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## Review Article

# A state of the art review on biomass processing and conversion technologies to produce hydrogen and its recovery via membrane separation

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## HIGHLIGHTS

- Thermochemical conversion technologies for hydrogen production.
- Gasification technologies review for hydrogen production.
- Biological routes for hydrogen production.
- Potential of membrane applications for hydrogen separation from syngas.
- Prospective of hydrogen as future of energy.

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## ABSTRACT

Hydrogen is a zero-emission green fuel containing sufficient energy potentially suitable for electricity generation. Currently, large quantities of hydrogen are produced using classical fossil fuels. Nevertheless, the finite quantities of these resources have compelled the global community to look into using more sustainable and environmentally friendly resources such as bio-based waste. There are several approaches, to convert biomass to hydrogen, among which the thermochemical and biological processes are considered as the most important ones. The aim of this review paper is twofold, namely, (a) to evaluate hydrogen

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production and biomass processing methods to give a better insight into their potential merits and identify gaps for sustainable hydrogen generation, and (b) to evaluate current and future opportunities in membrane technology for hydrogen separation and purification from biomass processing. By fulfilling these gaps, the objectives of economical, sustainable, and environmentally-friendly resources for hydrogen production and separation can be recommended.

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## Introduction

Hydrogen is ever-growing in its demand over other conventional fuels due to its wide range of diverse applications [1,2]. Its high energy content offers a comprehensive benefit [3], in terms of lower heating value (LHV)/kg over their fossil fuel-based counterparts such as methane and gasoline, which are 2.4 and 2.8 times higher respectively [4]. Furthermore, hydrogen is extensively used in fuel cells, which have minimal emissions and merely release water-vapor as the net emissions and might be regarded as zero-

emission green fuel [5,6]. On the other hand, fossil fuels have contributed to global warming by supplementing the CO<sub>2</sub> release with additional SO<sub>x</sub> and NO<sub>x</sub> into the environment [7]. Additionally, hydrogen is a principal component of many chemical and fuel products such as ammonia, methane, urea, ethanol, etc [8,9]. Due to these reasons, further research in the domain of hydrogen production is necessary so that future technology will meet these requirements [10]. Moreover, the hydrogen is useful in fuel cell applications and many integrated processes have been investigated for hydrogen production processes with fuel cells [11–13].

The hydrogen economy is known as a system in which hydrogen is used as a prime energy source and becomes a key component of future power generation [14]. Many countries have started to determine the value of the hydrogen economy and make efforts to take significant steps towards a hydrogen economy and planned the policies and methods as reviews by many researchers, such as, for Malaysia [15], Pakistan [16], Taiwan [17], China [18], Portugal [19], and Canada [20], etc. The value of the hydrogen economy was 107 billion \$ in 2016 [21], 115.25 billion \$ in 2017 and is expected to rise to 154.74 billion \$ by 2022 [10]. In a recent research report, world hydrogen demand has been reported as 50 million metric tons/year or 45 billion kg/year in 2006 and has been increasing at the rate of 10% annually [11]. Currently the worldwide cumulative hydrogen consumption is in the range 400–500 million Nm<sup>3</sup> per annum [12,13] and will continue beyond 2025 [14]. It is anticipated that in the near future hydrogen will be the most important energy carrying fuel for the reasons that it is environmentally friendly and possesses efficient burning characteristics [15,16]. Additionally, hydrogen is used as a major constituent in the synthesis of ammonia and methanol for many decades, which is conventionally obtained from the methane-steam reforming reaction [17,22].

Hydrogen is obtained from both fossil and non-fossil fuels and about 96% of the total hydrogen produced is obtained from carbonaceous raw materials, which are comprised mainly fossil fuels [21]. The continuing supply of fuel is under threat due to the finite sources of fossil fuels, hence the world must divert its dependence from fossil to non-fossil renewable sources [23,24]. Reforming and pyrolysis are the major processes to produce hydrogen from fossil fuels [3,25]. On the other hand, it can be produced using non-fossil fuel either by thermochemical or biological methods [26]. Among the non-fossil fuels, biomass is an abundant renewable source of energy that is available in many forms such as; agricultural, forest, and biowastes, etc. Biomass has been utilized in many ways for energy production for centuries and it is still contributing about 10–14% of the total energy supply of the world, whereas, for the developed countries, this share is substantially higher, i.e., 40–45% [27,28]. Biomass may be processed in numerous ways depending on the end-use and required products, which are obtained through chemical, thermal, thermochemical and biochemical pathways [25,29]. The resultant amount of hydrogen from biomass may reach 20% by volume via different conversion strategies [30,31].

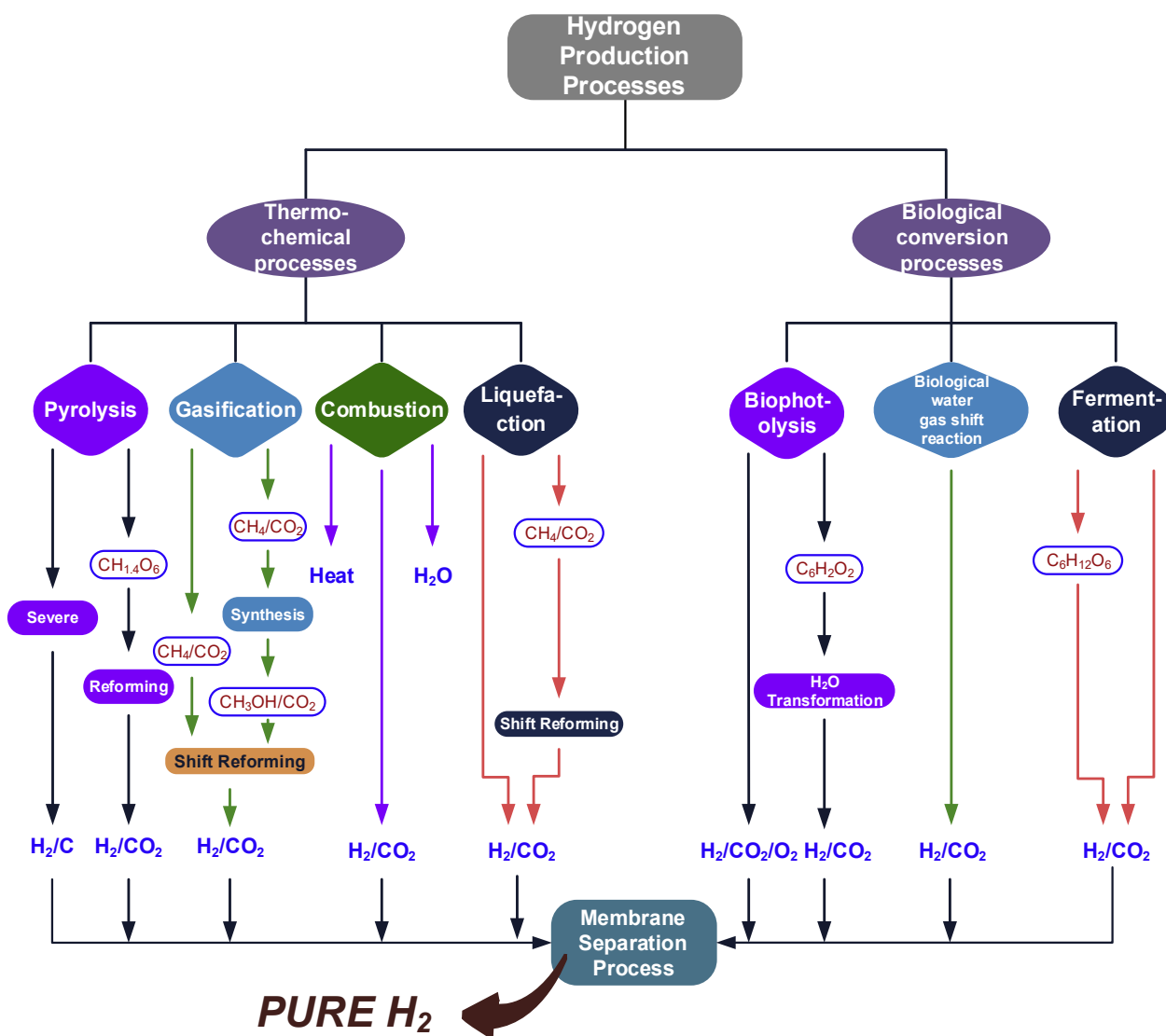
Biomass processing routes, in principle, depend on the state of the available feedstock [32]. Hydrogen from bio-resources can be produced using gasification, pyrolysis, fermentation, anaerobic digestion or even the steam reforming process [33]. A scheme of the different routes from biomass to hydrogen is shown in Fig. 1. The quantity of hydrogen produced depends on the source of biomass and the efficiency of the process method/route utilized [34]. The technologies, to convert biomass into hydrogen, are useful and acceptable as compared to other typical technologies incorporating fossil fuels due to less and/or zero emissions into the environment [27,35].

Several reviews have been published over time to study the developments in the area of hydrogen production. A detailed

analysis of these review papers published for hydrogen production from biomass using thermochemical or biological conversion technologies is shown in Table 1, which also indicates how these insightful reviews have served to this domain of knowledge especially in the case of the separation of hydrogen through membrane technology. Most of these reviews are based on a single technology for hydrogen production. No review paper has been found which compares all available technologies for hydrogen production. Singh et al. [36] discussed hydrogen production through both direct and indirect bio-photolysis processes with the effect of catalysts. The most important reviews covering biological methods were presented by Mudhoo et al. [37] and Anoop et al. [38]. The hydrogen production processes by thermochemical based techniques have been reviewed and are available for pyrolysis and gasification [25,39,40]. A review was published in 2009, which gives a very brief review of the thermochemical and biological conversion processes for hydrogen production, as most of the technologies were at the initial stages of development [25]. Most of the literature studies available are for gasification processes such as steam gasification, supercritical water gasification, solar gasification, etc [41–44]. Based on the extensive literature reviews, there has not been a critical discussion, assessment, and comparison of the operating principles. Also, the costs relating to H<sub>2</sub> production for most processes are missing in the literature. The major contribution of this review paper lies in providing an in-depth analysis of hydrogen production and biomass processing methods for relevant advantages and shortcomings for a sustainable energy future. Furthermore, the usefulness of membrane technology for hydrogen separation and purification specifically obtained via biomass processing are included as a key highlight, followed by the future potential in this area of research. Within this context, the remainder of this review is categorized as follows. In section **Thermochemical methods**, a literature survey on thermochemical methods is presented which will assist researchers and the scientific community to select the suitable process according to type of biomass and applications. Section **Non-Thermal/biological methods** addresses the non-thermal/biological methods of hydrogen production and its usage. The separation of hydrogen via membranes through biomass based processes is reviewed in Section **Implementation of membrane for biomass-based Hydrogen Separation**. The next section discusses the challenges to continue the way forward to sustainable hydrogen production.

## Thermochemical methods

Thermochemical processes are typically considered as viable and effective to produce hydrogen from biomass [23,35,48], whereas, these processes have many challenges in terms of commercialization [49]. These technologies mainly include pyrolysis [50], gasification [51], combustion [52] and liquefaction [53]. Fig. 1 also shows the schematic diagram for pathways of biomass thermochemical technologies with subsequent downstream processes for hydrogen production and purification using membrane technology.



**Fig. 1 – Schematic diagram for the pathway of biomass thermochemical technologies with subsequent downstream processes for hydrogen production.**

### Biomass combustion

The process of burning any fuel in the presence of air to release its energy in the form of heat of reaction is termed a combustion process. In this process, the biomass burns directly in the presence of excess air in a boiler or furnace, which might be used to produce steam and the resultant steam serve as the driver for turbines, pumps or compressors in any chemical process, and represents the conversion of heat energy into mechanical energy [48]. Due to the less efficacy of thermal power plants, i.e., 40%, this process is considered as an energy-inefficient process [49]. Furthermore, biomass combustion is typically not preferred for hydrogen production due to high formation of carbon dioxide. The hydrogen production was 9.56 vol% for the combustion of algal biomass [54]. In practice, however, many other gases such as  $\text{CO}_x$ ,  $\text{SO}_x$ ,  $\text{NO}_x$ , and  $\text{CH}_4$  are also emitted which depend upon the source and composition of the biomass.

Among these,  $\text{SO}_x$  forms, if the sulfur is present in biomass,  $\text{CO}$  due to incomplete combustion and  $\text{NO}_x$  in case of nitrogen present either in air or biomass [50]. The effective implementation of environmental laws helps in maintaining the amount of these pollutants to a certain level to avoid both environmental and health problems. The cost of remedial treatment for these unwanted gases is very high, which adversely increases the overall cost of this process [48]. Correspondingly, the cost per unit of energy is intensified. Additionally, this is an inefficient energy process for the reason of wasting a large amount of energy in the form of flue gas enthalpy [51]. Nevertheless, this wastage of energy can be controlled by installing a waste heat recovery boiler/economizer. These options have limited applications due to the little amount of heat which can be recovered [52]. The combustion process has certain other limitations, such as the high value of acid dew point (ADP) and water dew point (WDP), and emissions of un-wanted polluted gases and ashes [53]. Generally,

**Table 1 – The review papers published for hydrogen production from biomass in last.**

Reviews	Description	Thermochemical conversion methods					Biological conversion methods					Separation via membrane	
		combustion	Pyrolysis	Liquefaction	Gasification			Photo-fermentation		Bio-Photolysis			Biological water gas shift reaction
					Gasification	Solar- gasification	Water – gasification	Photo	Dark	Direct	Indirect		
Pandey et al. 2019 [40]	Recent development in gasification, pyrolysis process for H <sub>2</sub> production		✓		✓		✓						
Singh et al.2018 [36]	Detail about the use of catalyst and mechanism									✓		✓	
Rezania et al. 2017 [41]	Detail about the effect of parameters, optimization, wheat straw, rice husk, etc							✓	✓				
Arregi et al. 2018 [1]	This is about reactor designs, process parameters, and use of catalysts		✓		✓		✓						
Rafal et al. 2018 [9]	Use of many wastes for substrate and operating parameters issues								✓				
Kalinci et al. 2009 [25]	A brief review on H <sub>2</sub> production process with gasification case study		✓		✓	✓	✓	✓	✓	✓	✓	✓	✓
Azwar et al. 2014 [45]	This covers theoretical principals, bacterial selection of strains and substrates, operating parameters and mathematical models							✓	✓	✓	✓		
Singh et al. 2014 [46]	Review covers pre-treatment, cell immobilization, sequential and combined fermentation,							✓	✓				
Chen et al. 2011 [39]	It covers the use of bio-oil. CO <sub>2</sub> reduction, thermodynamic principle to enhanced H <sub>2</sub> , catalysts used		✓		✓	✓	✓	✓					
Mudhoo et al. 2010 [37]	This deals in detail about pre- treatments, modifications in the design of reactors and process to enhance yield							✓	✓	✓	✓		
Anoop et al. 2015 [38]	This covers biological method with some LCA based study and kinetic models							✓	✓	✓	✓		
(continued on next page)													

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Table 1 – (continued)

Reviews	Description	Thermochemical conversion methods				Biological conversion methods				Separation via membrane		
		combustion	Pyrolysis	Liquefaction	Gasification		Photo-fermentation		Bio-Photolysis		Biological water gas shift reaction	
					Gasification	Solar-gasification	Photo	Dark				Direct
Prakash et al. [42]	This deals for biomass type, particle size, reaction parameters temperature, and catalyst				✓							
Tanksale et al. [47]	This review described the catalytic h production using biomass		✓			✓						✓
This review	A comparative study for all process with membrane process for H <sub>2</sub> separation	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

the main purpose of the combustion process is for energy production, however, research is in high demand for technology resulting in the lower production of greenhouse gases (GHG), and the utilization of flue gas heat for energy production. Some new processes have been proposed with the integration of power and energy production such as the chemical looping process to economize the process for hydrogen production [55,56]. The main challenge is the lower content of H<sub>2</sub> in the flue gas, that make it unattractive in the case of hydrogen production.

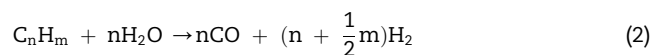
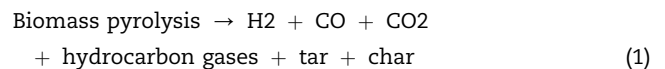
### Biomass pyrolysis

Pyrolysis is the process in which biomass is thermally treated in the temperature range of 400–600 °C and at atmospheric pressure in the absence of air to convert biomass feedstocks into liquid(bio-oils), solid(char), and gaseous components(syngas) [57,58]. The pyrolysis process consists of devolatilization, fragmentation and product formation that effects the yield of the process [59]. Pyrolysis may also be further classified into slow and fast types [57]. Slow pyrolysis normally occurs at a temperature between 400 and 450 °C, with a low heating rate of 1–5 °C/s and longer residence time (4–8 min). Whereas, in the case of fast pyrolysis, the temperature is maintained in the range of 450–950 °C, along with a higher heating rate and shorter residence time, which are in the range of 100–300 °C/s and 1–5 s respectively [60].

The process of pyrolysis and its product is demonstrated in Fig. 2; these products may occur in gas, liquid or solid phases, which are outlined below:

- Gaseous products: mixtures of H<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>, and other gases, which depend upon the organic nature of the biomass [57].
- Liquid products: tar and oils left over in liquid form at room temperature.
- Solid products: char and inorganic components, where the char is almost pure carbon and the latter contains ash and alkali metals from the biomass.

The major objective of the pyrolysis process is to produce bio-oil, nevertheless, it may lead to the production of hydrogen either directly via flashing or fast pyrolysis at high temperatures and a suitable residence time [61]. The following reactions are involved in biomass pyrolysis for hydrogen production.



The yield of hydrogen from biomass pyrolysis is strictly dependent upon the feedstock nature, catalyst type, process temperature and residence time [62]. Both the organic liquid and solid products of pyrolysis process can be processed to produce hydrogen. The pyrolysis oil can be separated into two



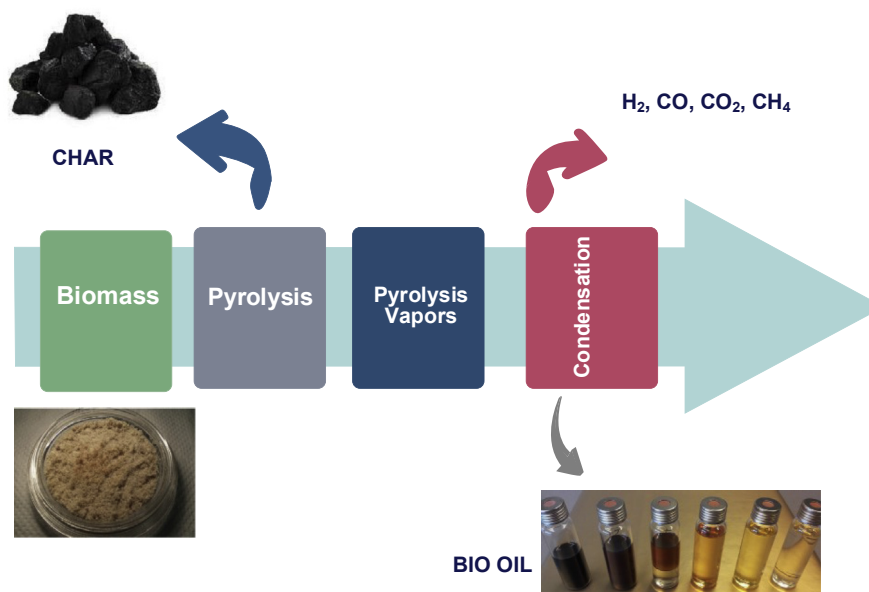


Fig. 2 – Biomass pyrolysis route for hydrogen production.

fractions based on water solubility [1]. These fractions can be used either separately or as mixtures for hydrogen production through the gasification or steam reforming process [63,64]. The expected cost of hydrogen production from the pyrolysis process lies in the range of (1.25–2.220 \$/kg) depending on biomass type and the production facility type [65].

To evaluate the hydrogen production from biomass pyrolysis, various catalysts have been tested through ex-situ or in-situ processes [66–68]. Table 2 summarizes the information about hydrogen yield from the pyrolysis for various types of biomass in the presence of various catalysts and reactor types, as reported in the literature. The pyrolysis technology has been under consideration by researchers and it has developed from laboratory scale to pilot scale that involved tubular reactors, fixed bed reactors, and fluidized bed reactors [59]. In Table 2 it can be observed that the type of reactor, catalyst, biomass and process conditions affect the hydrogen yield.

Char is a byproduct of pyrolysis, which is generated during slow pyrolysis; therefore this type of pyrolysis is not preferred for hydrogen production, while bio-oil is produced as a result of fast pyrolysis, making it a desirable and feasible process for hydrogen production [65]. The fast pyrolysis of biomass results in a mixture of gases and liquids [87]. For hydrogen production, fast pyrolysis is integrated with steam reforming [30]. This is a two-step process, where bio-oil is the intermediate product obtained from first stage and may lead to hydrogen and carbon dioxide generation through reforming in the presence of a catalyst and steam [88]. Fast pyrolysis is advantageous over slow pyrolysis in many ways. Firstly, it is easy to transport bio-oil instead of biomass (charcoal) [89]. Secondly, valuable products have been recovered from bio-oil along with hydrogen. Furthermore, fast pyrolysis produces highly efficient fuels [30]. Bio-oil produced in fast pyrolysis is further reformed in the presence of steam in fluidized bed reactors. Vortex and fluidized bed reactors are currently the subjects of research and it appears that they will be

economically viable options [90]. Catalysts are used to improve the process conditions as well as the product quality of the process. Experimental results have shown that at 850 °C, 90% of the stoichiometric hydrogen is recovered when a Ni-based catalyst of 300–350 µm size was used with 9:1 steam to biomass carbon ratio. Another type of Ni catalyst was reported by Waheed et al. [81]. The estimated cost of hydrogen produced from this process is \$7.7/GJ, which is considerably less than that of hydrogen produced from wind electrolysis (\$20/GJ) [30]. Considering the technology readiness level of the pyrolysis process is still on par for bio-oil production, but for the application of hydrogen production it is still not popular. The most likely reason of this is that most of the research and technology development has been focused towards bio-oil and char production [58,91]. It is concluded that there is a need to further explore some new technology developments: such as microwave pyrolysis as well as more development on the catalyst and reactor for hydrogen production. In addition, there are some techno-economic and life cycle assessment analyses still needed to compare its cost with other technologies.

### Biomass liquefaction

Liquefaction of biomass is another thermochemical process that can be used to produce hydrogen. Liquefaction of biomass can be classified into two processes, namely: direct liquefaction and hydrothermal liquefaction [92]. Hydrothermal liquefaction, also known as hydrous pyrolysis [93], is defined as the conversion of biomass into liquid fuels in the presence of water, while maintaining a temperature between 226 and 362 °C and a pressure ranging from 5 to 20 MPa, preferably in the presence of a catalyst [94]. The positive point about hydrothermal liquefaction over pyrolysis is that the biomass prerequisite treatment such as drying is eliminated, thus resulting in energy savings. Only due to this reason, this

**Table 2 – Different biomass pyrolysis for the synthesis of hydrogen production.**

Biomass	Catalyst	Reactor type	Reaction Temperature (°C)	Hydrogen yield	References
Wheat straw	0.25 5KCl/CaO	Two-stage reactor	500 (1st stage) 650 (2nd stage)	55.5 vol%	[69]
Pine wood	Ni/MgO	Spouted bed reactor + fluidized bed reactor	500 (SBR) 600 (FBR)	9.08 wt%	[70]
Pine wood	Blast-furnace slag	Rotary pyrolysis reactor	800	45.4 vol%	[71]
Corn cob	Limonite ore	Two-stage fixed bed quartz reactor	650	21.65 mmol/g	[72]
Wood sawdust	35NiZn4Al	Two-stage fixed bed reactor	800	20.1 mmol/g	[73]
Pine wood sawdust	Ni commercial	Spouted bed reactor + fluidized bed reactor	500 (SBR) 600 (FBR)	110 g/kg	[74]
Wood sawdust	Ni/CaAlOx	Two-stage fixed bed quartz reactor	800	15.57 mmol/g	[75]
Rice Husk	10 wt%Ni-dolomite	Two-stage fixed reactor	850–1050	20.03–30.62 mmol/g	[76]
Japsnese cedar	20 wt%Mo2C/biochar	Fixed-bed reactor	650	20 mmol/g	[77]
Water hyacinth	Ni-based catalyst	Two-stage pyrolyzer	600 (1st) 800 (2nd)	59.96 g/kg biomass (1st) 101.17 g/kg biomass (2nd)	[78]
Sawdust	NiO/MgO	Three-stage integrated reactor	700–850	43.58–75.96 g/kg biomass	[79]
Bagasse	12%Ni6%Fe/Al <sub>2</sub> O <sub>3</sub>	Dual stage bed microreactor	850	15 mol. %	[80]
Bagasse, Rice Husk, wheat straw	10 wt% Ni-dolomite	Two-stage pyrolyzer	950	25.41 mmol/g, 25.44 mmol/g, 24.47 mmo/g	[81]
Rice stalk	Molten alkali	Stainless steel tank reactor	550	66.5 g/kg biomass	[82]
Pine	NiMo/Al <sub>2</sub> O <sub>3</sub>	Dual-particle powder fluidized-bed	500	33.6 g/kg biomass	[83]
Wood	Cu–Al-MCM-41	Fixed bed	500	9 vol%	[84]
Oil palm wastes	Ni, La/Al <sub>2</sub> O <sub>3</sub>	Fixed bed	900	37.28 vol% (Ni) 38.45 vol% (La/Al <sub>2</sub> O <sub>3</sub> )	[68]
Rice straw, Sawdust	Cr <sub>2</sub> O <sub>3</sub>	Fixed bed	850	49.5 wt% (RS), 51.4 wt% (SD)	[67]
Pine sawdust	Ni/slag	Entrained flow fixed bed	900	29.0 vol%	[85]
Coconut shell	ReC	Fixed bed	800	57 vol%	[86]



**Table 3 – Hydrogen production through liquefaction process from different biomass.**

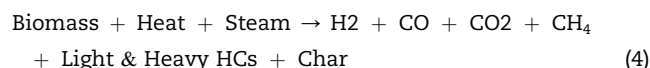
Feed	Catalyst	Reactor type and conditions	Hydrogen yield	References
Glucose	Ni/activated charcoal	Packed-bed reactor, 28 MPa, 650 °C	15.6 mmol/g	[103]
Olive mill waste water	–	Coiled tubular reactor, 25 MPa, 600 °C	10.79 mol%	[104]
Switchgrass biocrude	Ni/ZrO <sub>2</sub>	Packed-bed reactor, 600 °C, 25 MPa	81.67 mol/g carbon reacted	[105]
Bark	Ni/hydrotalcite	Batch reactor, 380 °C, 23 MPa	2.05 mmol/g	[106]
Sewage sludge	KOH	Fluidized bed reactor, 540 °C, 30 MPa	15.49 mmol/g	[107]
Maize silage hydrochar	K <sub>2</sub> CO <sub>3</sub>	Micro-autoclaves, 400 °C, 30 MPa	8.9 mol%	[94]
Coconut shell	K <sub>2</sub> CO <sub>3</sub>	Tubular batch reactor, 600 °C, 23–25 MPa	4.8 mmol/g	[93]
Fruit pulp	RU/activated charcoal	Batch reactor, 600 °C, 25 MPa	54.8 mmol/g	[95]
Microalgae		Batch reactor, 385 °C, 26 MPa.	4 mmol/g	[108]
(Cenedesmus quadricauda)	Nickel/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	Batch microreactor, 440 °C, 25 MPa	12.28 mmol/g	[109]
Microalgae		Continuous reactor, 600 °C, 25 MPa	40 vol%	[110]

process is highly desirable for processing aquatic biomass, garbage, and organic sludge for hydrogen production. This process has some serious concerns, which originate from the severe reaction conditions that may not be easily achieved and the low yield of hydrogen from the reformation of oil produced as a result of hydrothermal liquefaction. Due to these facts, no commercial-scale plant has been implemented so far [95]. Table 3 provides insights to the published hydrogen yields obtained via biomass liquefaction. From Table 3, it can be concluded that the effect of process parameters such as temperature, pressure, catalyst loading, biomass type and its ratio with solvent, and heating rate and residence time are significantly important for H<sub>2</sub> production [96–98]. Besides, it can be observed that liquefaction is mostly focused on liquid fuel production. Furthermore, the research level is still at a laboratory scale and a pilot-scale experience still needs to be investigated and eventually, it will be necessary to progress

from a batch process to a continuous process. Elliott et al. [99] pointed out the limitation of a continuous process for the liquefaction of biomass. The case of issues of design and performance of reactors has been identified by Tran et al. [100,101], who suggested the use of plug flow reactors for more research. In addition, Fernandes et al. [102] proposed an integrated gasification and liquefaction system for hydrogen production and presented an exergy analysis to economize the process. The main challenge for its commercialization is the cost of a process that is very rarely studied. The economic and environmental feasibility needs to be assessed in terms of techno-economic analysis and a life cycle assessment.

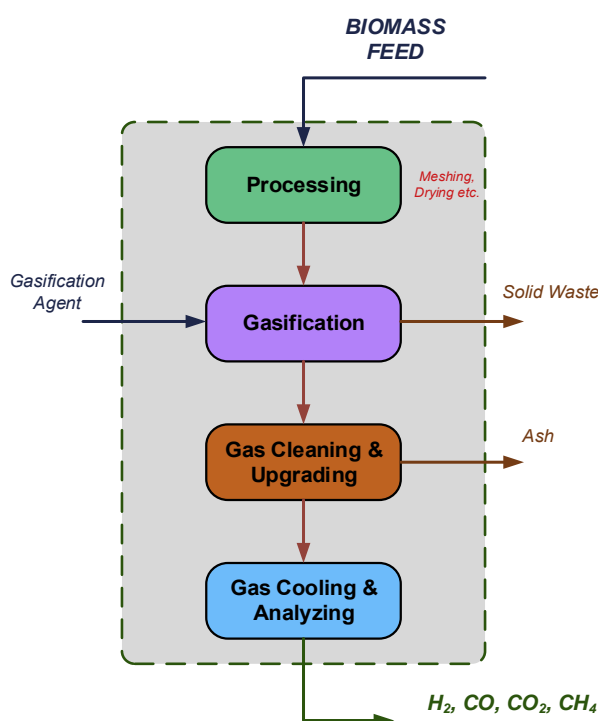
### Biomass gasification

Gasification is a thermochemical process, which converts biomass into gaseous fuels at elevated temperatures, and may occur both in the presence or absence of a catalyst [111]. In this process, the energy contained in the biomass is not directly released but converted into bond energies of lighter fuels rather than into the sensible heat of combustion products. Fossil or non-fossil carbonaceous materials are heated at high temperatures (almost 700 °C or above) in the presence of steam/air/O<sub>2</sub> or combination of those known as gasifying agents. The resulting product is comprised of a mixture of H<sub>2</sub>, CO, and CO<sub>2</sub> gases and more commonly known as syngas and some solid product known as char [42,112]. The process flow of gasification is shown in Fig. 3. The product gas obtained can be either used as a fuel directly or it may be converted into other fuels and chemicals such as methane, methanol, ethanol, dimethyl ether and diesel [2,113]. Hydrogen can be separated from the product gas [114]. The general conversion process can be expressed by the following equations [112,115,116]:



The reactions that take place during the gasification process are given in Table 4 [26,117,118].

In liquefaction, the moisture contents of biomass limit the process effectiveness, however, in gasification the moisture contents are also critical it also should be less than 35%, as highlighted by Demirbas et al. [115]. Other important issues related to biomass gasification are discussed below.



**Fig. 3 – Biomass gasification route for hydrogen production.**

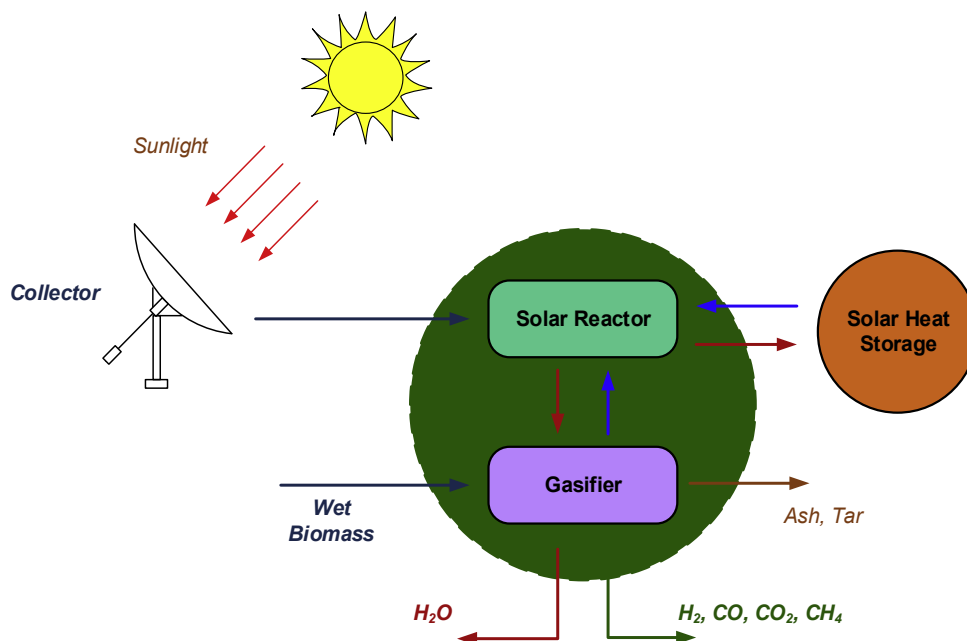


Fig. 4 – Solar gasification route for hydrogen production.

#### Tar formation

Hydrogen production through steam gasification is effected by tar production [115]. Tar is a mixture of higher hydrocarbons produced during the gasification process [116]. Tar, produced along with synthetic gas during gasification of biomass, cannot be easily separated via physical methods proposed for dust removal. Therefore, the removal of tar seems necessitated both for the reasons of qualitative hydrogen production and process economics [115]. The most frequently employed parameters for this purpose are listed below [119,120].

- (i) engineered design of the gasifier [121,122];
- (ii) suitable process control and/or operation [123,124];
- (iii) additives/catalysts [125,126].

Besides operating parameters, i.e., temperature and residence time, gasifying agents have a significant role in the formation and decomposition of tar which needs to be

optimized. Operating temperaturea of about 1273 °C could enhance thermal cracking of produced tar [120,127] and the utilization of a catalyst and other additives could reduce the tar formation, improve the efficiency of the process and the quality of the product as well [127]. The catalyst positively impacts the process through enhanced cracking of higher hydrocarbons into lighter ones as well as augmenting the hydrogen yield via enhancing the water gas - shift reaction [128]. Dolomite, the source of CaO, has been used for tar reduction, as reported by many researchers, to increase the hydrogen yield in the gasification process [119,129]. Abu et al. [115] have discussed nine groups of catalysts both synthesized and mineral types for tar reduction. The use of catalysts is not only good for tar reduction as well as enhancing the yield of H<sub>2</sub> but it has some issues in terms of cost and regeneration that should be addressed to enhance the hydrogen yield through the gasification process. Mazumder et al. [130] discussed the operating conditions and aspects of tar reduction in the gasification process to enhance the yield of hydrogen. It can be concluded that tar reduction appears to be the main challenge that needs to be addressed not only at the laboratory scale but

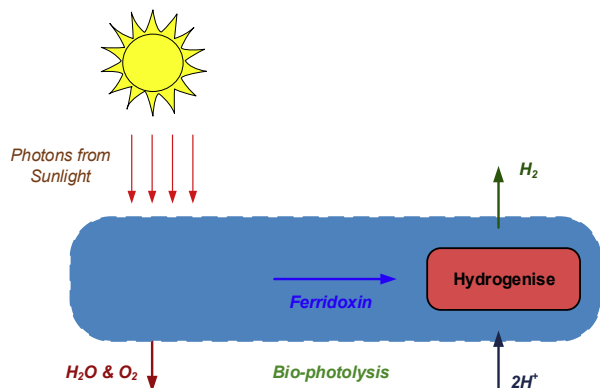


Fig. 5 – Direct bio-photolysis route for hydrogen production.

Table 4 – Reactions present in biomass gasification [26,117,118].

Name	Chemical Reactions
Combustion reaction	$C + O_2 \rightarrow CO_2$ $C + 1/2O_2 \rightarrow CO$
Boudouard reaction	$C + CO_2 \leftrightarrow 2CO$
water-gas reaction	$C + H_2O \leftrightarrow CO + H_2$ $CO + H_2O \leftrightarrow CO_2 + H_2$
Reforming reaction	$CH_4 + H_2O \leftrightarrow CO + 3H_2$ $CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$
Tar reforming reaction	$C_nH_m + nH_2O \leftrightarrow (n + (m/2))H_2 + nCO$ $C_nH_m + nCO_2 \leftrightarrow (m/2)H_2 + 2nCO$

also during testing at the pilot-scale. Many researchers have reviewed the work leading to a reduction in the tar content using catalysts [131,132] and other mechanical and thermal methods both experimental and modeling [133–136]. Although much R&D has been undertaken in tar reduction, there is still a gap in simulation modeling that needs to be addressed for a general tar reduction model for biomass instead of a specific component model.

### Catalytic steam gasification

Catalytic steam reforming of the intermediate volatiles formed is carried out either by fractionation of pyrolysis bio-oil or biomass gasification that enhanced the hydrogen yield [130]. Catalysts are very important to enhance the hydrogen yield by accelerating the water gas shift reaction, steam reforming reaction [132]. Two groups of catalysts are mainly used for biomass gasification [131,137,138], which are categorized based upon their function. These categories are (i) pre-catalyze the raw biomass termed as group-1 catalysts (ii) post-catalyze the gases produces as a result of gasification classified as group-2 catalysts [139].

#### Group-1

These catalysts are better known as the primary catalysts [140] and are typically added directly to the raw biomass before gasification either through wet impregnation or via dry mixing with biomass. The primary purpose of these catalysts is to reduce the tar content, however, these have little effect on the conversion of tar into lighter gases [141]. Group 1 catalysts aid the gasification reaction and enhance the yield of the product and operate under the same condition as the gasifier [142–144]. Three types of primary catalysts have been commonly used in gasification processes. Shahbaz et al. [132] have reviewed the effect of catalysts in the gasification process for hydrogen yield and tar reduction. Dolomite and alkali metal have been reported as primary catalysts [145]. In this context, dolomite ( $\text{MgCO}_3 \cdot \text{CaCO}_3$ ) is used in the gasifier for the reasons that it is cheap, easy to dispose of and reduces the tar content significantly [125]. Orto et al. [146] have also reported different dolomite catalysts with variations of  $\text{Fe}_2\text{O}_3$  in the steam reforming of wood in a catalytic reactor at 805–850 °C. A few other works on dolomite catalyst are also available in the literature [146–150]. Dolomite is a very useful catalyst as it provides aid for improving the hydrogen yield as well as reducing  $\text{CO}_2$  through the carbonation reaction [151–153]. The removal of  $\text{CO}_2$  is directly related to the cost of gasification process. In this regard, Khan et al. [154] used in-situ removal of  $\text{CO}_2$  with the help of a dolomite catalyst for the steam gasification of palm kernel shell and obtained 82 vol% hydrogen with significant reduction of  $\text{CO}_2$  [144,155,156]. Therefore, dolomite has emerged as a popular in-situ catalyst. Many experimental and modeling studies were made to investigate dolomite (catalyst) effect on the gasification process for hydrogen production [142,157]. Inayat et al. [158] made the mathematical model for the steam gasification of empty fruit bunches (EFB) using  $\text{CaO}$  which resulted in 76 vol% of hydrogen production [159,160]. Additionally, alkali metals have a positive contribution to tar reduction, and the quality

and quantity of the product yields [161,162]. In some cases, its recovery is difficult and may multiply the operational cost. The challenges associated with the use of catalysts have also been pointed out by many researchers [115,148,163–165]. Each type of catalyst has some pros and cons associated with it, among which the regeneration and the cost of catalysts are of the utmost importance [140]. Coal bottom ash is a waste product of the power generating industry. Its typical characterization reveals that it contains reasonable amounts of alkaline metals as well as  $\text{CaO}$  and may serve as a catalyst [137,166,167]. The use of bottom ash in gasification has demonstrated very prominent results in terms of hydrogen production, i.e., 79 vol% and might be considered as a cheap catalyst for the gasification process [143,168,169].

The plant biomass contains a certain amount of ash which consists of Mg, Ca, and K [170,171]. According to thermodynamic principles, the ash formed a liquid solution with the molten salt known as the melted salt, which did not reduce the tar formation [170,172]. The molten salt directly affected the kinetics of the reaction and enhanced the reactivity of reactions from the conversion of biomass into gaseous products [173]. Brandon et al. [170] performed the steam gasification of switchgrass cellulose using the molten salt of Li, K, and Na and a 25% increase in syngas was observed and a 77% decrease in tar formation, which is due to an increase in the reactivity of reactions and was confirmed by the 49% increase in the reactivity index. Kirtania et al. [174] investigated the kinetics of different alkaline salts in the catalytic gasification of char and reported the effect on reaction rates of different alkali salt types and loading. Jin et al. [175] reported the increase in 16.2 vol% of  $\text{H}_2$  using the molten salts of Li, Na, and K carbonated in the steam gasification of biomass due to the excellent heat and mass transfer. Many researchers have shown the effective use of molten salt for hydrogen production in biomass gasification [176–178]. Franginei et al. [171] reviewed the application of molten salt in the biomass gasification process.

#### Group-2

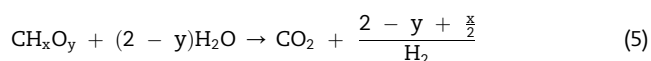
These catalysts, also known as secondary catalysts, which are placed in reactors situated after the gasification reactors [179]. These catalyze the reforming reactions and also enhance the energy quality of the final product [180]. The reactors, which engage these catalysts, are independent of the type of gasifier and may have the same or even different operating conditions. Transition metals are frequently used as secondary catalysts in secondary reformers [181]. A lot of research has been done on these metals since it has been an area of concern for many years [75]. Nickel is a widely used metal in the gasification industry and it plays an important role in reducing tar content, at the same time it reforms the methane in the product gas. At temperatures higher than 750 °C,  $\text{H}_2$  and  $\text{CO}$  contents increase quite significantly [182–184]. Ni is one of the commercial catalysts used for hydrogen production however it has limitations in terms of its sintering potential [185]. To avoid this problem many other metals with Ni are used for its productive usage [140]. The metals such as Rh [141,142], Fe [143], Pt [144], dolomite [145,146], Mg [130,148], Al [147,149], and Zn [150] are used with Ni to overcome this issue and further enhance the hydrogen contents in the product gas.

### Supercritical water gasification

The supercritical water gasification of biomass is one of the most widely used and commercially exploited techniques for hydrogen production from biomass. Water has been used as a gasifying medium due to the reasons that it is abundantly and easily available, non-toxic, inexpensive, and environmentally friendly. It has an important advantage in that, the feed to be used does not require any pre-drying, therefore it saves time as well as energy and cost [186]. Sewage sludge, sea algae, waste vegetables, and fruits can be gasified using this process. The products of gasification in this type have a high molar fraction of hydrogen which makes it easier to be separated from other gases. The production of char and tar is very low, however, these may have the problem of plugging in the apparatus. This problematic issue can be reduced by the efficient use of catalysts. Corrosion of reactor walls due to the formation of hydrogen peroxide is a major issue in this technique and much less information is available regarding this issue [153]. This process was also discussed by Modell et al. [151] in a patent released in 1978 for the gasification of glucose and the sawdust of the maple tree. Gasafi et al. [152] studied and found that sewage sludge may be a potential market for supercritical water gasification and might have a bright future [152]. Supercritical water is used as a gasifying agent in this technique, as the critical point of water is at 374 °C temperature and 22.1 MPa pressure. Under these conditions, there is no distinction between water and steam and only a single phase exists, which is better known as supercritical water [153,155]. Reactors used for these processes have been operated at different conditions. An example is the continuously operating tubular flow reactor that operates at 700 °C and pressures up to 35 MPa [31]. There are two methods for the supercritical gasification of biomass [156], as described below.

#### Non-Catalytic supercritical water gasification (NCSCWG)

Non-catalytic supercritical water gasification (NCSCWG) is also called the high-temperature supercritical gasification or steam-only gasification process because the temperature for this process ranges from 500 to 750 °C [157]. It has been shown that the amount of hydrogen is governed by two parameters namely reaction temperature and steam to carbon ratio. The hydrogen fraction increases with reaction temperature up to 900 °C [159,160]. Some authors have observed that the fraction of hydrogen decreases as the temperature exceeds 1100 °C [161]. The overall reaction is provided by Guo et al. and is given in Eq. (5) [187].



This reaction is divided into two steps [162]. The first is steam reforming while the second is the water-gas shift reaction. The advantage of this method is that these two reactions are carried out in a single reactor. The previous researchers demonstrated in their studies that the water-gas shift reaction is necessary only for steam gasification [164,165]. Supercritical water gasification is a very important hydrogen production technique, but a lot of improvement is needed in this field to make it viable for future applications. Suzuki et al. [181] has shown from their studies that one of the

important factors affecting the efficiency of the process is the recovery of the process water and the reactivity of steam that is less than that of air/oxygen. For this type of gasification, a fluidized bed gasifier is preferred because in fluidized bed gasifier, moving particles assist in homogenizing the temperature of the gasifier by shifting heat from char combustion to an endothermic gasification reaction [166]. Djesus et al. [168] studied the effect of particle size and his investigation explained the effect of particle size on the efficiency of the process. It was observed that a decrease in feed particle size increases hydrogen yield, which also results in efficient heat and mass transfer due to increased reactive surface area. In future, this technology could be more attractive and promising, if it is integrated with solar energy to achieve the supercritical conditions of water [169].

#### Catalytic supercritical water gasification (CSCWG)

Catalytic Supercritical Water Gasification (CSCWG) is also known as low-temperature catalytic gasification due to its low temperature operating ranges, i.e., 350–600 °C. The catalyst along with reduced reaction temperature also reduces the formation of char and tar. Resende et al. [188] studied and presented the result for the use of metal catalysts for the supercritical water gasification of cellulose and lignin. Laboratory scale experiments have been conducted by several researchers which laid the foundation for implementation of the concept on pilot and commercial scales. The first pilot plant for CSCWG was established by Jesus et al. and Rauzan et al. [168,169] in San Diego at the General Atomics facility to explore the earlier results of laboratory-scale experiments. It was found that the yield of hydrogen was comparable with the results of laboratory experiments as 10 g of hydrogen per 100 g of feed was produced [43]. The catalysts are very useful in the water gasification process that enhances hydrogen production [189,190]. Watanabe et al. [191] found that the amount of hydrogen produced in the case of catalytic supercritical water gasification was doubled when compared with non-catalytic supercritical gasification. Park et al. [192] used RuO<sub>2</sub> for aromatic compounds. It was concluded from this investigation that RuO<sub>2</sub> provided all the activity mechanism for the K<sub>2</sub>CO<sub>3</sub> catalyst. In the gasification of cellulose in catalytic supercritical water gasification, K<sub>2</sub>CO<sub>3</sub> was more active than Ca(OH)<sub>2</sub> but did not capture CO<sub>2</sub> [193]. Metallic nickel catalysts have been used for many years for the conventional gasification of fossil fuels and are still used for biomass catalytic supercritical gasification [137]. The cost of hydrogen production is very important for the development of a technology; a very comprehensive study was made by considering all parameters and the cost of hydrogen was 3.4 \$/kg for the hydrogasification of biomass wastes [194]. Zhang et al. [195] documented the literature about the exergy efficiencies of the SCWG process and reported values in the range of 0.04–42.05%. Table 5 summarizes the hydrogen production from supercritical gasification process for numerous biomass types.

#### Solar biomass gasification

In this process, biomass is milled and dried to remove moisture contents. After drying it is placed in a high-temperature reactor at the temperature about 700–750 °C [196,197]. The



**Table 5 – Hydrogen production through supercritical biomass gasification from different biomass.**

Feed	Catalyst	Reactor type and conditions	Hydrogen yield	References
Glucose	Ni/activated charcoal	Packed-bed reactor, 28 MPa, 650 °C	15.6 mmol/g	[103]
Olive mill wastewater	–	Coiled tubular reactor, 25 MPa, 600 °C	10.79 mol%	[104]
Switchgrass biocrude	Ni/ZrO <sub>2</sub>	Packed-bed reactor, 600 °C, 25 MPa	81.67 mol/g carbon reacted	[105]
Bark	Ni/hydrotalcite	Batch reactor, 380 °C, 23 MPa	2.05 mmol/g	[106]
Sewage sludge	KOH	Fluidized bed reactor, 540 °C, 30 MPa	15.49 mmol/g	[107]
Maize silage hydrochar	K <sub>2</sub> CO <sub>3</sub>	Micro-autoclaves, 400 °C, 30 MPa	8.9 mol%	[94]
Coconut shell	K <sub>2</sub> CO <sub>3</sub>	Tubular batch reactor, 600 °C, 23–25 MPa	4.8 mmol/g	[93]
Fruit pulp	RU/activated charcoal	Batch reactor, 600 °C, 25 MPa	54.8 mmol/g	[95]
Microalgae ( <i>Cenedesmus quadricauda</i> )	Nickel/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	Batch reactor, 385 °C, 26 MPa.	4 mmol/g	[108]
Microalgae <i>Enteromorpha intestinalis</i>	Fe–Ni–Ru/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Batch microreactor, 440 °C, 25 MPa	12.28 mmol/g	[109]
Sewage sludge	–	Continuous reactor, 600 °C, 25 MPa	40 vol%	[110]

molecules of the biomass are broken in the reactor and synthesis gas is produced that is integrated with the char combustor. The gas consists of a mixture of H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, and some other molecules. Peter et al. [44] reviewed the advantages and disadvantages of solar gasification with all aspects such as yield, type of process, and process parameters. Exhaust gas coming out of the char combustor is used to dry the biomass. The exhaust gas coming from the char combustor and superheated steam coming from the combustor, in which methane and carbon monoxide are burnt, is recycled through the gasification chamber. As a result, the synthesis gas is produced in the gasification chamber having a temperature around 800 °C which is cooled in the heat exchanger with the saturated steam coming out from the solar field. The saturated steam is heated to a temperature of 700 °C [169]. The synthesis gas is cleaned in the water scrubber and hydrogen is separated from the CO<sub>2</sub> in the separator. Other gases like carbon monoxide and methane are introduced to the combustor from the separating chamber, where they are burnt to raise the temperature of steam from 700 °C to 800 °C, which is used for fluidization purposes of the gasification bed [198]. In this way, steam is recycled throughout the process. Saturated steam is produced in the solar thermal field and then with the help of heat exchangers, it is superheated for heat integration and optimization. A feasibility study of this process was carried out by Antal et al. [199]. The high reaction temperature for promoting a high hydrogen yield is the main concern of this technology due to the extensive energy required for process initiation. To meet this challenge many researchers intended to utilize solar energy to attain the reaction temperature. Shahbazov et al. and Midilli et al. [200,201] used parabolic mirror reflectors for agriculture waste biomass to increase the yield of hydrogen. Solar gasification is emerging as an alternative source of conventional gasification to utilize the solar heat that has the potential to reduce the overall cost of the process. The main challenge in this field is to use the solar field area, storage capacity to attain a high temperature inside the reactor [202]. The combustion looping process with gasification is effective for hydrogen production through gasification and combustion which resulted in a cost reduction for the process [203,204]. The continuous driven solar reactor system was investigated, which increased the carbon conversion rate into gaseous

products about 74% and 70 mmol/g biomass was obtained [205]. Many modeling processes have been developed to study and encourage the utilization of solar heat for biomass gasification, such as the irradiated fluidized bed [206] and hybrid solar/autothermal operation [207], that enhances hydrogen enriched syngas production [208,209]. Hydrogen production from solar gasification has been studied by different researchers and a summary of the achievements is given in Table 6. Solar gasification is an important alternative that should be utilized in warm and hot countries to save the heating duty required during the gasification process to make it comparable to H<sub>2</sub> obtained through fossil fuel gasification.

### Non-thermal/biological methods

Hydrogen production from biological conversion of biomass is another important element of future bio-refinery systems. The production of hydrogen using biological methods was discussed by Levin et al. [212] and it gained prominence in the mid of 1970's when the oil crises shook the world economy. During that decade, many biological processes were developed and employed for hydrogen production. These processes are able to produce the hydrogen to meet the increasing demand for hydrogen and numerous research studies have documented these results in many review articles for further research, challenges, and commercialization [213–215]. It has some distinction as compared to other processes due to the zero accumulation of CO<sub>2</sub> and a wide range of waste materials available for hydrogen production. Among other methods, it was considered to be less energy-intensive, as it is carried out at ambient pressure and temperature [216]. However, the biological route has limitations of low hydrogen production rate and low hydrogen yield. In this section, the biological route incorporating photolysis, fermentation, and the biological water-gas shift reaction has been discussed for further research.

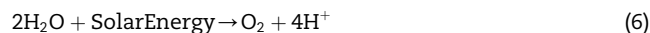
#### Direct bio-photolysis

In this process, a microalgae photosynthesis system converts the solar energy into chemical energy, which results in hydrogen production from biomass and this process involves a photo-autotrophic organism. Regularly, freshwater algae are

Table 6 – Hydrogen production through solar gasification from different biomass.

Feed	Light Source/Catalyst	Reactor type and conditions	Hydrogen yield	References
Glucose, corn meal, wheat stalk	Solar power/NaOH	Snake like tubular reactor, 500 °C, 24 MPa, DNI: 610 W/m <sup>2</sup> (Direct normal irradiation) Supercritical water gasification	11 mmol/g	[210]
Glucose, corn cob	Solar power/KOH	Spiral tube tubular reactor, 636 °C, 24 MPa, DNI (Direct normal irradiation): 571 W/m <sup>2</sup> Supercritical water gasification	27.1 mmol/g	[211]
Switchgrass biocrude	Ni/ZrO <sub>2</sub>	Packed-bed reactor, 600 °C, 25 MPa	81.67 mol/g carbon reacted	[105]
Bark	Ni/hydrotalcite	Batch reactor, 380 °C, 23 MPa	2.05 mmol/g	[106]
Sewage sludge	KOH	Fluidized bed reactor, 540 °C, 30 MPa	15.49 mmol/g	[107]
Maize silage hydrochar	K <sub>2</sub> CO <sub>3</sub>	Micro-autoclaves, 400 °C, 30 MPa	8.9 mol%	[94]
Coconut shell	K <sub>2</sub> CO <sub>3</sub>	Tubular batch reactor, 600 °C, 23–25 MPa	4.8 mmol/g	[93]
Fruit pulp	RU/activated charcoal	Batch reactor, 600 °C, 25 MPa	54.8 mmol/g	[95]
Microalgae (Cenedesmus quadricauda)	Nickel/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	Batch reactor, 385 °C, 26 MPa	4 mmol/g	[108]
Microalgae Enteromorpha intestinalis	Fe–Ni–Ru/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Batch microreactor, 440 °C, 25 MPa	12.28 mmol/g	[109]
Sewage sludge	–	Continuous reactor, 600 °C, 25 MPa	40 vol%	[110]
Microalgae	Solar heat by high flux simulator	Batch reactor, 905 °C	64 vol%	[208]

used in fermentation, while marine algae are utilized in seawater. This bio-system offers some advantages, such as no need for substrate and it is a CO<sub>2</sub> neutral system with the use of sunlight [45]. Therefore, direct bio-photolysis is considered as both a renewable and environmentally friendly process. Biological hydrogen production is carried out in two steps, in the first step, growth of the cell takes place and in the second step, hydrogen is evolved as shown in Fig. 5 [217]. Two photosynthetic systems are used in producing hydrogen when water is utilized as feed: photosystem-1 and photosystem-2. Photosystem-1 is used for CO<sub>2</sub> reduction while photosystem-2 is engaged to split water for O<sub>2</sub> liberation. Two photons are produced to form either CO<sub>2</sub> or H<sub>2</sub> in the presence of hydrogenase. The equations involved are provided below.



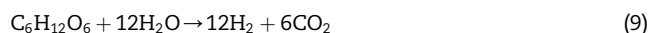
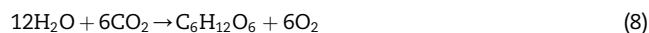
In this photosynthetic process, photosynthetic electrons reduce a proton to an atomic state and then molecular hydrogen. The oxygen produced in this process has some adverse impacts such as the hydrogen is poisoned and the photosynthetic system is disturbed, which is the major shortcoming of this process. To avoid these issues, oxygen-absorbing species, for instance, glucose oxidase, are used [218]. To address this issue, the electrochemical photoreactor for spirulina has been developed and hydrogen rate increase four times as well, and in another study, in order to solve the reduction of the increase in oxygen, four different reducing agents were used for the microalgae culture [219,220]. Many research studies have been reported to solve this problem [221,222], however, there has not been a commercial success due to the issues of limited production of hydrogen and low solar energy conversion efficiency. However, for hydrogen production, the employment of mutants can assist in overcoming the efficiency limitation, and efficiency has been increased significantly [223]. Benemann et al. [224] estimated the cost of direct bio-photolysis to produce hydrogen to be \$ 20/GJ, by assuming that the capital cost is about \$ 60/m<sup>2</sup> with a total solar conversion efficiency around 10%. In another report, the capital cost was proposed to be \$ 100/m<sup>2</sup> [225]. Despite these facts, this process has not yet been proved to be industrially economical, however, it has attracted the attention of researchers as it assists in understanding the basic concepts involved in the bio-hydrogen production process.

#### Indirect bio-photolysis

In this process, Cyanobacteria convert the biomass into hydrogen by coupling two stages of the biological processes namely photosynthesis and fermentation, in the presence of hydrogenase. The whole system results in environmental CO<sub>2</sub> fixation into carbohydrates and then their conversion into H<sub>2</sub> by the action of hydrogenase in darkness and sunlight as well. Solar energy is utilized for CO<sub>2</sub> fixation. For this purpose, the overall efficiency of solar light must be greater than 10% to compete with other processes [217,226]. A maximum of 16.3% conversion efficiency has been achieved until now [227]. Markov et al. [228] provided an estimate that requires light



intensities of 45–55  $\mu\text{mol}\cdot\text{m}^{-2}$  and 170–180  $\mu\text{mol}\cdot\text{m}^{-2}$ . This process is completed in a two-stage process as shown in Fig. 6 and mentioned in the following equations.



The first reaction is responsible for the fixation of environmental  $\text{CO}_2$  to glucose while the later one for fermentation of glucose to  $\text{H}_2$ . Commonly used cyanobacteria are the species of *Oscillatoria*, *Anabaena* and *Calothrix* [229]. The photoproduction rate of hydrogen increases with light intensity and optimized yield were reported with light intensity of 12.5 ml  $\text{H}_2/\text{g (cdw)h}$  (cdw implies cell dry weight) and pH value ranging from 6.8 to 8.3. By increasing the temperature from 30 to 40  $^\circ\text{C}$ , the production of hydrogen is doubled. The estimated overall cost has reached up to 10\$/GJ of hydrogen [218]. Variation in cost depends on the technology used to produce hydrogen. This technology is still immature as the overall efficiency is as low as 1–2%. It is currently being investigated by many research groups [230], and outstanding research efforts seems necessitated to commercialize this technology for hydrogen production.

#### Photo-fermentation

In the photo-fermentation process, photosynthetic bacteria utilize the nitrogenous matter to convert biomass into hydrogen only and only if the sunlight is present. Photosynthetic bacteria donate electrons by undergoing an-oxygeno photosynthetic process with an organic acid or a reducing sulfur compound. The rate of  $\text{H}_2$  production increases with the intensity of light, while on the contrary, the light conversion efficiency decreases. The photosynthetic bacteria used in the photo-fermentation has a comparatively high light conversion efficiency to cyanobacteria, which is used in indirect bio-photolysis. Basak et al. [231] studied purple non-sulfur bacteria that are used in an oxygen-deficient environment in the presence of nitrogenase whereas an organic acid is used as the reducing agent for the production of hydrogen. There are certain shortcomings of this method, which are listed below:

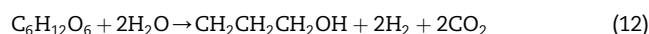
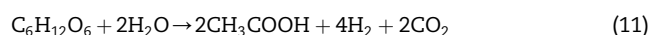
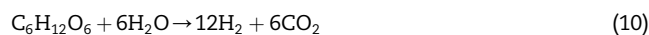
- The low conversion efficiency of solar energy (3–10%);
- Demand for anaerobic photo-bioreactors, which cover a large area;
- The use of nitrogenase enzymes requires high energy for their activation.

Nitrogenase activity plays a very important role in the production of hydrogen by photosynthetic bacteria. Hydrogenase is active under the same condition for hydrogen production and hydrogen uptake. The major benefit of this

process is that the high concentration of  $\text{H}_2$  in the product gas stream is significant; around 96% of  $\text{H}_2$  concentration was reported by Tao et al. [232]. Another advantage of this process is that the organic acid, used as a substrate, could be found in the effluent wastewaters of different industries. The effluent of dark fermentation can also be used as the substrate for photo-fermentation [233,234]. Different types of biomass wastes could also be employed for hydrogen production via this process [235]. The  $\text{H}_2$  production was found to be increased by 2–3 times using a sole carbon sources [236]. The bacteria system and the hydrogen conversion efficiency for different feedstocks have been provided by Fedorov et al. [237] and are shown in Table 7. The schematic for the photo-fermentation to produce hydrogen is provided in Fig. 7. There have been many research efforts reported in the literature for photosynthetic bacteria; however, the photo-fermentation process has never been identified as an economically viable method. Photo fermentation processes have some advantages such as large amount of feedstock and utilization of abundant heat available in the form of sunlight. The challenges which still need to be addressed include the lower volumetric flowrate of hydrogen, the conversion efficiency as well as wide surface area requirement.

#### Dark-fermentation

From the name of this type, it is evident that darkness is a key element in this process. For dark fermentation, anaerobic bacteria and micro-algae are used to produce hydrogen where the temperature is maintained in the range of 30  $^\circ\text{C}$ –80  $^\circ\text{C}$  [238]. The simple process flow diagram is given in Fig. 8 for biomass processing and its conversion to hydrogen. This process has some merits, such as its simplicity, a continuous hydrogen production rate, a low energy requirement, and the use of low grade or waste biomass [45,239]. Along with hydrogen and carbon dioxide, a few other gases are also produced which are dependent upon the type of biomass substrate. A large number of substrates i.e., glucose, sucrose starch, and cellulose and anaerobic fermentative bacteria i.e., thermophilic, mesophilic and facultative are available for utilization in this process as compared to the process of photo fermentation [45,46]. For glucose as a substrate, theoretically, 12 mol of hydrogen can be produced, as shown in Eq. (10). On the contrary, practically only a maximum of 4 mol of  $\text{H}_2$  are produced per mole of glucose because of acetic acid production, as demonstrated in Eqs. 10–12 [240].



**Table 7 – Bacteria system and hydrogen conversion efficiency for different feeds.**

Biomass type	Bacteria system	Hydrogen conversion efficiency
Lactic acid	Rhodobacter spheroids immobilized	86%
Lactate feedstock	Rhodobacter capsulatus	30%
Wastewater	Rhodobacter spheroids immobilized	53%

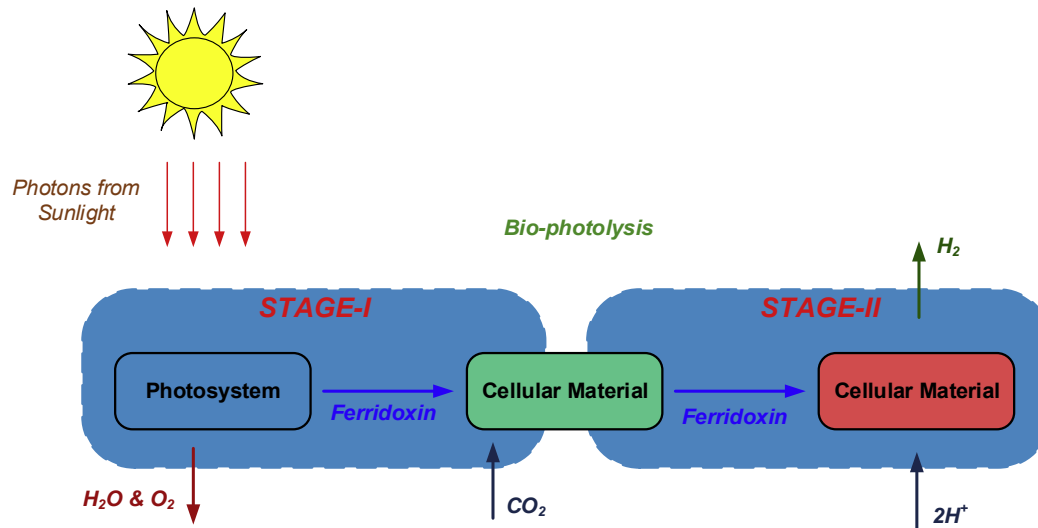


Fig. 6 – Indirect bio-photolysis route for hydrogen production.

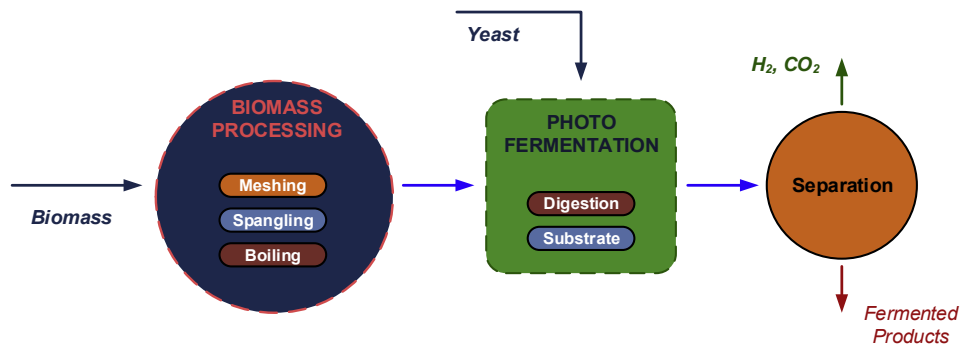


Fig. 7 – Hydrogen production mechanism through photo-fermentation.

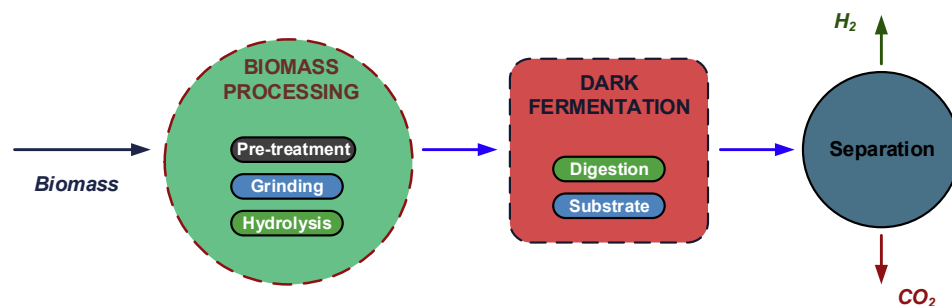


Fig. 8 – Hydrogen production mechanism through dark fermentation.

Production of H<sub>2</sub> depends on the hydraulic retention time, pH value and partial pressure of gas. The pH value is a crucial parameter and must be controlled carefully; ranging between 5 and 6 [241]. Dark fermentation has some drawbacks, such as low yield and less energy efficient, longer residence time and production of byproducts. All these factors considerably influence the overall cost of the process [45]. Attention should also be paid to the hydraulic retention time, which also plays an important role in the production of hydrogen [240]. A hydraulic retention time of 0.5 day is optimal in the dark fermentation of wastewater. Hydrogen production decreases

with an increase in reaction time. Two types of reactors have been studied for this process, the continuous stirred tank reactor (CSTR) and the upflow anaerobic sludge blanket reactor (UASBR). Under the same condition, the yield from a UASBR is higher than that of the CSTR using a comparatively low retention time [242,243]. Although the yield for the hydrogen production from this process is high compared to other processes, however, the product gases have a low concentration of hydrogen (40–46%) [235]. Due to this reason, the purification of the product seems necessary to improve the concentration of hydrogen before it can be used in a fuel cell.

**Table 8 – Summary of hydrogen yield with dark and photo-fermentation process.**

Fermentation process	Reactor	bacterial strain	Substrate	Process condition	Hydrogen yield	References
Dark	CSTR	Microbial consortium/digester	Tofu waste (Glucose)	HRT 4, pH 5.5, 110 °C	12.01 H <sub>2</sub> L/day	[250]
Dark & photo	Batch	Clostridium butyricum (C. butyricum)	Grounded wheat (Glucose)	pH 7.0 ± 0.002, 35 °C	1.59 mol H <sub>2</sub> /mol glucose, 4.16 molH <sub>2</sub> /mol glucose	[251]
Dark	CSTR	sorghum extract.	Sorghum bicolor L. Moench (glucose)	HRT 12, pH 4.7, 35 °C	0.93 ± 0.03 mol H <sub>2</sub> /mol glucose, 3.50 H <sub>2</sub> L/day	[252]
Dark & photo	Batch	Clostridium species, (anaerobic), Rhodopseudomonas palustris species	Cassava starch	pH 6.3, 31.3 °C,	351 ml H <sub>2</sub> /g starch, 489 ml H <sub>2</sub> /g starch	[253]
Dark	Batch	Silage grass based Ruminobacillus xylanolyticum, Acetanaerobacterium, Ongatum	Silage grass	pH 7, 35 °C	37.8 ml H <sub>2</sub> /g silage	[254]
Dark	Batch	Rhodobacter sphaeroides-RV	Grounded wheat (Glucose)	HRT 17 h, pH 6.3, 37 °C	4.55 mol H <sub>2</sub> /mol glucose	[255]
Photo	Tubular bio reactor	bacterium, Rhodobacter capsulatus	Acetate	pH, 10–35 °C	0.6 mol H <sub>2</sub> /mol acetate	[256]
Dark	Batch	Bacterial hydrolysis seed microorganism	Dry grass (Glucose)	pH 7, 37 °C	72.21 mL/g-dry grass	[257]
Photo	Tubular reactor	(Rhodospirillum rubrum, Rhodobacter sphaeroides	Corn stove	pH 4.9, 30 °C	211.9 mL/L-material	[258]
Photo	CSTR	bacteria HAU-M1w	Corn stove	pH 5.4, 30 °C	58.73 mL/g	[259]
Dark	Bio-chemical reactor	Enterobacter aerogenes	Humulus scandens	pH 6.59, 35 °C	64.08 mL H <sub>2</sub> /g	[260]
Dark	CSTR	Seacoast sludge	Sucrose	pH 5.5–6, 35 °C	120 mol/m <sup>3</sup> -d	[249]

**Table 9 – Comparison of separation technologies.**

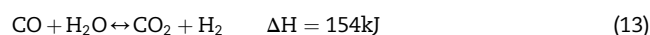
Separation technologies	Advantages	Dis advantages	References
Pressure swing adsorption (PSA)	<ul style="list-style-type: none"> <li>• Very effective separation is &gt;99.99% in part per million</li> <li>• Useful at small and large scale, commercially available</li> </ul>	<ul style="list-style-type: none"> <li>• The 20% produced hydrogen lost during the separation</li> <li>• Very high-cost process about 50% of the total H<sub>2</sub> production process.</li> <li>• Energy-intensive process</li> </ul>	[275–279]
Temperature swing adsorption (TSA)	<ul style="list-style-type: none"> <li>• Useful at a higher temperature</li> <li>• Commercially available</li> </ul>	<ul style="list-style-type: none"> <li>• Dilution of the separated gas</li> </ul>	[280–283]
Electric Swing adsorption	<ul style="list-style-type: none"> <li>• Energy-efficient than TSA</li> <li>• An improved form of TSA</li> </ul>	<ul style="list-style-type: none"> <li>• Energy and cost-intensive process</li> <li>• Dilution of separated gas</li> </ul>	[281,284]
Cryogenic separation technologies	<ul style="list-style-type: none"> <li>• Suitable for large scale</li> <li>• Work at high pressure on</li> </ul>	<ul style="list-style-type: none"> <li>• Intensive energy and cost process</li> <li>• Purity is less than 99%</li> <li>• Required many equipment's and costly process</li> </ul>	[285–288]
Amine based separation	<ul style="list-style-type: none"> <li>• Old and commercialize the technology.</li> <li>• Available technology for separation.</li> </ul>	<ul style="list-style-type: none"> <li>• Suitable for only large scale</li> <li>• Corrosive and harmful,</li> <li>• Affected by the SO<sub>x</sub> and NO<sub>x</sub> in flue gases,</li> <li>• Loss of amine solution due to volatility, Degradation issues</li> </ul>	[289,290]
Membrane separation	<ul style="list-style-type: none"> <li>• Low cost, lightweight, simple and easy operation. Less maintenance and operation</li> <li>• less energy-intensive, less carbon footprint, and environment issue</li> <li>• No problem for scale-up, effective in every system</li> </ul>	<ul style="list-style-type: none"> <li>• Still not able to industrial level due to permeability level is still less than 100 barrer</li> </ul>	[288,291–293]

Bélafi-Bakó et al. [244] reported that by using a two-stage gas membrane separation system 73% H<sub>2</sub> concentration can be achieved in the biogas. Balachandar et al. [245] successfully scaled up the dark-fermentation process from bench to pilot scale and observed a 1.2 times increase in H<sub>2</sub> production with a good energy gain 4.6 kJ g<sup>-1</sup> COD, which is good news for its technological development. This process has certain advantages, as solar energy is not required, land requirements are low and the weather conditions do not affect the process. Recently, a study utilized the corn stove for hydrogen production through the following processes: photo fermentation, dark fermentation and dark photo co-fermentation and reported the H<sub>2</sub> production as 141.2, 36.02, and 90.13 mL H<sub>2</sub>/g respectively [246]. Recently, many pilot scale studies in the range of 380–3000 L reactor size for commercialization have

been performed [247–249]. Table 8 summarizes some important reported research work in terms of hydrogen yield through dark and photo-fermentation. In the case of hydrogen production, dark fermentation has some advantages such as higher production rates, ease in operation, bearable cost due to no need of light for fermentation, but the main changes are still questionable such as higher content of by-products, a large amount of CO<sub>2</sub> and electricity requirement is high [41].

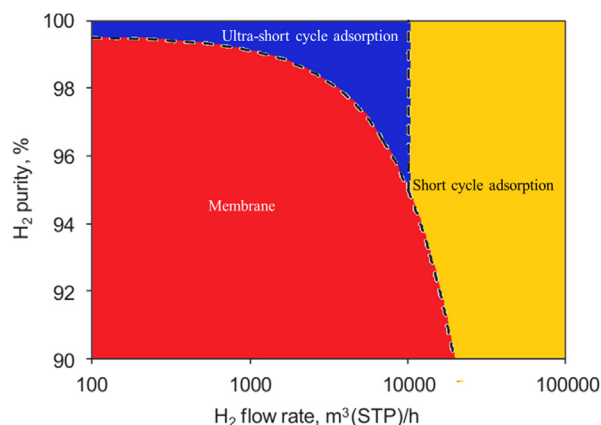
#### Biological water–gas shift reaction

Biological water gas shift reaction based technology is developed for hydrogen production using some photo-heterotrophic bacteria like *Rhodospirillum rubrum* feedstock or *Rubrivivax gelatinosus*, which is non-sulfur, purple photosynthetic bacteria, and can perform the water-gas shift reaction at 25 °C and 4 atm [261]. These bacteria do not require light and use CO as a raw carbon source to reduce the H<sup>+</sup> ion, hence producing H<sub>2</sub>.

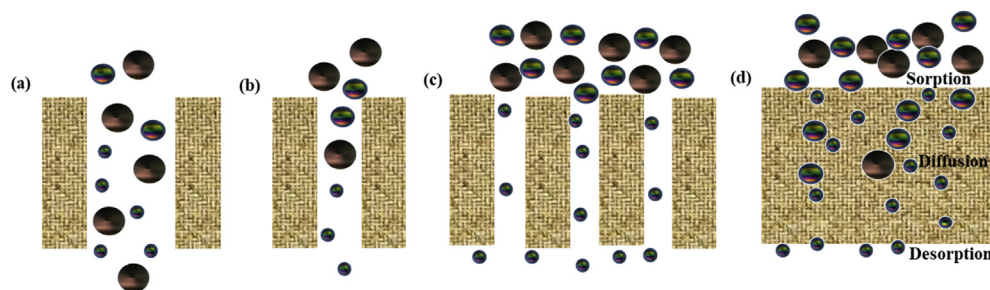


In this process, the main products are CO<sub>2</sub> and H<sub>2</sub>, hence it favors the production of hydrogen. Currently, this process is reported at laboratory scale for which only research works are available so far. The challenge of this study was to identify the suitable microorganisms for high CO uptake and to estimate high rate of production. Non-sulfur purple bacteria have the ability to perform the bacterial reaction in darkness and convert up to 100% of the CO based on the stoichiometric value. For this process industrial effluents are used as the substrate.

A higher rate of hydrogen production has been observed compared to other process. The literature reports that 96 mmol H<sub>2</sub> L<sup>-1</sup> h<sup>-1</sup> has been produced by the biological water-



**Fig. 9 – Technological zones for hydrogen purification processes. Modified from Ref. [271]. Copyright 2015 Elsevier.**



**Fig. 10 – Gas separation mechanisms through porous and dense membranes; (a) Convective flow, (b) Knudsen diffusion, (c) Molecular sieving, (d) Solution-diffusion.**

gas shift reaction, which was considerably high compared to 20–50 mmol  $\text{H}_2 \text{ L}^{-1}\text{h}^{-1}$  obtained via anaerobic fermentation process [29]. It was reported that this reaction could be economically viable, if the methane concentration is below 3%. The cost of hydrogen production from this process ranges from 1.75 to 2.25 \$/kg when the concentration of methane is between 1 and 10% [262]. In another report, 3.4\$/kg was estimated as the cost of hydrogen production for this process. This cost of hydrogen production is comparatively much less than that for other biological processes (12–20 \$/kg) [19]. The cost of the biological water-gas shift process is lower as compared to thermochemical water-gas shift process for the reason that fewer equipment items are involved. Due to the low cost of hydrogen production, this process has become an area of interest of several researchers [263–265].

### Implementation of membrane for biomass-based hydrogen separation

Membrane, absorption, adsorption such as pressure swing adsorption (PSA), temperature swing adsorption (TSA), electrical swing adsorption (ESA) and cryogenic technologies are often used at an industrial scale for the separation and purification of hydrogen produced from biomass [266–269]. Although the above-mentioned technologies are commercialized, but they are facing many issues of cost and energy-intensive performance. Membrane separation is a very good, important and emerging technology, successfully tested at laboratory and pilot scale and has the potential for commercialization. Table 9 provides the pros and cons of different  $\text{H}_2$  separation technologies. Membranes, ultra-short cycle adsorption, and short cycle adsorption are less energy intensive processes and technological zones for optimal target purity of product and installed productivity are established for

these, depicted in Fig. 9. Membrane technology for  $\text{H}_2$  recovery and purification provides a broad range opportunity in comparison to the other ones as shown in Fig. 9. Membrane technology occupies a particular place because energy is not required for phase transitions. Among all available technologies for hydrogen recovery in biomass processing, membrane separation has unique opportunities such as reduced energy consumption, small footprint, simplicity and continuity of operation, improved efficiency and low cost. In particular, a combination of a membrane separation process and a catalytic reactor would result in enhanced shifted reaction equilibrium, concentrated products and higher conversion [270]. The first flat sheet membrane to separate gases was developed at industrial scale in 1977 in Russia and membrane technology for  $\text{H}_2$  separation and recovery was introduced in the market in 1980 for the first time [271]. In recent years, more than 500 patents are covered on hydrogen selective membranes and syntheses of polymeric membranes are dedicated with more than 50% patents. The non-porous inorganic membranes covered around 25% patents and also about 25% patents are dedicated to porous inorganic membranes [272–274].

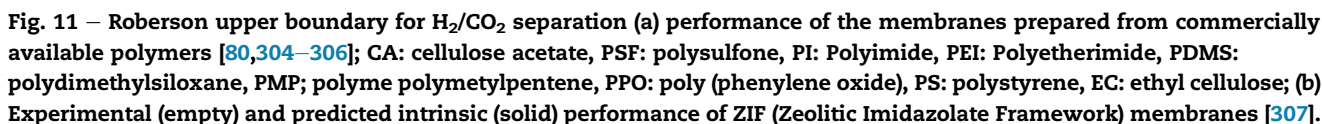
### Theoretical background

A membrane is a selective barrier that is dependent on the selective permeation of hydrogen from mixed gases and the selectivity depends on the membrane properties. The typical driving force for the permeation is the  $\text{H}_2$  partial pressure in the feed stream, which is balanced by the permeate's side  $\text{H}_2$  partial pressure. The membranes, inorganic - manufactured from such materials as metallic or ceramic, and organic - such as polymer or carbon, are applied for hydrogen separation [294,295]. Generally, hydrogen separation, using membranes, is based on three mechanisms including Knudsen diffusion, molecular sieving and solution diffusion (Fig. 10). The gas

**Table 10 – Commercially available polymeric membranes and their selectivity.**

Polymer	Selectivity			
	$\text{H}_2/\text{CO}_2$	$\text{H}_2/\text{N}_2$	$\text{H}_2/\text{CO}$	$\text{H}_2/\text{CH}_4$
Cellulose acetate (Separex)	2.4	72–80	30–66	60–80
Polysulfone (Permea)	2.5	56–80	40–56	80
Polyaramide (Medal)		>200	100	>200
Tetrabromopolycarbonate (MG)	3.5	90	100–123	120
Polyimide (Ube)	3.8	88–200	50–125	100–200
Silicon rubber	0.2	22	0.69	0.8





Polymeric membranes for hydrogen separation from biomass processing can be divided into two types; the first one is the hydrogen-selective membranes, which are synthesized with polymers including ethylcellulose, polyetherimide, polyphenylene oxide, polysulfone, polystyrene, polyvinylidene fluoride, and polymethyl methacrylate; the second one is the hydrogen rejecting membranes comprising polymers such as poly trimethylsilyl propane, poly 4-methyl-2-pentyne, polyphosphazene, polyamide-6-b-ethylene oxide, polyethylene glycol diacrylate, crosslinked PEG copolymer, polyether, poly styrene-co-butadiene, polyethylene oxide-poly butylene terephthalate and poly dimethyl siloxane [303]. As shown in Fig. 11, Roberson upper boundary lines reveal the selectivity permeability trade-off limits for the hydrogen and carbon dioxide pair for the polymeric membranes and most membranes prepared from available commercial polymers are still far from the attractive region [304]. However, ZIF (Zeolitic Imidazolate Framework) membrane showed better separation performance of  $H_2/CO_2$ . Experimental (empty) and predicted intrinsic (solid) performance of ZIF membranes are



demonstrated in the Roberson upper boundary lines in Fig. 11. Recently, polyimide (PI) and polybenzimidazole (PBI) showed promising performance for hydrogen separation, because of better thermal and structural stabilities under harsh operating conditions [80,305]. However, there is still a need to develop new polymers and modify existing polymers to fulfill industrial needs in harsh conditions.

Recently, several strategies; such as polymer blending to form an integrated membrane, chemical crosslinking and mixed matrix membranes (MMMs) using organic polymers and inorganic fillers (zeolites, metal-organic frameworks, etc.); have been applied to achieve simultaneously higher permeability and selectivity [297]. Apart from several opportunities for hydrogen separation and purification using membranes in biomass processing, polymeric membranes have some limitations such as physical aging, plasticization as well as chemical and thermal stability could be a key bottleneck limiting the applications in biomass processing [306].

### Dense metal membranes

Dense metal membranes are prepared from the metals such as nickel, palladium and platinum and their metallic alloys. The higher hydrogen selectivity and production of ultra-pure hydrogen is the prominent advantage of these membranes. This feature is associated with the innate ability of metals and its alloys structure to permit selective diffusion of hydrogen while rejecting other gases [308–310]. Therefore, many dense metal membranes have been introduced at commercial scale to provide highly purified hydrogen. However, the permeability of hydrogen is relatively lower than that of other membranes because of the nonporous structure [310]. Among all dense metal membranes, palladium (Pd) based membranes have been extensively studied and were reported to have superior hydrogen solubility on the surface of the Pd at different temperatures, leading to excellent flux in comparison with other metal membranes. However, the high cost of Pd membranes restricted their economic practicality [310]. Various techniques to synthesis dense metal membranes have been used in literature, such as chemical vapor deposition (CVD), electroless plating (ELP) and physical vapor deposition (PVD). Research and industrial interest recently been emphasized to fabricate integrated supported metal membranes as well as a variety of porous substrates, such as glass, alumina and stainless steel, have also been considered [297]. However, the formation of the defect-free supported metal membrane is challenging due to the lack of compatibility between the supports and metal materials, particularly at high temperatures.

Although dense metal membranes provide a promising alternative to achieve high selectivity and purity of hydrogen, there are several issues in practical applications. The hydrogen embrittlement phenomenon and the poisoning of membranes due to chemical contaminants such as carbon monoxide, Sulfur, and hydrocarbons etc. are major limitations of the dense metal membranes particularly Pd membranes [308,310,311]. Among the metal elements, Copper (Cu) is considered to have the ability to resist contaminants poisoning and to suppress the phenomenon of hydrogen embrittlement. In addition, Cu could reduce the cost relative

to the cost of pure Pd membranes [312]. Recently, composite Pd-alloy membranes outperformed the single pure metal membranes and were also found to be suitable when applied in a large scale hydrogen purification plant during long-term operation [309].

## Research development and future direction

In this section, the research gaps, current challenges, and future research direction of biomass processing methods as well as for the separation of hydrogen using membranes are discussed.

### Research and development needs in biomass hydrogen separation using membranes

Membrane technology for the separation and purification of  $H_2$  derived from biomass processing has the potential to improve efficiency, manufacturing flexibility, robustness and reduce costs. The hydrogen separation membranes can produce ultra-high pure hydrogen for fuel cell applications. The practical feasibility required high hydrogen flux with low-pressure drop across the membranes, operation at higher temperature and tolerance to contaminants especially sulfur and carbon monoxide. Moreover, the principle is to improve the  $H_2$  selectivity along with maximizing its diffusivity for hydrogen-selective membranes. Therefore, the development of new materials for hydrogen separation membranes is needed. In addition, more robust membrane fabrication methods are also greatly needed to develop a more permeable and selective membrane with high mechanical strength. Current research works are focusing on the development of hydrogen separation membranes to employ under the operation conditions of biomass processing for hydrogen production to overcome the challenges lacking to practical feasibility such as inability to fabricate defect-free membranes at an industrial scale, catalyst or material failure due to thermal cycling and/or contaminants and the lack of suitable seals to apply under higher pressure.

### Research and development needs in biological and thermochemical conversion technologies

- Pyrolysis processes are mostly focused on bio-oil production. There is a challenge to make the pyrolysis process commercially viable for  $H_2$  production both at the laboratory and pilot-scale; more effort is required especially in the techno-economic analysis to show the cost of  $H_2$  while including the selling revenue of the char and bio-oil.
- Gasification is the most promising method for  $H_2$  production. But it also has some challenges to overcome in relation to the cost of  $H_2$  production as compared to fossil fuel  $H_2$ . There is a need to make more progress in developing a new type of gasification such as solar gasification, water gasification as well as achieving further improvements in process optimization and tar reduction. In addition, more LCA and techno-economic analysis are required with the integration of the power production process.

- Liquefaction is an emerging potential route for hydrogen production, but it is still at an initial stage. Many areas need to be explored, such as the reaction mechanism, thermal and kinetic behaviors, optimization of process parameters, design of reactors and most important economic –analysis.
- The H<sub>2</sub> yield is still very low from the photo and dark fermentation processes and is in the range of 4–8 mol H<sub>2</sub>/mol (biomass) [313]. The production cost is very high per kg H<sub>2</sub> is in the range 3.70–18.72 \$ [314]. In this regard, it is important to work on yield improvement as well as an improved design and operational cost reduction. In the case of commercialization, the production cost is the main obstacle for its scaling-up. Techno-economic and LCA should be made to compare the H<sub>2</sub> production cost with other methods [315].
- Hydrogen production from the photolysis method is a promising method but it is still at the laboratory scale due to its high cost. There is a big gap for the researcher to improve the process upscaling parameters specially the use of sunlight efficiently with the integration fuel cell.

## Conclusions

This study reviewed the biomass processing and conversion technologies for hydrogen production. Biomass is typically converted to hydrogen via two main routes, either thermochemical or biological. The thermochemical route is credible via combustion, pyrolysis, and liquefaction, catalytic steam reforming of raw gases, gasification, supercritical water gasification, and solar gasification. The merits and demerits, process parameters, types and routes of all processes have been critically discussed in terms of processing and conversion technologies from both research and commercial points of view. Among the thermochemical studies, pyrolysis, gasification, and solar gasification appear to be the most feasible and economically viable methods. Research gaps have also been suggested for solar gasification to improve the efficiency of solar heat and intensity. For the biological routes for hydrogen production from biomass included: covered direct and indirect bio-photolysis, photo fermentation, dark fermentation, and biological water gas shift reaction. Among the processes, photo fermentation and dark fermentation methods seem to be more suitable for hydrogen production, due to their high conversion yield and possible commercial application. Furthermore, the biological water gas shift reaction has also been shown to have economic viability. Direct and indirect photolysis and biological water gas shift reaction are potential areas of interest for efficient and sustainable bio-hydrogen production. Membrane technology is a promising alternative to conventional technologies for hydrogen production and purification from biomass processing because it has considerable advantages than other ones. First, membrane systems have been well investigated and commercialized. The current available membrane systems in the market could meet the demands of hydrogen separation from biomass-derived gases including CO<sub>2</sub>, CH<sub>4</sub>, and CO, etc. Moreover, the cost of the membrane separation is lower in comparison to other separation processes because of the

relative ease in membrane development and the low-cost of the system operation. However, more research efforts are required to develop new industrial membrane materials to maximize the permeability and selectivity as well as to overcome the limitations to meet practical feasibility.

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## REFERENCES

- [1] Arregi A, Amutio M, Lopez G, Bilbao J, Olazar M. Evaluation of thermochemical routes for hydrogen production from biomass: a review. *Energy Convers Manag* 2018;165:696–719.
- [2] Shahbaz M, Yusup S, Inayat A, Ammar M, Patrick DO, Pratama A, et al. Syngas production from steam gasification of palm kernel shell with subsequent CO<sub>2</sub> capture using CaO sorbent: an aspen plus modeling. *Energy Fuel* 2017;31:12350–7.
- [3] Khan Z, Yusup S, Ahmad MM, Chok VS, Uemura Y, Sabil KM. Review on hydrogen production technologies in Malaysia. *Int J Eng Technol* 2010;10:111–8.
- [4] Abbas HF, Wan Daud WMA. Hydrogen production by methane decomposition: a review. *Int J Hydrogen Energy* 2010;35:1160–90.
- [5] Sengodan S, Lan R, Humphreys J, Du D, Xu W, Wang H, et al. Advances in reforming and partial oxidation of hydrocarbons for hydrogen production and fuel cell applications. *Renew Sustain Energy Rev* 2018;82:761–80.
- [6] Martins RF, Martins DAA, Costa LAC, Matencio T, Paniago RM, Montoro LA. Copper hexacyanoferrate as cathode material for hydrogen peroxide fuel cell. *Int J Hydrogen Energy* 2020. <https://doi.org/10.1016/j.ijhydene.2020.01.077>. in press.
- [7] Houghton J. *Global warming: the complete briefing*. Cambridge University Press; 2009.
- [8] Shahbaz M, Yusup S, Inayat A, Patrick DO, Ammar M, Pratama A. Cleaner production of hydrogen and syngas from catalytic steam palm kernel shell gasification using cao sorbent and coal bottom ash as a catalyst. *Energy Fuel* 2017;31:13824–33.
- [9] Łukajtis R, Hołowacz I, Kucharska K, Glinka M, Rybarczyk P, Przyjazny A, et al. Hydrogen production from biomass using dark fermentation. *Renew Sustain Energy Rev* 2018;91:665–94.
- [10] Balat H, Kırtay E. Hydrogen from biomass – present scenario and future prospects. *Int J Hydrogen Energy* 2010;35:7416–26.
- [11] Ullvius NC, Rokni M. A study on a polygeneration plant based on solar power and solid oxide cells. *Int J Hydrogen Energy* 2019;44:19206–23.
- [12] He Q, Yu J, Xu H, Zhao D, Zhao T, Ni M. Thermal effects in H<sub>2</sub>O and CO<sub>2</sub> assisted direct carbon solid oxide fuel cells. *Int J Hydrogen Energy* 2020;45(22):12459–75.
- [13] Xu H, Chen B, Zhang H, Sun Q, Yang G, Ni M. Modeling of direct carbon solid oxide fuel cells with H<sub>2</sub>O and CO<sub>2</sub> as gasification agents. *Int J Hydrogen Energy* 2017;42:15641–51.

- [14] Abe JO, Popoola API, Ajenifuja E, Popoola OM. Hydrogen energy, economy and storage: review and recommendation. *Int J Hydrogen Energy* 2019;44:15072–86.
- [15] Mah AXY, Ho WS, Bong CPC, Hassim MH, Liew PY, Asli UA, et al. Review of hydrogen economy in Malaysia and its way forward. *Int J Hydrogen Energy* 2019;44:5661–75.
- [16] Shah SAA. Feasibility study of renewable energy sources for developing the hydrogen economy in Pakistan. *Int J Hydrogen Energy* 2019. <https://doi.org/10.1016/j.ijhydene.2019.09.153>. in press.
- [17] Chen Y-T, Hsu C-W. The key factors affecting the strategy planning of Taiwan's hydrogen economy. *Int J Hydrogen Energy* 2019;44:3290–305.
- [18] Ren X, Dong L, Xu D, Hu B. Challenges towards hydrogen economy in China. *Int J Hydrogen Energy* 2020. <https://doi.org/10.1016/j.ijhydene.2020.01.163>. in press.
- [19] Murray ML, Hugo Seymour E, Pimenta R. Towards a hydrogen economy in Portugal. *Int J Hydrogen Energy* 2007;32:3223–9.
- [20] Hajimiragha A, Fowler MW, Cañizares CA. Hydrogen economy transition in Ontario – Canada considering the electricity grid constraints. *Int J Hydrogen Energy* 2009;34:5275–93.
- [21] Bakenne A, Nuttall W, Kazantzis N. Sankey-Diagram-based insights into the hydrogen economy of today. *Int J Hydrogen Energy* 2016;41:7744–53.
- [22] Shahbaz M, Yusup S, Al-Ansari T, Inayat A, Inayat M, Zeb H, et al. Characterization and reactivity study of coal bottom ash for utilization in biomass gasification as an adsorbent/catalyst for cleaner fuel production. *Energy Fuel* 2019;33:11318–27.
- [23] Mah Abdallah, Asfour SS, Veziroglu TN. Solar–hydrogen energy system for Egypt. *Int J Hydrogen Energy* 1999;24:505–17.
- [24] Inayat A, Inayat M, Shahbaz M, Sulaiman SA, Raza M, Yusup S. Parametric analysis and optimization for the catalytic air gasification of palm kernel shell using coal bottom ash as catalyst. *Renew Energy* 2020;145:671–81.
- [25] Kalinci Y, Hepbasli A, Dincer I. Biomass-based hydrogen production: a review and analysis. *Int J Hydrogen Energy* 2009;34:8799–817.
- [26] Shahbaz M, Yusup S, Inayat A, Patrick DO, Pratama A, Ammar M. Optimization of hydrogen and syngas production from PKS gasification by using coal bottom ash. *Bioresour Technol* 2017;241:284–95.
- [27] Demirbaş A. Biomass resource facilities and biomass conversion processing for fuels and chemicals. *Energy Convers Manag* 2001;42:1357–78.
- [28] McKendry P. Energy production from biomass (part 1): overview of biomass. *Bioresour Technol* 2002;83:37–46.
- [29] Saxena RC, Adhikari DK, Goyal HB. Biomass-based energy fuel through biochemical routes: a review. *Renew Sustain Energy Rev* 2009;13:167–78.
- [30] Czernik S, French R, Feik C, Chornet E. Production of hydrogen from biomass by pyrolysis/steam reforming. In: Grégoire Padró CE, Lau F, editors. *Advances in hydrogen energy*. Boston, MA: Springer US; 2002. p. 87–91.
- [31] Guo LJ, Lu YJ, Zhang XM, Ji CM, Guan Y, Pei AX. Hydrogen production by biomass gasification in supercritical water: a systematic experimental and analytical study. *Catal Today* 2007;129:275–86.
- [32] Vassilev SV, Baxter D, Andersen LK, Vassileva CG, Morgan TJ. An overview of the organic and inorganic phase composition of biomass. *Fuel* 2012;94:1–33.
- [33] Ahmed TY, Ahmad MM, Yusup S, Inayat A, Khan Z. Mathematical and computational approaches for design of biomass gasification for hydrogen production: a review. *Renew Sustain Energy Rev* 2012;16:2304–15.
- [34] Van de Velden M, Baeyens J, Brems A, Janssens B, Dewil R. Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction. *Renew Energy* 2010;35:232–42.
- [35] Basu P. Biomass gasification and pyrolysis: practical design and theory. Elsevier Science; 2010.
- [36] Singh R, Dutta S. A review on H<sub>2</sub> production through photocatalytic reactions using TiO<sub>2</sub>/TiO<sub>2</sub>-assisted catalysts. *Fuel* 2018;220:607–20.
- [37] Mudhoo A, Forster-Carneiro T, Sánchez A. Biohydrogen production and bioprocess enhancement: a review. *Crit Rev Biotechnol* 2011;31:250–63.
- [38] Singh A, Sevdia S, Abu Reesh IM, Vanbroekhoven K, Rathore D, Pant D. Biohydrogen production from lignocellulosic biomass: technology and sustainability. *Energies* 2015;8:13062–80.
- [39] Chen D, He L. Towards an efficient hydrogen production from biomass: a review of processes and materials. *ChemCatChem* 2011;3:490–511.
- [40] Pandey B, Prajapati YK, Sheth PN. Recent progress in thermochemical techniques to produce hydrogen gas from biomass: a state of the art review. *Int J Hydrogen Energy* 2019;44:25384–415.
- [41] Rezanian S, Din MFM, Taib SM, Sohaili J, Chelliapan S, Kamyab H, et al. Review on fermentative biohydrogen production from water hyacinth, wheat straw and rice straw with focus on recent perspectives. *Int J Hydrogen Energy* 2017;42:20955–69.
- [42] Parthasarathy P, Narayanan KS. Hydrogen production from steam gasification of biomass: influence of process parameters on hydrogen yield – a review. *Renew Energy* 2014;66:570–9.
- [43] Antal MJ, Allen SG, Schulman D, Xu X, Divilio RJ. Biomass gasification in supercritical water. *Ind Eng Chem Res* 2000;39:4040–53.
- [44] Loutzenhiser PG, Muroyama AP. A review of the state-of-the-art in solar-driven gasification processes with carbonaceous materials. *Sol Energy* 2017;156:93–100.
- [45] Azwar MY, Hussain MA, Abdul-Wahab AK. Development of biohydrogen production by photobiological, fermentation and electrochemical processes: a review. *Renew Sustain Energy Rev* 2014;31:158–73.
- [46] Singh L, Wahid ZA. Methods for enhancing bio-hydrogen production from biological process: a review. *J Ind Eng Chem* 2015;21:70–80.
- [47] Tanksale A, Beltramini JN, Lu GM. A review of catalytic hydrogen production processes from biomass. *Renew Sustain Energy Rev* 2010;14:166–82.
- [48] Demirbas A. Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues. *Prog Energy Combust Sci* 2005;31:171–92.
- [49] Sengupta S, Datta A, Duttagupta S. Exergy analysis of a coal-based 210 MW thermal power plant. *Int J Energy Res* 2007;31:14–28.
- [50] Finkelman RB. Potential health impacts of burning coal beds and waste banks. *Int J Coal Geol* 2004;59:19–24.
- [51] Saidur R, Ju Ahamed, Masjuki HH. Energy, exergy and economic analysis of industrial boilers. *Energy Pol* 2010;38:2188–97.
- [52] Huijbregts WMM, Leferink RGI. Latest advances in the understanding of acid dewpoint corrosion: corrosion and stress corrosion cracking in combustion gas condensates. *Anti-Corros Method Mater* 2004;51:173–88.
- [53] Blanco JM, Peña F. Increase in the boiler's performance in terms of the acid dew point temperature: environmental advantages of replacing fuels. *Appl Therm Eng* 2008;28:777–84.



- [54] Ripoll N, Silvestre C, Paredes E, Toledo M. Hydrogen production from algae biomass in rich natural gas-air filtration combustion. *Int J Hydrogen Energy* 2017;42:5513–22.
- [55] Ghayur A, Verheyen TV. Technical evaluation of post-combustion CO<sub>2</sub> capture and hydrogen production industrial symbiosis. *Int J Hydrogen Energy* 2018;43:13852–9.
- [56] Ajiwibowo MW, Darmawan A, Aziz M. A conceptual chemical looping combustion power system design in a power-to-gas energy storage scenario. *Int J Hydrogen Energy* 2019;44:9636–42.
- [57] Naqvi SR, Tariq R, Hameed Z, Ali I, Naqvi M, Chen W-H, et al. Pyrolysis of high ash sewage sludge: kinetics and thermodynamic analysis using Coats-Redfern method. *Renew Energy* 2019;131:854–60.
- [58] Elkhailifa S, Al-Ansari T, Mackey HR, McKay G. Food waste to biochars through pyrolysis: a review. *Resour Conserv Recycl* 2019;144:310–20.
- [59] Chan YH, Cheah KW, How BS, Loy ACM, Shahbaz M, Singh HKG, et al. An overview of biomass thermochemical conversion technologies in Malaysia. *Sci Total Environ* 2019;680:105–23.
- [60] Naqvi SR, Uemura Y, Yusup S, Sugiura Y, Nishiyama N. In situ catalytic fast pyrolysis of paddy husk pyrolysis vapors over MCM-22 and ITQ-2 zeolites. *J Anal Appl Pyrolysis* 2015;114:32–9.
- [61] Naqvi SR, Prabhakara HM, Bramer EA, Dierkes W, Akkerman R, Brem G. A critical review on recycling of end-of-life carbon fibre/glass fibre reinforced composites waste using pyrolysis towards a circular economy. *Resour Conserv Recycl* 2018;136:118–29.
- [62] Duman G, Uddin MA, Yanik J. Hydrogen production from algal biomass via steam gasification. *Bioresour Technol* 2014;166:24–30.
- [63] Lan P, Xu Q, Zhou M, Lan L, Zhang S, Yan Y. Catalytic steam reforming of fast pyrolysis bio-oil in fixed bed and fluidized bed reactors. *Chem Eng Technol* 2010;33:2021–8.
- [64] Setiabudi HD, Aziz MAA, Abdullah S, Teh LP, Jusoh R. Hydrogen production from catalytic steam reforming of biomass pyrolysis oil or bio-oil derivatives: a review. *Int J Hydrogen Energy* 2019. <https://doi.org/10.1016/j.ijhydene.2019.10.141>. in press.
- [65] Ni M, Leung DY, Leung MKH, Sumathy K. An overview of hydrogen production from biomass. *Fuel Process Technol* 2006;87:461–72.
- [66] Demirbaş A. Gaseous products from biomass by pyrolysis and gasification: effects of catalyst on hydrogen yield. *Energy Convers Manag* 2002;43:897–909.
- [67] Chen G, Andries J, Spliethoff H. Catalytic pyrolysis of biomass for hydrogen rich fuel gas production. *Energy Convers Manag* 2003;44:2289–96.
- [68] Yang H, Yan R, Chen H, Lee DH, Liang DT, Zheng C. Pyrolysis of palm oil wastes for enhanced production of hydrogen rich gases. *Fuel Process Technol* 2006;87:935–42.
- [69] Yang H, Wang D, Li B, Zeng Z, Qu L, Zhang W, et al. Effects of potassium salts loading on calcium oxide on the hydrogen production from pyrolysis-gasification of biomass. *Bioresour Technol* 2018;249:744–50.
- [70] Santamaria L, Lopez G, Arregi A, Amutio M, Artetxe M, Bilbao J, et al. Influence of the support on Ni catalysts performance in the in-line steam reforming of biomass fast pyrolysis derived volatiles. *Appl Catal B Environ* 2018;229:105–13.
- [71] Luo S, Fu J, Zhou Y, Yi C. The production of hydrogen-rich gas by catalytic pyrolysis of biomass using waste heat from blast-furnace slag. *Renew Energy* 2017;101:1030–6.
- [72] Zhao X-Y, Ren J, Cao J-P, Wei F, Zhu C, Fan X, et al. Catalytic reforming of volatiles from biomass pyrolysis for hydrogen-rich gas production over limonite ore. *Energy Fuel* 2017;31:4054–60.
- [73] Dong L, Wu C, Ling H, Shi J, Williams PT, Huang J. Promoting hydrogen production and minimizing catalyst deactivation from the pyrolysis-catalytic steam reforming of biomass on nanosized NiZnAlOx catalysts. *Fuel* 2017;188:610–20.
- [74] Arregi A, Lopez G, Amutio M, Barbarias I, Bilbao J, Olazar M. Hydrogen production from biomass by continuous fast pyrolysis and in-line steam reforming. *RSC Adv* 2016;6:25975–85.
- [75] Chen F, Wu C, Dong L, Vassallo A, Williams PT, Huang J. Characteristics and catalytic properties of Ni/CaAlOx catalyst for hydrogen-enriched syngas production from pyrolysis-steam reforming of biomass sawdust. *Appl Catal B Environ* 2016;183:168–75.
- [76] Waheed QMK, Wu C, Williams PT. Pyrolysis/reforming of rice husks with a Ni–dolomite catalyst: influence of process conditions on syngas and hydrogen yield. *J Energy Inst* 2016;89:657–67.
- [77] Kaewpanha M, Guan G, Ma Y, Hao X, Zhang Z, Reubroychareon P, et al. Hydrogen production by steam reforming of biomass tar over biomass char supported molybdenum carbide catalyst. *Int J Hydrogen Energy* 2015;40:7974–82.
- [78] Liu S, Zhu J, Chen M, Xin W, Yang Z, Kong L. Hydrogen production via catalytic pyrolysis of biomass in a two-stage fixed bed reactor system. *Int J Hydrogen Energy* 2014;39:13128–35.
- [79] Ma Z, Zhang S-p, Xie D-y, Yan Y-j. A novel integrated process for hydrogen production from biomass. *Int J Hydrogen Energy* 2014;39:1274–9.
- [80] Hojjat Ansari M, Jafarian S, Tavasoli A, Karimi A, Rashidi M. Hydrogen rich gas production via nano-catalytic pyrolysis of bagasse in a dual bed reactor. *J Nat Gas Sci Eng* 2014;19:279–86.
- [81] Waheed QMK, Williams PT. Hydrogen production from high temperature pyrolysis/steam reforming of waste biomass: rice husk, sugar cane bagasse, and wheat straw. *Energy Fuel* 2013;27:6695–704.
- [82] Jiang H, Wu Y, Fan H, Ji J. Hydrogen production from biomass pyrolysis in molten alkali. *AASRI Procedia* 2012;3:217–23.
- [83] Qinglan H, Chang W, Dingqiang L, Yao W, Dan L, Guiju L. Production of hydrogen-rich gas from plant biomass by catalytic pyrolysis at low temperature. *Int J Hydrogen Energy* 2010;35:8884–90.
- [84] Antonakou E, Lappas A, Nilsen MH, Bouzga A, Stöcker M. Evaluation of various types of Al-MCM-41 materials as catalysts in biomass pyrolysis for the production of bio-fuels and chemicals. *Fuel* 2006;85:2202–12.
- [85] Liu Y, Yu H, Liu J, Chen D. Catalytic characteristics of innovative Ni/slag catalysts for syngas production and tar removal from biomass pyrolysis. *Int J Hydrogen Energy* 2019;44:11848–60.
- [86] Granados-Fitch MG, Quintana-Melgoza JM, Juarez-Arellano EA, Avalos-Borja M. Mechanism to H<sub>2</sub> production on rhenium carbide from pyrolysis of coconut shell. *Int J Hydrogen Energy* 2019;44:2784–96.
- [87] Naqvi SR, Uemura Y, Yusup SB. Catalytic pyrolysis of paddy husk in a drop type pyrolyzer for bio-oil production: the role of temperature and catalyst. *J Anal Appl Pyrolysis* 2014;106:57–62.
- [88] Demirbas MF. Hydrogen from various biomass species via pyrolysis and steam gasification processes. *Energy Sources, Part A Recovery, Util Environ Eff* 2006;28:245–52.
- [89] Bridgwater AV, Meier D, Radlein D. An overview of fast pyrolysis of biomass. *Org Geochem* 1999;30:1479–93.

- [90] Lathouwers D, Bellan J. Modeling of biomass pyrolysis for hydrogen production: the fluidized bed reactor. *Proc 2001 DOE Hydrogen Prog Rev* 2001;1–35.
- [91] Bridgwater AV. Review of fast pyrolysis of biomass and product upgrading. *Biomass Bioenergy* 2012;38:68–94.
- [92] Behrendt F, Neubauer Y, Oevermann M, Wilmes B, Zobel N. Direct liquefaction of biomass. *Chem Eng Technol* 2008;31:667–77.
- [93] Nanda S, Isen J, Dalai AK, Kozinski JA. Gasification of fruit wastes and agro-food residues in supercritical water. *Energy Convers Manag* 2016;110:296–306.
- [94] Castello D, Kruse A, Fiori L. Supercritical water gasification of hydrochar. *Chem Eng Res Des* 2014;92:1864–75.
- [95] Elif D, Nezihe A. Hydrogen production by supercritical water gasification of fruit pulp in the presence of Ru/C. *Int J Hydrogen Energy* 2016;41:8073–83.
- [96] Chan YH, Cheah KW, How BS, Loy ACM, Shahbaz M, Singh HKG, et al. An overview of biomass thermochemical conversion technologies in Malaysia. *Sci Total Environ* 2019;680:105–23.
- [97] Akhtar J, Amin NAS. A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass. *Renew Sustain Energy Rev* 2011;15:1615–24.
- [98] Brand S, Hardi F, Kim J, Suh DJ. Effect of heating rate on biomass liquefaction: differences between subcritical water and supercritical ethanol. *Energy* 2014;68:420–7.
- [99] Elliott DC, Biller P, Ross AB, Schmidt AJ, Jones SB. Hydrothermal liquefaction of biomass: developments from batch to continuous process. *Bioresour Technol* 2015;178:147–56.
- [100] Tran K-Q. Fast hydrothermal liquefaction for production of chemicals and biofuels from wet biomass—the need to develop a plug-flow reactor. *Bioresour Technol* 2016;213:327–32.
- [101] Tran NTT, Uemura Y, Chowdhury S, Ramli A. Vapor-phase hydrodeoxygenation of guaiacol on Al-MCM-41 supported Ni and Co catalysts. *Appl Catal Gen* 2016;512:93–100.
- [102] Fernandes A, Woudstra T, Aravind PV. System simulation and exergy analysis on the use of biomass-derived liquid-hydrogen for SOFC/GT powered aircraft. *Int J Hydrogen Energy* 2015;40:4683–97.
- [103] Lee I-G, Ihm S-K. Catalytic gasification of glucose over Ni/activated charcoal in supercritical water. *Ind Eng Chem Res* 2009;48:1435–42.
- [104] Kıpçak E, Söğüt ÖÖ, Akgün M. Hydrothermal gasification of olive mill wastewater as a biomass source in supercritical water. *J Supercrit Fluids* 2011;57:50–7.
- [105] Byrd AJ, Kumar S, Kong L, Ramsurn H, Gupta RB. Hydrogen production from catalytic gasification of switchgrass biocrude in supercritical water. *Int J Hydrogen Energy* 2011;36:3426–33.
- [106] Azadi P, Khan S, Strobel F, Azadi F, Farnood R. Hydrogen production from cellulose, lignin, bark and model carbohydrates in supercritical water using nickel and ruthenium catalysts. *Appl Catal B Environ* 2012;117–118:330–8.
- [107] Chen Y, Guo L, Cao W, Jin H, Guo S, Zhang X. Hydrogen production by sewage sludge gasification in supercritical water with a fluidized bed reactor. *Int J Hydrogen Energy* 2013;38:12991–9.
- [108] Tiong L, Komiyama M, Uemura Y, Nguyen TT. Catalytic supercritical water gasification of microalgae: comparison of *Chlorella vulgaris* and *Scenedesmus quadricauda*. *J Supercrit Fluids* 2016;107:408–13.
- [109] Norouzi O, Safari F, Jafarian S, Tavasoli A, Karimi A. Hydrothermal gasification performance of *Enteromorpha intestinalis* as an algal biomass for hydrogen-rich gas production using Ru promoted Fe–Ni/ $\gamma$ - $\text{Al}_2\text{O}_3$  nanocatalysts. *Energy Convers Manag* 2017;141:63–71.
- [110] Amrullah A, Matsumura Y. Supercritical water gasification of sewage sludge in continuous reactor. *Bioresour Technol* 2018;249:276–83.
- [111] Alipour Moghadam R, Yusup S, Azlina W, Nehzati S, Tavasoli A. Investigation on syngas production via biomass conversion through the integration of pyrolysis and air–steam gasification processes. *Energy Convers Manag* 2014;87:670–5.
- [112] Milne TA, Elam CC, Evans RJ. Hydrogen from biomass: state of the art and research challenges. Golden, CO (US): National Renewable Energy Lab.; 2002.
- [113] Shahbaz M, Yusup S, Inayat A, Patrick D, Partama A. System analysis of poly-generation of SNG, power and district heating from biomass gasification system. *Chem Eng Trans* 2016;52:781–6.
- [114] Ghiat I, AlNouss A, McKay G, Al-Ansari T. Biomass-based integrated gasification combined cycle with post-combustion  $\text{CO}_2$  recovery by potassium carbonate: techno-economic and environmental analysis. *Comput Chem Eng* 2020:106758.
- [115] Demirbaş A. Hydrogen Production from biomass by the gasification process. *Energy Sources* 2002;24:59–68.
- [116] Inayat A, Ahmad MM, Mutalib MA. Effect of process parameters on hydrogen production and efficiency in biomass steam gasification with in-situ  $\text{CO}_2$  capture. *Prec Int Conf Proc Eng Adv Mater* 2010:15–7.
- [117] AlNouss A, McKay G, Al-Ansari T. A comparison of steam and oxygen fed biomass gasification through a techno-economic-environmental study. *Energy Convers Manag* 2020;208:112612.
- [118] AlNouss A, McKay G, Al-Ansari T. Production of syngas via gasification using optimum blends of biomass. *J Clean Prod* 2020;242:118499.
- [119] Encinar JM, Beltrán FJ, Ramiro A, González JF. Pyrolysis/gasification of agricultural residues by carbon dioxide in the presence of different additives: influence of variables. *Fuel Process Technol* 1998;55:219–33.
- [120] Zevenhoven-Onderwater M, Backman R, Skrifvars B-J, Hupa M. The ash chemistry in fluidised bed gasification of biomass fuels. Part I: predicting the chemistry of melting ashes and ash–bed material interaction. *Fuel* 2001;80:1489–502.
- [121] Milne TA, Evans RJ, Abatzoglou N. Biomass Gasifier“Tars”: their nature, formation, and conversion. Golden, CO (US): National Renewable Energy Laboratory; 1998.
- [122] Herman AP, Yusup S, Shahbaz M, Patrick DO. Bottom ash characterization and its catalytic potential in biomass gasification. *Proced Eng* 2016;148:432–6.
- [123] Arvelakis S, Koukios EG. Physicochemical upgrading of agroresidues as feedstocks for energy production via thermochemical conversion methods. *Biomass Bioenergy* 2002;22:331–48.
- [124] Lahijani P, Zainal ZA, Mohamed AR, Mohammadi M. Ash of palm empty fruit bunch as a natural catalyst for promoting the  $\text{CO}_2$  gasification reactivity of biomass char. *Bioresour Technol* 2013;132:351–5.
- [125] Mitsuoka K, Hayashi S, Amano H, Kayahara K, Sasaoaka E, Uddin MA. Gasification of woody biomass char with  $\text{CO}_2$ : the catalytic effects of K and Ca species on char gasification reactivity. *Fuel Process Technol* 2011;92:26–31.
- [126] Umeki K, Moilanen A, Gómez-Barea A, Kontinen J. A model of biomass char gasification describing the change in catalytic activity of ash. *Chem Eng J* 2012;207–208:616–24.
- [127] Inayat A, Ahmad MM, Mutalib MIA, Yusup S. Process modeling for parametric study on oil palm empty fruit bunch steam gasification for hydrogen production. *Fuel Process Technol* 2012;93:26–34.

- [128] Shen Y, Zhao P, Shao Q, Takahashi F, Yoshikawa K. In situ catalytic conversion of tar using rice husk char/ash supported nickel–iron catalysts for biomass pyrolytic gasification combined with the mixing-simulation in fluidized-bed gasifier. *Appl Energy* 2015;160:808–19.
- [129] Kelelepole L, Sun R, Liao J. Fly ash and coal char reactivity from Thermo-gravimetric (TGA) experiments. *Fuel Process Technol* 2011;92:1178–86.
- [130] Aznar MP, Caballero MA, Gil J, Martín JA, Corella J. Commercial steam reforming catalysts to improve biomass gasification with steam–oxygen mixtures. 2. catalytic tar removal. *Ind Eng Chem Res* 1998;37:2668–80.
- [131] Abu El-Rub Z, Bramer EA, Brem G. Review of catalysts for tar elimination in biomass gasification processes. *Ind Eng Chem Res* 2004;43:6911–9.
- [132] Shahbaz M, Yusup S, Inayat A, Patrick DO, Ammar M. The influence of catalysts in biomass steam gasification and catalytic potential of coal bottom ash in biomass steam gasification: a review. *Renew Sustain Energy Rev* 2017;73:468–76.
- [133] Anis S, Zainal ZA. Tar reduction in biomass producer gas via mechanical, catalytic and thermal methods: a review. *Renew Sustain Energy Rev* 2011;15:2355–77.
- [134] Devi L, Ptasiński KJ, Janssen FJJG. A review of the primary measures for tar elimination in biomass gasification processes. *Biomass Bioenergy* 2003;24:125–40.
- [135] Rios MLV, González AM, Lora EES, del Olmo OAA. Reduction of tar generated during biomass gasification: a review. *Biomass Bioenergy* 2018;108:345–70.
- [136] Palma CF. Modelling of tar formation and evolution for biomass gasification: a review. *Appl Energy* 2013;111:129–41.
- [137] Sutton D, Kelleher B, Ross JRH. Review of literature on catalysts for biomass gasification. *Fuel Process Technol* 2001;73:155–73.
- [138] Mevissen N, Schulzke T, Unger CA, an Bhaïrd SM. Thermodynamics of autothermal wood gasification. *Environ Prog Sustain Energy* 2009;28:347–54.
- [139] Bulushev DA, Ross JRH. Catalysis for conversion of biomass to fuels via pyrolysis and gasification: a review. *Catal Today* 2011;171:1–13.
- [140] Yu MM, Masnadi MS, Grace JR, Bi XT, Lim CJ, Li Y. Co-gasification of biosolids with biomass: thermogravimetric analysis and pilot scale study in a bubbling fluidized bed reactor. *Bioresour Technol* 2015;175:51–8.
- [141] Tomishige K, Asadullah M, Kunimori K. Syngas production by biomass gasification using Rh/CeO<sub>2</sub>/SiO<sub>2</sub> catalysts and fluidized bed reactor. *Catal Today* 2004;89:389–403.
- [142] Miyazawa T, Kimura T, Nishikawa J, Kunimori K, Tomishige K. Catalytic properties of Rh/CeO<sub>2</sub>/SiO<sub>2</sub> for synthesis gas production from biomass by catalytic partial oxidation of tar. *Sci Technol Adv Mater* 2005;6:604–14.
- [143] Nishikawa J, Nakamura K, Asadullah M, Miyazawa T, Kunimori K, Tomishige K. Catalytic performance of Ni/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> modified with noble metals in steam gasification of biomass. *Catal Today* 2008;131:146–55.
- [144] Efika CE, Wu C, Williams PT. Syngas production from pyrolysis–catalytic steam reforming of waste biomass in a continuous screw kiln reactor. *J Anal Appl Pyrolysis* 2012;95:87–94.
- [145] Pfeifer C, Hofbauer H. Development of catalytic tar decomposition downstream from a dual fluidized bed biomass steam gasifier. *Powder Technol* 2008;180:9–16.
- [146] Corella J, Aznar MP, Caballero MA, Molina G, Toledo JM. 140 gH<sub>2</sub>/kg biomass d.a.f. by a CO-shift reactor downstream from a FB biomass gasifier and a catalytic steam reformer. *Int J Hydrogen Energy* 2008;33:1820–6.
- [147] Lü P, Kong X, Wu C, Yuan Z, Ma L, Chang J. Modeling and simulation of biomass air-steam gasification in a fluidized bed. *Front Chem Eng China* 2008;2:209–13.
- [148] García R, Pizarro C, Lavín AG, Bueno JL. Characterization of Spanish biomass wastes for energy use. *Bioresour Technol* 2012;103:249–58.
- [149] Nahil MA, Wang X, Wu C, Yang H, Chen H, Williams PT. Novel bi-functional Ni–Mg–Al–CaO catalyst for catalytic gasification of biomass for hydrogen production with in situ CO<sub>2</sub> adsorption. *RSC Adv* 2013;3:5583–90.
- [150] Wang L, Lei H, Bu Q, Ren S, Wei Y, Zhu L, et al. Aromatic hydrocarbons production from ex situ catalysis of pyrolysis vapor over Zinc modified ZSM-5 in a packed-bed catalysis coupled with microwave pyrolysis reactor. *Fuel* 2014;129:78–85.
- [151] Modell M. Processing methods for the oxidation of organics in supercritical water. Google Patents; 1982.
- [152] Gasafi E, Reinecke M-Y, Kruse A, Schebek L. Economic analysis of sewage sludge gasification in supercritical water for hydrogen production. *Biomass Bioenergy* 2008;32:1085–96.
- [153] Reddy SN, Nanda S, Dalai AK, Kozinski JA. Supercritical water gasification of biomass for hydrogen production. *Int J Hydrogen Energy* 2014;39:6912–26.
- [154] Khan Z, Yusup S, Ahmad MM, Chin BLF. Hydrogen production from palm kernel shell via integrated catalytic adsorption (ICA) steam gasification. *Energy Convers Manag* 2014;87:1224–30.
- [155] Hao XH, Guo LJ, Mao X, Zhang XM, Chen XJ. Hydrogen production from glucose used as a model compound of biomass gasified in supercritical water. *Int J Hydrogen Energy* 2003;28:55–64.
- [156] Matsumura Y, Minowa T, Potic B, Kersten SRA, Prins W, van Swaaij WPM, et al. Biomass gasification in near- and supercritical water: status and prospects. *Biomass Bioenergy* 2005;29:269–92.
- [157] Koku H, Eroglu İ, Gündüz U, Yücel M, Türker L. Aspects of the metabolism of hydrogen production by *Rhodobacter sphaeroides*. *Int J Hydrogen Energy* 2002;27:1315–29.
- [158] Inayat A, Ahmad MM, Mutalib M, Yusup S. Process modeling for parametric study on oil palm empty fruit bunch steam gasification for hydrogen production. *Fuel Process Technol* 2012;93:26–34.
- [159] Walawender WP, Hoveland DA, Fan LT. Steam gasification of pure cellulose. 1. Uniform temperature profile. *Ind Eng Chem Process Des Dev* 1985;24:813–7.
- [160] Kaushal P, Tyagi R. Steam assisted biomass gasification—an overview. *Candain J Chem Eng* 2012;90:1043–58.
- [161] Jangsawang W, Klimanek A, Gupta AK. Enhanced yield of hydrogen from wastes using high temperature steam gasification. *J Energy Resources* 2005;128:179–85.
- [162] Wang Y, Yoshikawa K, Namioka T, Hashimoto Y. Performance optimization of two-staged gasification system for woody biomass. *Fuel Process Technol* 2007;88:243–50.
- [163] Kajitani S, Hara S, Matsuda H. Gasification rate analysis of coal char with a pressurized drop tube furnace. *Fuel* 2002;81:539–46.
- [164] Franco C, Pinto F, Gulyurtlu I, Cabrita I. The study of reactions influencing the biomass steam gasification process. *Fuel* 2003;82:835–42.
- [165] Wei L, Xu S, Liu J, Liu C, Liu S. Hydrogen production in steam gasification of biomass with CaO as a CO<sub>2</sub> absorbent. *Energy Fuel* 2008;22:1997–2004.
- [166] Wei L, Xu S, Liu J, Lu C, Liu S, Liu C. A novel process of biomass gasification for hydrogen-rich gas with solid heat Carrier: preliminary experimental results. *Energy Fuel* 2006;20:2266–73.



- [167] Wei L, Xu S, Zhang L, Liu C, Zhu H, Liu S. Steam gasification of biomass for hydrogen-rich gas in a free-fall reactor. *Int J Hydrogen Energy* 2007;32:24–31.
- [168] D'Jesús P, Artiel C, Boukis N, Kraushaar-Czarnetzki B, Dinjus E. Influence of educt preparation on gasification of corn silage in supercritical water. *Ind Eng Chem Res* 2005;44:9071–7.
- [169] Razuan R, Chen Q, Zhang X, Sharifi V, Swithenbank J. Pyrolysis and combustion of oil palm stone and palm kernel cake in fixed-bed reactors. *Bioresour Technol* 2010;101:4622–9.
- [170] Hathaway BJ, Honda M, Kittelson DB, Davidson JH. Steam gasification of plant biomass using molten carbonate salts. *Energy* 2013;49:211–7.
- [171] Frangini S, Masi A. Molten carbonates for advanced and sustainable energy applications: Part II. Review of recent literature. *Int J Hydrogen Energy* 2016;41:18971–94.
- [172] Weihong Z, Bin B, Guanyi C, Longlong M, Beibei Y. Thermogravimetric characteristics and kinetics of sawdust pyrolysis catalyzed by potassium salt during the process of hydrogen preparation. *Int J Hydrogen Energy* 2019;44:15863–70.
- [173] Jin G, Iwaki H, Arai N, Kitagawa K. Study on the gasification of wastepaper/carbon dioxide catalyzed by molten carbonate salts. *Energy* 2005;30:1192–203.
- [174] Kirtania K, Axelsson J, Matsakas L, Christakopoulos P, Umeki K, Furusjö E. Kinetic study of catalytic gasification of wood char impregnated with different alkali salts. *Energy* 2017;118:1055–65.
- [175] Jin K, Ji D, Xie Q, Nie Y, Yu F, Ji J. Hydrogen production from steam gasification of tableted biomass in molten eutectic carbonates. *Int J Hydrogen Energy* 2019;44:22919–25.
- [176] Ratchahat S, Kodama S, Tanthapanichakoon W, Sekiguchi H. CO<sub>2</sub> gasification of biomass wastes enhanced by Ni/Al<sub>2</sub>O<sub>3</sub> catalyst in molten eutectic carbonate salt. *Int J Hydrogen Energy* 2015;40:11809–22.
- [177] Xiao P, Guo L, Zhang X, Zhu C, Ma S. Continuous hydrogen production by biomass gasification in supercritical water heated by molten salt flow: system development and reactor assessment. *Int J Hydrogen Energy* 2013;38:12927–37.
- [178] Xu D, Liu L, Wei N, Guo Y, Wang S, Wu Z, et al. Catalytic supercritical water gasification of aqueous phase directly derived from microalgae hydrothermal liquefaction. *Int J Hydrogen Energy* 2019;44:26181–92.
- [179] Moghadam RA, Yusup S, Lam HL, Al Shoaibi A, Ahmad MM. Hydrogen production from mixture of biomass and polyethylene waste in fluidized bed catalytic steam co-gasification process. *Chem Eng Trans* 2013;35.
- [180] Su S, Chi Y, Chang R, Hu R, Li N. Analysis of the catalytic steam gasification mechanism of biomass. *Int J Hydrogen Energy* 2015;40:935–40.
- [181] Suzuki T, Ohme H, Watanabe Y. Alkali metal catalyzed carbon dioxide gasification of carbon. *Energy Fuel* 1992;6:343–51.
- [182] Lamacz A, Krztoń A, Djéga-Mariadassou G. Steam reforming of model gasification tars compounds on nickel based ceria-zirconia catalysts. *Catal Today* 2011;176:347–51.
- [183] Berguerand N, Lind F, Israelsson M, Seemann M, Biollaz S, Thunman H. Use of nickel oxide as a catalyst for tar elimination in a chemical-looping reforming reactor operated with biomass producer gas. *Ind Eng Chem Res* 2012;51:16610–6.
- [184] Guan G, Chen G, Kasai Y, Lim EWC, Hao X, Kaewpanha M, et al. Catalytic steam reforming of biomass tar over iron- or nickel-based catalyst supported on calcined scallop shell. *Appl Catal B Environ* 2012;115–116:159–68.
- [185] Mazumder J, de Lasa HI. Fluidizable La<sub>2</sub>O<sub>3</sub> promoted Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst for steam gasification of biomass: effect of catalyst preparation conditions. *Appl Catal B Environ* 2015;168–169:250–65.
- [186] Zhang W. Automotive fuels from biomass via gasification. *Fuel Process Technol* 2010;91:866–76.
- [187] Barreto L, Makihira A, Riahi K. The hydrogen economy in the 21st century: a sustainable development scenario. *Int J Hydrogen Energy* 2003;28:267–84.
- [188] Resende FLP, Savage PE. Effect of metals on supercritical water gasification of cellulose and lignin. *Ind Eng Chem Res* 2010;49:2694–700.
- [189] Güngören Madenoğlu T, Boukis N, Sağlam M, Yüksel M. Supercritical water gasification of real biomass feedstocks in continuous flow system. *Int J Hydrogen Energy* 2011;36:14408–15.
- [190] Azadi P, Farnood R. Review of heterogeneous catalysts for sub- and supercritical water gasification of biomass and wastes. *Int J Hydrogen Energy* 2011;36:9529–41.
- [191] Watanabe M, Inomata H, Arai K. Catalytic hydrogen generation from biomass (glucose and cellulose) with ZrO<sub>2</sub> in supercritical water. *Biomass Bioenergy* 2002;22:405–10.
- [192] Park KC, Tomiyasu H. Gasification reaction of organic compounds catalyzed by RuO<sub>2</sub> in supercritical water. *Chem Commun* 2003:694–5.
- [193] Sinağ A, Kruse A, Schwarzkopf V. Key compounds of the hydrolysis of glucose in supercritical water in the presence of K<sub>2</sub>CO<sub>3</sub>. *Ind Eng Chem Res* 2003;42:3516–21.
- [194] Paidá VR, Kersten SRA, van der Ham AGJ, Brilman DWF. A two-step approach to the hydrothermal gasification of carbohydrate-rich wastes: process design and economic evaluation. *Int J Hydrogen Energy* 2019;44:25524–41.
- [195] Zhang Y, Li L, Xu P, Liu B, Shuai Y, Li B. Hydrogen production through biomass gasification in supercritical water: a review from exergy aspect. *Int J Hydrogen Energy* 2019;44:15727–36.
- [196] Gokon N, Izawa T, Abe T, Kodama T. Steam gasification of coal cokes in an internally circulating fluidized bed of thermal storage material for solar thermochemical processes. *Int J Hydrogen Energy* 2014;39:11082–93.
- [197] Müller F, van Eyk P, Haueter P, Steinfeld A. Experimental study of solar driven steam-gasification using a vortex flow reactor directly and indirectly irradiated. 11th SOLLAB Doctoral Colloquium. 2015. p. 17.
- [198] Bockris JOM, Veziroglu TN. A solar-hydrogen energy system for environmental compatibility. *Environ Conserv* 1982;12:105–118.
- [199] Antal Jr M, Feber R, Tinkle M. Synthetic fuels from solid wastes and solar energy. 1st World Hydrogen Energy Conference, Volume 11976. p. 3A-69A.
- [200] Shahbazov SS, Usubov I. Heliothermic unit for gasification agricultural product wastes. *Hydrogen energy progress XI*. In: Proceedings of the world hydrogen energy conference, 11th, Stuttgart; 1996. p. 951–4.
- [201] Midilli A, Rzaev P, Olgun H, Ayhan T. Solar hydrogen production from hazelnut shells. *Int J Hydrogen Energy* 2000;25:723–32.
- [202] Nathan GJ, Dally BB, Alwahabi ZT, van Eyk PJ, Jafarian M, Ashman PJ. Research challenges in combustion and gasification arising from emerging technologies employing directly irradiated concentrating solar thermal radiation. *Proc Combust Inst* 2017;36:2055–74.
- [203] Jafarian M, Arjomandi M, Nathan GJ. A hybrid solar and chemical looping combustion system for solar thermal energy storage. *Appl Energy* 2013;103:671–8.
- [204] Lim JH, Nathan GJ, Hu E, Dally BB. Analytical assessment of a novel hybrid solar tubular receiver and combustor. *Appl Energy* 2016;162:298–307.
- [205] Bellouard Q, Rodat S, Abanades S, Ravel S, Frayssines P-É. Design, simulation and experimental study of a directly-

- irradiated solar chemical reactor for hydrogen and syngas production from continuous solar-driven wood biomass gasification. *Int J Hydrogen Energy* 2019;44:19193–205.
- [206] Bellan S, Gokon N, Matsubara K, Cho HS, Kodama T. Numerical and experimental study on granular flow and heat transfer characteristics of directly-irradiated fluidized bed reactor for solar gasification. *Int J Hydrogen Energy* 2018;43:16443–57.
- [207] Boujjat H, Yuki Junior GM, Rodat S, Abanades S. Dynamic simulation and control of solar biomass gasification for hydrogen-rich syngas production during allothermal and hybrid solar/autothermal operation. *Int J Hydrogen Energy* 2020. <https://doi.org/10.1016/j.ijhydene.2020.01.072>. in press.
- [208] Arribas L, Arconada N, González-Fernández C, Löhr L, C, González-Aguilar J, Kaltschmitt M, et al. Solar-driven pyrolysis and gasification of low-grade carbonaceous materials. *Int J Hydrogen Energy* 2017;42:13598–606.
- [209] Salemm L, Simeone M, Chirone R, Salatino P. Analysis of the energy efficiency of solar aided biomass gasification for pure hydrogen production. *Int J Hydrogen Energy* 2014;39:14622–32.
- [210] Chen J, Lu Y, Guo L, Zhang X, Xiao P. Hydrogen production by biomass gasification in supercritical water using concentrated solar energy: system development and proof of concept. *Int J Hydrogen Energy* 2010;35:7134–41.
- [211] Liao B, Guo L, Lu Y, Zhang X. Solar receiver/reactor for hydrogen production with biomass gasification in supercritical water. *Int J Hydrogen Energy* 2013;38:13038–44.
- [212] Levin DB, Pitt L, Love M. Biohydrogen production: prospects and limitations to practical application. *Int J Hydrogen Energy* 2004;29:173–85.
- [213] Bičáková O, Straka P. Production of hydrogen from renewable resources and its effectiveness. *Int J Hydrogen Energy* 2012;37:11563–78.
- [214] Liu Y, Lin R, Man Y, Ren J. Recent developments of hydrogen production from sewage sludge by biological and thermochemical process. *Int J Hydrogen Energy* 2019;44:19676–97.
- [215] Kumar G, Mathimani T, Rene ER, Pugazhendhi A. Application of nanotechnology in dark fermentation for enhanced biohydrogen production using inorganic nanoparticles. *Int J Hydrogen Energy* 2019;44:13106–13.
- [216] Basak N, Das D. Microbial biohydrogen production by *Rhodobacter sphaeroides* OU 001 in photobioreactor. In: *Proceedings of world congress on eng and computer sci*, San Francisco, USA; 2007.
- [217] Karthic P, Joseph S. Comparison and limitations of biohydrogen production processes. *Res J Biotechnol* 2012;7:59–71.
- [218] Benemann JR. Process analysis and economics of biophotolysis of water. IEA Hydrogen Program Paris; 1998.
- [219] Márquez-Reyes LA, Sánchez-Saavedra MdP, Valdez-Vazquez I. Improvement of hydrogen production by reduction of the photosynthetic oxygen in microalgae cultures of *Chlamydomonas gloeopara* and *Scenedesmus obliquus*. *Int J Hydrogen Energy* 2015;40:7291–300.
- [220] Hasnaoui S, Pauss A, Abdi N, Grib H, Mameri N. Enhancement of bio-hydrogen generation by spirulina via an electrochemical photo-bioreactor (EPBR). *Int J Hydrogen Energy* 2020;45:6231–42.
- [221] Ghirardi ML, Zhang L, Lee JW, Flynn T, Seibert M, Greenbaum E, et al. Microalgae: a green source of renewable H<sub>2</sub>. *Trends Biotechnol* 2000;18:506–11.
- [222] Benemann J. Biohydrogen: approaches and potential. In: *Proceedings of the 11th Canadian hydrogen conference*, Victoria, BC June; 2001. p. 17–20.
- [223] Hallenbeck PC, Benemann JR. Biological hydrogen production; fundamentals and limiting processes. *Int J Hydrogen Energy* 2002;27:1185–93.
- [224] Venkata Mohan S, Vijaya Bhaskar Y, Sarma PN. Biohydrogen production from chemical wastewater treatment in biofilm configured reactor operated in periodic discontinuous batch mode by selectively enriched anaerobic mixed consortia. *Water Res* 2007;41:2652–64.
- [225] Epstein M, Spiewak I, Funken KH, Ortner J. Review of the technology for solar gasification of carbonaceous materials. United States: American Society of Mechanical Engineers; 1994.
- [226] Benemann JR. Feasibility analysis of photobiological hydrogen production. *Int J Hydrogen Energy* 1997;22:979–87.
- [227] Prince RC, Kheshgi HS. The photobiological production of hydrogen: potential efficiency and effectiveness as a renewable fuel. *Crit Rev Microbiol* 2005;31:19–31.
- [228] Markov SA, Thomas AD, Bazin MJ, Hall DO. Photoproduction of hydrogen by cyanobacteria under partial vacuum in batch culture or in a photobioreactor. *Int J Hydrogen Energy* 1997;22:521–4.
- [229] Lopes Pinto FA, Troshina O, Lindblad P. A brief look at three decades of research on cyanobacterial hydrogen evolution. *Int J Hydrogen Energy* 2002;27:1209–15.
- [230] Lindblad P, Christensson K, Lindberg P, Fedorov A, Pinto F, Tsygankov A. Photoproduction of H<sub>2</sub> by wildtype *Anabaena PCC 7120* and a hydrogen uptake deficient mutant: from laboratory experiments to outdoor culture. *Int J Hydrogen Energy* 2002;27:1271–81.
- [231] Basak N, Das D. The prospect of purple non-sulfur (PNS) photosynthetic bacteria for hydrogen production: the present state of the art. *World J Microbiol Biotechnol* 2007;23:31–42.
- [232] Tao Y, He Y, Wu Y, Liu F, Li X, Zong W, et al. Characteristics of a new photosynthetic bacterial strain for hydrogen production and its application in wastewater treatment. *Int J Hydrogen Energy* 2008;33:963–73.
- [233] Zhu H, Suzuki T, Tsygankov AA, Asada Y, Miyake J. Hydrogen production from tofu wastewater by *Rhodobacter sphaeroides* immobilized in agar gels. *Int J Hydrogen Energy* 1999;24:305–10.
- [234] Yetis M, Gündüz U, Eroglu I, Yücel M, Türker L. Photoproduction of hydrogen from sugar refinery wastewater by *Rhodobacter sphaeroides* O.U. 001. *Int J Hydrogen Energy* 2000;25:1035–41.
- [235] Tao Y, Chen Y, Wu Y, He Y, Zhou Z. High hydrogen yield from a two-step process of dark- and photo-fermentation of sucrose. *Int J Hydrogen Energy* 2007;32:200–6.
- [236] Hakobyan L, Gabrielyan L, Trchounian A. Biohydrogen by *Rhodobacter sphaeroides* during photo-fermentation: mixed vs. sole carbon sources enhance bacterial growth and H<sub>2</sub> production. *Int J Hydrogen Energy* 2019;44:674–9.
- [237] Fedorov AS, Tsygankov AA, Rao KK, Hall DO. Hydrogen photoproduction by *Rhodobacter sphaeroides* immobilised on polyurethane foam. *Biotechnol Lett* 1998;20:1007–9.
- [238] Singh J. Management of the agricultural biomass on decentralized basis for producing sustainable power in India. *J Clean Prod* 2017;142:3985–4000.
- [239] Chen W-H, Chen S-Y, Kumar Khanal S, Sung S. Kinetic study of biological hydrogen production by anaerobic fermentation. *Int J Hydrogen Energy* 2006;31:2170–8.
- [240] Hawkes FR, Dinsdale R, Hawkes DL, Hussy I. Sustainable fermentative hydrogen production: challenges for process optimisation. *Int J Hydrogen Energy* 2002;27:1339–47.
- [241] Venkata Mohan S, Vijaya Bhaskar Y, Murali Krishna P, Chandrasekhara Rao N, Lalit Babu V, Sarma PN. Biohydrogen production from chemical wastewater as

- substrate by selectively enriched anaerobic mixed consortia: influence of fermentation pH and substrate composition. *Int J Hydrogen Energy* 2007;32:2286–95.
- [242] Ren N-Q, Tang J, Liu B-F, Guo W-Q. Biological hydrogen production in continuous stirred tank reactor systems with suspended and attached microbial growth. *Int J Hydrogen Energy* 2010;35:2807–13.
- [243] Diamantis VI, Kapagiannidis AG, Ntougias S, Tataki V, Melidis P, Aivasidis A. Two-stage CSTR–UASB digestion enables superior and alkali addition-free cheese whey treatment. *Biochem Eng J* 2014;84:45–52.
- [244] Bélafi-Bakó K, Búcsú D, Pientka Z, Bálint B, Herbel Z, Kovács KL, et al. Integration of biohydrogen fermentation and gas separation processes to recover and enrich hydrogen. *Int J Hydrogen Energy* 2006;31:1490–5.
- [245] Balachandar G, Varanasi JL, Singh V, Singh H, Das D. Biological hydrogen production via dark fermentation: a holistic approach from lab-scale to pilot-scale. *Int J Hydrogen Energy* 2020;45:5202–15.
- [246] Zhang T, Jiang D, Zhang H, Jing Y, Tahir N, Zhang Y, et al. Comparative study on bio-hydrogen production from corn stover: photo-fermentation, dark-fermentation and dark-photo co-fermentation. *Int J Hydrogen Energy* 2020;45:3807–14.
- [247] Lu C, Zhang H, Zhang Q, Chu C-y, Tahir N, Ge X, et al. An automated control system for pilot-scale biohydrogen production: design, operation and validation. *Int J Hydrogen Energy* 2020;45:3795–806.
- [248] Ren N, Li J, Li B, Wang Y, Liu S. Biohydrogen production from molasses by anaerobic fermentation with a pilot-scale bioreactor system. *Int J Hydrogen Energy* 2006;31:2147–57.
- [249] Lin C-Y, Wu S-Y, Lin P-J, Chang J-S, Hung C-H, Lee K-S, et al. Pilot-scale hydrogen fermentation system start-up performance. *Int J Hydrogen Energy* 2010;35:13452–7.
- [250] Kim M-S, Lee D-Y. Fermentative hydrogen production from tofu-processing waste and anaerobic digester sludge using microbial consortium. *Bioresour Technol* 2010;101:S48–52.
- [251] Su H, Cheng J, Zhou J, Song W, Cen K. Combination of dark- and photo-fermentation to enhance hydrogen production and energy conversion efficiency. *Int J Hydrogen Energy* 2009;34:8846–53.
- [252] Antonopoulou G, Gavala HN, Skiadas IV, Lyberatos G. Influence of pH on fermentative hydrogen production from sweet sorghum extract. *Int J Hydrogen Energy* 2010;35:1921–8.
- [253] Cheng J, Su H, Zhou J, Song W, Cen K. Hydrogen production by mixed bacteria through dark and photo fermentation. *Int J Hydrogen Energy* 2011;36:450–7.
- [254] Li Y-C, Nissilä ME, Wu S-Y, Lin C-Y, Puhakka JA. Silage as source of bacteria and electrons for dark fermentative hydrogen production. *Int J Hydrogen Energy* 2012;37:15518–24.
- [255] Argun H, Kargi F. Photo-fermentative hydrogen gas production from dark fermentation effluent of ground wheat solution: effects of light source and light intensity. *Int J Hydrogen Energy* 2010;35:1595–603.
- [256] Boran E, Özgür E, van der Burg J, Yücel M, Gündüz U, Eroglu I. Biological hydrogen production by *Rhodobacter capsulatus* in solar tubular photo bioreactor. *J Clean Prod* 2010;18:S29–35.
- [257] Gao N, Li A, Quan C, Qu Y, Mao L. Characteristics of hydrogen-rich gas production of biomass gasification with porous ceramic reforming. *Int J Hydrogen Energy* 2012;37:9610–8.
- [258] Jiang D, Ge X, Lin L, Zhang T, Liu H, Hu J, et al. Continuous photobioreactor using corn stalk pith hydrolysate with a consortium. *Int J Hydrogen Energy* 2020;45:3776–84.
- [259] Zhu S, Zhang Z, Zhang H, Jing Y, Li Y, Zhang Q. Rheological properties of corn stover hydrolysate and photo-fermentation bio-hydrogen producing capacity under intermittent stirring. *Int J Hydrogen Energy* 2020;45:3721–8.
- [260] Zhang Y, Zhang T, Zhang Z, Tahir N, Zhang Q. Biohydrogen production from *Humulus scandens* by dark fermentation: potential evaluation and process optimization. *Int J Hydrogen Energy* 2020;45:3760–8.
- [261] Wolfrum EJ, Vanzin G, Huang J, Watt AS, Smolinski S, Maness P-C. Biological water gas shift development. DOE hydrogen, fuel cell, and infrastructure technologies program review. 2003.
- [262] Wolfrum E, Manese P, Watt A, Vanzin G, Huang J, Smolinski S. Biological water gas shift DOE hydrogen, fuel cell, and infrastructure technologies program review. 2003.
- [263] Mendes D, Chibante V, Zheng J-M, Tosti S, Borgognoni F, Mendes A, et al. Enhancing the production of hydrogen via water–gas shift reaction using Pd-based membrane reactors. *Int J Hydrogen Energy* 2010;35:12596–608.
- [264] Yi N, Si R, Saltsburg H, Flytzani-Stephanopoulos M. Active gold species on cerium oxide nanoshapes for methanol steam reforming and the water gas shift reactions. *Energy Environ Sci* 2010;3:831–7.
- [265] Zhai Y, Pierre D, Si R, Deng W, Ferrin P, Nilekar AU, et al. Alkali-stabilized Pt-OHx species catalyze low-temperature water-gas shift reactions. *Science* 2010;329:1633–6.
- [266] Sircar S, Waldron WE, Anand M, Rao MB. Hydrogen recovery by pressure swing adsorption integrated with adsorbent membranes. Google Patents. 1998.
- [267] Baker RW, Lokhandwala KA, He Z, Pinnau I. Process, including PSA and membrane separation, for separating hydrogen from hydrocarbons. Google Patents. 2001.
- [268] Yang RT. Adsorbents: fundamentals and applications. Wiley; 2003.
- [269] Amosova OL, Malykh OV, Teplyakov VV. Integrated membrane/PSA systems for hydrogen recovery from gas mixtures. *Desalin Water Treatment* 2010;14:119–26.
- [270] Gallucci F, Fernandez E, Corengia P, van Sint Annaland M. Recent advances on membranes and membrane reactors for hydrogen production. *Chem Eng Sci* 2013;92:40–66.
- [271] Shalygin MG, Abramov SM, Netrusov AI, Teplyakov VV. Membrane recovery of hydrogen from gaseous mixtures of biogenic and technogenic origin. *Int J Hydrogen Energy* 2015;40:3438–51.
- [272] Lu GQ, Diniz da Costa JC, Duke M, Giessler S, Socolow R, Williams RH, et al. Inorganic membranes for hydrogen production and purification: a critical review and perspective. *J Colloid Interface Sci* 2007;314:589–603.
- [273] Ockwig NW, Nenoff TM. Membranes for hydrogen separation. *Chem Rev* 2007;107:4078–110.
- [274] Ritter JA, Ebner AD. State-of-the-art adsorption and membrane separation processes for hydrogen production in the chemical and petrochemical industries. *Separ Sci Technol* 2007;42:1123–93.
- [275] Relvas F, Whitley RD, Silva C, Mendes A. Single-stage pressure swing adsorption for producing fuel cell grade hydrogen. *Ind Eng Chem Res* 2018;57:5106–18.
- [276] Ye F, Ma S, Tong L, Xiao J, Bénard P, Chahine R. Artificial neural network based optimization for hydrogen purification performance of pressure swing adsorption. *Int J Hydrogen Energy* 2019;44:5334–44.
- [277] Zhu X, Shi Y, Li S, Cai N. Elevated temperature pressure swing adsorption process for reactive separation of CO/CO<sub>2</sub> in H<sub>2</sub>-rich gas. *Int J Hydrogen Energy* 2018;43:13305–17.
- [278] Fakhroleslam M, Bozorgmehry Boozarjomehry R, Fatemi S. Design of a dynamical hybrid observer for pressure swing adsorption processes. *Int J Hydrogen Energy* 2017;42:21027–39.



- [279] Shukla A, Sahoo S, Moharir AS. Non-isothermal Multi-cell Model for pressure swing adsorption process. *Int J Hydrogen Energy* 2017;42:5150–67.
- [280] Yong Z, Mata V, Rodrigues ArE. Adsorption of carbon dioxide at high temperature—a review. *Separ Purif Technol* 2002;26:195–205.
- [281] Zhao R, Liu L, Zhao L, Deng S, Li S, Zhang Y. A comprehensive performance evaluation of temperature swing adsorption for post-combustion carbon dioxide capture. *Renew Sustain Energy Rev* 2019;114:109285.
- [282] Joss L, Hefti M, Bjelobrk Z, Mazzotti M. On the potential of phase-change adsorbents for CO<sub>2</sub> capture by temperature swing adsorption. *Energy Proced* 2017;114:2271–8.
- [283] He J, Deng S, Zhao L, Zhao R, Li S. A numerical analysis on energy-efficiency performance of temperature swing adsorption for CO<sub>2</sub> capture. *Energy Proced* 2017;142:3200–7.
- [284] Ribeiro RPPL, Grande CA, Rodrigues AE. Electric swing adsorption for gas separation and purification: a review. *Separ Sci Technol* 2014;49:1985–2002.
- [285] Wang B, Zhou R, Yu L, Qiu L, Zhi X, Zhang X. Evaluation of mass transfer correlations applying to cryogenic distillation process with non-equilibrium model. *Cryogenics* 2019;97:22–30.
- [286] Yousef AM, El-Maghlany WM, Eldrainy YA, Attia A. New approach for biogas purification using cryogenic separation and distillation process for CO<sub>2</sub> capture. *Energy* 2018;156:328–51.
- [287] Bhattacharyya R, Bhanja K, Mohan S. Simulation studies of the characteristics of a cryogenic distillation column for hydrogen isotope separation. *Int J Hydrogen Energy* 2016;41:5003–18.
- [288] Bernardo G, Araújo T, da Silva Lopes T, Sousa J, Mendes A. Recent advances in membrane technologies for hydrogen purification. *Int J Hydrogen Energy* 2020;45:7313–38.
- [289] Gouedard C, Picq D, Launay F, Carrette PL. Amine degradation in CO<sub>2</sub> capture. I. A review. *Int J GHG Cont* 2012;10:244–70.
- [290] Dutcher B, Fan M, Russell AG. Amine-based CO<sub>2</sub> capture technology development from the beginning of 2013-A review. *ACS Appl Mater Interfaces* 2015;7:2137–48.
- [291] Sazali N, Salleh WNW, Ismail AF. Carbon tubular membranes from nanocrystalline cellulose blended with P84 co-polyimide for H<sub>2</sub> and He separation. *Int J Hydrogen Energy* 2017;42:9952–7.
- [292] Tseng H-H, Shiu P-T, Lin Y-S. Effect of mesoporous silica modification on the structure of hybrid carbon membrane for hydrogen separation. *Int J Hydrogen Energy* 2011;36:15352–63.
- [293] Adams JS, Itta AK, Zhang C, Wenz GB, Sanyal O, Koros WJ. New insights into structural evolution in carbon molecular sieve membranes during pyrolysis. *Carbon* 2019;141:238–46.
- [294] Sinha P, Pandey A. An evaluative report and challenges for fermentative biohydrogen production. *Int J Hydrogen Energy* 2011;36:7460–78.
- [295] Sołowski G, Shalaby MS, Abdallah H, Shaban AM, Cenian A. Production of hydrogen from biomass and its separation using membrane technology. *Renew Sustain Energy Rev* 2018;82:3152–67.
- [296] Saqib S, Rafiq S, Chawla M, Saeed M, Muhammad N, Khurram S, et al. Facile CO<sub>2</sub> separation in composite membranes. *Chem Eng Technol* 2019;42:30–44.
- [297] Yin H, Yip ACK. A review on the production and purification of biomass-derived hydrogen using emerging membrane technologies. *Catalysts* 2017;7:297.
- [298] Strathmann H. Membrane separation processes: current relevance and future opportunities. *AIChE J* 2001;47:1077–87.
- [299] Bernardo P, Drioli E, Golemme G. Membrane gas separation: a review/state of the art. *Ind Eng Chem Res* 2009;48:4638–63.
- [300] Drioli E, Giorno L, Fontananova E. Comprehensive membrane science and engineering. Elsevier Science; 2017.
- [301] Bhattacharya A, Misra BN. Grafting: a versatile means to modify polymers: techniques, factors and applications. *Prog Polym Sci* 2004;29:767–814.
- [302] Lalia BS, Kochkodan V, Hashaikh R, Hilal N. A review on membrane fabrication: structure, properties and performance relationship. *Desalination* 2013;326:77–95.
- [303] Perry JD, Nagai K, Koros WJ. Polymer membranes for hydrogen separations. *MRS Bull* 2006;31:745–9.
- [304] Robeson LM. Correlation of separation factor versus permeability for polymeric membranes. *J Membr Sci* 1991;62:165–85.
- [305] Low BT, Xiao Y, Chung TS, Liu Y. Simultaneous occurrence of chemical grafting, Cross-linking, and etching on the surface of polyimide membranes and their impact on H<sub>2</sub>/CO<sub>2</sub> separation. *Macromolecules* 2008;41:1297–309.
- [306] Huang X, Yao H, Cheng Z. Hydrogen separation membranes of polymeric materials. Nanostructured materials for next-generation energy storage and conversion. Springer; 2017. p. 85–116.
- [307] Thornton AW, Dubbeldam D, Liu MS, Ladewig BP, Hill AJ, Hill MR. Feasibility of zeolitic imidazolate framework membranes for clean energy applications. *Energy Environ Sci* 2012;5:7637–46.
- [308] Yun S, Ted Oyama S. Correlations in palladium membranes for hydrogen separation: a review. *J Membr Sci* 2011;375:28–45.
- [309] Li H, Caravella A, Xu HY. Recent progress in Pd-based composite membranes. *J Mater Chem* 2016;4:14069–94.
- [310] Conde JJ, Maroño M, Sánchez-Hervás JM. Pd-Based Membranes for hydrogen separation: review of alloying elements and their influence on membrane properties. *Separ Purif Rev* 2017;46:152–77.
- [311] Al-Mufachi NA, Rees NV, Steinberger-Wilkens R. Hydrogen selective membranes: a review of palladium-based dense metal membranes. *Renew Sustain Energy Rev* 2015;47:540–51.
- [312] Zhang K, Way JD. Palladium-copper membranes for hydrogen separation. *Separ Purif Technol* 2017;186:39–44.
- [313] Nikolaidis P, Poullikkas A. A comparative overview of hydrogen production processes. *Renew Sustain Energy Rev* 2017;67:597–611.
- [314] Sharma M, Kaushik A. Biohydrogen economy: challenges and prospects for commercialization. In: Singh A, Rathore D, editors. Biohydrogen production: sustainability of current technology and future perspective. New Delhi: Springer India; 2017. p. 253–67.
- [315] Hsu C-W, Lin C-Y. Commercialization model of hydrogen production technology in Taiwan: dark fermentation technology applications. *Int J Hydrogen Energy* 2016;41:4489–97.