production yield using hybrid systems with DF, such as microbial electrolysis cells (MECs), PF, anaerobic digester, and DF with a cell-free enzymatic system [117].

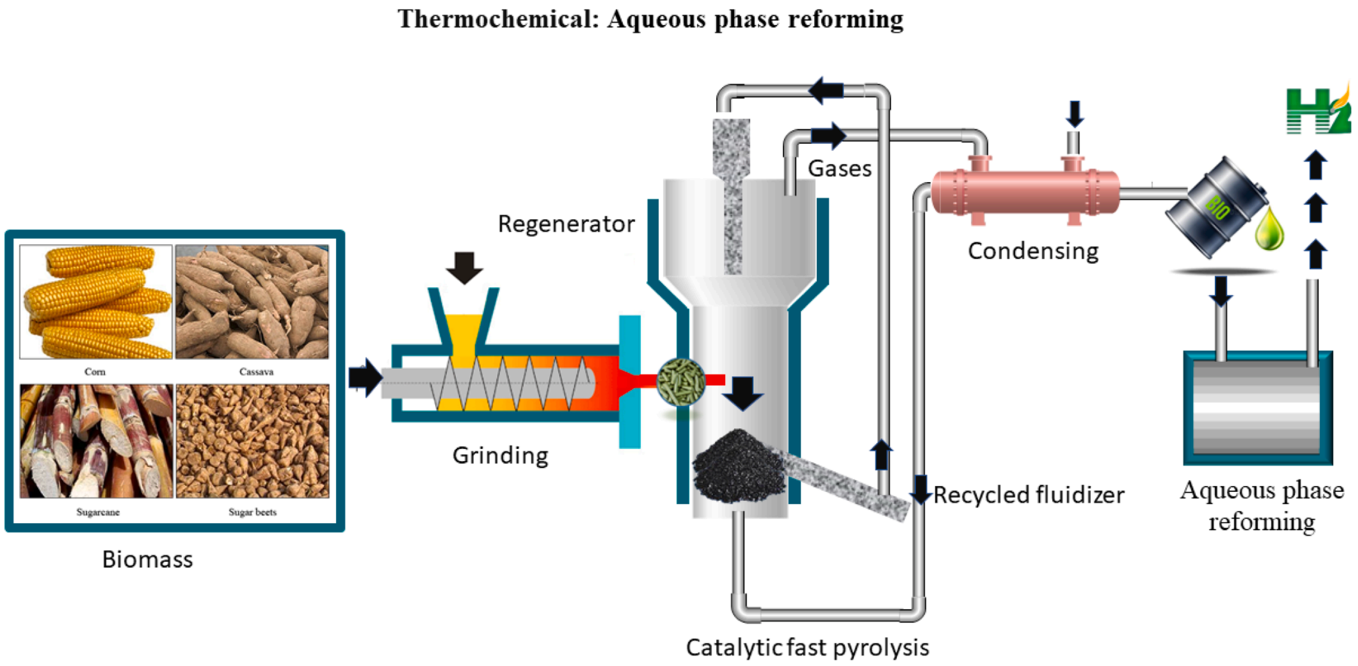

Fig. 6. Schematic diagram for thermochemical (aqueous phase reforming) process.

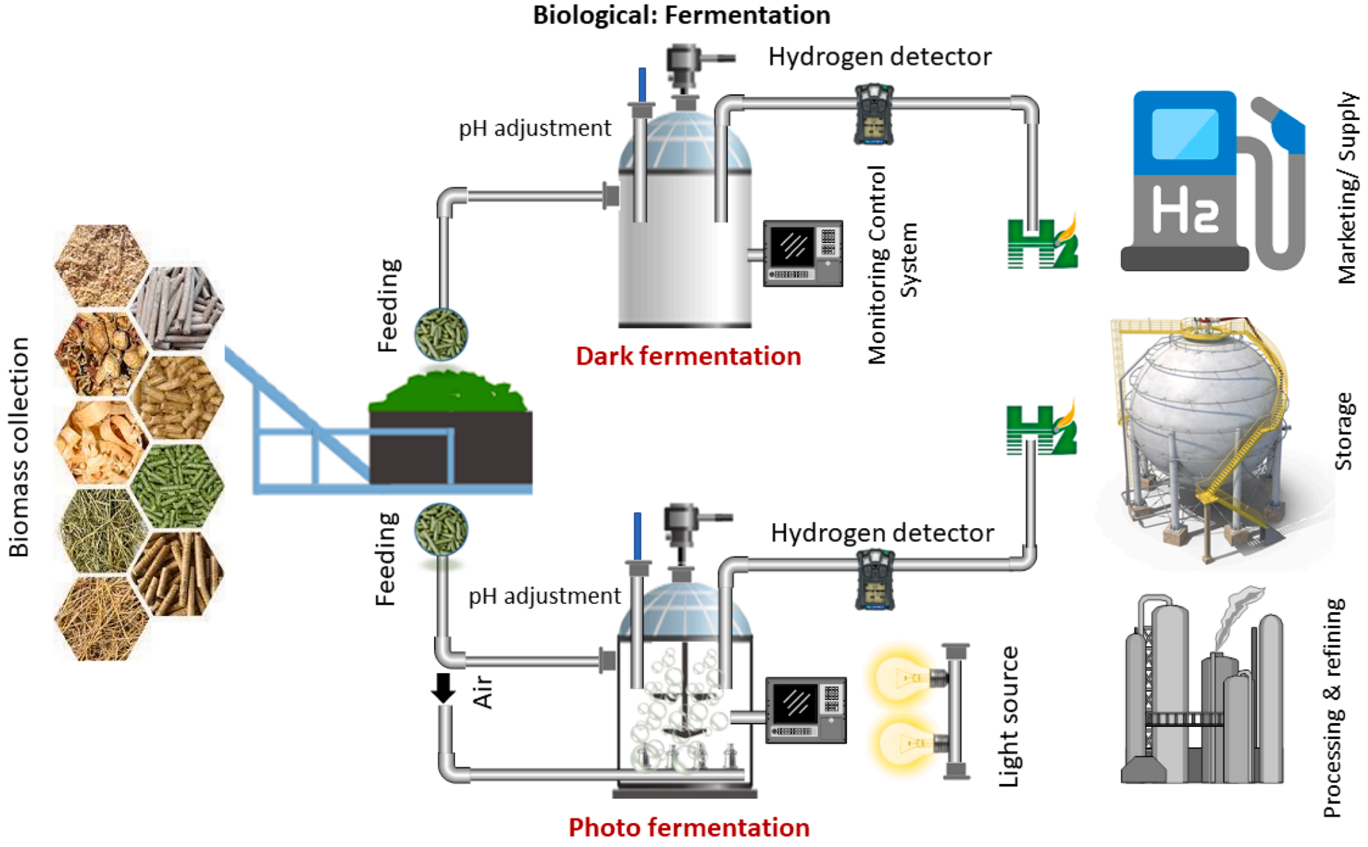

Fig. 7. Schematic diagram for biological (fermentation) process.

Hydrolysis, acidogenic fermentation, acetogenesis, and methanogenesis are all part of the anaerobic digestion (AD) process [118]. Indeed, both fermentation and AD processes are anaerobic processes. DF process is composed of the first two phases of AD (hydrolysis and acidogenesis) to produce H_2, whilst in anaerobic AD process, the objective is to produce biogas which can be further upgraded to biomethane. The major differences between them are in their operational parameters. Methanogens (H_2 consumers) must be suppressed to create H_2 in an anaerobic environment. With the help of extracellular hydrolytic enzymes, complex organic molecules that bacteria cannot directly consume are broken into soluble monomers such as monosaccharides, amino acids, and other simple organic components in the first phase. Obligate anaerobes such as *Bacteroides, Clostridia*, and other facultative bacteria do this phase. During the hydrolysis process, the rate of degradation is mostly determined by the substrate's type. Hemicellulose and cellulose degradation occur more slowly than protein decomposition [119]. Acidogenic fermentation bacteria transform the hydrolysis products into short-chain organic acids such as butyric acids (C_3H_7COOH), propanoic acids (CH_3CH_2COOH), and acetic acids (CH_3COOH), alcohols, H_2, and CO_2 in the second stage. Simple sugars, fatty acids, and amino acids are generally transformed into acetate, CO_2, and H_2 (70%), as well as volatile fatty acids (VFAs) and alcohols, during this phase (30%).

DF process may be employed to convert biomass-based resources directly to H_2 in a one- or two-stage process. The simplest technique is the one-stage AD process, which allows all phases (hydrolysis, acidogenesis, and acetogenesis) to take place in a single reactor. The most difficult aspect of this method is maintaining microbial equilibrium during the whole procedure. The two groups of organisms differ significantly in terms of physiology, dietary requirements, growth kinetics, and susceptibility to environmental factors, as previously documented [120]. To separate the hydrolysis/ acidogenesis and acetogenesis phases, a multistage process employs two or more reactors for digestion. Acidogenic bacteria make organic acids proliferate and reproduce more quickly than methanogenic bacteria. The multistage method is used to improve each digestive phase, resulting in more stable functioning, increased organic loading capacity, and increased resistance to toxicants and inhibitory chemicals [121–123]. As a result, compared to a one-stage approach, this technique demands a larger initial investment and ongoing operating expenditures.

DF pathway can take place at temperatures ranging from 26 to 40 °C, or in hyperthermophilic settings (temperatures above 70 °C). Because the benefits of operating outside of mesophilic environments (26–40 °C) are uncertain, most DF operational studies are carried out around 35–37 °C [68]. At 29–70 °C, the temperature was observed to be more variable during DF of different biomass and organic solid wastes [124]. To obtain ideal conditions during DF, researchers looked at not just temperature but also several important environmental elements such as pre-treatment, pH, hydraulic retention time (HRT), organic loading rate (OLR), biomass composition, partial pressure, and reactor type. On a larger scale, the selection of raw resources is equally critical. Because of their biodegradable substrates, the DF process focuses on carbon sources comprising monosaccharides, such as glucose, and disaccharides, such as lactose or sucrose. Many studies have reported on the use of biomass and organic solid waste for H_2 generation, as indicated in Table 7. According to a recent development, more research is needed to determine the best reactor configuration, supports for augmenting microbial immobilization, novel microbial strains, inhibitory effect mitigation, and an integrated fermentation mechanism that could potentially convert biomass to H_2 [125].

Additionally, similar to anaerobic conversion, PF process is the fermentative conversion of organic substrate to bio-H_2 by diverse photosynthetic bacteria through a three-step series of biochemical events. Through the action of their nitrogenase, photosynthetic bacteria including *Rhodospirillum, Rhodobacter, Rhodobium*, and *Rhodopseudomonas* may create H_2. Because of its major benefits of extensive

Table 7
Dark fermentation has been used to produce hydrogen from biomass and organic solid wastes.

Biomass	Reactor type	Pre-treatment	pH, Temp	Hydrogen yield	References
Rice waste	Anaerobic bioreactor	Thermal	5.5, 55 °C	40 mL-H_2/g-VS	[252]
Kitchen waste	Inclined plug-flow	Inoculum; thermal	5.5	72 mL-H_2/g-VS	[253]
Corn stover	Glass reactor (batch)	Inoculum	6.5, 35 °C	36.1 mL-H_2/g-biomass	[254]
Rice waste	Anaerobic bioreactor	Thermal	5.5, 55 °C	40 mL-H_2/g-VS	[252]
Duckweed	Serum bottle (batch)	Inoculum; thermal; acid-alkaline	7.0, 35 °C	169.3 mL-H_2/g	[255]
Empty fruit bunch	Batch reactor	Inoculum; thermal	7.0, 35 °C	287.0 mL-H_2/g-biomass	[256]
Grass waste	Blass bottle (batch)	Inoculum; ionizing radiation, acid or both combined	7.0, 37 °C	68.0 mL-H_2/g-biomass	[257]

material sources and thorough substrate consumption, photo-fermentation H_2 generation has attracted international study attention in recent years [126].

The rate of H_2 synthesis increases as light intensity increases, whereas light conversion efficiency declines. In comparison to cyanobacteria, which are employed in indirect bio-photolysis, the photosynthetic bacteria used in PF pathway have relatively high light conversion efficiency. Basak et al. [127] investigated purple non-sulfur bacteria grown in an O_2-deficient environment using nitrogenase and an organic acid as a reducing agent for H_2 generation. This approach has several flaws, which are stated below: a) The low conversion efficiency of solar energy (3–10%); b) The demand for large-area anaerobic photo-bioreactors; and c) The usage of nitrogenase enzymes, which require a lot of energy to activate.

Nitrogenase activity is critical in photosynthetic bacteria's generation of H_2. Hydrogenase is active in both H_2 synthesis and H_2 absorption under the same conditions. The main advantage of this method is the high concentration of H_2 in the product gas stream; Tao et al. [128] reported a concentration of roughly 96% of H_2 in the product gas stream. Another advantage of this technique is that the organic acid utilized as a substrate might be found in many industries' discharge wastewater. DF effluent can also be employed as a substrate for PF [129,130]. This procedure might potentially be used to produce H_2 from many forms of biomass waste [131]. Using just carbon sources, H_2 production was shown to be increased by 2–3 times [132]. Fedorov et al. [133] presented the bacterium system and the H_2 conversion efficiency for various feedstock. Many research attempts for photosynthetic bacteria have been documented in the literature; nevertheless, the PF process has never been discovered as an economically feasible approach. PF techniques offer several advantages, including the use of a large volume of feedstock and the usage of plentiful heat in the form of sunshine. The issues that remain to be solved are the reduced volumetric flow rate of H_2, conversion efficiency, and the demand for a large surface area.

2.2.2. Biophotolysis

In the biophotolysis process, solar energy is used by the photosystem to break water into O_2, energy, and a reducing agent (Fig. 8). This agent is used to produce H_2 by reducing protons utilizing nitrogenase or hydrogenase enzymes. The possibility of producing clean, carbon-free renewable energy from readily available natural resources such as sunshine and water has aroused interest in photosynthetic bacteria producing photobiological H_2. Photosynthesis catalyzed by hydrogenases can be used to create H_2 from solar energy. Through biochemical processes, this photobiological process, also known as biophotolysis, transforms organic molecules to H_2 using different microorganisms (such as cyanobacteria and microalgae) photosynthetic groups [134]. Photosynthesis uses sunlight as an energy source to separate H_2 from water or other chemical molecules. The key inputs for growing organisms in the photobiological process provided by the hydrogenase enzyme are sunlight and CO_2. During photosynthesis, chlorophyll pigments in photosynthetic organisms' thylakoid membranes absorb light

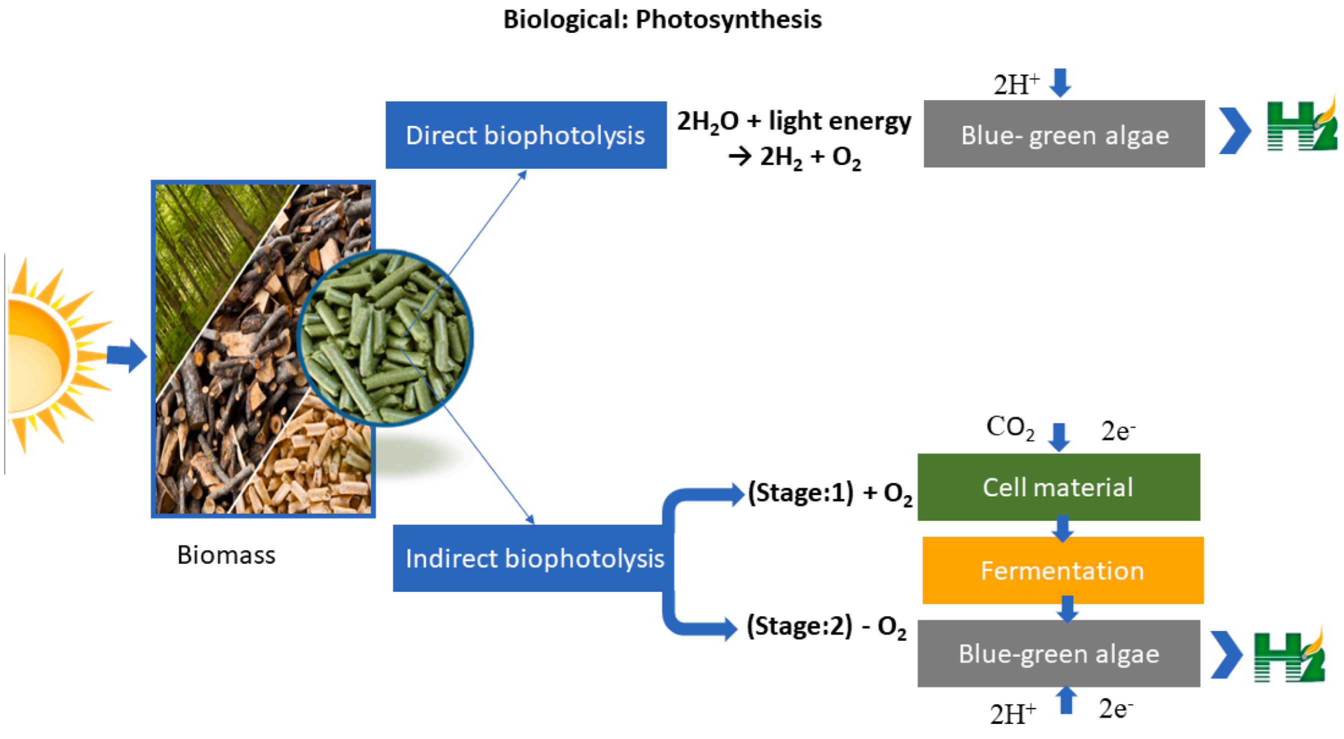

Fig. 8. Schematic diagram for biological (biophotolysis) process.

and create molecular O_2. CO_2 is subsequently converted to triose phosphate via enzymatic activities with the aid of ATP and NADPH [135]. Direct and indirect biophotolysis are two types of biophotolysis used to produce H_2. In the direct biophotolysis, water molecules are split using sunlight as a source of energy in the photosystem. After transferring the residual e^- to photosystem I, the hydrogenase helps to generate H_2 without releasing harmful GHG. This process also simultaneously releases O_2 into the atmosphere as displayed below:

$$2H_2O + \text{light energy} \rightarrow 2H_2 + O_2$$

Indirect biophotolysis is performed by microalgae under anoxic conditions. Under these conditions, microalgae can produce bio-H_2 through fermentation or respiration. Indirect biophotolysis is a two-step process: (i) the first stage involves O_2 producing and CO_2 fixing into chemical energy carbohydrates, and lipids; and (ii) the second stage functionally produces H_2 by the fermentation of stored carbohydrates. Cyanobacteria and microalgae have garnered the greatest attention among the microorganisms capable of producing H_2 [136]. Vargas et al. [137] produced H_2 by nitrogen deprivation in two experimental stages of development utilizing the *cyanobacterium Anabaena* sp. They discovered that optimizing biomass in the first phase of culture enhanced production by 18.3%, and heterocyst development was 3.4 times greater under nitrogen-deficient circumstances. Furthermore, fundamental research related to increasing the efficiency of H_2 production by photosynthetic cultures and increasing the reaction rate of this process is required to solve the problems associated with the simultaneous release of O_2 and H_2, ensuring the process's high sensitivity to O_2. In this context, research aiming at boosting the rate of H_2 production by photosynthetic bacteria is now highly important.

Kossalbayev et al. [136] examined the synthesis of biological H_2 from several strains of cyanobacteria. After 166 h of incubation in the presence of light, *Desertifilum* sp. IPPAS B-1220 produced 0.229 mmol-H2/mg-Chl·h. A 10-mM concentration of 3-(3,4-dichlorophenyl)-1,1-dimethylurea might boost H_2 production (0.348 mmol-H_2/mg-Chl·h) by *Desertifilum* sp. IPPAS B-1220 by 1.5-fold. Desertifilum sp. IPPAS B-1220 was discovered to have a 20-fold larger quantity of H_2 generated in the light than in the dark in research to locate novel *cyanobacterial* strains that can create and optimize conditions for H_2 production. It was found that cyanobacteria had the potential to efficiently convert solar energy to molecular H_2 as an environmentally acceptable fuel.

In theory, technological conversion using chemical catalysis, biocatalysts, or a mix of the two may generate 12 mol of H_2 per mole of glucose from biomass sugars. However, most experimental research using those approaches failed to obtain optimal H_2 production, owing to unwanted products and harsh reaction conditions [138]. Researchers also studied an enzymatic approach to improving H_2 performance from biomass. Zhang et al. [139] demonstrated a strong performance of the enzymatic process using starch and water, with the H_2 output being roughly 70% of the theoretical estimate. Furthermore, 13 enzymes facilitated the investigation, which took place at a temperature of 30 °C.

H_2 may be produced by converting substrates using certain enzymes that do not produce unwanted byproducts. The needed H_2 gas may then be easily extracted from the reactor, allowing for long-term production. Because the enzymatic process does not include cellular membranes that might hinder mass transfer, as in the microbial process, it can function more quickly to increase H_2 generation [140]. This approach produces more than DF, has a quicker production rate, and can accelerate non-natural processes. Several experiments on enzymatic H_2 generation have been conducted by researchers [140].

One of the challenges associated with bio-H_2 production is the. The presence of produced O_2 throughout the process is a significant obstacle to the creation of H_2 from biomass and organic solid waste [141]. In the presence of O_2, enzyme action, transcription, and protein maturation can be inhibited [142]. Researchers are attempting to maximize H_2 synthesis from biomass and organic solid waste while overcoming the presence of O_2 molecules. Melis [143] demonstrated that the enzyme hydrogenase activity in algae cultures, such as *Chlamydomonas*, needs the lack of O_2. To boost H_2 generation from green algae, *Paramesh* and *Chandrasekhar* [144] used O_2 scavengers such as sodium sulfite, sodium metabisulfite, and sodium dithionite. They discovered that all three scavengers might boost H_2 generation. Because of its high O_2 consumption, sodium sulfite produced the greatest results. $NaHSO_3$ has previously been used to boost H_2 generation in *Chlamydomonas reinhardtii* [145]. The results demonstrated that a small dose of sodium bisulfite in the studied algae could efficiently extract O_2. Surzycki et al. [146] examined the use of O_2 blockers containing copper to increase H_2 generation in algae cultivation.

Effective bioreactor and genetic engineering are also critical components in developing a sustainable biological process for H_2 generation. The latter is regarded as ground-breaking research in terms of increasing H_2 output throughout the process [141]. Some photosynthetic bacteria, such as cyanobacteria and *Rhodobacter sphaeroides*, have been genetically engineered [147,148]. Because most research is done in a laboratory size, the reactor's effective design must be done on a bigger scale. Temperature control, agitation system, bioreactor performance with the same volume but varied area-volume ratio, and ability to handle consortium organisms are some critical criteria to consider when designing bioreactors [149].

2.3. *Electrochemical production pathways*

Biomass may also be converted electrochemically (Fig. 9). The reaction at the anode is what distinguishes water electrolysis from biomass electrolysis. Instead of creating gaseous O_2 from water, the feedstock is oxidized. MECs and Proton Exchange Membrane Electrolysis Cells (PEMECs) are two technologies that may be used to electrolyze biomass. For bio-based compounds such as ethanol and glycerol, both PEMECs and MECs are routinely utilized. Electrolysis cannot directly transform polymeric compounds such as cellulose or wood sawdust. These systems necessitate a single or two chambers with an anode/cathode coupling. At the anode, organic matter is converted via an oxidation process that releases protons (H^+). At the cathode, a reduction process occurs, permitting the production of H_2 [147].

MECs are a new biochemical technique to produce H_2 from biomass in a cleaner form. An anode and a cathode electrode in an anaerobic environment connected to a power supply make up the MECs [150]. MECs look like microbial fuel cells (MFCs); they have similar electrodes and reactions setup. The main differences between the MECs and MFCs systems are no air is needed for the cathode in MECs and the end products are different [151]. MFCs produce electricity directly, while in MECs, bio-H_2 is generated on the exterior of the cathode [152]. In the MECs scheme, the microbial reactions on the anode have a significant influence on the H_2 generation process [152]. An electrochemically active bacterium (EAB) is an electrogenic microorganism that spreads on the surface of the anode and reacts with the organic wastes. EAB oxidizes the substrate then protons and electrons are produced. Electrons go across the wires to the cathode while the protons travel to the cathode through the solution, at which they interact with electrons for producing H_2 [153]. The H_2 generation in the MECs system is not spontaneous; a small voltage is needed to start the reaction around 0.2–0.8 V [154]. This voltage is still far lower than the 1.2 V needed for water electrolysis [153].

The EAB has a significant impact on the total power generation in the MECs system by enhancing the passage of electrons or production on the surface of the anode. Exoelectrogens are a kind of microbe that exists on the surface of the anode or anode compartment of MECs for the transmission of electrons from feedstocks to electron acceptors [155,156]. EAB has been identified in soil and household wastewater and industrial wastewater [151]. In MECs, a variety of inoculation microorganism approaches are frequently used, such as; (i) Cells were run in MFCs mode

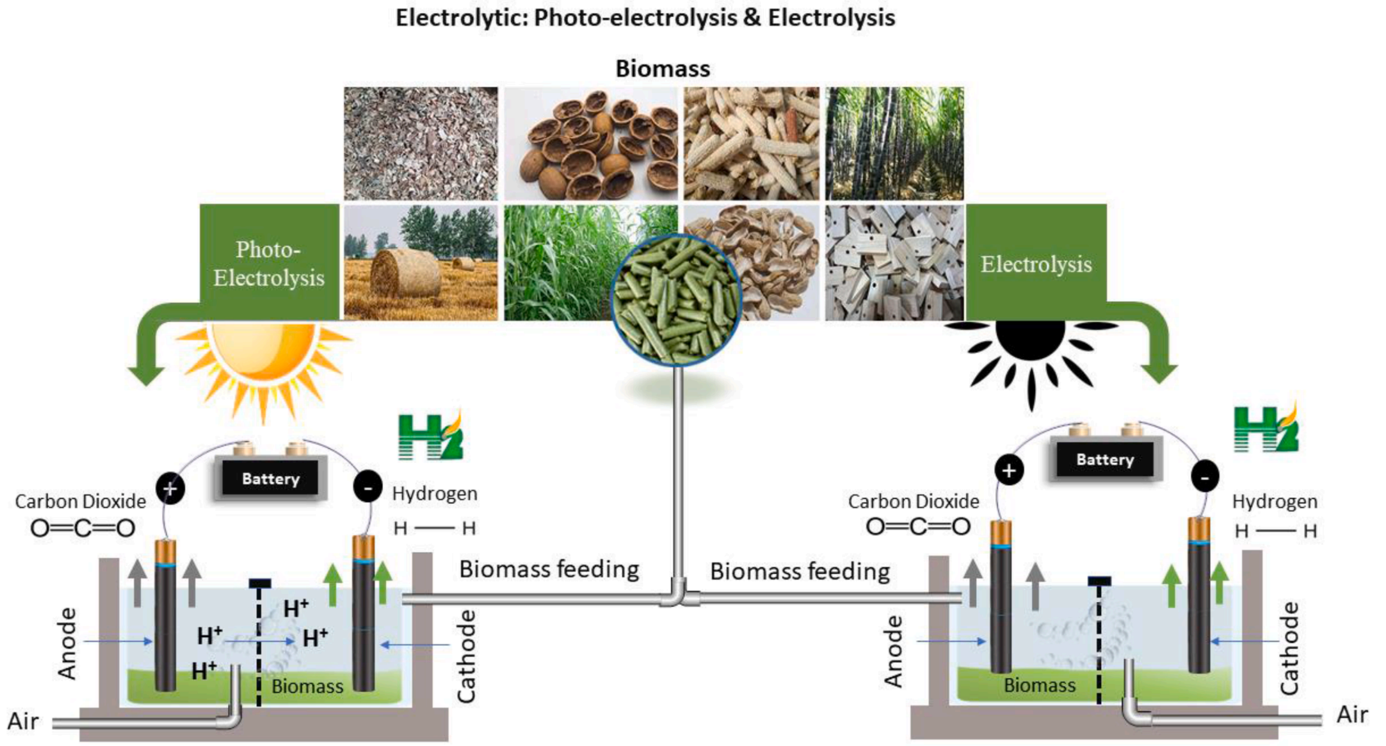

Fig. 9. Schematic diagram for electrochemical process.

until consistent power generation was achieved. Moving anodes to MECs exoelectrogenic microorganisms on anodes are enriched, and MEC operation may begin quickly [155], (ii) scraping biofilms off from anodes of operating MFCs/MECs or using the effluent from them, and (iii) using wastewater or anaerobic sludge directly as a source of large levels of microorganisms that are well suited for the MECs process [157].

Because of its availability and renewability, lignocellulose has gotten a lot of attention as a prospective fuel for H_2 generation in MECs. Complex carbohydrates found in lignocellulosic biomass may be utilized to feed microorganisms that produce renewable sources of energy like H_2 and methane [158]. But microorganisms cannot be used in a direct way for H_2 production from lignocellulose. Pretreatment techniques (such as acid or enzymatic pretreatment) are required to use lignocellulosic materials by microorganisms effectively. Using DF process, lignocellulose was converted to acetic and formic acids, as well as ethanol, that far more readily degrade organic molecules in MECs via electrochemically active bacteria [153]. VFAs from DF discharges can be treated in MECs cells to produce H_2. The lignocellulose effluent of corn stover and a cellobiose effluent from DF were treated in MECs. H_2 generation rates of lignocellulose effluent were 1 L-H_2/L-d while the

Table 8
The production of Hydrogen from different biomass through microbial electrolysis cells.

Biomass type	Anode	Cathode	Eap (V)	volume (mL)	MEC type	Operation mode	Hydrogen production	Reference
Cellobiose	graphite fiber brush	Pt/carbon cloth	0.5	28	Single chamber	Fed-batch	0.96 L/L-day	[258]
Lignocellulose	graphite fiber brush	Pt/carbon cloth	0.5	28	Single chamber	Fed-batch	1.00 L/L-day	[258]
Cornstalk fermentation effluent) acetate(	graphite felts	Carbon cloth coated with Pt and a Nafion	0.8	64	Single chamber	batch mode	3.43 m^3/m^3-day	[176]
Rice straw	carbon cloth	Pt/ carbon cloth	0.8	358	dual chamber	Fed-batch	2.46 mmol/L Day	[259]
Rice straw	carbon cloth	carbon cloth impregnated with Pt	0.8	360	dual chamber	Fed-batch	1.95 mmol	[260]
Vegetable waste	carbon cloth	carbon cloth impregnated with Pt	0.8	360	dual chamber	Fed-batch	2.31 mmol	[260]
1:1 mixture of Rice straw and vegetable waste	carbon cloth	carbon cloth impregnated with Pt	0.8	360	dual chamber	Fed-batch	2.56 mmol	[260]
Galactose	carbon cloth	carbon cloth containing 0.5 mg cm^2 Pt	0.7	17	Single chamber	batch mode	0.07 m^3/ m^3-day	[158]
Cellobiose	carbon cloth	carbon cloth containing 0.5 mg cm2 Pt	0.7	17	Single chamber	batch mode	0.09 m^3/m^3-day	[158]
Palm oil mill effluent (acetate and butyrate)	graphite fiber felt	carbon cloth	0.7	600	Single chamber	batch mode/ single chamber	7.81 L/ L -day	[159]
fermented sugar beet juice	carbon fibers	Stainless steel mesh	0.4	–	dual chamber	batch-mode	1088 mL	[261]
fermented corn stover	carbon felt	Pt deposited carbon disk with a stainless-steel wire mesh	−0.2 versus Ag/AgCl	16	two-chamber	continuous-fed	20.1 L/L-day	[262]

cellobiose fermentation effluent produced 0.96 L-H_2/L-d in the MECs [153]. Bio-H_2 generation from palm oil mill effluent (POME) was studied using two-stage DF and MECs. Continuous two-stage DF with MECs produced three times more H_2 than DF alone [159]. Recently, It was possible to attain a high rate of H_2 generation of 20.2 L/L/D from fermented corn stover [159]. Single-chamber MECs were recently used to generate H_2 from different carbohydrates in lignocellulosic biomass. The highest production rate from cellobiose was about 0.09 m^3 H_2/m^3 d after 14 d of operation [158]. Table 8 displays the production of H_2 from different biomass through MECs.

Graphite or carbon cloth are carbon-based electrodes, commonly known as the most popular anode materials used in MECs. Higher electrical conductivity, form and size flexibility, compatibility in biological terms, a large reaction surface area, as well as economical, and resistance to chemicals with minimal overpotential are advantages of these electrodes [153,160]. Also, these electrode materials showed an improvement in the yield and overall performance of MECs. The cathode materials have a significant influence on the overall efficiency of MECs since H_2 is generated on the cathode surface. On graphite or carbon-cloth materials, the H_2 evolution reaction (HER) is impracticable due to the low activity rate, so a catalyst modifies these materials. In MFCs, platinum has been employed as a catalyst for the cathode. This catalyst increases the HER rate and reduces electrode overpotential or overcomes the thermodynamic barrier during the reduction reaction [161]. Another critical component for successful MECS operation is the membrane. Membranes in MECs usually separate the cathode and anode chambers physically and permit ions or particles to flow through according to their pore size. Except for H^+, membranes are also utilised to inhibit mass, H_2, CH_4, substrate movement, and microbes from flowing between anode and cathode chambers [162]. Anion-exchange membranes (AEM) and cation-exchange membranes (CEM) are the most investigated membrane types in MECs systems [163]. A drawback of the membrane is that it generates a pH gradient, which reduces MECs efficiency by lowering the pH in the anode compartment while increasing the pH in the cathode compartment.

High pH is needed for electrochemically active bacteria EAB for growth and activity. Controlling the pH inside the MECs is challenging and important. The pH also regulates both the anode and cathode processes and the thermodynamics and kinetics of the reactions. In MECs, pH 9 is favorable for COD decomposition and increases H_2 gas generation [164]. Temperature is another important factor in the MECs activity as it affects the H_2 generation by influencing the activity and choice of microorganisms. The effect of temperature on MECs performance by examining the MECs at different temperatures found that 30 °C had the greatest Coulombic efficiency. Currently, MECs experiments are often carried out at a regulated temperature of roughly 30 °C, where the H_2 yield is directly affected [164]. At the cathode of MECs, the H_2 evolution rate HER is a thermodynamically unfavorable reaction, so H_2 gas generation requires a voltage range of 0.3–1. 0 V [165]. When the applied voltage is lower than 0.3 V, the results showed that the H_2 production rate decreased. Also, the usage of 1.1 V has not been suggested since the electric power input is very high that the MECs approach a water electrolysis process [164]. The reactor geometry and configuration have a direct effect on current density and H_2 yield. Various MECs configurations have been created recently employing a variety of materials such as single-chamber and two-chamber cells. Internal resistance in MECs configurations might directly impact H_2 production output. Internal resistance in MECs is affected by a variety of variables such as raising the anode conductivity, decreasing contact resistance, and reducing the total distance of electrons in the anode [166]. In single-chamber MECs, the internal resistance can be prevented, but H_2 cannot be separated efficiently [167]. During the reactions, the substrate concentration decreases. The anodic bacteria reprocess H_2 as an electron donor that creates a side reaction between the electrodes; H_2 extraction and energy efficiency are both reduced [168]. Another drawback is H_2 methanation which reduces the H_2 production rate. There are a variety of methods for overcoming these problems, including decreasing the temperature and/or pH, use of antibiotics and presence of a more positive anode. Other modifications to lower the internal resistance, such as irregular shaped electrodes, are being used in MECs to minimize electrode resistance and boost electrode area/volume ratio, decreasing the space between the electrodes [169].

For lab-scale experiments, many MECs reactor setups have been developed, although they all operate on the same principles [151]. The most extensively used design, consisting of two chambers separated by an ion-exchange membrane between the anode and cathode compartments, is the two-chamber MECs. In recent years, various designs have been configured, such as H-type, cylindrical-shaped, or rectangular. The main advantage of two-chamber MECs is the ability to H_2 recover due to the use of a membrane.

Separating the anode and cathode using a proton exchange membrane (PEM) is a great idea, as it can effectively decrease the access of O_2 which prevents O_2 infiltration. If a tiny amount of "hydrogen infiltration" occurs as a result of employing porous membranes in MECs, electrons will not be removed from the organic matter, therefore not affecting coulombic efficiency. The influence of permeable membranes on MECs mass transfer varies according to the membrane material, pore size, and operating parameters [169]. A polymeric membrane in PEMEC devices transports protons to produce a high H_2 gaseous percentage [148]. In MEC systems, organic matter is oxidized to create H^+utilizing electrochemically active microbes as catalysts, resulting in a "bio--electrochemical" system [170]. Classic PEMEC systems necessitate the use of a costly noble metal catalyst, which is particularly sensitive to CO and other contaminants generated by biomass during electrolysis. Furthermore, PEMECs use a large number of alkaline molecules to neutralize the organic acids created during biomass electrolysis, increasing the cost of the process. The same results have been found for MECs systems in which microbes are unable to directly consume the biomass. Biomass must be fermented and transformed into organic acids or alcohols before being turned to H_2 via the MECs. Furthermore, although having lower energy consumption than water electrolysis, the conversion rate of MECs is too slow for the process to be competitive. These disadvantages have hindered the development of electrolysis devices that produce H_2 from biomass [149]. Even if electricity consumption may be decreased by utilizing bioethanol instead of water (e. g., Chen et al. reduced it by 26.5 kWh/kg H_2 converting ethanol using palladium nanoparticles coated on titanium nanotubes), bioethanol production influences the whole energy balance. Indeed, this problem reduces interest in this technique since producing economically viable bioethanol from biomass, particularly lignocellulose, is difficult [171]. In the future, research on the direct electrolysis of biomass should be conducted.

To increase H_2 generation from biomass and organic solid waste, several hybrid biological conversion methods have been developed. As previously stated, a poor output during DF can be enhanced by combining it with other processes such as PF, MECs, enzymatic systems, and AD. DF process is still appealing because of its simple design and high output rates. The second phase is usually concerned with treating the DF effluent to attain the best outcome of 12 H_2 atoms per glucose. To achieve an optimal operation with a yield of 5–7 mol-H_2/mol-hexose, the combination of DF and PF can be accomplished using two consecutive reactors [172,173]. Excess nitrogen during DF, on the other hand, can hinder the solar fermentation process, particularly nitrogenase, a crucial enzyme. As a result, extra treatment expenditures are incurred to neutralize and dilute the effluent before the second phase.

Yan et al. used a combination of DF and MECs to create H_2 utilizing two bacteria, *Moorella thermoacetica* and *Geobacter sulfurreducens* [174]. Other investigations [175,176] indicated an increase in H_2 yield during this combination, but a decrease in yield for complex organic waste and wastewater [177,178]. Khongkliang et al. [159] studied hemophilic H_2 generation from POME using two-stage DF and MECs. The findings seemed encouraging, with high H_2 output; the H_2 yield rose thrice when compared to DF alone. Due to the presence of methanogens, a mixture of H_2 and methane can be created in the combination of DF and AD. The combination of DF and AD from diverse wastes such as bio-waste [179], food waste [180,181], and home solid waste [182] has shown promise and improved performance. Albini et al. [183] observed an increase in biological stability and efficiency over a single-stage approach. In general, a hybrid biological process can enhance H_2 production with a more intricate design than a single conversion approach [172]. Table 9 compares the advantages and disadvantages of MEC and PEMECs.

3. Circular economy, current trends, and prospects of bio-hydrogen

H_2 council report in 2017 [184] anticipated that 18% of the global energy demand will be fulfilled by H_2 by 2050. This energy is estimated to be 78 EJ (10^{12} MJ). Additionally, World Energy Outlook (WEO) in 2020 [185] envisaged that countries would achieve Net Zero Emissions by 2050 (NZE2050) as a sustainable development scenario. Thus, relying on fossil fuels drastically reduces as the H_2-based fuels are going to be central in particular for aviation and maritime shipping applications despite being in the early stages with some demonstration projects [185,186]. For example, UK's H_2 strategy report [187] in 2021 mentioned that the government's commitment is to produce low carbon H_2 of 5 GW by 2030 dealing with industry to endure the H_2 economy. Bio-hydrogen is regarded as one of the growing eco-friendly energy sources in recent years due to its advantages in offering a clean and sustainable form of energy. H_2 is a distinctive energy carrier with a high calorific value of 120 MJ/kg at room temperature which is nearly three times as much as fossil fuels (e.g., gasoline 44 MJ/kg) [188,189]. This offers a high energy content which makes it considered the best alternative to petroleum fuels releasing only water from the combustion process supplying sustainable energy and minimizing waste. Fig. 10 depicts the circular economy, current trends, and prospects of bio-hydrogen applications. Industrial applications now depend on H_2, albeit it mostly focuses on H_2 produced from SMR [190] or electrolysis [191,192]. For instance, the UK currently is producing (10–27) TWh of H_2 using SMR without carbon capture and storage (CCS) and all are employed in the petrochemical sector [187]. Only a few trial projects using H_2 from electrolysis such as: blending H_2 in domestic heating and gas grid.

Materazzi et al. [193] proposed a model for a pilot biomass waste gasification plant to produce bio-H_2 with a gross efficiency of 78%. Grid-quality and high purity H_2 of 360 and 23 GWh for the transportation section. The authors suggested that the combination of waste to H_2 technology with CCS technology will meet the requirements for net-zero emissions in the future. Zhang et al. [194] found that the bio-H_2 produced via biological methods of DF and PF processes of *Platanus Orientalis* leaves is not enough to be employed in industrial applications due to the low energy conversion efficiency. They utilised the effluents produced from bio-H_2 production via fermentation to produce bio-methane. They found that this co-generation of bio-H_2 and bio-methane enhance the energy conversion efficiency by 10 to 18%. Despite the production of bio-H_2 worldwide, the application of bio-H_2 in many sectors doesn't have yet a firm footing.

Table 9
Advantages and disadvantages of microbial electrolysis cells and proton exchange membrane electrolysis cell.

	MEC	PEMEC
Advantages	• no need to purify • low energy consumption • moderate operational conditions • low potential losses • high H_2 production rate • low pH gradient impact	• no need to purify • low energy consumption • moderate operational conditions • prevent back diffuses of H_2 • high Purity of hydrogen
Disadvantages	• Expensive catalyst • Production of methane • Low Purity of hydrogen	• Large internal resistance • High pH gradient impact • High cost of H_2 generation

3.1. Applications of bio-hydrogen in power generation and transportation sectors

Indeed, the contribution of bio-H_2 in decarbonising the transport sector is a must. Reducing emissions, especially in heavy-duty transportation, and replacing it with fuel cell electric vehicles (FCEVs) will follow the demand for sustainable energy. Fuel cell vehicles (FCVs) are considered the future vehicles for a zero-emission environment and high performance. International Renewable Energy Agency (IRENA) report [195] suggested that most of the global H_2 economic potential would be applied in the transport sector, with industrial use in the chemical and steel sectors. There are few wastes to H_2 projects, however, they are mostly on a pilot scale and even smaller. PEM fuel cells have great attention in employing bio-H_2 in fuel cell technology. PEM has a compact structure containing high power density and very low operation temperature below 100° C, and it showed a good demonstration portably in some small units [196,197] despite some challenges regarding the stack that can only tolerate CO and H_2S at certain levels. If these levels are higher, this may end up blocking the catalyst sites and reducing the performance of the fuel cell.

SGH2-energy [198] is launching the world's largest production project of bio-H_2 from waste via a patented plasma-thermal catalytic conversion process of wastes including mixed paper, plastics, tires, and textiles in the city of Lancaster, California. The process utilises a pressure swing absorber system to separate and purify H_2 at 99.99% from the syngas produced before employing in PEM- FCVs. The facility can produce 11,000 kg/day of H_2 equivalent to 3800 tons/year from 42,000 tons of feedstock if it operates 8000 h/year making it nearly larger than any other project even finished or still under development. The project is in the front-end engineering and design (FEED) phase and Iwatani Company in Japan has commissioned to use SGH2 - H_2 in its refueling stations. California Energy Commission (CEC) and the air resources board (ARB) are intending to establish 200 H_2 refueling stations by 2025 [199]. SGH2 is negotiating on projects in Europe, Asia, South America, and Australia.

Ways2H [200,201] is a joint venture between US and Japan to produce bio-H_2 from municipal solid waste, biomass, sewage sludge, hazardous medical, and plastic wastes. The system relays on the distinctive thermochemical process via a two-stage process that includes the thermal cracking of the organic wastes by solid heat carriers as ceramic beads at high temperature indirectly in an inert atmosphere, and the SR to break down the methane into H_2. A mobile demonstration unit is currently working in Japan known as AGM Model 5. The unit is transportable and of a size fitted into three stackable 50 cm shipping containers producing 50 kg of H_2/1 tpd of biomass. This is equivalent to a 40 kW power generator or 12 FCVs tanks. A commercial plant located in Sunamachi Water Reclamation Center-Japan has been established after four demonstration plants to process 1 ton/day of sewage sludge into 50 kg/day of H_2 sufficient to fuel 10 FCVs.

An experimental study was carried out by Pedro Farrancha [202] on integrated bio-H_2 with a fuel cell. Food waste DF was used to produce bio-H_2 from a small-scale system with a total volume of 45 Litres after 14 days and the maximum energy generation from the PEM fuel cell was 1.6 Wh/L. The study suggests a further study with more than one cell with some trials to assess the performance of the bio-H_2 application in fuel cells.

Chung et al. [203] studied experimentally the effect of purification of bio-H_2 produced from Palm Oil Mill Effluent through fermentation on the power generation from a proton exchange membrane fuel cell. Two different separation techniques were employed in the study; absorption and membrane separation. The study has proven that the absorption technique is more efficient than the membrane separation as the purified

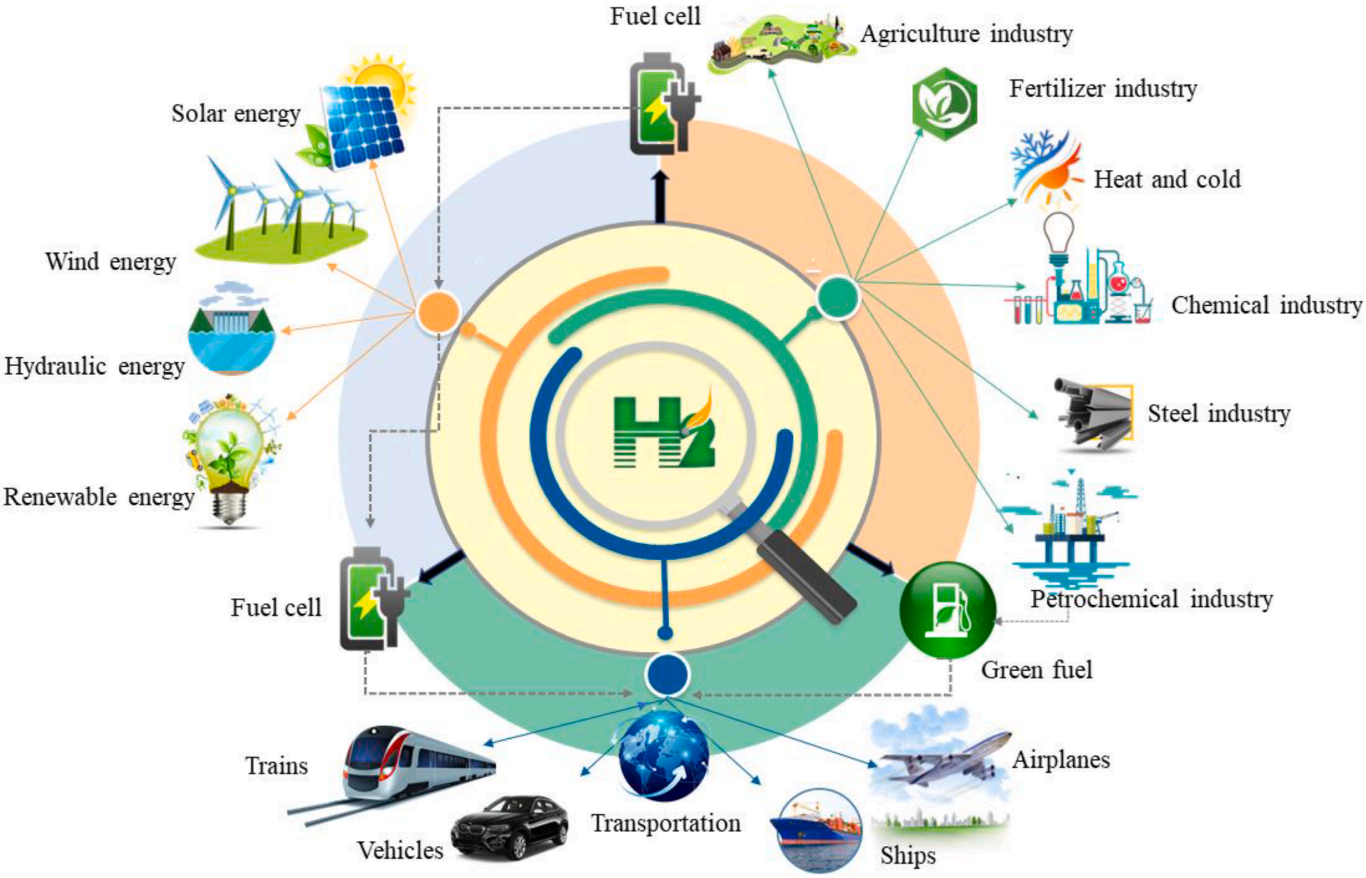

Fig. 10. Circular economy, current trends, and prospects of bio-hydrogen applications.

bio-H_2 from absorption was 100% H_2. H_2 was fed directly to the PEM fuel cell. The current and power generated from the absorption technique were 1.6 A and 9.3 W whilst using membrane was 0.69 A and 3 W.

The H2-W project is established in Wuppertal, Germany by WSW Mobil GmbH to produce H_2 powered-bus from municipal solid waste incineration [204]. The technology relays on the electricity produced from the waste incinerator to release the H_2 via electrolysis. An 85 kW fuel cell is equipped to convert H_2 into electricity to power the bus [205]. AWG mbH Wuppertal plant is producing nearly 400 kg H_2/day for the refueling system supplied by Belgian manufacturer Van Hool of the ten-fuel cell buses.

3.2. Applications of bio-hydrogen in combined heat and power (CHP) systems

Tokyu Hotel in Kawasaki, Japan is now 30% powered by H_2 produced from waste plastics gasification [206]. By supplying H_2 to Toshiba's H2Rex fuel cell system, the electric power and heat are generated without CO_2 emissions. The remaining 70% comes from food waste recycling using the bio-methanation method by microorganisms. The hotel is providing 300,000 nm^3/y of H_2 offering 450 MWh equivalent to the annual energy consumption of 82 households.

Metacon AB company [207] has developed a product named ''H2PS-5'' system at its subsidiary Helbio in Greece consists of a CHP generation unit. The patented technology consists of two steps; the fuel processing step whereas the H_2 is produced through the SR of biogas or other feeding fuels. The second step is the power generation step where a low-temperature PEM fuel cell is equipped for the system. H2PS-5 is producing 5 kW of electricity and 7 kW of thermal power in the form of hot water. Annually, the estimated energy production is nearly 43 MWh of electricity and 60 MWh of heat equivalence to 70–80 °C hot water. The system has a maximum electrical efficiency of 35% and the operating costs are two times lower than conventional diesel generators [208]. H2PS-5 is applicable for telecommunication stations, on or off-grid households, sailing yachts and boats, trucks, and small farms.

3.3. Operational challenges regarding the bio-hydrogen implementation in applications

The situation of using bio-H_2 in different sectors is facing some obstacles needed to be overcome, such as in the transportation sector where FCEVs are still in an early commercial-stage due to main factors are main parameters that hurdle the wide usage of bio-H_2 in various applications such as the cost of fuel and vehicle materials and infrastructure of the H_2 system. Fig. 11 depicts some of the main obstacles that show some challenges and require more research studies to be done.

3.3.1. Large scale application

Despite the attractive biological methods of producing bio-H_2, low production yield is still one of the main obstacles that impede the ability to have wide large, and commercial-scale applications. In addition, starting up the bio-reactor of a large residence time would limit the high yield and require larger reactors and extra cost. There are some promising solutions to overcome this obstacle such as the creation of new biocatalysts [209] that can work under difficult conditions of temperature, pH, and others to offer short residence time and also reactor volume with a higher rate of substrate conversions. Another solution is to rely on nanotechnology and the employment of nanoparticles seizing the distinctive geometry and quantum size such as gold, and iron nanoparticles. These particles during the fermentation process may turn into metal ions which enhance the microbial and biocatalyst activities as well [210,211]. Another obstacle that limits the large-scale application

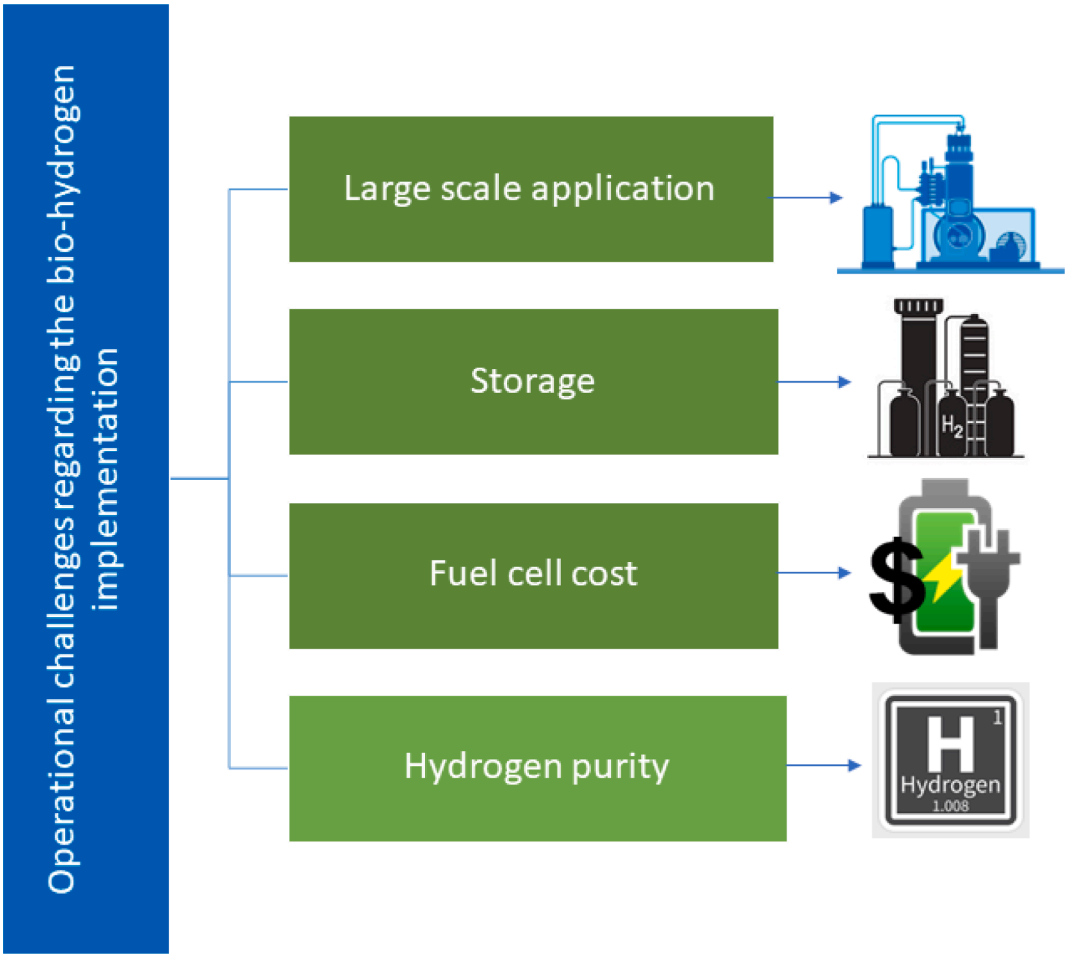

Fig. 11. Operational challenges regarding biohydrogen production.

is technical and managerial including the design of the system and optimum operating conditions and difficulties in high yields. This could be solved by Artificial intelligence (AI) to set optimization algorithms to predict bio-H_2 production yield from the system [209]. Nutshell, research is still going in the field of bio-H_2 to acquire a higher yield.

3.3.2. *Storage*

Despite the high energy density by weight of H_2, it has a low volumetric energy density (8 Mj/l) which is approximately one-fourth the gasoline (32 Mj/l) at room temperature [189,212]. This means storing and transporting liquid H_2 needs large and also cryogenic tanks. For example, jets need a liquified H_2 combined with O_2 to work as a propellant. The liquefaction process is accompanied by high cost and also keeping H_2 in a liquid phase. Even storing H_2 in a gaseous phase requires elevated pressure of up to (700–1000) bar especially in-vehicle applications [213] and this demands different H_2 storage materials.

In addition, the pressurization process consumes about 10% of the H_2 energy content [214]. Special expensive metal or crystalline alumino-silicate materials and alloys are used to store H_2 such as zeolites, and metal hydride. The most promising metal hydride are MgH_2, $LaNi_5$, $ZrFe_2$, and $NaAlH_4$ which can be employed in a wide variety of applications including thermal storage neuron moderation, electrochemical processes, and others [215]. Metal hydride is considered the safest method of storing due to its low operating temperature and endothermic behavior [216]. However, Hydrogen storage and transportation still need further condensed research.

3.3.3. *Fuel cell costs*

Although H_2 fuel cells are used in different applications such as transportation and CHP offering great advantages in vehicles such as high thermal efficiencies, good fuel efficiency, no engine noise, zero emissions, and few moving parts still the vehicles are more expensive than their low-carbon rivals. CHP applications are mostly running on natural gas and could be converted to H_2-powered (FC—CHPs) with little modifications but, are still expensive.

3.3.4. *Hydrogen purity*

To utilize produced H_2, purification is substantial. As seen by Chung et al. [203] that efficient power system requires a high-quality H_2. Purity requirements remain essential in some applications as there would be some implications due to the existing impurities. For example, fuel cells require CO_2 removal from bio-H_2 with an allowable concentration of less than 2 mmol/mol [192,217,218]. The onset of impurities in the fuel cell system could irreversibly deteriorate the performance and running life [219]. Thus, ISO and SAE released the ISO 14,687–3 and SAE J2719–20, 511 for the purity characteristics of H_2 used in vehicles that must meet the minimum requirements of purity of PEMFCs (99.97 mol%) [197, 220]. Many research studies have been carried out on H_2 purification systems and are still ongoing [220–222]. H_2 purification can be physical like adsorption and membrane separation, and also chemical like catalysis and metal hydride separation [223]. Some studies revealed that absorption is a preferable technique due to the low temperature and pressure operation [203,224]. However, still, the cost of the purification process remains an issue that is required to be addressed for using low-cost membrane materials for instance. Research is still on-going for example novel adsorption materials and poison-free metal hydrides to guarantee cost-effectiveness and endpoint application tolerance improvement for H_2 purification.

3.3.5. Future directions

Biomass is an effective feedstock for carbon management for carbon neutrality, which provides a significant prospect for renewable development. Sustainability, natural availability, bio-renewability, and recyclability. The creation of more compact, effective distribution facilities that use the gasification process to create hydrogen at a reasonable cost should be the main focus of research efforts in this field. Because oxygen hinders the creation of hydrogen, it is crucial to develop organisms that are less sensitive to oxygen to produce hydrogen at a higher rate. The creation of innovative engineered strains and advancements in combined/hybrid fermentation techniques open up new opportunities for higher production efficiencies of bio-H_2. Another great option to improve the technological and financial aspects of the production of bio-H_2 is the concurrent synthesis of biomethane and other compounds with value-added. Pre-treatment reduces the lag phase of anaerobic fermentation by removing stiff and inhibitory substrate components that impede the fermentation process. This increases the efficiency of the bioprocess. Pre-treatment procedures are helpful, but they raise production costs, thus their usage must be justified. Also, hybrid systems of bio-H_2 production are considered one of the best solutions to reduce the cost of production and increase the productivity of bio-H_2.

Metal hydrides are the best methods for storing a large amount of hydrogen because of their fast kinetics for releasing and storing hydrogen at low temperatures. The development of materials that could promote the storage of high-density hydrogen at low temperatures needs extensive research. As a result, it can be concluded that inexpensive, safe, and environmentally friendly hydrogen production and separation, as well as hydrogen storage, is required to promote the hydrogen economy. While the development of low-cost, effective systems for the separation, purification, and storage of hydrogen can be very valuable, more emphasis needs to be paid to manufacturing methods. According to the author's vision, optimal processing for the manufacture of bio-H_2 requires the integration of several production processes, various biomass waste streams, and modeling. This will promote environmental benefits such as the creation of bio-H_2 from sustainable waste materials and afterward work toward the zero-carbon economy, helping to ease problems related to fossil-based fuel. To sum up, continued research and innovation regarding the biomass-to-H_2 strategy with emphasis considering their merits is urgently needed to enhance the mercantile sustainable H_2 production rates from renewables.

4. Conclusion

Bio-hydrogen is regarded as one of the growing eco-friendly energy sources in recent years due to its advantages in offering a clean and sustainable form of energy. This review illustrates a detailed mechanistic insight into hydrogen production routes from bio-renewable resources. Therefore, the present review has systematically taken up the recent progress in various bio-sourced H_2 production pathways (i.e., thermochemical, biological, and electrochemical). Both thermochemical processes, such as pyrolysis, liquefaction, and gasification, as well as biological processes can produce hydrogen from biomass (i.e., direct or indirect biophotolysis, photo- and dark-fermentation). For the most promising identified biomass-to-hydrogen conversion pathways, the biological methods showed favorable environmental performances compared to thermochemical and electrochemical methods. Dark and photo-fermentation by strict anaerobes, facultative anaerobes microalgae, cyanobacteria, and bacteria are the most widely used methods for biological hydrogen production. Research is still on-going for example novel adsorption materials and poison-free metal hydrides to guarantee cost-effectiveness and endpoint application tolerance improvement for H_2 purification. According to the reviewed articles, Solar pyrolysis can provide a very high temperature of up to 2000 °C, which was found to promote the gas yield. Moreover, hot radiofrequency plasma pyrolysis research succeeded to investigate a temperature range of 900–2000 °C and achieved high syn gas productivity. Supercritical water gasification is an alternative thermochemical technique that has been designed to be more resilient for the biomass type, including wet biomass (moisture $>$ 35%), such as carbohydrates and wood. In several investigations, the combined fermentation routes have also produced encouraging outcomes. Hydraulic retention time, pH, temperature, and substrate pretreatment all play a significant role in determining the best path for producing bio-H_2. With a good yield of bio-H_2 produced from waste feedstock under low-temperature settings, the MEC approach demonstrated encouraging results. However, using these procedures for large-scale production is still difficult. Additionally, the current developments in the well-developed H_2 generation based on biomass in terms of the bio-circular economy were briefly covered. The high energy content of hydrogen makes it considered the best alternative to petroleum fuels releasing only water from the combustion process supplying sustainable energy and minimizing wastes. Overall, recent developments in bio-H_2 production offer a promising future alternative to traditional fossil fuels.

Funding

The authors received no financial support for the research, authorship, and/or publication of this article.

Availability of data and materials section

Not applicable

CRediT authorship contribution statement

M.G. Eloffy: Methodology, Investigation, Data curation, Writing – original draft. **Ahmed M. Elgarahy:** Conceptualization, Methodology, Investigation, Data curation, Writing – original draft. **Ayman N. Saber:** Methodology, Investigation, Data curation, Writing – original draft. **Ahmed Hammad:** Methodology, Investigation, Data curation, Writing – original draft. **Dina M. El-Sherif:** Methodology, Investigation, Data curation, Writing – original draft. **Moustafa Shehata:** Methodology, Investigation, Data curation, Writing – original draft. **Ahmed Mohsen:** Methodology, Investigation, Data curation, Writing – original draft. **Khalid Z. Elwakeel:** Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no competing interests.

Data Availability

Not applicable

References

[1] A.B.A. Ibrahim, H. Akilli, Supercritical water gasification of wastewater sludge for hydrogen production, Int. J. Hydrogen Energy 44 (21) (2019) 10328–10349, https://doi.org/10.1016/j.ijhydene.2019.02.184.

[2] S.J. Malode, K.K. Prabhu, R.J. Mascarenhas, N.P. Shetti, T.M. Aminabhavi, Recent advances and viability in biofuel production, Energy Conver. Manag. X 10 (2021), 100070, https://doi.org/10.1016/j.ecmx.2020.100070.

[3] L. Christiansen, O.B. von Kursk, J.A. Haselip, UN environment emissions gap report 2018, (2018).

[4] V. Parravicini, K. Svardal, J. Krampe, Greenhouse gas emissions from wastewater treatment plants, Energy Procedia 97 (2016) 246–253, https://doi.org/10.1016/j.egypro.2016.10.067.

[5] D. Gielen, F. Boshell, D. Saygin, M.D. Bazilian, N. Wagner, R. Gorini, The role of renewable energy in the global energy transformation, Energy Strategy Rev. 24 (2019) 38–50, https://doi.org/10.1016/j.esr.2019.01.006.

[6] S. Mona, S.S. Kumar, V. Kumar, K. Parveen, N. Saini, B. Deepak, A. Pugazhendhi, Green technology for sustainable biohydrogen production (waste to energy): a review, Sci. Total Environ. 728 (2020), 138481, https://doi.org/10.1016/j.scitotenv.2020.138481.

[7] T. CLIMA, WMO statement on the state of the global climate in 2018, (2019).

[8] R.K. Srivastava, N.P. Shetti, K.R. Reddy, T.M. Aminabhavi, Biofuels, biodiesel and biohydrogen production using bioprocesses. A review, Environ. Chem. Lett. 18 (4) (2020) 1049–1072, https://doi.org/10.1007/s10311-020-00999-7.

[9] S. Sharma, A. Kundu, S. Basu, N.P. Shetti, T.M. Aminabhavi, Sustainable environmental management and related biofuel technologies, J. Environ. Manage. 273 (2020), 111096, https://doi.org/10.1016/j.jenvman.2020.111096.

[10] N. Andryeyeva, O. Nikishyna, B. Burkynskyi, N. Khumarova, O. Laiko, H. Tiutiunnyk, Methodology of analysis of the influence of the economic policy of the state on the environment, Insights Reg. Devel. 3 (2) (2021) 198–212, https://doi.org/10.9770/ird.2021.3.2(3).

[11] B. Xu, D. Chen, M. Venkateshkumar, Y. Xiao, Y. Yue, Y. Xing, P. Li, Modeling a pumped storage hydropower integrated to a hybrid power system with solar-wind power and its stability analysis, Appl. Energy 248 (2019) 446–462, https://doi.org/10.1016/j.apenergy.2019.04.125.

[12] R.K. Srivastava, N.P. Shetti, K.R. Reddy, E.E. Kwon, M.N. Nadagouda, T. M. Aminabhavi, Biomass utilization and production of biofuels from carbon neutral materials, Environ. Pollut. 276 (2021), 116731, https://doi.org/10.1016/j.envpol.2021.116731.

[13] Renewable Energy Growth Rate Up 45% Worldwide In 2020; IEA Sees 'New Normal', 2021. https://www.npr.org/2021/05/11/995849954/renewable-energy-capacity-jumped-45-worldwide-in-2020-iea-sees-new-normal. (Accessed 5/30/2022).

[14] M. Aziz, A. Darmawan, F.B. Juangsa, Hydrogen production from biomasses and wastes: a technological review, Int. J. Hydrogen Energy 46 (68) (2021) 33756–33781, https://doi.org/10.1016/j.ijhydene.2021.07.189.

[15] S. Sharma, S. Basu, N.P. Shetti, M. Kamali, P. Walvekar, T.M. Aminabhavi, Waste-to-energy nexus: a sustainable development, Environ. Pollut. 267 (2020), 115501, https://doi.org/10.1016/j.envpol.2020.115501.

[16] A.M. Elgarahy, A. Hammad, D.M. El-Sherif, M. Abouzid, M.S. Gaballah, K. Z. Elwakeel, Thermochemical conversion strategies of biomass to biofuels, techno-economic and bibliometric analysis: a conceptual review, J. Environ. Chem. Eng. 9 (6) (2021), https://doi.org/10.1016/j.jece.2021.106503.

[17] R.K. Srivastava, N.P. Shetti, K.R. Reddy, T.M. Aminabhavi, Sustainable energy from waste organic matters via efficient microbial processes, Sci. Total Environ. 722 (2020), 137927, https://doi.org/10.1016/j.scitotenv.2020.137927.

[18] M. Zborowska, H. Waliszewska, B. Waliszewska, S. Borysiak, J. Brozdowski, A. Stachowiak-Wencek, Conversion of carbohydrates in lignocellulosic biomass after chemical pretreatment, Energies 15 (1) (2022), https://doi.org/10.3390/en15010254.

[19] S. Jung, N.P. Shetti, K.R. Reddy, M.N. Nadagouda, Y.-.K. Park, T.M. Aminabhavi, E.E. Kwon, Synthesis of different biofuels from livestock waste materials and their potential as sustainable feedstocks – a review, Energy Convers. Manage. 236 (2021), 114038, https://doi.org/10.1016/j.enconman.2021.114038.

[20] D.-.C. Li, H. Jiang, The thermochemical conversion of non-lignocellulosic biomass to form biochar: a review on characterizations and mechanism elucidation, Bioresour. Technol. 246 (2017) 57–68, https://doi.org/10.1016/j.biortech.2017.07.029.

[21] G. Velvizhi, C. Goswami, N.P. Shetti, E. Ahmad, K. Kishore Pant, T. M. Aminabhavi, Valorisation of lignocellulosic biomass to value-added products: paving the pathway towards low-carbon footprint, Fuel 313 (2022), 122678, https://doi.org/10.1016/j.fuel.2021.122678.

[22] G. Velvizhi, K. Balakumar, N.P. Shetti, E. Ahmad, K. Kishore Pant, T. M. Aminabhavi, Integrated biorefinery processes for conversion of lignocellulosic biomass to value added materials: paving a path towards circular economy, Bioresour. Technol. 343 (2022), 126151, https://doi.org/10.1016/j.biortech.2021.126151.

[23] A. Rabiee, A. Keane, A. Soroudi, Technical barriers for harnessing the green hydrogen: a power system perspective, Renew. Energy 163 (2021) 1580–1587, https://doi.org/10.1016/j.renene.2020.10.051.

[24] S. Singla, N.P. Shetti, S. Basu, K. Mondal, T.M. Aminabhavi, Hydrogen production technologies - Membrane based separation, storage and challenges, J. Environ. Manage. 302 (2022), 113963, https://doi.org/10.1016/j.jenvman.2021.113963.

[25] P. Sampath, Brijesh, K.R. Reddy, C.V. Reddy, N.P. Shetti, R.V. Kulkarni, A. V. Raghu, Biohydrogen production from organic waste – a review, Chem. Eng. Technol. 43 (7) (2020) 1240–1248, https://doi.org/10.1002/ceat.201900400.

[26] J. Remón, P. Arcelus-Arrillaga, L. García, J. Arauzo, Simultaneous production of gaseous and liquid biofuels from the synergetic co-valorisation of bio-oil and crude glycerol in supercritical water, Appl. Energy 228 (2018) 2275–2287, https://doi.org/10.1016/j.apenergy.2018.07.093.

[27] S. Sharma, S. Basu, N.P. Shetti, T.M. Aminabhavi, Waste-to-energy nexus for circular economy and environmental protection: recent trends in hydrogen energy, Sci. Total Environ. 713 (2020), 136633, https://doi.org/10.1016/j.scitotenv.2020.136633.

[28] H. Wang, J. Xu, L. Sheng, X. Liu, Y. Lu, W. Li, A review on bio-hydrogen production technology, Int. J. Energy Res. 42 (11) (2018) 3442–3453, https://doi.org/10.1002/er.4044.

[29] P.A. Harris, R. Taylor, B.L. Minor, V. Elliott, M. Fernandez, L. O'Neal, L. McLeod, G. Delacqua, F. Delacqua, J. Kirby, S.N. Duda, The REDCap consortium: building an international community of software platform partners, J. Biomed. Inform. 95 (2019), 103208, https://doi.org/10.1016/j.jbi.2019.103208.

[30] S.I. Ngo, Y.-.I. Lim, W. Kim, D.J. Seo, W.L. Yoon, Computational fluid dynamics and experimental validation of a compact steam methane reformer for hydrogen production from natural gas, Appl. Energy 236 (2019) 340–353, https://doi.org/10.1016/j.apenergy.2018.11.075.

[31] L. Zou, Y. Liu, Y. Wang, X. Hu, Assessment and analysis of agricultural non-point source pollution loads in China: 1978–2017, J. Environ. Manage. 263 (2020), 110400, https://doi.org/10.1016/j.jenvman.2020.110400.

[32] M.A. Abdelkareem, K. Elsaid, T. Wilberforce, M. Kamil, E.T. Sayed, A. Olabi, Environmental aspects of fuel cells: a review, Sci. Total Environ. 752 (2021), 141803, https://doi.org/10.1016/j.scitotenv.2020.141803.

[33] T. Lepage, M. Kammoun, Q. Schmetz, A. Richel, Biomass-to-hydrogen: a review of main routes production, processes evaluation and techno-economical assessment, Biomass Bioenergy 144 (2021), 105920, https://doi.org/10.1016/j.biombioe.2020.105920.

[34] D.E. Resasco, B. Wang, D. Sabatini, Distributed processes for biomass conversion could aid UN Sustainable Development Goals, Nature Catalysis 1 (10) (2018) 731–735, https://doi.org/10.1038/s41929-018-0166-6.

[35] P.-.S. Yap, T.-.T. Lim, Effect of aqueous matrix species on synergistic removal of bisphenol-A under solar irradiation using nitrogen-doped TiO2/AC composite, Appl. Catal. B 101 (3) (2011) 709–717, https://doi.org/10.1016/j.apcatb.2010.11.013.

[36] J.U. Ani, K.G. Akpomie, U.C. Okoro, L.E. Aneke, O.D. Onukwuli, O.T. Ujam, Potentials of activated carbon produced from biomass materials for sequestration of dyes, heavy metals, and crude oil components from aqueous environment, Appl. Water Sci. 10 (2) (2020) 69, https://doi.org/10.1007/s13201-020-1149-8.

[37] M. Karimi, M. Shirzad, J.A.C. Silva, A.E. Rodrigues, Biomass/Biochar carbon materials for CO2 capture and sequestration by cyclic adsorption processes: a review and prospects for future directions, J. CO2 Utiliz. 57 (2022), 101890, https://doi.org/10.1016/j.jcou.2022.101890.

[38] Z. Usmani, M. Sharma, A.K. Awasthi, N. Sivakumar, T. Lukk, L. Pecoraro, V. K. Thakur, D. Roberts, J. Newbold, V.K. Gupta, Bioprocessing of waste biomass for sustainable product development and minimizing environmental impact, Bioresour. Technol. 322 (2021), 124548, https://doi.org/10.1016/j.biortech.2020.124548.

[39] M.A. Islam, M.J. Ahmed, W.A. Khanday, M. Asif, B.H. Hameed, Mesoporous activated coconut shell-derived hydrochar prepared via hydrothermal carbonization-NaOH activation for methylene blue adsorption, J. Environ. Manage. 203 (2017) 237–244, https://doi.org/10.1016/j.jenvman.2017.07.029.

[40] W. Li, Q. Li, L. Zheng, Y. Wang, J. Zhang, Z. Yu, Y. Zhang, Potential biodiesel and biogas production from corncob by anaerobic fermentation and black soldier fly, Bioresour. Technol. 194 (2015) 276–282, https://doi.org/10.1016/j.biortech.2015.06.112.

[41] P. Wang, Y. Guo, C. Zhao, J. Yan, P. Lu, Biomass derived wood ash with amine modification for post-combustion CO2 capture, Appl. Energy 201 (2017) 34–44, https://doi.org/10.1016/j.apenergy.2017.05.096.

[42] M. Balat, M. Balat, E. Kırtay, H. Balat, Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 1: pyrolysis systems, Energy Convers. Manage. 50 (12) (2009) 3147–3157, https://doi.org/10.1016/j.enconman.2009.08.014.

[43] R.P. Rastogi, A. Pandey, C. Larroche, D. Madamwar, Algal Green Energy – R&D and technological perspectives for biodiesel production, Renew. Sustain. Energy Rev. 82 (2018) 2946–2969, https://doi.org/10.1016/j.rser.2017.10.038.

[44] R.S. El-Emam, H. Özcan, Comprehensive review on the techno-economics of sustainable large-scale clean hydrogen production, J. Clean. Prod. 220 (2019) 593–609, https://doi.org/10.1016/j.jclepro.2019.01.309.

[45] R.-.X. Yang, K.-.H. Chuang, M.-.Y. Wey, Effects of temperature and equivalence ratio on carbon nanotubes and hydrogen production from waste plastic gasification in fluidized bed, Energy Fuels 32 (4) (2018) 5462–5470, https://doi.org/10.1021/acs.energyfuels.7b04109.

[46] E. Barbuzza, G. Buceti, A. Pozio, M. Santarelli, S. Tosti, Gasification of wood biomass with renewable hydrogen for the production of synthetic natural gas, Fuel 242 (2019) 520–531, https://doi.org/10.1016/j.fuel.2019.01.079.

[47] M.L.N.M. Carneiro, M.S.P. Gomes, Energy, exergy, environmental and economic analysis of hybrid waste-to-energy plants, Energy Convers. Manage. 179 (2019) 397–417, https://doi.org/10.1016/j.enconman.2018.10.007.

[48] R. Sha'Ato, S.Y. Aboho, F.O. Oketunde, I.S. Eneji, G. Unazi, S. Agwa, Survey of solid waste generation and composition in a rapidly growing urban area in Central Nigeria, Waste Manage. 27 (3) (2007) 352–358, https://doi.org/10.1016/j.wasman.2006.02.008.

[49] D. Brounen, N. Kok, J.M. Quigley, Energy literacy, awareness, and conservation behavior of residential households, Energy Econ. 38 (2013) 42–50, https://doi.org/10.1016/j.eneco.2013.02.008.

[50] C. Liu, Y. Huang, M. Niu, H. Pei, L. Liu, Y. Wang, L. Dong, L. Xu, Influences of equivalence ratio, oxygen concentration and fluidization velocity on the characteristics of oxygen-enriched gasification products from biomass in a pilot-scale fluidized bed, Int. J. Hydrogen Energy 43 (31) (2018) 14214–14225, https://doi.org/10.1016/j.ijhydene.2018.05.154.

[51] A. Ayol, O. Tezer Yurdakos, A. Gurgen, Investigation of municipal sludge gasification potential: gasification characteristics of dried sludge in a pilot-scale downdraft fixed bed gasifier, Int. J. Hydrogen Energy 44 (32) (2019) 17397–17410, https://doi.org/10.1016/j.ijhydene.2019.01.014.

[52] H. Ge, H. Zhang, W. Guo, T. Song, L. Shen, System simulation and experimental verification: biomass-based integrated gasification combined cycle (BIGCC) coupling with chemical looping gasification (CLG) for power generation, Fuel 241 (2019) 118–128, https://doi.org/10.1016/j.fuel.2018.11.091.

[53] I. Ul Hai, F. Sher, A. Yaqoob, H. Liu, Assessment of biomass energy potential for SRC willow woodchips in a pilot scale bubbling fluidized bed gasifier, Fuel 258 (2019), 116143, https://doi.org/10.1016/j.fuel.2019.116143.

[54] T. Zhou, S. Yang, Y. Wei, J. Hu, H. Wang, Impact of wide particle size distribution on the gasification performance of biomass in a bubbling fluidized bed gasifier, Renew. Energy 148 (2020) 534–547, https://doi.org/10.1016/j.renene.2019.10.059.

[55] F. Meng, Q. Ma, H. Wang, Y. Liu, D. Wang, Effect of gasifying agents on sawdust gasification in a novel pilot scale bubbling fluidized bed system, Fuel 249 (2019) 112–118, https://doi.org/10.1016/j.fuel.2019.03.107.

[56] Y. Chen, L. Guo, W. Cao, H. Jin, S. Guo, X. Zhang, Hydrogen production by sewage sludge gasification in supercritical water with a fluidized bed reactor, Int. J. Hydrogen Energy 38 (29) (2013) 12991–12999, https://doi.org/10.1016/j.ijhydene.2013.03.165.

[57] H. de Lasa, E. Salaices, J. Mazumder, R. Lucky, Catalytic steam gasification of biomass: catalysts, thermodynamics and kinetics, Chem. Rev. 111 (9) (2011) 5404–5433, https://doi.org/10.1021/cr200024w.

[58] P. Simell, E. Kurkela, P. Ståhlberg, J. Hepola, Catalytic hot gas cleaning of gasification gas, Catal. Today 27 (1) (1996) 55–62, https://doi.org/10.1016/0920-5861(95)00172-7.

[59] A. Erkiaga, G. Lopez, M. Amutio, J. Bilbao, M. Olazar, Steam gasification of biomass in a conical spouted bed reactor with olivine and γ-alumina as primary catalysts, Fuel Process. Technol. 116 (2013) 292–299, https://doi.org/10.1016/j.fuproc.2013.07.008.

[60] H. Balat, E. Kırtay, Hydrogen from biomass – present scenario and future prospects, Int. J. Hydrogen Energy 35 (14) (2010) 7416–7426, https://doi.org/10.1016/j.ijhydene.2010.04.137.

[61] C. Pirez, W. Fang, M. Capron, S. Paul, H. Jobic, F. Dumeignil, L. Jalowiecki-Duhamel, Steam reforming, partial oxidation and oxidative steam reforming for hydrogen production from ethanol over cerium nickel based oxyhydride catalyst, Appl. Catal. A 518 (2016) 78–86, https://doi.org/10.1016/j.apcata.2015.10.035.

[62] D. Rennard, R. French, S. Czernik, T. Josephson, L. Schmidt, Production of synthesis gas by partial oxidation and steam reforming of biomass pyrolysis oils, Int. J. Hydrogen Energy 35 (9) (2010) 4048–4059, https://doi.org/10.1016/j.ijhydene.2010.01.143.

[63] J.R. Salge, G.A. Deluga, L.D. Schmidt, Catalytic partial oxidation of ethanol over noble metal catalysts, J. Catal. 235 (1) (2005) 69–78, https://doi.org/10.1016/j.jcat.2005.07.021.

[64] M. Tóth, E. Varga, A. Oszkó, K. Baán, J. Kiss, A. Erdőhelyi, Partial oxidation of ethanol on supported Rh catalysts: effect of the oxide support, J. Mol. Catal. A: Chem. 411 (2016) 377–387, https://doi.org/10.1016/j.molcata.2015.11.010.

[65] L. He, J. Yang, D. Chen, L. Gandia, Hydrogen from biomass: Advances in Thermochemical Processes, Elsevier, Amsterdam, Netherlands, 2013.

[66] R.M. Navarro, M.C. Sanchez-Sanchez, M.C. Alvarez-Galvan, J.L.G. Fierro, S.M. Al-Zaharani, H2 production from renewables, Energy Prod. Storage: Inorg. Chem. Strat. Warming World 3 (2013).

[67] M. Kumar, A.O. Oyedun, A. Kumar, A comparative analysis of hydrogen production from the thermochemical conversion of algal biomass, Int. J. Hydrogen Energy 44 (21) (2019) 10384–10397, https://doi.org/10.1016/j.ijhydene.2019.02.220.

[68] B.R. Pinkard, D.J. Gorman, K. Tiwari, E.G. Rasmussen, J.C. Kramlich, P. G. Reinhall, I.V. Novosselov, Supercritical water gasification: practical design strategies and operational challenges for lab-scale, continuous flow reactors, Heliyon 5 (2) (2019) e01269, https://doi.org/10.1016/j.heliyon.2019.e01269.

[69] M. Osada, T. Sato, M. Watanabe, M. Shirai, K. Arai, Catalytic gasification of wood biomass in subcritical and supercritical water, Combust. Sci. Technol. 178 (1–3) (2006) 537–552, https://doi.org/10.1080/00102200500290807.

[70] Y. Matsumura, T. Minowa, B. Potic, S.R.A. Kersten, W. Prins, W.P.M. van Swaaij, B. van de Beld, D.C. Elliott, G.G. Neuenschwander, A. Kruse, M. Jerry Antal Jr, Biomass gasification in near- and super-critical water: status and prospects, Biomass Bioenergy 29 (4) (2005) 269–292, https://doi.org/10.1016/j.biombioe.2005.04.006.

[71] F.L.P. Resende, P.E. Savage, Effect of metals on supercritical water gasification of cellulose and lignin, Ind. Eng. Chem. Res. 49 (6) (2010) 2694–2700, https://doi.org/10.1021/ie901928f.

[72] R. Razuan, Q. Chen, X. Zhang, V. Sharifi, J. Swithenbank, Pyrolysis and combustion of oil palm stone and palm kernel cake in fixed-bed reactors, Bioresour. Technol. 101 (12) (2010) 4622–4629, https://doi.org/10.1016/j.biortech.2010.01.079.

[73] R. Razuan, K.N. Finney, Q. Chen, V.N. Sharifi, J. Swithenbank, Pelletised fuel production from palm kernel cake, Fuel Process. Technol. 92 (3) (2011) 609–615, https://doi.org/10.1016/j.fuproc.2010.11.018.

[74] R. Razuan, Q. Chen, K.N. Finney, N.V. Russell, V.N. Sharifi, J. Swithenbank, Combustion of oil palm stone in a pilot-scale fluidised bed reactor, Fuel Process. Technol. 92 (12) (2011) 2219–2225, https://doi.org/10.1016/j.fuproc.2011.07.012.

[75] M.J. Antal, S.G. Allen, D. Schulman, X. Xu, R.J. Divilio, Biomass gasification in supercritical water, Ind. Eng. Chem. Res. 39 (11) (2000) 4040–4053, https://doi.org/10.1021/ie0003436.

[76] T. Güngören Madenoğlu, N. Boukis, M. Sağlam, M. Yüksel, Supercritical water gasification of real biomass feedstocks in continuous flow system, Int. J. Hydrogen Energy 36 (22) (2011) 14408–14415, https://doi.org/10.1016/j.ijhydene.2011.08.047.

[77] P. Azadi, R. Farnood, Review of heterogeneous catalysts for sub- and supercritical water gasification of biomass and wastes, Int. J. Hydrogen Energy 36 (16) (2011) 9529–9541, https://doi.org/10.1016/j.ijhydene.2011.05.081.

[78] M. Watanabe, H. Inomata, K. Arai, Catalytic hydrogen generation from biomass (glucose and cellulose) with ZrO2 in supercritical water, Biomass Bioenergy 22 (5) (2002) 405–410, https://doi.org/10.1016/S0961-9534(02)00017-X.

[79] K.C. Park, H. Tomiyasu, Gasification reaction of organic compounds catalyzed by RuO2 in supercritical water, Chem. Commun. (6) (2003) 694–695, https://doi.org/10.1039/B211800A.

[80] A. Sınağ, A. Kruse, V. Schwarzkopf, Key compounds of the hydropyrolysis of glucose in supercritical water in the presence of K2CO3, Ind. Eng. Chem. Res. 42 (15) (2003) 3516–3521, https://doi.org/10.1021/ie030079r.

[81] D. Sutton, B. Kelleher, J.R.H. Ross, Review of literature on catalysts for biomass gasification, Fuel Process. Technol. 73 (3) (2001) 155–173, https://doi.org/10.1016/S0378-3820(01)00208-9.

[82] V.R. Paida, S.R.A. Kersten, A.G.J. van der Ham, D.W.F. Brilman, A two-step approach to the hydrothermal gasification of carbohydrate-rich wastes: process design and economic evaluation, Int. J. Hydrogen Energy 44 (47) (2019) 25524–25541, https://doi.org/10.1016/j.ijhydene.2019.08.027.

[83] Y. Zhang, L. Li, P. Xu, B. Liu, Y. Shuai, B. Li, Hydrogen production through biomass gasification in supercritical water: a review from exergy aspect, Int. J. Hydrogen Energy 44 (30) (2019) 15727–15736, https://doi.org/10.1016/j.ijhydene.2019.01.151.

[84] X.-.Y. Zhao, J. Ren, J.-.P. Cao, F. Wei, C. Zhu, X. Fan, Y.-.P. Zhao, X.-.Y. Wei, Catalytic reforming of volatiles from biomass pyrolysis for hydrogen-rich gas production over limonite ore, Energy Fuels 31 (4) (2017) 4054–4060, https://doi.org/10.1021/acs.energyfuels.7b00005.

[85] L. Dong, C. Wu, H. Ling, J. Shi, P.T. Williams, J. Huang, Promoting hydrogen production and minimizing catalyst deactivation from the pyrolysis-catalytic steam reforming of biomass on nanosized NiZnAlOx catalysts, Fuel 188 (2017) 610–620, https://doi.org/10.1016/j.fuel.2016.10.072.

[86] S.R. Naqvi, H.M. Prabhakara, E.A. Bramer, W. Dierkes, R. Akkerman, G. Brem, A critical review on recycling of end-of-life carbon fibre/glass fibre reinforced composites waste using pyrolysis towards a circular economy, Resour. Conserv. Recy. 136 (2018) 118–129, https://doi.org/10.1016/j.resconrec.2018.04.013.

[87] A. Arregi, G. Lopez, M. Amutio, I. Barbarias, J. Bilbao, M. Olazar, Hydrogen production from biomass by continuous fast pyrolysis and in-line steam reforming, RSC Adv. 6 (31) (2016) 25975–25985, https://doi.org/10.1039/C6RA01657J.

[88] A.J. Byrd, S. Kumar, L. Kong, H. Ramsurn, R.B. Gupta, Hydrogen production from catalytic gasification of switchgrass biocrude in supercritical water, Int. J. Hydrogen Energy 36 (5) (2011) 3426–3433, https://doi.org/10.1016/j.ijhydene.2010.12.026.

[89] F. Chen, C. Wu, L. Dong, A. Vassallo, P.T. Williams, J. Huang, Characteristics and catalytic properties of Ni/CaAlOx catalyst for hydrogen-enriched syngas production from pyrolysis-steam reforming of biomass sawdust, Appl. Catal. B 183 (2016) 168–175, https://doi.org/10.1016/j.apcatb.2015.10.028.

[90] Q.M.K. Waheed, C. Wu, P.T. Williams, Pyrolysis/reforming of rice husks with a Ni–dolomite catalyst: influence of process conditions on syngas and hydrogen yield, J. Energy Inst. 89 (4) (2016) 657–667, https://doi.org/10.1016/j.joei.2015.05.006.

[91] M. Kaewpanha, G. Guan, Y. Ma, X. Hao, Z. Zhang, P. Reubroychareon, K. Kusakabe, A. Abudula, Hydrogen production by steam reforming of biomass tar over biomass char supported molybdenum carbide catalyst, Int. J. Hydrogen Energy 40 (25) (2015) 7974–7982, https://doi.org/10.1016/j.ijhydene.2015.04.068.

[92] J. Kim, B.-.G. Ryu, B.-.K. Kim, J.-.I. Han, J.-.W. Yang, Continuous microalgae recovery using electrolysis with polarity exchange, Bioresour. Technol. 111 (2012) 268–275, https://doi.org/10.1016/j.biortech.2012.01.104.

[93] W.-.H. Chen, W. Farooq, M. Shahbaz, S.R. Naqvi, I. Ali, T. Al-Ansari, N.A. Saidina Amin, Current status of biohydrogen production from lignocellulosic biomass, technical challenges and commercial potential through pyrolysis process, Energy 226 (2021), 120433, https://doi.org/10.1016/j.energy.2021.120433.

[94] P. Liu, Y. Wang, Z. Zhou, H. Yuan, T. Zheng, Y. Chen, Effect of carbon structure on hydrogen release derived from different biomass pyrolysis, Fuel 271 (2020), 117638, https://doi.org/10.1016/j.fuel.2020.117638.

[95] T.Y.A. Fahmy, Y. Fahmy, F. Mobarak, M. El-Sakhawy, R.E. Abou-Zeid, Biomass pyrolysis: past, present, and future, Environ. Dev. Sustain. 22 (1) (2020) 17–32, https://doi.org/10.1007/s10668-018-0200-5.

[96] J. Adam, M. Blazsó, E. Mészáros, M. Stöcker, M.H. Nilsen, A. Bouzga, J.E. Hustad, M. Grønli, G. Øye, Pyrolysis of biomass in the presence of Al-MCM-41 type catalysts, Fuel 84 (12) (2005) 1494–1502, https://doi.org/10.1016/j.fuel.2005.02.006.

[97] P. Prasertcharoensuk, S.J. Bull, A.N. Phan, Gasification of waste biomass for hydrogen production: effects of pyrolysis parameters, Renew. Energy 143 (2019) 112–120, https://doi.org/10.1016/j.renene.2019.05.009.

[98] S. Al Arni, Comparison of slow and fast pyrolysis for converting biomass into fuel, Renew. Energy 124 (2018) 197–201, https://doi.org/10.1016/j.renene.2017.04.060.

[99] Y. Yue, Q. Lin, M. Irfan, Q. Chen, X. Zhao, Characteristics and potential values of bio-oil, syngas and biochar derived from Salsola collina Pall. in a fixed bed slow pyrolysis system, Bioresour. Technol. 220 (2016) 378–383, https://doi.org/10.1016/j.biortech.2016.08.028.

[100] S. Cheng, J. Shu, H. Xia, S. Wang, L. Zhang, J. Peng, C. Li, X. Jiang, Q. Zhang, Pyrolysis of Crofton weed for the production of aldehyde rich bio-oil and combustible matter rich bio-gas, Appl. Therm. Eng. 148 (2019) 1164–1170, https://doi.org/10.1016/j.applthermaleng.2018.12.009.

[101] M.-.S. Safdari, E. Amini, D.R. Weise, T.H. Fletcher, Heating rate and temperature effects on pyrolysis products from live wildland fuels, Fuel 242 (2019) 295–304, https://doi.org/10.1016/j.fuel.2019.01.040.

[102] A. Bakhtyari, M.A. Makarem, M.R. Rahimpour, Hydrogen production through pyrolysis, in: T.E. Lipman, A.Z. Weber (Eds.), Fuel Cells and Hydrogen Production: A Volume in the Encyclopedia of Sustainability Science and Technology, 2nd Edition, Springer New York, New York, NY, 2019, pp. 947–973, https://doi.org/10.1007/978-1-4939-7789-5_956.

[103] S. Liu, J. Zhu, M. Chen, W. Xin, Z. Yang, L. Kong, Hydrogen production via catalytic pyrolysis of biomass in a two-stage fixed bed reactor system, Int. J. Hydrogen Energy 39 (25) (2014) 13128–13135, https://doi.org/10.1016/j.ijhydene.2014.06.158.

[104] R.M. Navarro, M.C. Sanchez-Sanchez, M.C. Alvarez-Galvan, J.L.G. Fierro, S.M. Al-Zaharani. (2013) 10.1002/9781119951438.eibc0450.

[105] S. Czernik, R. Evans, R. French, Hydrogen from biomass-production by steam reforming of biomass pyrolysis oil, Catal. Today 129 (3) (2007) 265–268, https://doi.org/10.1016/j.cattod.2006.08.071.

[106] A. Arregi, M. Amutio, G. Lopez, J. Bilbao, M. Olazar, Evaluation of thermochemical routes for hydrogen production from biomass: a review, Energy Convers. Manage. 165 (2018) 696–719, https://doi.org/10.1016/j.enconman.2018.03.089.

[107] P. Lan, Q. Xu, M. Zhou, L. Lan, S. Zhang, Y. Yan, Catalytic steam reforming of fast pyrolysis bio-oil in fixed bed and fluidized bed reactors, Chem. Eng. Technol. 33 (12) (2010) 2021–2028, https://doi.org/10.1002/ceat.201000169.

[108] V. Martínez-Merino, M.J. Gil, A. Cornejo, Chapter 5 - biomass sources for hydrogen production, in: L.M. Gandía, G. Arzamendi, P.M. Diéguez (Eds.), Renewable Hydrogen Technologies, Elsevier, Amsterdam, 2013, pp. 87–110, https://doi.org/10.1016/B978-0-444-56352-1.00005-2.

[109] G.W. Huber, J.A. Dumesic, An overview of aqueous-phase catalytic processes for production of hydrogen and alkanes in a biorefinery, Catal. Today 111 (1) (2006) 119–132, https://doi.org/10.1016/j.cattod.2005.10.010.

[110] R.D. Cortright, R.R. Davda, J.A. Dumesic, Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water, Nature 418 (6901) (2002) 964–967, https://doi.org/10.1038/nature01009.

[111] A. Tanksale, J.N. Beltramini, G.M. Lu, A review of catalytic hydrogen production processes from biomass, Renew. Sustain. Energy Rev. 14 (1) (2010) 166–182, https://doi.org/10.1016/j.rser.2009.08.010.

[112] R.R. Davda, J.W. Shabaker, G.W. Huber, R.D. Cortright, J.A. Dumesic, A review of catalytic issues and process conditions for renewable hydrogen and alkanes by aqueous-phase reforming of oxygenated hydrocarbons over supported metal catalysts, Appl. Catal. B 56 (1) (2005) 171–186, https://doi.org/10.1016/j.apcatb.2004.04.027.

[113] L. He, J. Yang, D. Chen, Chapter 6 - hydrogen from biomass: advances in thermochemical processes, in: L.M. Gandía, G. Arzamendi, P.M. Diéguez (Eds.), Renewable Hydrogen Technologies, Elsevier, Amsterdam, 2013, pp. 111–133, https://doi.org/10.1016/B978-0-444-56352-1.00006-4.

[114] D.P. Harrison, Sorption-enhanced hydrogen production: a review, Ind. Eng. Chem. Res. 47 (17) (2008) 6486–6501, https://doi.org/10.1021/ie800298z.

[115] D.B. Levin, L. Pitt, M. Love, Biohydrogen production: prospects and limitations to practical application, Int. J. Hydrogen Energy 29 (2) (2004) 173–185, https://doi.org/10.1016/S0360-3199(03)00094-6.

[116] R. Łukajtis, I. Hołowacz, K. Kucharska, M. Glinka, P. Rybarczyk, A. Przyjazny, M. Kamiński, Hydrogen production from biomass using dark fermentation, Renew. Sustain. Energy Rev. 91 (2018) 665–694, https://doi.org/10.1016/j.rser.2018.04.043.

[117] R. Luque, J. Clark, Handbook of Biofuels production: Processes and Technologies, Elsevier, 2010.

[118] Y. Li, Y. Chen, J. Wu, Enhancement of methane production in anaerobic digestion process: a review, Appl. Energy 240 (2019) 120–137, https://doi.org/10.1016/j.apenergy.2019.01.243.

[119] J. Ángel Siles López, Q. Li, I.P. Thompson, Biorefinery of waste orange peel, Crit. Rev. Biotechnol. 30 (1) (2010) 63–69, https://doi.org/10.3109/07388550903425201.

[120] B. Derimelk, O. Yenigun, Two-phase anaerobic digestion processes, J. Chem. Technol. & Biotechnol 10 (2002) 743–755.

[121] D.P. Van, T. Fujiwara, B.L. Tho, P.P.S. Toan, G.H. Minh, A review of anaerobic digestion systems for biodegradable waste: configurations, operating parameters, and current trends, Environ. Eng. Res. 25 (1) (2020) 1–17.

[122] M. Majid, Renewable energy for sustainable development in India: current status, future prospects, challenges, employment, and investment opportunities, Energy Sustain. Soc. 10 (1) (2020) 1–36.

[123] S. Aslanzadeh, K. Rajendran, M.J. Taherzadeh, A comparative study between single- and two-stage anaerobic digestion processes: effects of organic loading rate and hydraulic retention time, Int. Biodeterior. Biodegradation 95 (2014) 181–188, https://doi.org/10.1016/j.ibiod.2014.06.008.

[124] A. Ghimire, L. Frunzo, F. Pirozzi, E. Trably, R. Escudie, P.N.L. Lens, G. Esposito, A review on dark fermentative biohydrogen production from organic biomass: process parameters and use of by-products, Appl. Energy 144 (2015) 73–95, https://doi.org/10.1016/j.apenergy.2015.01.045.

[125] V. Martınez-Merino, M. Jose, A.C. Gil, Biomass sources for hydrogen production, renewable hydrogen technologies: production, purification, storage, Appl. Safety 87 (2013).

[126] C.N.C. Hitam, A.A. Jalil, A review on biohydrogen production through photo-fermentation of lignocellulosic biomass, Biomass Convers. Biorefin. (2020), https://doi.org/10.1007/s13399-020-01140-y.

[127] N. Basak, D. Das, The prospect of purple non-sulfur (PNS) photosynthetic bacteria for hydrogen production: the present state of the art, World J. Microbiol. Biotechnol. 23 (1) (2007) 31–42, https://doi.org/10.1007/s11274-006-9190-9.

[128] Y. Tao, Y. He, Y. Wu, F. Liu, X. Li, W. Zong, Z. Zhou, Characteristics of a new photosynthetic bacterial strain for hydrogen production and its application in wastewater treatment, Int. J. Hydrogen Energy 33 (3) (2008) 963–973, https://doi.org/10.1016/j.ijhydene.2007.11.021.

[129] H. Zhu, T. Suzuki, A.A. Tsygankov, Y. Asada, J. Miyake, Hydrogen production from tofu wastewater by Rhodobacter sphaeroides immobilized in agar gels, Int. J. Hydrogen Energy 24 (4) (1999) 305–310, https://doi.org/10.1016/S0360-3199(98)00081-0.

[130] M. Yetis, U. Gündüz, I. Eroglu, M. Yücel, L. Türker, Photoproduction of hydrogen from sugar refinery wastewater by Rhodobacter sphaeroides O.U. 001, Int. J. Hydrogen Energy 25 (11) (2000) 1035–1041, https://doi.org/10.1016/S0360-3199(00)00027-6.

[131] Y. Tao, Y. Chen, Y. Wu, Y. He, Z. Zhou, High hydrogen yield from a two-step process of dark- and photo-fermentation of sucrose, Int. J. Hydrogen Energy 32 (2) (2007) 200–206, https://doi.org/10.1016/j.ijhydene.2006.06.034.

[132] L. Hakobyan, L. Gabrielyan, A. Trchounian, Biohydrogen by Rhodobacter sphaeroides during photo-fermentation: mixed vs. sole carbon sources enhance bacterial growth and H2 production, Int. J. Hydrogen Energy 44 (2) (2019) 674–679, https://doi.org/10.1016/j.ijhydene.2018.11.082.

[133] A.S. Fedorov, A.A. Tsygankov, K.K. Rao, D.O. Hall, Hydrogen photoproduction by Rhodobacter sphaeroides immobilised on polyurethane foam, Biotechnol. Lett. 20 (11) (1998) 1007–1009, https://doi.org/10.1023/A:1005402904462.

[134] M.Y. Azwar, M.A. Hussain, A.K. Abdul-Wahab, Development of biohydrogen production by photobiological, fermentation and electrochemical processes: a review, Renew. Sustain. Energy Rev. 31 (2014) 158–173, https://doi.org/10.1016/j.rser.2013.11.022.

[135] L.B. Brentner, J. Peccia, J.B. Zimmerman, Challenges in developing biohydrogen as a sustainable energy source: implications for a research agenda, Environ. Sci. Technol. 44 (7) (2010) 2243–2254, https://doi.org/10.1021/es9030613.

[136] B.D. Kossalbayev, T. Tomo, B.K. Zayadan, A.K. Sadvakasova, K. Bolatkhan, S. Alwasel, S.I. Allakhverdiev, Determination of the potential of cyanobacterial strains for hydrogen production, Int. J. Hydrogen Energy 45 (4) (2020) 2627–2639, https://doi.org/10.1016/j.ijhydene.2019.11.164.

[137] S.R. Vargas, P.V.d. Santos, M. Zaiat, M.d.C. Calijuri, Optimization of biomass and hydrogen production by Anabaena sp. (UTEX 1448) in nitrogen-deprived cultures, Biomass Bioenergy 111 (2018) 70–76, https://doi.org/10.1016/j.biombioe.2018.01.022.

[138] Y.H.P. Zhang, J. Sun, J.-.J. Zhong, Biofuel production by in vitro synthetic enzymatic pathway biotransformation, Curr. Opin. Biotechnol. 21 (5) (2010) 663–669, https://doi.org/10.1016/j.copbio.2010.05.005.

[139] Y.H.P. Zhang, B.R. Evans, J.R. Mielenz, R.C. Hopkins, M.W.W. Adams, High-yield hydrogen production from starch and water by a synthetic enzymatic pathway, PLoS One 2 (5) (2007) e456, https://doi.org/10.1371/journal.pone.0000456.

[140] J.A. Rollin, T.K. Tam, Y.H.P. Zhang, New biotechnology paradigm: cell-free biosystems for biomanufacturing, Green Chem. 15 (7) (2013) 1708–1719, https://doi.org/10.1039/C3GC40625C.

[141] R.S. Poudyal, I. Tiwari, A.R. Koirala, H. Masukawa, K. Inoue, T. Tomo, M. M. Najafpour, S.I. Allakhverdiev, T.N. Veziroğlu, 10 - Hydrogen production using photobiological methods, in: V. Subramani, A. Basile, T.N. Veziroğlu (Eds.), Compendium of Hydrogen Energy, Woodhead Publishing, Oxford, 2015, pp. 289–317, https://doi.org/10.1016/B978-1-78242-361-4.00010-8.

[142] I. Cohen, J.A. Knopf, V. Irihimovitch, M. Shapira, A proposed mechanism for the inhibitory effects of oxidative stress on rubisco assembly and its subunit expression, Plant Physiol 137 (2) (2005) 738–746, https://doi.org/10.1104/pp.104.056341.

[143] A. Melis, Photosynthetic H2 metabolism in Chlamydomonas reinhardtii (unicellular green algae), Planta 226 (5) (2007) 1075–1086, https://doi.org/10.1007/s00425-007-0609-9.

[144] K. Paramesh, T. Chandrasekhar, Improvement of photobiological hydrogen production in Chlorococcum minutum using various oxygen scavengers, Int. J. Hydrogen Energy 45 (13) (2020) 7641–7646, https://doi.org/10.1016/j.ijhydene.2019.05.216.

[145] L. Wei, J. Yi, L. Wang, T. Huang, F. Gao, Q. Wang, W. Ma, Light intensity is important for hydrogen production in NaHSO3-treated chlamydomonas reinhardtii, Plant Cell Physiol. 58 (3) (2017) 451–457, https://doi.org/10.1093/pcp/pcw216.

[146] R. Surzycki, L. Cournac, G. Peltier, J.-.D. Rochaix, Potential for hydrogen production with inducible chloroplast gene expression in Chlamydomonas, Proc. Natl. Acad. Sci. 104 (44) (2007) 17548–17553, https://doi.org/10.1073/pnas.0704205104.

[147] H. Bothe, O. Schmitz, M.G. Yates, E.Newton William, Nitrogen fixation and hydrogen metabolism in cyanobacteria, Microbiol. Mol. Biol. Rev. 74 (4) (2010) 529–551, https://doi.org/10.1128/MMBR.00033-10.

[148] A.V. Nguyen, J. Toepel, S. Burgess, A. Uhmeyer, O. Blifernez, A. Doebbe, B. Hankamer, P. Nixon, L. Wobbe, O. Kruse, Time-course global expression profiles of chlamydomonas reinhardtii during photo-biological H2 production, PLoS One 6 (12) (2011) e29364, https://doi.org/10.1371/journal.pone.0029364.

[149] C.N. Dasgupta, J.Jose Gilbert, P. Lindblad, T. Heidorn, S.A. Borgvang, K. Skjanes, D. Das, Recent trends on the development of photobiological processes and photobioreactors for the improvement of hydrogen production, Int. J. Hydrogen Energy 35 (19) (2010) 10218–10238, https://doi.org/10.1016/j.ijhydene.2010.06.029.

[150] A. Kadier, A.K. Chaurasia, S.M. Sapuan, R.A. Ilyas, P.C. Ma, K.F.S. Alabbosh, P. K. Rai, W. Logroño, A.A. Hamid, H.A. Hasan, Essential factors for performance improvement and the implementation of microbial electrolysis cells (MECs), in: P. Kumar, C. Kuppam (Eds.), Bioelectrochemical Systems: Vol.1 Principles and Processes, Springer Singapore, Singapore, 2020, pp. 139–168, https://doi.org/10.1007/978-981-15-6872-5_7.

[151] J.L. Varanasi, R. Veerubhotla, S. Pandit, D. Das, Chapter 5.7 - biohydrogen production using microbial electrolysis cell: recent advances and future prospects, in: S.V. Mohan, S. Varjani, A. Pandey (Eds.), Microbial Electrochemical Technology, Elsevier, 2019, pp. 843–869, https://doi.org/10.1016/B978-0-444-64052-9.00035-2.

[152] G. Kumar, R.G. Saratale, A. Kadier, P. Sivagurunathan, G. Zhen, S.-.H. Kim, G. D. Saratale, A review on bio-electrochemical systems (BESs) for the syngas and value added biochemicals production, Chemosphere 177 (2017) 84–92, https://doi.org/10.1016/j.chemosphere.2017.02.135.

[153] A. Kadier, M.S. Kalil, P. Abdeshahian, K. Chandrasekhar, A. Mohamed, N. F. Azman, W. Logroño, Y. Simayi, A.A. Hamid, Recent advances and emerging challenges in microbial electrolysis cells (MECs) for microbial production of hydrogen and value-added chemicals, Renew. Sustain. Energy Rev. 61 (2016) 501–525, https://doi.org/10.1016/j.rser.2016.04.017.

[154] L. Lu, Z.J. Ren, Microbial electrolysis cells for waste biorefinery: a state of the art review, Bioresour. Technol. 215 (2016) 254–264, https://doi.org/10.1016/j.biortech.2016.03.034.

[155] A. Kadier, M.S. Kalil, P.K. Rai, S.S. Kumar, P. Abdeshahian, P. Sivagurunathan, H. A. Hasan, A.A. Hamid, A. Mohamed, Microbial electrolysis cells; a promising and green approach for bioenergy and biochemical production from waste resources, Bioelectrochem. Interface Eng. (2019) 209–234, https://doi.org/10.1002/9781119611103.ch12. Wiley.

[156] R.G. Saratale, G.D. Saratale, A. Pugazhendhi, G. Zhen, G. Kumar, A. Kadier, P. Sivagurunathan, Microbiome involved in microbial electrochemical systems (MESs): a review, Chemosphere 177 (2017) 176–188, https://doi.org/10.1016/j.chemosphere.2017.02.143.

[157] O. Sosa-Hernández, S.C. Popat, P. Parameswaran, G.S. Alemán-Nava, C.I. Torres, G. Buitrón, R. Parra-Saldívar, Application of microbial electrolysis cells to treat spent yeast from an alcoholic fermentation, Bioresour. Technol. 200 (2016) 342–349, https://doi.org/10.1016/j.biortech.2015.10.053.

[158] T. Catal, Comparison of various carbohydrates for hydrogen production in microbial electrolysis cells, Biotechnol. Biotechnol. Equip. 30 (1) (2016) 75–80, https://doi.org/10.1080/13102818.2015.1081078.

[159] P. Khongkliang, A. Jehlee, P. Kongjan, A. Reungsang, S. O-Thong, High efficient biohydrogen production from palm oil mill effluent by two-stage dark fermentation and microbial electrolysis under thermophilic condition, Int. J. Hydrogen Energy 44 (60) (2019) 31841–31852, https://doi.org/10.1016/j.ijhydene.2019.10.022.

[160] A. Escapa, R. Mateos, E.J. Martínez, J. Blanes, Microbial electrolysis cells: an emerging technology for wastewater treatment and energy recovery. From laboratory to pilot plant and beyond, Renew. Sustain. Energy Rev. 55 (2016) 942–956, https://doi.org/10.1016/j.rser.2015.11.029.

[161] A. Kadier, W. Logrono, P.K. Rai, M.S. Kalil, A. Mohamed, H. Abu Hasan, A. Abdul Hamid, None-platinum electrode catalysts and membranes for highly efficient and inexpensive H2 production in microbial electrolysis cells (MECS): a review, Iranian J. Catal. 7 (2) (2017) 89–102.

[162] S.-.G. Park, K.-.J. Chae, M. Lee, A sulfonated poly(arylene ether sulfone)/polyimide nanofiber composite proton exchange membrane for microbial electrolysis cell application under the coexistence of diverse competitive cations and protons, J. Membr. Sci. 540 (2017) 165–173, https://doi.org/10.1016/j.memsci.2017.06.048.

[163] N.G. Yasri, G. Nakhla, The performance of 3-D graphite doped anodes in microbial electrolysis cells, J. Power Sources 342 (2017) 579–588, https://doi.org/10.1016/j.jpowsour.2016.12.081.

[164] P. Kumar, C. Kuppam, Bioelectrochemical Systems: Vol. 1 Principles and Processes, Springer Nature, 2021.

[165] T.H. Chung, M.N.A. Meshref, F.I. Hai, A. Al-Mamun, B.R. Dhar, Microbial electrochemical systems for hydrogen peroxide synthesis: critical review of process optimization, prospective environmental applications, and challenges, Bioresour. Technol. 313 (2020), 123727, https://doi.org/10.1016/j.biortech.2020.123727.

[166] A. Miller, L. Singh, L. Wang, H. Liu, Linking internal resistance with design and operation decisions in microbial electrolysis cells, Environ. Int. 126 (2019) 611–618, https://doi.org/10.1016/j.envint.2019.02.056.

[167] R. Rousseau, L. Etcheverry, E. Roubaud, R. Basséguy, M.-.L. Délia, A. Bergel, Microbial electrolysis cell (MEC): strengths, weaknesses and research needs from electrochemical engineering standpoint, Appl. Energy 257 (2020), 113938, https://doi.org/10.1016/j.apenergy.2019.113938.

[168] N. Yasri, E.P.L. Roberts, S. Gunasekaran, The electrochemical perspective of bioelectrocatalytic activities in microbial electrolysis and microbial fuel cells, Energy Rep. 5 (2019) 1116–1136, https://doi.org/10.1016/j.egyr.2019.08.007.

[169] N. Zhao, D. Liang, S. Meng, X. Li, Bibliometric and content analysis on emerging technologies of hydrogen production using microbial electrolysis cells, Int. J. Hydrogen Energy 45 (58) (2020) 33310–33324, https://doi.org/10.1016/j.ijhydene.2020.09.104.

[170] T. Kondo, M. Arakawa, T. Hirai, T. Wakayama, M. Hara, J. Miyake, Enhancement of hydrogen production by a photosynthetic bacterium mutant with reduced pigment, J. Biosci. Bioeng. 93 (2) (2002) 145–150, https://doi.org/10.1016/S1389-1723(02)80006-8.

[171] B. Yildiz, M.S. Kazimi, Efficiency of hydrogen production systems using alternative nuclear energy technologies, Int. J. Hydrogen Energy 31 (1) (2006) 77–92, https://doi.org/10.1016/j.ijhydene.2005.02.009.

[172] C. Ding, K.L. Yang, J. He, 11 - Biological and fermentative production of hydrogen, in: R. Luque, C.S.K. Lin, K. Wilson, J. Clark (Eds.), Handbook of Biofuels Production, (2nd Edition), Woodhead Publishing, 2016, pp. 303–333, https://doi.org/10.1016/B978-0-08-100455-5.00011-4.

[173] P.C. Hallenbeck, Chapter 7 - photofermentative biohydrogen production, in: A. Pandey, J.-S. Chang, P.C. Hallenbecka, C. Larroche (Eds.), Biohydrogen, Elsevier, Amsterdam, 2013, pp. 145–159, https://doi.org/10.1016/B978-0-444-59555-3.00007-6.

[174] D. Yan, X. Yang, W. Yuan, Electricity and H2 generation from hemicellulose by sequential fermentation and microbial fuel/electrolysis cell, J. Power Sources 289 (2015) 26–33, https://doi.org/10.1016/j.jpowsour.2015.04.164.

[175] X. Zhang, S. Cheng, X. Huang, B.E. Logan, Improved performance of single-chamber microbial fuel cells through control of membrane deformation, Biosens. Bioelectron. 25 (7) (2010) 1825–1828, https://doi.org/10.1016/j.bios.2009.11.018.

[176] X.-.H. Li, D.-.W. Liang, Y.-.X. Bai, Y.-.T. Fan, H.-.W. Hou, Enhanced H2 production from corn stalk by integrating dark fermentation and single chamber microbial electrolysis cells with double anode arrangement, Int. J. Hydrogen Energy 39 (17) (2014) 8977–8982, https://doi.org/10.1016/j.ijhydene.2014.03.065.

[177] B.R. Dhar, Y. Gao, H. Yeo, H.-.S. Lee, Separation of competitive microorganisms using anaerobic membrane bioreactors as pretreatment to microbial electrochemical cells, Bioresour. Technol. 148 (2013) 208–214, https://doi.org/10.1016/j.biortech.2013.08.138.

[178] W. Liu, S. Huang, A. Zhou, G. Zhou, N. Ren, A. Wang, G. Zhuang, Hydrogen generation in microbial electrolysis cell feeding with fermentation liquid of waste activated sludge, Int. J. Hydrogen Energy 37 (18) (2012) 13859–13864, https://doi.org/10.1016/j.ijhydene.2012.04.090.

[179] C. Cavinato, D. Bolzonella, P. Pavan, F. Fatone, F. Cecchi, Mesophilic and thermophilic anaerobic co-digestion of waste activated sludge and source sorted biowaste in pilot- and full-scale reactors, Renew. Energy 55 (2013) 260–265, https://doi.org/10.1016/j.renene.2012.12.044.

[180] G. Chinellato, C. Cavinato, D. Bolzonella, S. Heaven, C.J. Banks, Biohydrogen production from food waste in batch and semi-continuous conditions: evaluation of a two-phase approach with digestate recirculation for pH control, Int. J. Hydrogen Energy 38 (11) (2013) 4351–4360, https://doi.org/10.1016/j.ijhydene.2013.01.078.

[181] M.T. Anwar, X. Yan, S. Shen, N. Husnain, F. Zhu, L. Luo, J. Zhang, Enhanced durability of Pt electrocatalyst with tantalum doped titania as catalyst support, Int. J. Hydrogen Energy 42 (52) (2017) 30750–30759, https://doi.org/10.1016/j.ijhydene.2017.10.152.

[182] D. Liu, D. Liu, R.J. Zeng, I. Angelidaki, Hydrogen and methane production from household solid waste in the two-stage fermentation process, Water Res. 40 (11) (2006) 2230–2236, https://doi.org/10.1016/j.watres.2006.03.029.

[183] E. Albini, I. Pecorini, G. Ferrara, Improvement of digestate stability using dark fermentation and anaerobic digestion processes, Energies 12 (18) (2019), https://doi.org/10.3390/en12183552.

[184] H. Council, Hydrogen scaling up: a sustainable pathway for the global energy transition, 2017. https://www.h2knowledgecentre.com/content/policypaper1201?crawler=redirect&mimetype=application/pdf.

[185] L. Cozzi, T. Gould, S. Bouckart, D. Crow, T. Kim, C. Mcglade, P. Olejarnik, B. Wanner, D. Wetzel, World Energy Outlook 2020 2050 (2020) 1–461.

[186] N. Gray, S. McDonagh, R. O'Shea, B. Smyth, J.D. Murphy, Decarbonising ships, planes and trucks: an analysis of suitable low-carbon fuels for the maritime, aviation and haulage sectors, Advances in Applied Energy 1 (2021), 100008.

[187] UK Hydrogen strategy: presented to parliament by the secretary of state for business, energy & industrial strategy by command of her majesty, 2021. https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/1011283/UK-Hydrogen-Strategy_web.pdf.

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

[189] I. Vincent, D. Bessarabov, Low cost hydrogen production by anion exchange membrane electrolysis: a review, Renew. Sustain. Energy Rev. 81 (2018) 1690–1704, https://doi.org/10.1016/j.rser.2017.05.258.

[190] L. Chen, Z. Qi, S. Zhang, J. Su, G.A. Somorjai, Catalytic hydrogen production from methane: a review on recent progress and prospect, Catalysts 10 (8) (2020), https://doi.org/10.3390/catal10080858.

[191] A.R. Limongi, E. Viviano, M. De Luca, R.P. Radice, G. Bianco, G. Martelli, Biohydrogen from microalgae: production and applications, Appl. Sci. 11 (4) (2021) 1616.

[192] F. Dawood, M. Anda, G.M. Shafiullah, Hydrogen production for energy: an overview, Int. J. Hydrogen Energy 45 (7) (2020) 3847–3869, https://doi.org/10.1016/j.ijhydene.2019.12.059.

[193] M. Materazzi, R. Taylor, M. Cairns-Terry, Production of biohydrogen from gasification of waste fuels: pilot plant results and deployment prospects, Waste Manage. 94 (2019) 95–106, https://doi.org/10.1016/j.wasman.2019.05.038.

[194] Z. Zhang, Y. Li, H. Zhang, C. He, Q. Zhang, Potential use and the energy conversion efficiency analysis of fermentation effluents from photo and dark fermentative bio-hydrogen production, Bioresour. Technol. 245 (2017) 884–889, https://doi.org/10.1016/j.biortech.2017.09.037.

[195] R.E.S. IRENA, International Renewable Energy Agency, Renewable Energy Target Setting, Abu Dhabi, UAE, 2015.

[196] S.N.A. Rahman, M.S. Masdar, M.I. Rosli, E.H. Majlan, T. Husaini, S.K. Kamarudin, W.R.W. Daud, Overview biohydrogen technologies and application in fuel cell technology, Renew. Sustain. Energy Rev. 66 (2016) 137–162, https://doi.org/10.1016/j.rser.2016.07.047.

[197] Z. Du, C. Liu, J. Zhai, X. Guo, Y. Xiong, W. Su, G. He, A review of hydrogen purification technologies for fuel cell vehicles, Catalysts 11 (3) (2021), https://doi.org/10.3390/catal11030393.

[198] SGH2 energy. https://www.sgh2energy.com/projects/, 2022. (Accessed 31 May 2022).

[199] Green car congress. https://www.greencarcongress.com/, 2022. (Accessed 31 May 2022).

[200] Ways2h from waste to hydrogen. https://ways2h.com/, 2022. (Accessed 31 May 2022).

[201] A. Chanthakett, M.T. Arif, M.M.K. Khan, A.M.T. Oo, Chapter 9 - Hydrogen production from municipal solid waste (MSW) for cleaner environment, in: A. K. Azad, M.M.K. Khan (Eds.), Bioenergy Resources and Technologies, Academic Press, 2021, pp. 261–289, https://doi.org/10.1016/B978-0-12-822525-7.00017-2.

[202] P.N.P. Farrancha, Operation of a fuel cell with biohydrogen obtained from food waste, 2019.

[203] Y. Chung, R. Rosiah, N.M. Izzati, S.M. Mohd, S.T. Mohd, Biohydrogen purification from palm oil mill effluent fermentation for fuel cell application, Malaysian J. Anal. Sci 23 (1) (2019) 80–89.

[204] H2-W project https://www.wsw-online.de/wsw-mobil/, 2022 (Accessed 31 May 2022).

[205] I.F.J. Selvaraj, Hydrogen buses: an analysis with a focus on India's hydrogen roadmap, (2022).

[206] https://www.global.toshiba/ww/products-solutions/hydrogen.html?utm_source=www&utm_medium=web&utm_campaign=since202202ess, 2022. (Accessed 31 May 2022).

[207] Metacon AB company. https://metacon.se/small-chp-systems/#content, 2022. (Accessed 31 May 2022).

[208] H2planet. https://www.h2planet.eu/nl, 2022. (Accessed 31 May 2022).

[209] M.M. Habashy, E.S. Ong, O.M. Abdeldayem, E.G. Al-Sakkari, E.R. Rene, Food waste: a promising source of sustainable biohydrogen fuel, Trends Biotechnol. 39 (12) (2021) 1274–1288, https://doi.org/10.1016/j.tibtech.2021.04.001.

[210] Y. Sun, J. He, G. Yang, G. Sun, V. Sage, A review of the enhancement of biohydrogen generation by chemicals addition, Catalysts 9 (4) (2019) 353.

[211] S.K.S. Patel, J.-K. Lee, V.C. Kalia, Nanoparticles in biological hydrogen production: an overview, Indian J. Microbiol. 58 (1) (2018) 8–18, https://doi.org/10.1007/s12088-017-0678-9.

[212] X. Zhang, C. Bauer, C.L. Mutel, K. Volkart, Life cycle assessment of power-to-gas: approaches, system variations and their environmental implications, Appl. Energy 190 (2017) 326–338, https://doi.org/10.1016/j.apenergy.2016.12.098.

[213] H. Barthelemy, M. Weber, F. Barbier, Hydrogen storage: recent improvements and industrial perspectives, Int. J. Hydrogen Energy 42 (11) (2017) 7254–7262, https://doi.org/10.1016/j.ijhydene.2016.03.178.

[214] O.S. Burheim, Engineering Energy Storage, Academic press, 2017.

[215] I.A. Hassan, H.S. Ramadan, M.A. Saleh, D. Hissel, Hydrogen storage technologies for stationary and mobile applications: review, analysis and perspectives, Renew. Sustain. Energy Rev. 149 (2021), 111311, https://doi.org/10.1016/j.rser.2021.111311.

[216] N. Rajesh Jesudoss Hynes, R. Sankaranarayanan, P. Senthamarai Kannan, A. Khan, A.A.P. Khan, A.M. Asiri, H. Dzudzevic-Cancar, 14 - Solid-state hydrides for hydrogen storage, in: F. Sen, A. Khan, A.M. Asiri (Eds.), Nanomaterials For Hydrogen Storage Applications, Elsevier, 2021, pp. 249–264, https://doi.org/10.1016/B978-0-12-819476-8.00021-9.

[217] F.U. Nigiz, N.D. Hilmioglu, Enhanced hydrogen purification by graphene - Poly (Dimethyl siloxane) membrane, Int. J. Hydrogen Energy 45 (5) (2020) 3549–3557, https://doi.org/10.1016/j.ijhydene.2018.12.215.

[218] T. Bacquart, A. Murugan, M. Carré, B. Gozlan, F. Auprêtre, F. Haloua, T. A. Aarhaug, Probability of occurrence of ISO 14687-2 contaminants in hydrogen: principles and examples from steam methane reforming and electrolysis (water and chlor-alkali) production processes model, Int. J. Hydrogen Energy 43 (26) (2018) 11872–11883, https://doi.org/10.1016/j.ijhydene.2018.03.084.

[219] Y. Zhao, Y. Mao, W. Zhang, Y. Tang, P. Wang, Reviews on the effects of contaminations and research methodologies for PEMFC, Int. J. Hydrogen Energy 45 (43) (2020) 23174–23200, https://doi.org/10.1016/j.ijhydene.2020.06.145.

[220] A. Murugan, A.S. Brown, Review of purity analysis methods for performing quality assurance of fuel cell hydrogen, Int. J. Hydrogen Energy 40 (11) (2015) 4219–4233, https://doi.org/10.1016/j.ijhydene.2015.01.041.

[221] M.R. Rahimpour, F. Samimi, A. Babapoor, T. Tohidian, S. Mohebi, Palladium membranes applications in reaction systems for hydrogen separation and purification: a review, Chem. Eng. Process: Process Intensif. 121 (2017) 24–49, https://doi.org/10.1016/j.cep.2017.07.021.

[222] H. Wang, X. Wang, B. Meng, X. Tan, K.S. Loh, J. Sunarso, S. Liu, Perovskite-based mixed protonic–electronic conducting membranes for hydrogen separation: recent status and advances, J. Ind. Eng. Chem. 60 (2018) 297–306, https://doi.org/10.1016/j.jiec.2017.11.016.

[223] M. Aasadnia, M. Mehrpooya, B. Ghorbani, A novel integrated structure for hydrogen purification using the cryogenic method, J. Clean. Prod. 278 (2021), 123872, https://doi.org/10.1016/j.jclepro.2020.123872.

[224] A.M.N. Azira, A.U. Aisah, Purification of biohydrogen from fermentation gas mixture using two-stage chemical absorption, E3S Web of Conferences, EDP Sci. (2019) 01012.

[225] A. Big, World Almond Production by Country- AtlasBig.com. https://www.atlasbig.com/en-ie/countries-by-almond-production, 2022. (Accessed Feb. 14, 2022).

[226] A. Big, World's Leading Olive Producing Countries - AtlasBig.com. https://www.atlasbig.com/en-in/countries-by-olive-production, 2022. (Accessed Feb. 14, 2022).

[227] M. Meghana, Y. Shastri, Sustainable valorization of sugar industry waste: status, opportunities, and challenges, Bioresour. Technol. 303 (2020), 122929, https://doi.org/10.1016/j.biortech.2020.122929.

[228] T. Silalertruksa, S.H. Gheewala, Competitive use of sugarcane for food, fuel, and biochemical through the environmental and economic factors, Int. J. Life Cycle Assess 25 (7) (2020) 1343–1355, https://doi.org/10.1007/s11367-019-01664-0.

[229] A. Big, World's leading peanut producing countries - AtlasBig.com. https://www.atlasbig.com/en-in/countries-by-peanut-production, 2022. (Feb. 14, 2022).

[230] Statista, Top countries based on production of milled rice | Statista, (2021) https://www.statista.com/statistics/255945/top-countries-of-destination-for-us-rice-exports-2011/. (Feb. 14, 2022).

[231] A. Big, Countries by Oat Production - AtlasBig.com. https://www.atlasbig.com/en-in/countries-by-oat-production, 2022. (Accessed Feb. 14, 2022).

[232] P. Saosee, B. Sajjakulnukit, S.H. Gheewala, Life cycle assessment of wood pellet production in Thailand, Sustainability 12 (17) (2020), https://doi.org/10.3390/su12176996.

[233] EOS, EOS - European organisation of the sawmill industry | sawmill industry - annual reports. https://www.eos-oes.eu/en/sawmill_industry_annual_reports.php, 2022. (Accessed Feb. 14, 2022).

[234] D.S. Bajwa, G. Pourhashem, A.H. Ullah, S.G. Bajwa, A concise review of current lignin production, applications, products and their environmental impact, Ind. Crops Prod. 139 (2019), 111526, https://doi.org/10.1016/j.indcrop.2019.111526.

[235] Statista, Coconut production worldwide by leading country 2020, Statista, 2021. https://www.statista.com/statistics/1040499/world-coconut-production-by-leading-producers/. (Accessed Feb. 14, 2022).electrohydrogenesis, Int. J. Hydrogen Energy 34(15) (2009) 6201-6210.

[236] M.M. Parascanu, M. Puig-Gamero, G. Soreanu, J.L. Valverde, L. Sanchez-Silva, Comparison of three Mexican biomasses valorization through combustion and gasification: environmental and economic analysis, Energy 189 (2019), 116095, https://doi.org/10.1016/j.energy.2019.116095.

[237] C. Liu, L. Chen, W. Tang, S. Peng, M. Li, N. Deng, Y. Chen, Predicting potential distribution and evaluating suitable soil condition of oil tea camellia in China, Forests 9 (8) (2018), https://doi.org/10.3390/f9080487.

[238] E. Cassou, D.N. Tran, T.H. Nguyen, T.X. Dinh, C.V. Nguyen, B.T. Cao, S. Jaffee, J. Ru, An overview of agricultural pollution in Vietnam, (2017). doi: 10.1596/29244.

[239] D. Barisano, G. Canneto, F. Nanna, A. Villone, E. Fanelli, C. Freda, M. Grieco, G. Cornacchia, G. Braccio, V. Marcantonio, E. Bocci, P.U. Foscolo, S. Heidenreich, Investigation of an intensified thermo-chemical experimental set-up for hydrogen production from biomass: gasification process performance—part I, Processes 9 (7) (2021), https://doi.org/10.3390/pr9071104.

[240] V. Marcantonio, M. De Falco, M. Capocelli, E. Bocci, A. Colantoni, M. Villarini, Process analysis of hydrogen production from biomass gasification in fluidized bed reactor with different separation systems, Int. J. Hydrogen Energy 44 (21) (2019) 10350–10360, https://doi.org/10.1016/j.ijhydene.2019.02.121.

[241] X. Fan, L. Yang, J. Jiang, Experimental study on industrial-scale CFB biomass gasification, Renew. Energy 158 (2020) 32–36, https://doi.org/10.1016/j.renene.2020.05.145.

[242] E. Kıpçak, O.Ö. Söğüt, M. Akgün, Hydrothermal gasification of olive mill wastewater as a biomass source in supercritical water, J. Supercrit. Fluids 57 (1) (2011) 50–57, https://doi.org/10.1016/j.supflu.2011.02.006.

[243] I.-.G. Lee, S.-.K. Ihm, Catalytic gasification of glucose over Ni/activated charcoal in supercritical water, Ind. Eng. Chem. Res. 48 (3) (2009) 1435–1442, https://doi.org/10.1021/ie8012456.

[244] O. Norouzi, F. Safari, S. Jafarian, A. Tavasoli, A. Karimi, Hydrothermal gasification performance of Enteromorpha intestinalis as an algal biomass for hydrogen-rich gas production using Ru promoted Fe–Ni/γ-Al2O3 nanocatalysts, Energy Convers. Manage. 141 (2017) 63–71, https://doi.org/10.1016/j.enconman.2016.04.083.

[245] D. Castello, A. Kruse, L. Fiori, Supercritical water gasification of hydrochar, Chem. Eng. Res. Des. 92 (10) (2014) 1864–1875, https://doi.org/10.1016/j.cherd.2014.05.024.

[246] D. Elif, A. Nezihe, Hydrogen production by supercritical water gasification of fruit pulp in the presence of Ru/C, Int. J. Hydrogen Energy 41 (19) (2016) 8073–8083, https://doi.org/10.1016/j.ijhydene.2015.12.005.

[247] L. Tiong, M. Komiyama, Y. Uemura, T.T. Nguyen, Catalytic supercritical water gasification of microalgae: comparison of Chlorella vulgaris and Scenedesmus quadricauda, J. Supercrit. Fluids 107 (2016) 408–413, https://doi.org/10.1016/j.supflu.2015.10.009.

[248] S. Nanda, J. Isen, A.K. Dalai, J.A. Kozinski, Gasification of fruit wastes and agro-food residues in supercritical water, Energy Convers. Manage. 110 (2016) 296–306, https://doi.org/10.1016/j.enconman.2015.11.060.

[249] A. Amrullah, Y. Matsumura, Supercritical water gasification of sewage sludge in continuous reactor, Bioresour. Technol. 249 (2018) 276–283, https://doi.org/10.1016/j.biortech.2017.10.002.

[250] K. Akubo, M.A. Nahil, P.T. Williams, Pyrolysis-catalytic steam reforming of agricultural biomass wastes and biomass components for production of hydrogen/syngas, J. Energy Inst. 92 (6) (2019) 1987–1996, https://doi.org/10.1016/j.joei.2018.10.013.

[251] T.K. Tran, N. Kim, H.J. Leu, M.P. Pham, N.A. Luong, H.K. Vo, The production of hydrogen gas from modified water hyacinth (Eichhornia Crassipes) biomass through pyrolysis process, Int. J. Hydrogen Energy 46 (27) (2021) 13976–13984, https://doi.org/10.1016/j.ijhydene.2020.08.225.

[252] A. Sattar, C. Arslan, C. Ji, S. Sattar, M. Umair, S. Sattar, M.Z. Bakht, Quantification of temperature effect on batch production of bio-hydrogen from rice crop wastes in an anaerobic bio reactor, Int. J. Hydrogen Energy 41 (26) (2016) 11050–11061, https://doi.org/10.1016/j.ijhydene.2016.04.087.

[253] S. Jayalakshmi, K. Joseph, V. Sukumaran, Bio hydrogen generation from kitchen waste in an inclined plug flow reactor, Int. J. Hydrogen Energy 34 (21) (2009) 8854–8858, https://doi.org/10.1016/j.ijhydene.2009.08.048.

[254] T. Zhang, D. Jiang, H. Zhang, Y. Jing, N. Tahir, Y. Zhang, Q. Zhang, Comparative study on bio-hydrogen production from corn stover: photo-fermentation, dark-fermentation and dark-photo co-fermentation, Int. J. Hydrogen Energy 45 (6) (2020) 3807–3814, https://doi.org/10.1016/j.ijhydene.2019.04.170.

[255] D. Mu, H. Liu, W. Lin, P. Shukla, J. Luo, Simultaneous biohydrogen production from dark fermentation of duckweed and waste utilization for microalgal lipid production, Bioresour. Technol. 302 (2020), 122879, https://doi.org/10.1016/j.biortech.2020.122879.

[256] C. Wu, M. Yin, R. Zhang, Z. Li, Z. Zou, Z. Li, Further studies of photodegradation and photocatalytic hydrogen production over Nafion-coated Pt/P25 sensitized by rhodamine B, Int. J. Hydrogen Energy 45 (43) (2020) 22700–22710, https://doi.org/10.1016/j.ijhydene.2020.06.098.

[257] G. Yang, J. Wang, Various additives for improving dark fermentative hydrogen production: a review, Renew. Sustain. Energy Rev. 95 (2018) 130–146, https://doi.org/10.1016/j.rser.2018.07.029.

[258] E. Lalaurette, S. Thammannagowda, A. Mohagheghi, P.-.C. Maness, B.E. Logan, Hydrogen production from cellulose in a two-stage process combining fermentation and electrohydrogenesis, Int. J. Hydrogen Energy 34 (15) (2009) 6201–6210, https://doi.org/10.1016/j.ijhydene.2009.05.112.

[259] Y.-.Z. Wang, L. Zhang, T. Xu, K. Ding, Influence of initial anolyte pH and temperature on hydrogen production through simultaneous saccharification and fermentation of lignocellulose in microbial electrolysis cell, Int. J. Hydrogen Energy 42 (36) (2017) 22663–22670, https://doi.org/10.1016/j.ijhydene.2017.07.214.

[260] L. Zhang, Y.-.Z. Wang, T. Zhao, T. Xu, Hydrogen production from simultaneous saccharification and fermentation of lignocellulosic materials in a dual-chamber microbial electrolysis cell, Int. J. Hydrogen Energy 44 (57) (2019) 30024–30030, https://doi.org/10.1016/j.ijhydene.2019.09.191.

[261] B.R. Dhar, E. Elbeshbishy, H. Hafez, H.-.S. Lee, Hydrogen production from sugar beet juice using an integrated biohydrogen process of dark fermentation and microbial electrolysis cell, Bioresour. Technol. 198 (2015) 223–230, https://doi.org/10.1016/j.biortech.2015.08.048.

[262] S.J. Satinover, D. Schell, A.P. Borole, Achieving high hydrogen productivities of 20L/L-day via microbial electrolysis of corn stover fermentation products, Appl. Energy 259 (2020), 114126, https://doi.org/10.1016/j.apenergy.2019.114126.