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# Biorenewable hydrogen production through biomass gasification: A review and future prospects



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#### ABSTRACT

Hydrogen is recognized as one of the cleanest energy carriers, which can be produced from renewable biomass as a promising feedstock to achieve sustainable bioeconomy. Thermochemical technologies (e.g., gasification and pyrolysis) are the main routes for hydrogen production from biomass. Although biomass gasification, including steam gasification and supercritical water gasification, shows a high potential in field-scale applications, the selectivity and efficiency of hydrogen production need improvement to secure cost-effective industrial applications with high atom economy. This article reviews the two main-stream biomass-to-hydrogen technologies and discusses the significance of operating conditions and considerations in the catalytic system design. Challenges and prospects of hydrogen production via biomass gasification are explored to advise on the critical information gaps that require future investigations.

#### 1. Introduction

With rapid economic development and continuous growth of world population, consumption of energy is sharply increasing. At present, fossil fuels still dominate the energy market, accounting for 87% of global energy consumption (Zhou et al., 2019). However, there are increasing environmental concerns over the depletion of fossil resources and significant greenhouse gas emissions (Zhai et al., 2018), which should be alleviated by developing and utilizing clean and renewable energy. Hydrogen energy is the cleanest among alternative energy sources producing water as the only combustion product, which enables to truly achieve "zero emission" of pollutants (Li et al., 2018; Yiin et al., 2018). The combustion calorific value of hydrogen is 142.3 MJ/kg, which is three times higher than that of gasoline (Remon et al., 2018), making it a clean, efficient, and renewable energy.

Nowadays, industrial hydrogen production methods mainly include water electrolysis, methanol steam reforming, and steam catalytic conversion of heavy oil and natural gas (Yiin et al., 2018; Terrell and

Theegala, 2019; Ju et al., 2018a; Wang et al., 2018). The electrolytic water process consumes massive amount of electricity incurring a high cost (Chen et al., 2019). Although methanol steam reforming is currently the most economical method, it uses non-renewable fossil fuels as the raw material and generates CO<sub>2</sub> as a by-product (Lv et al., 2019; Zhang, 2018). Steam catalytic conversion of heavy oil and natural gas is also not sustainable. In comparison, biomass hydrogen production is an efficient, energy-saving, and environmentally friendly hydrogen production route (Chan et al., 2019a; Barbuzza et al., 2019; Shayan et al., 2019). Biomass is a renewable natural resource of biological origin that is easily accessible from various industries. Agricultural, forestry, fishery, livestock, and municipal wastes such as straw, rice husk, cellulose, sawdust, and animal manure are common types of biomass in large quantities, emerging as a sustainable feedstock for biorefinery (Resasco et al., 2018; Zhang et al., 2018a). Biomass contains organic materials with abundant carbon, oxygen, and hydrogen. The mass fraction of H element in biomass is ~6%, which is equivalent to 0.672 m<sup>3</sup> gaseous hydrogen produced by 1 kg biomass, accounting for

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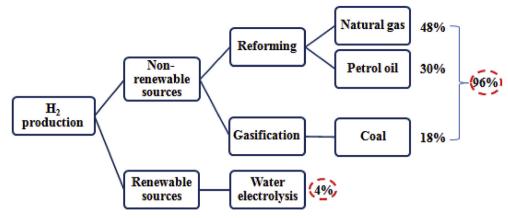


Fig. 1. Proportion of non-renewable or renewable sources for the present H<sub>2</sub> production technologies.

more than 40% of the total energy of biomass (El-Emam and Ozcan, 2019). At present, biomass-based hydrogen production technology mainly includes thermochemical, biological, and electrolysis methods (Lin et al., 2018; Ju et al., 2018a). While biological and electrolysis hydrogen production are difficult for scale-up and have low production rates (Yang et al., 2018), thermochemical hydrogen production is gaining attention (Barbuzza et al., 2019; Shayan et al., 2019).

The main routes of biomass thermochemical conversion consist of gasification and pyrolysis. Compared with pyrolysis, biomass gasification occurs at higher temperature in the presence of oxidizing agent, and mainly produces gaseous products, which is recognized as a more effective way to produce syngas (H<sub>2</sub> and CO) (Yang et al., 2018; Catalan-Martinez et al., 2018; Houcinat et al., 2018; Qiu et al., 2018). Syngas can be used for heating, power generation, and production of synthetic chemicals such as methanol, dimethyl ether, and ammonia (Chan et al., 2019a, 2019b; George et al., 2018). In addition, hydrogen of high purity obtained by further conversion of CO in syngas can be used in fuel cells (Jeong et al., 2019; Sharma, 2019). At present, fossil resources account for 96% of the main sources of hydrogen and methane steam reforming accounts for about 48% (Fig. 1) (Chan et al., 2019a).

Therefore, it is imperative to develop efficient gasification technologies using biomass feedstock, securing clean energy with low-carbon emission to help combat global warming and achieve waste recovery. In this regard, this paper comprehensively reviews the recent research advances on hydrogen production from biomass gasification. This paper summarizes the updated researches on biomass gasification, compares the routes of two mainstream biomass-to-hydrogen technologies (i.e., steam gasification and supercritical water gasification), and critically discusses the roles of operating conditions as well as novel catalysts. This manuscript provides an overview of the state-of-the-art researches of biomass-to-hydrogen gasification, and subsequently puts forward challenges and prospects for improving the process efficiencies as well as product qualities (e.g., hydrogen-rich syngas), which is of great significance for achieving green and sustainable development.

#### 2. Hydrogen production from biomass

#### 2.1. Various biomass as feedstock

Biomass, originally an ecological term, has broadened its definition when the concept of renewable energy was introduced after the oil crisis (Arun et al., 2019). Biomass is a variety of biological organisms derived from natural and non-fossil materials synthesized through photosynthesis. It includes plants, animals, and microorganisms as well as their associated waste. Biomass also refers to waste generated in the agricultural and forestry activities, such as agricultural residues, forest residues, energy crops, agro-industrial waste, and municipal waste

Table 1
Ultimate and proximate analyses (wt%) of various biomass.

Biomass	С	Н	N	S	0	Ash	Moisture	Organic fraction
Wood	50.8	6.06	42.7	0.07	42.7	1.84	19.8	78.4
Legume straw	43.3	5.62	0.61	0.12	50.35	9.8	1.62	73.74
Apricot stone	44.39	5.74	0.37	0.05	49.45	8.52	0.17	75.14
Hornbeam shell	41.78	5.36	0.60	0	52.26	9.52	2.28	78.83
Hornbeam sawdust	45.18	6.59	0	0	48.23	0.45	8.78	78.14
Rice husk	42.0	5.4	0.4	0	39.3	12.9	1.1	70.5
Straw	48.9	5.97	0.82	0.15	43.9	6.37	12.7	80.9
Safflower seed	60.46	9.08	3.10	0	27.36	2.2	5.7	80.8
Sludge	50.2	7.09	5.63	1.77	34.9	25.7	32.5	41.8
Sawdust	52	6.07	0.28	0	41.55	0.1	_	_
Manure	50.2	6.50	6.50	0.85	34.6	17.2	43.6	39.2
Vegetable oils	75.4	11.7	0	12.9	0	0	0	100

Sources: Ahmed et al. (2012); Alvarez et al. (2014); Li et al. (2004); Morali et al. (2016); Onay, 2007.

(Table 1) (Cao et al., 2018b; Lam et al., 2018; Mak et al., 2018). Biomass is renewable carbon-based resources with broad distributions and species, which do not require strict conditions and grow steadily in the environment (Lee et al., 2019). The abundant and wide availability of waste biomass around the world does not compete with food crops nor interrupt the environmental life cycle in terms of land occupation and water consumption. Valorization of waste biomass is an environmentally friendly approach of waste management and sustainable energy production, which effectively reduce greenhouse gas emissions and mitigate climate change. Therefore, biomass is emerging as an important source of renewable energy in place of fossil-based energy to power a green and sustainable community and boost the development of circular bioeconomy, as promoted by different jurisdictions (Chan et al., 2019a; Yan et al., 2019a, 2019b; Zhang et al., 2019). For example, the U.S. Department of Energy aims to replace 20% of fossil fuel with biomass energy by 2030; the European Union expects that biomass energy will account for no less than 10% of energy consumption by 2020. China has also listed biomass alternative fuel as one of the key renewable energy projects (Chan et al., 2019a).

The main way to produce hydrogen from biomass is thermochemical routes (Fig. 2) which include steam gasification, supercritical water gasification, and fast pyrolysis (Ebadi et al., 2019). Compared with pyrolysis, gasification is recognized to be more promising in industrial production because of their higher efficiency and  $\rm H_2$  yield (Table 2) (Gai et al., 2016; Shahbaz et al., 2017). There are various types of biomass as potential feedstocks for hydrogen production via gasification, which are discussed in the following sections (Section 2.1.1 to 2.1.4).

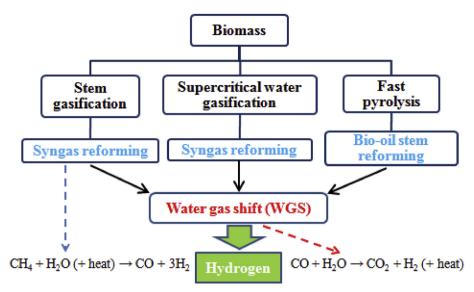


Fig. 2. Main routes of thermochemical processes for biomass based H<sub>2</sub> production.

#### 2.1.1. Lignocellulosic biomass

Lignocellulose (mainly agroforestry biomass) is composed of tightly bound biopolymers, i.e., cellulose, hemicelluloses, and lignin (Supanchaiyamat et al., 2019; Lee et al., 2017). Global farmland and forests produce about 11.4 billion of biomass annually, of which agricultural production accounts for 40%, pasture output accounts for 30%, timber accounts for 18%, and 12% from by-products (Zhu et al., 2019). Hydrogen production from lignocelluloses gasification (e.g., energy crop (Helianthus tuberosus L. (Smolinski et al., 2018)), agricultural waste (palm kernel shell (Khan et al., 2018; Yahaya et al., 2019)), and forestry waste beech-wood (Zhu et al., 2019)) has been extensively studied, which is a promising approach for the utilization/valorization of these wastes generated in huge amount.

#### 2.1.2. Algae biomass

According to Food and Agriculture Organization of the United Nations, the world produces 150–600 tons of fresh algae per hectare annually, with an annual output of 12 million tons of dry matter, (Adnan et al., 2019), representing a good opportunity for biomass-to-hydrogen industry (Cao et al., 2019). Compared with traditional direct combustion, algae biomass gasification is recognized as a more effective way of resource utilization, because the produced syngas can be used for various purposes (Adnan and Hossain, 2018). Recent studies have demonstrated the potential of hydrogen production from different algae species through gasification (De Clercq et al., 2017).

#### 2.1.3. Food waste

Food waste is a large group of municipal solid waste that generates

during the food supply chain from production to consumption. It was estimated that 1.3 billion tons food waste was generated annually over the world. In China, about 140 million tons of food wastes are produced annually, 98% of which are directly disposed of by landfill or incineration, causing serious environmental threats (Chen et al., 2019). Unlike hazardous solid waste, food waste contains a large amount of reusable organic components, such as carbohydrates (starch, sugar, and cellulose), proteins, and oils (Duman et al., 2018). Therefore, the scientific community has drawn great attention to food waste valorization, which sustainably convert waste as renewable resources into valueadded products (Xiong et al., 2019; Yu and Tsang, 2017; Chen et al., 2017). Based on the characteristics of high organic and moisture content of food waste, hydrogen production from food waste through gasification (especially supercritical gasification) has attracted wide attention and shown good application prospect (Yan et al., 2019; Zheng et al., 2018).

#### 2.1.4. Municipal solid waste

With the development of economy and the improvement of living quality, the annual output of global municipal solid waste (MSW) is growing rapidly. For example, MSW in China has reached 191 million tons in 2015 (Hoornweg et al., 2013) and is expected to reach 510 million tons by 2025 (Zhou et al., 2014). Typical components of MSW include food residues, paper, plastics, wood waste, rubber, textiles, and non-combustible materials (Irfan et al., 2019). In recent years, MSW gasification has become a promising alternative to MSW incineration, since this method can not only produce value-added products (i.e., syngas, char, and tar), but also reduce the emissions of dioxins and

**Table 2**Different strategies for hydrogen production from biomass by thermochemical processes.

	Steam gasification	Supercritical water gasification	Fast pyrolysis
Average H <sub>2</sub> production (wt%, g	Without catalyst: 4 g	Without catalyst: 3 g	Without catalyst: 2 g
$H_2/100$ g biomass)	With catalyst: 7 g	With catalyst: 5 g	With catalyst: 3 g
Reactor	Upper/lower ventilation gasifier; Fluidized bed	Batch reactor, Continuous reactor	Fluidized bed; Fixed bed; Rotary furnaces; Ablation reactor; Drainage bed
Advantage	Suitable for large-scale industrial production with high gasification rate and low ash production.	High conversion and hydrogen concentration without tar and coke formation and secondary pollution.	Oxygen free and relatively high hydrogen concentration.
Disadvantage	Separation and purification of gas products are difficult.	Difficult to recycle alkaline catalysts and strict operating conditions.	High equipment requirement and energy consumption with low hydrogen yield.
Challenge	Decrease the tar content; Optimize the catalyst composition to reduce its deactivation; Reduce energetic and material costs	Technological development; Reduce energetic costs	Raw bio-oil feeding; Scale up of the process; Optimize the catalyst composition to reduce its deactivation

nitrogen oxides due to the reductive environment during the gasification process (Hoornweg et al., 2013; Shao et al., 2019).

## 2.2. Comparison of thermochemical method with other techniques for hydrogen production

Bioconversion is another method to produce hydrogen from biomass. The main biological methods for producing biomass hydrogen include fermentation, photosynthesis, and water gas shift reactions (Mishra et al., 2019; Pachapur et al., 2019; Rodrigues et al., 2019). Fermented hydrogen production is a multi-enzyme system that uses a variety of bacterial populations to convert organic substrates into hydrogen. It includes dark fermentation and photoheterotrophic fermentation (Mishra et al., 2019). Dark fermentation uses abundant and lowcost anaerobic bacteria to produce hydrogen in the dark. It can produce hydrogen from carbohydrate-rich biomass between 30 °C and 80 °C. However, some impurities, such as CH<sub>4</sub> or H<sub>2</sub>S, are mixed into the product. In order to expand practical application, it is necessary to establish a benign method for separating and purifying gases from mixtures. Photo-fermentative process is different from dark fermentation because it requires light and is similar to the production of photosynthetic hydrogen. Photosynthetic hydrogen production can produce hydrogen in aquatic environments under ambient temperatures and pressures (Magnin and Deseure, 2019; Menia et al., 2019). However, it is inefficient for microalgae or cyanobacteria to use light energy to decompose water molecules into oxygen and hydrogen ions (Assawamongkholsiri et al., 2019). This is one of the main barriers that restrict the application. Nowadays, more attention has been paid to the production of hydrogen by water gas shift (Remon et al., 2018; Zhang et al., 2018b). This method involves the reaction of carbon monoxide and water vapour through certain bacteria to form carbon dioxide and hydrogen. Improving hydrogen production rate is one of the main research directions. When a steel autoclave is used as a reactor, the biological method is also affected by slow heating and long reaction time. Biological hydrogen production from biomass takes the advantages of safety, low cost, and pollution-free. However, this process is still in the stage of laboratory-scale research due to its low H2 yield, poor controllability, long duration time and high operating cost (Rodrigues

Besides bioconversion, electrolytic hydrogen production from biomass is a new technology which can obtain H<sub>2</sub> directly from protoplasmic biomass such as starch, cellulose, and lignin (Kaya et al., 2012). Compared with other approaches, electrolytic hydrogen production from biomass can be carried out at lower temperature and pure H<sub>2</sub> can be obtained without further purification (Caravaca et al., 2019). However, the intermediates and final products of the electrolysis process are not yet clear, and the reaction mechanism needs to be elucidated. There are many organic substances generated in the anode solution after electrolysis. So far, no robust method has been established to separate and dispose of them, which will cause environmental pollution (Kaya et al., 2012; Lewis and Borole, 2019). Therefore, compared with biological and electrolytic routes, thermochemical conversion via gasification shows excellent performance with higher efficiency and H<sub>2</sub> yield as well as feasibility of scale-up (Rapagna et al., 2018).

#### 3. Hydrogen production from biomass gasification

#### 3.1. Reaction routes

#### 3.1.1. Steam gasification of biomass

Biomass steam gasification involves the conversion of raw biomass materials into combustible gases ( $H_2$ , CO,  $CO_2$ ,  $CH_4$  and hydrocarbons) under high temperature facilitating the introduction of water vapour as a gasification agent (Fig. 3) (Table 3). Biomass characteristics and gasification operating conditions, such as reaction temperature, and steam-to-biomass ratio, play a key role in regulating the hydrogen

content in syngas (Zhang and Pang, 2017). It is generally accepted that steam is the most suitable gasification agent for production of hydrogen-rich syngas. Biomass steam gasification mainly contains the reactions of carbon gasification (Equation (1)), water-gas conversion (Equation (2)), methane reforming (Equation (3)), and hydrocarbon reforming (Equation (4)). Under the conditions of introducing water vapour, the hydrogen content in syngas can be further increased by adding catalysts and absorbents (Schweitzer et al., 2018; Hernandez et al., 2012).

$$C + H_2O \rightarrow H_2 + CO \Delta H_{298K} = 131 \text{ kJ/mol}$$
 (1)

$$CO + H_2O \rightarrow H_2 + CO_2 \Delta H_{298K} = -40.9 \text{ kJ/mol}$$
 (2)

$$CH_4 + H_2O \rightarrow 3H_2 + CO \Delta H_{298K} = 206.3 \text{ kJ/mol}$$
 (3)

$$C_a H_b + a H_2 O \rightarrow a CO + (a+b/2) H_2$$
 (4)

#### 3.1.2. Supercritical water gasification of biomass

Supercritical water gasification is the hydrothermal gasification of biomass in a liquid water processing medium, when the properties of the liquid and gaseous phases existing above the critical point are referred to as supercritical state (Heidenreich et al., 2016). In supercritical water, biomass can be decomposed by pyrolysis, hydrolysis, condensation, and dehydrogenation to produce hydrogen, carbon monoxide, carbon dioxide, methane, and other gases (Fig. 4). The reaction process mainly includes steam reforming reaction (Equation (5)), water-gas conversion (Equation (6)), and methanation (Equations (7) and (8)) (Sharma, 2019; Okolie et al., 2019). In this process, water acts as both a reaction medium and a reactant, so it is unnecessary to dry the raw material before supercritical water gasification, which significantly reduces the energy consumption (Nanda et al., 2019).

$$CH_n O_m + (1-m) H_2 O \rightarrow (n/2 + 1 - m) H_2 + CO$$
 (5)

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{6}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$
 (7)

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$
 (8)

#### 3.2. Catalysts used for hydrogen production from biomass gasification

For both steam gasification (SG) and supercritical water gasification (SWCG), the use of catalysts can decrease the reaction temperature and improve the carbon gasification rate and hydrogen selectivity from biomass (Cao et al., 2018a; Colmenares et al., 2016; Xiong et al., 2017). The biggest disadvantage of SG compared with SWCG and fast pyrolysis is the high likelihood of tar formation during the process (Ebadi et al., 2019). Tar is a complex mixture consisting of alcohols, phenols, aldehydes, and aromatic compounds. Its formation will cause problems such as pipeline blockage which increases operation and maintenance costs (Qiu et al., 2018). Nevertheless, tar contains energy components. If it can be converted, the gasification efficiency will be greatly improved. Adding catalyst is an effective way to promote tar cracking and reforming of condensable fractions. Catalysts commonly used in both gasification routes include alkaline earth metallic catalysts, metal-based catalysts (e.g., Ni, Ce, La), and mineral catalysts. During gasification, catalysts can be added by directly mixing with raw materials, or they can be placed in a secondary reactor to crack newly formed tar (Grams and Ruppert, 2017).

#### 3.2.1. Alkaline earth metallic catalysts

Alkali catalysts are the most widely used catalysts for biomass gasification, such as KOH, NaOH, K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, KHCO<sub>3</sub>, and Ca(OH)<sub>2</sub>. The use of alkali metal catalysts not only can increase the volatility of the gaseous phase, but also enhance the steam reforming reactions. Ebadi et al. (2019) investigated the effect of alkali and alkaline earth

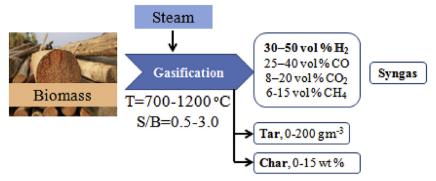


Fig. 3. Biomass-based hydrogen production through steam gasification process.

metal catalysts (e.g., NaOH, KHCO $_3$ , Na $_3$ PO $_4$ , and MgO) on the syngas yield and tar content of the steam gasification of algal (*Cladophora glomerata* L.). The results showed that the catalysts had a strong promoting effect on hydrogen production, char conversion, and tar destruction. Cao et al. (2017) observed a synergetic effect during co-gasification of black and liquor coal, where both the hydrogen production and gasification efficiency were improved by efficient catalysis of coal gasification by the alkali compounds in black liquor. The additional benefit of this processing is the simultaneous handling of black liquor. The conversion efficiency was improved with an increase of temperature and the optimal carbon conversion rate (79.5%) was achieved at 750 °C.

Alkali metal catalysts not only catalyze natural biomass gasification, but also show more effective catalytic activity on the gasification of hydrochar. Gai et al. (2016) investigated the steam gasification of sewage sludge derived hydrochar for hydrogen production. The hydrogen-rich gas production from both sewage sludge and its hydrochar was improved in the presence of alkali catalysts, especially for the hydrochar. Qiu et al. (2018) reported the steam gasification of char derived from low-rank coal catalyzed by Na and Ca alkali catalysts. The results indicated that both Na and Ca species could significantly increase H2 production. However, Na and Ca catalysts have different catalytic reaction mechanisms and deactivation pathways. During Nachar gasification, the loss of Na is the main reason for the decrease of H<sub>2</sub> production as temperature increases. While the promotion of H2 production during Ca-char gasification is attributed to the enhanced Ca activity. The catalytic effect of LiOH is similar in the process of hydrogen production by biomass gasification and also increases hydrogen production through water-gas shift reaction (Cao et al., 2018; Miyaoka et al., 2015). Nanou et al. (2013) added 9.5 wt% KOH to the steam gasification reactor and studied the kinetics by changing the parameters of carbon particle size, bed height, and steam flow rate. The reaction followed the first-order kinetics. Alkali metal catalysts can significantly improve the conversion of carbon in biomass gasification process and inhibit the tar formation (Tang et al., 2016). Alkali metal catalysts play an important role in improving H2 production through biomass gasification by influencing the steam reforming process.

#### 3.2.2. Metal and metallic oxides catalysts

In addition to alkali metals, metals and metal oxides can also catalyze the production of hydrogen from biomass gasification. They have a great potential as catalysts with high selectivity, recyclability, and earth abundance (Mishra et al., 2019; Pachapur et al., 2019). Metalbased catalysts could be synthesized by impregnation of active metals onto the carbon supports, such as biochar (Sun et al., 2019; Wan et al., 2019; Yu et al., 2019). Nickel-based catalysts allow good carbon conversion for syngas or hydrogen from biomass gasification. In addition, they can promote the rapid pyrolysis of hydrocarbons during steam reforming and water-gas shift reaction, exhibiting high catalytic activity (Gai et al., 2018) and good practical application potential (Gao

et al., 2016). Recent findings on using these catalysts in hydrogen production from biomass conversion are shown in Table 4.

Ni was one of the earliest catalysts used in biomass gasification, and it has been used to improve the gasification efficiency of glucose (Niu et al., 2017) In order to study the catalytic effect of Ni, Said et al. (2017) impregnated Ni (0.1 wt%) into biomass (willow) and pyrolyzed it to produce biochar. In the gasification test of willow biochar, it was found that at the temperature of 450 °C–600 °C Ni promoted the gasification rate of biochar and the syngas yield, and the presence of Ni also lowered the gasification temperature of biochar by 100 °C. Stonor et al. (2017) reported the screening of Ni, Fe, Cu, Pd, Pt, and Co for catalyzing cellulose gasification and verified that Ni could significantly increase H<sub>2</sub> production when used *in-situ* or *ex-situ*.

As mentioned above, Ni-based catalysts give an excellent performance in hydrogen production from biomass gasification. When mixed metals are used as catalysts, synergistic effects can further improve the catalytic performance. Gholkar et al. (2019) studied the use of Ni-Rh/y-Al<sub>2</sub>O<sub>3</sub> catalyst for catalyzing the steam gasification of microalgae Scenedesnws sp. The effects of temperature and steam content on the gasification efficiency and the composition of syngas were studied. The results showed that H<sub>2</sub> (65% (v/v)) rich syngas was produced at 650 °C with carbon-to-steam ratio being 0.12. The gasification efficiency was 83% and there was no tar formation. The molar ratio of H2 to CO in hydrogen-rich syngas was 10.9. These results were superior to those from using Ni/γ-Al<sub>2</sub>O<sub>3</sub> catalyst. In addition, strong metal-support interactions of Ni-Fe composite catalysts reduced carbon deposition rate and particle size during gasification (Oemar et al., 2013). Shen et al. (2015) used Ni-Fe catalyst to catalyze the gasification and transformation of rice husk charcoal and optimized the reaction conditions with the conversion rate of tar reaching 92.3%. Jafarian et al. (2017) also obtained similar results, proving that Ni-Fe/γ-Al<sub>2</sub>O<sub>3</sub> nanocatalyst can significantly improve the total gas yield and hydrogen content of bagasse gasification.

Skoulou and Zabaniotou (2012) studied the application of mixed iron slag and pyrolytic carbon as catalysts in biomass gasification. The effects of reaction temperature, heating rate, iron concentration, steam ratio, and other parameters were investigated. It was found that high temperature and high heating rate favoured hydrogen production. In this catalytic system, tar cracking rate was high and iron oxide was active for hydrogen production and tar conversion. Duman et al. (2014a,b) investigated a CeO<sub>2</sub>-FeO<sub>3</sub> catalyst mixed at a ratio of 50/ 50 wt% and showed that this catalyst had a good activity for biomass gasification. The addition of CeO<sub>2</sub> can improve the redox performance of the catalyst, which is conducive to the conversion of tar during gasification. At the same time, the presence of iron oxide changes the structure and surface area of the catalyst, thus promoting tar pyrolysis (Skoulou and Zabaniotou, 2012; Jiang et al., 2015). Lang et al. (2017) used La<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> to improve hydrogen production in supercritical water gasification process. The results showed that La improves the catalytic activity by enhancing the metal dispersion. The addition of Ni,

Table 3 Recent studies on biomass steam gasification and maximum H<sub>2</sub> production.

Biomass	Operating conditions	Catalyst	$\mathrm{H}_2$ production (wt%) <sup>a</sup>	$\rm H_2$ production $(wt\%)^3$ $$ Gas yield $(Nm^3/kg_{biomass})$ $$ Tar content $(g/Nm^3)$ $$ References	Tar content (g/Nm³)	References
Waste wood	$T = 900  ^{\circ}C; S/B = 1$	Silica sand	5.9	1.22	12.5	Fremaux et al. (2015)
Wood pellets	$T = 815  ^{\circ}C;  S/B = 0.84$	Primary: Olivine	0.76	2.2	4.4	Vilches et al. (2016)
Pine wood	T = 850 °C	None	6.2	1.4	ı	Niu et al. (2017)
Pine wood pellets	$T = 820  ^{\circ}C; S/B = 2$	Silica sand	1.8	0.82	10.3	(Zhang and Pang, 2017)
Pinewood sawdust	$T = 800-900  ^{\circ}C;  S/B = 0-2$	None	3.3	0.96	142	Erkiaga et al. (2014)
Pinewood sawdust	$T = 900  ^{\circ}C;  S/B = 1$	<i>Primary:</i> Olivine; $\gamma$ - Al <sub>2</sub> O <sub>3</sub>	4.4	1.15	22.4	Erkiaga et al. (2013)
Almond shells	$T = 820  ^{\circ}C;  S/B = 0.72$	Primary: Olivine (0.9)/dolomite (0.1)	7.3	1.58	2.13	Rapagna et al. (2018)
Almonds shells	Gasifier: $T = 808-813$ °C; S/B = 1.03-1.28	<i>Primary:</i> Olivine <i>Secondary:</i> NiO/Al <sub>2</sub> O <sub>3</sub>	14.5	2.9	0.15	Rapagna et al. (2012)
Palm shells	$T = 850  ^{\circ}C;  S/B = 0.6-1$	None	3.7	0.8	1.2	Iovane et al. (2013)
Sewage sludge	$T = 820  ^{\circ}C;  S/B = 1.5$	Silica sand	3.6	0.85	122	Schweitzer et al. (2018)
Dealcoholised marc of grape	$T = 1050 ^{\circ}C;  S/B = 1.02-3.19$	None	1.3	9.0	1	Hernandez et al. (2012)

<sup>a</sup> Based on biomass.

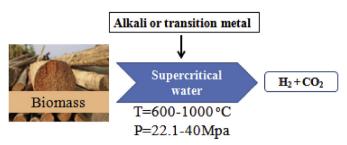


Fig. 4. Biomass-based hydrogen production through supercritical water gasification process.

NiO, and NiAlO<sub>2</sub> is helpful to the gasification of biochar in supercritical water by enhancing the cracking of intermediate tar. Chowdhury et al. (2018) also studied the addition of Ni to  $\rm La_2O_3/Al_2O_3$ . The obtained catalyst showed high hydrogen production at high temperature, long residence time, and low feed concentration. Similarly, La and Ce play a synergistic role in the cracking process of heavy oil. The production of reactive oxygen species is enhanced by the presence of  $\rm Ce^{4+}/\rm Ce^{3+}$  oxidative couples and the breakage of C–C bond (Sanchez-Sanchez et al., 2007). Mazumder and de Lasa (2015) optimized the preparation conditions of  $\rm La_2O_3/Al_2O_3$  catalyst and the gasification activity of the catalyst could be improved by modifying the structure and morphology of the catalyst. The results showed that at the concentration of  $\rm La_2O_3$  of 5%, the carbon conversion could reach 97%.

#### 3.2.3. Natural mineral catalysts

Some natural minerals, such as dolomite (MgCO<sub>3</sub>·CaCO<sub>3</sub>) and olivine (2MgO·SiO<sub>2</sub>) also have catalytic effects on biomass gasification (Basu and Pradhan, 2019; Ma et al., 2019). Under the catalysis of olivine and dolomite, the content of hydrogen increases and carbon monoxide decreases. However, when olivine is used as catalyst, the volume fraction of carbon dioxide usually reaches about 50%, suggesting that olivine has no selectivity for hydrogen (Wang et al., 2017). The catalytic mechanism is that calcined mineral catalyst forms CaO–MgO complex in the form of particles. The surface of these particles has active polar sites which can adsorb hydrocarbons, break C–C and C–H bonds, promote water-gas shift reaction, and change the product distribution in the reaction, thereby yielding small molecular gas and liquid products. Natural minerals can catalyze the decomposition of macromolecular hydrocarbons in tar and char (Ma et al., 2019; Zhang et al., 2017).

#### 3.2.4. Hybrid catalysts

Hybrid catalysts are also applicable for hydrogen production from biomass gasification. Ryczkowski et al. (2016) investigated the effect of  $\rm ZrO_2$  catalysts containing 20% nickel and 1% calcium, magnesium, sodium, or potassium (as oxides) on the composition of gaseous products. The results showed that the addition of alkali metals and alkaline earth metals in  $\rm Ni/ZrO_2$  catalyst had an explicit effect on the catalytic conversion of cellulose at high temperatures. The hydrogen production was significantly increased by introducing alkali metals and alkaline earth metals on the surface of nickel catalysts, and the effect on calcium modified catalysts was the most obvious. Chan and Tanksale (2016) investigated the production of syngas via steam gasification of pinewood and eucalyptus sawdust over hybrid catalysts. The catalytic effects of alkali metals and alkaline earth metals species further reduced the coke deposition on the  $\rm Ni$  catalysts, making the effect of  $\rm Ni$  catalysts even more significant.

#### 3.2.5. Comparison and selection of catalysts

In biomass gasification, suitable catalysts can be selected according to the given situation for the purpose of improving the carbon conversion and hydrogen production. Traditional alkali metal catalysts can effectively promote biomass gasification (both steam and supercritical

nable 4
Typical Ni-based and other metal catalysts used in biomass gasification.

Catalyst	T (°C)	S/C ratio	T (°C) S/C ratio Carbon conversion (%) Remarks	Remarks	Refs
Ni/Al <sub>2</sub> O <sub>3</sub>	550-650	8	62–90	Steam reforming of glycerol in the fixed-bed reactor	(Iriondo et al., 2010; Sanchez and Comelli, 2012; Bobadilla et al., 2012)
Ni-Na/Al <sub>2</sub> O <sub>3</sub>	400	7.5	Na: 93.8	K addition into catalyst presents high activity for acetic acid steam reforming	(Hu and Lu, 2007)
$Ni-K/Al_2O_3$			K: 100		
$Ni-Mg/A_{12}O_3$			Mg: 47.8		
Ni/Al	650	4.35	100	High activity for the steam reforming of acetic acid	Sun et al. (2013)
Ni/Zn/Al	009	2	1	Low coke formation ( $< 3.2\%$ ) by coprecipitation method	Nieva et al. (2014)
Ni/Al/Zn	200	1.4	100	Catalyst of 8 wt% Ni/20 wt% Zn showed highest activity	(Men and Yang, 2012)
Ni/B/Al	800	1	61	Boron improved conversion and stability	Xu et al. (2009)
Cu/Zn/Zr	260	1.2	100	High activity for methanol steam reforming	Zhang et al. (2013)
Rh/Zr/Ce	200	4	95.2	High conversion at lower temperature with low S/C ratio	Li et al. (2015)
Co/La/Al <sub>2</sub> O <sub>3</sub>	400	1	85	18 wt% Co loading in catalyst was best for steam reforming	(Hu and Lu, 2010)
Rh/CeO <sub>2</sub> -ZrO <sub>2</sub>	650	3	06	0.5 wt% Rh loading in catalyst had highest activity and selectivity	(Vagia and Lemonidou, 2010)
Ru/SrO-Al <sub>2</sub> O <sub>3</sub>	009	2.0	80	Superior catalytic activity for steam gasification of biomass tar	Iida et al. (2015)
Pt/Co/CeO <sub>2</sub>	350	3	100	High activity and selectivity for bioethanol steam reforming	(Iulianelli et al., 2018)

water gasification), but some drawbacks exist such as difficult recovery, large amount of loading, easy scaling, and blockage (Okolie et al., 2019). Although noble metals such as Ru and Rh have high catalytic activity in both routes, they cannot be put into use on a large scale due to economic consideration (Chan et al., 2019a). Ni-based catalysts have been widely used as effective catalysts, and it is better to utilize them in combination with other metals (Shen et al., 2015; Gai et al., 2018). The commonly used Al-based catalysts in steam gasification are not preferential in supercritical water gasification because they are soluble in water at high temperatures. Metal oxides not only have catalytic activity, but also can be used as effective supports for exogenous metal catalysts. For instance, the stability of Ni-based catalysts can be improved by using metal oxide supporter (Gholkar et al., 2019). Natural mineral catalysts are more suitable for steam gasification of biomass, but their catalytic activity in supercritical water gasification is obviously lower than that of other catalysts (Okolie et al., 2019). Besides, to further achieve a green and sustainable production, catalyst synthesis could be combined with biomass valorization. Biochar derived from pyrolysis or gasification of waste biomass is regarded as a cost-effective alternative as carbon supports for synthesizing catalysts (Cao et al., 2018, 2020; Shen et al., 2019; Zhao et al., 2018). Further research should focus on synergizing the processes of hydrogen production and catalyst synthesis by adjusting the operating conditions and infrastructure to fully utilize the gaseous and solid products of biomass gasification.

#### 3.3. Effect of operating conditions

#### 3.3.1. Steam gasification

3.3.1.1. Biomass characteristics. The main biomass characteristics affecting gasification performance are biomass type, particle size, and water content (Fremaux et al., 2015). Ash content is a critical issue that must be paid special attention to because it strongly affects the gasification process. High ash content will unfavourably increase the coke production as well as release of particulate matter that needs to be removed through downstream gas purification processes (Chan et al., 2019a). However, these adverse effects of ash content on the gasifier do not necessarily inhibit the net yield of hydrogen, the opposite being often true instead. Wei et al. (2007) compared the gasification hydrogen production from leguminous straw and pine sawdust. Although the higher ash content of leguminous straw resulted in lower natural gas production and higher coke and tar production, higher H<sub>2</sub> content was found in the produced gases. The H<sub>2</sub> contents were 50% of the gaseous products from leguminous straw and 44% from sawdust at 850 °C, the corresponding net hydrogen production rates were 5.2 wt% and 4.5 wt%, respectively. Duman et al. (2014a,b) studied the hydrogen production by steam gasification of three different types of algae. The feasibility of steam gasification was affirmed, and the hydrogen production capacity of macroalgae (Charcotylus verticillata and Laminaria palmata, ash content ~18%) was much higher than that of microalgae (Coccoid green algae, ash content ~3%). The maximum hydrogen production from macroalgae could reach 1036 mL/g, while the hydrogen production of microalgae was only 413 mL/g. This was attributed to the different inorganic substances in the raw materials, which shows that the material characteristics of the raw materials have a vital impact on the hydrogen production capacity.

The particle size of biomass also has a great influence on gasification performance. Usually, smaller particles provide a larger surface area per unit mass which increase the heat and mass transfer, thereby increasing the gasification rate and promoting the gas products with higher  $\rm H_2$  and lower tar content (Chan et al., 2019a; Menia et al., 2019). However, such increase in gasification efficiency of small particles also results in high energy consumption (especially below 1 mm) (Menia et al., 2019). Therefore, it is necessary to develop advanced gasifiers which can deal with large biomass particles without unacceptable compromise of heat and mass transfer. Erkiaga et al. (2014) reported

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the conical spouted bed to treat the biomass with particle size ranging from 0.75 to 4 mm, and the particle size hardly affected the gasification rate. Michel et al. (2011) treated wood pellets in a bubbling fluidized bed with a particle size of 6–8 mm. This reactor has proved to be particularly suitable for treating different types of wastes (e.g., plastics (Erkiaga et al., 2013a,b) and biomass/plastics mixtures (Lopez et al., 2015)).

The moisture content of biomass should be considered in gasification conversion. In general, biomass with water content less than 35 wt % can be treated by a gasifier, and the best designed water content treatment range is 10-15 wt%. Excessive moisture content of raw materials (> 40%) would result in lower operating temperatures and lower gasification efficiency (Kaushal and Tyagi, 2012). It is reported that when the moisture content of raw biomass was changed from 6 wt % to 40 wt%, the concentration of hydrogen in gas products increased slightly from 34 vol% at 6 wt% to 38 vol% at 40 wt% (Barbuzza et al., 2019). Hu et al. (2015) investigated the gasification process of biomass with different moisture contents without steam and evaluated the influence of steam on the gasification results with the water content varying from 10 wt% to 60 wt%. The study showed that 40 wt% of water content was the optimum condition, at which the volume fraction of hydrogen and hydrogen yield reached the maximum values. Further increase in the water content inevitably increased the energy consumption and reduced the temperature of reaction system, which was not conducive to gas and hydrogen production.

3.3.1.2. Temperature. It is acknowledged that because the reaction is basically an endothermic process requiring a large amount of heat supply, more energy-intensive operational conditions can improve gasification performance and minimize tar content. HH Li et al. (2015) pointed out in the study of sludge steam gasification that the increase of reaction temperature from 600 °C to 900 °C had a significant effect on increasing the gas yield and hydrogen concentration, and the maximum gas yield and hydrogen concentration were 49.4 wt% and 46.4 vol% obtained at 900 °C, respectively. Erkiaga et al. (Pachapur et al., 2019) carried out biomass gasification in a conical jet-bed reactor and concluded that the gas yield and H2 concentration increased from  $0.73 \text{ m}^3/\text{kg}$  biomass and 28 vol% to  $0.96 \text{ m}^3/\text{kg}$  and 38 vol% at 900 °C (equivalent to 1.8-3.3 wt% in H2 production). It can be interpreted that the reactions involved in gasification such as carbon gasification reaction (Equation (1)), methane reforming reaction (Equation (3)), and hydrocarbon reforming reaction (Equation (4)) are endothermic reactions. The increase of temperature is conducive to the reaction, thus increasing gas production and volume fraction of hydrogen.

However, the increase of hydrogen is not always proportional to temperature. Niu et al. (2017) studied the production of hydrogen-rich syngas from pine sawdust steam gasification in a downdraft gasifier. With the increase of temperature, the volume fraction of hydrogen increased at first and then decreased, reaching a maximum value of 44.79 vol% at 950 °C. Although the increase of temperature can promote the gasification of raw materials, raising temperature suppresses the water-gas conversion reaction (Equation (2)), since it is an exothermic reaction. As a result, the integral fraction of hydrogen in gas products decreased. The same results were obtained in the study of Gai et al. (2016), in which the volume fraction of hydrogen tended to decrease when the temperature rose to 1000 °C.

Therefore, the choice of temperature is very important for the gasification process. Low temperature indicates low gasification reaction rate and low hydrogen production. However, excessively high temperature would lead to the reduction of hydrogen content and incur more rigorous equipment (capital cost) as well as energy consumption (operational cost). In addition, in the laboratory-scale research, the reaction temperature is usually precisely controlled by an electrical heating program, but this may be not suitable for external heating in large-scale applications. Therefore, the renewable supply of heat source is very important for actualizing sustainable biorefinery.

3.3.1.3. Steam-to-biomass ratio. Theoretically, the more water vapour is added, the more positive the reaction will be. Thus, the higher hydrogen production can be obtained (i.e., H2 and CO2 formation is promoted while the production of CO and hydrocarbons is reduced (Zhang et al., 2015)). However, the energy consumption in the process of water gasification requires an increase in steam flow. High energy consumption is not economically applicable, and the volume fraction of hydrogen in syngas does not always increase in proportional to the increase of vapour volume. A study on the steam gasification of wetbased biomass showed that when the mass ratio of steam-to-biomass (S/B) increased from 0 to 0.5, the volume fraction of hydrogen increased by 20%, and the hydrogen yield reached 116 mL/g, which was 3.7 times higher than that without steam (Zhang et al., 2015). When the ratio further increased to 2.5, the volume fraction of hydrogen displayed a downward trend, while the hydrogen yield reached the maximum value of 142 mL/g, but the increase was not significant. Han et al. (2011, 2013) gasified wood sawdust at atmospheric and pressurized steam in fluidized bed. The atmospheric pressure results showed that with the increase of S/B from 1.2 to 2.18, the volume fraction of hydrogen increased from 50.3% to 62.2%, and the hydrogen yield increased from 54 g/kg to 72 g/kg. Despite the overall upward trend, the most suitable ratio was 1.3 in view of empirical deduction of sawdust chemistry, optimum gas composition, and energy consumption. In the pressurized experiment, the volume fraction of hydrogen and hydrogen yield also increased with the ratio of S/B. When the ratio was 0.89, the volume fraction of hydrogen could reach 62.4%, and the hydrogen yield was 52 g/kg. Iovane et al. (2013) reported the gasification in a rotary gasifier with S/B ratios increasing from 0.6 to 1, in which the gas yield (0.8 m<sup>3</sup>/kg biomass) was hardly affected by this parameter, while the H<sub>2</sub> produced increased from 2.9 to 3.7 wt%.

Based on the above it can be concluded that the amount of vapour is as important as the temperature, which requires comprehensive consideration of energy consumption and gasification results. Increasing the amount of vapour increases the content of hydrogen while the content of carbon dioxide also increases. Carbon dioxide has no contribution to the calorific value and gas utilization. The lower the content, the higher the quality of the gas produced. Therefore, it is necessary to determine the appropriate amount of vapour added to maintain the gasification efficiency with a low-carbon emission. The ideal gas composition can be simultaneously obtained.

#### 3.3.2. Supercritical water gasification

3.3.2.1. Temperature. Temperature is one of the key parameters in hydrogen production from biomass through supercritical water gasification. At low temperatures, the hydrogen yield, gasification rate, and carbon gasification rate are low, and with the increase of temperature the hydrogen gasification rate notably increases (Nanda et al., 2019). The main reason is that the dielectric constant of supercritical water decreases with the increase of temperature, which enhances the dissolution of organic components, decreases the density and ionic product of supercritical water, and promotes the free radical reaction, which are conducive to the formation of gas products (Okolie et al., 2019). However, at high temperatures the yield of  $\rm H_2$  can be expensed by methane formation (Equations (7) and (8)).

Ortiz et al. (2015) carried out supercritical water gasification experiments of glycerol under the conditions of 500 °C, 24 MPa, 5% mass fraction, and 1.0 L/h of feeding. It was found that the yield of hydrogen was 1.14 mol/mol. When the temperature was increased to 550, 600, 700, and 800 °C, the yield of hydrogen increased to 2.43, 3.27, 5.70, and 6.52 mol/mol, respectively. Ding et al. (2014a) gasified cellulose to produce hydrogen, in which the gasification rate was 7.2% at 400 °C and increased to 10.2% at 470 °C and 20.3% at 550 °C. Ding et al. (2014b) also used glucose as a raw material and found that the rate of carbon gasification was low (9.0%) at 400 °C. When the temperature increased to 500 °C, the carbon gasification rate increased by

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approximately two times (16.1%). Nanda et al. (2015) used fructose as a model compound of fruit or vegetable. When the mass fraction of fructose was 4%, the carbon gasification rate was 23%. With the increase of temperature to 600, 650, and 700  $^{\circ}$ C, the carbon gasification rate increased to 41%, 67%, and 88%, respectively.

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In order to obtain more hydrogen and improve gasification efficiency, high temperature is indispensable. However, excessively high temperature will increase the operation cost and energy consumption, which does not meet the requirements of low-energy and environmentally friendly production. Therefore, it is necessary to determine the appropriate reaction temperature striking a balance between energy consumption and gasification efficiency.

3.3.2.2. Operating pressure. The effect of reaction pressure on biomass supercritical water gasification process is relatively minor (Okolie et al., 2019). With increasing pressure, the dielectric constant of supercritical water increases, which weakens the dissolution of organic components, increases the density and ionic product of supercritical water, and promotes ionic reaction, which are undesirable for the formation of gas products (Okolie et al., 2019; Nanda et al., 2015). Gokkaya et al. (2015) studied the supercritical water gasification of phenol as a model compound for plant biomass. The results showed that the carbon gasification rate was 29.5% at 22.0 MPa, and it dropped to 26.2%, 22.5%, and 22.0% at 27.5, 34.5, and 42.0 MPa, respectively. It is obvious that with the increase in pressure, the carbon gasification rate decreases and then the effect of pressure approaches the critical point above which increasing pressure can hardly change the volume fraction of gas product. Continuous elevation of pressure did not affect the gasification rate further at 650 °C.

In order to satisfy the supercritical condition, the reaction pressure should be greater than 22 MPa. Nevertheless, to improve the gasification efficiency, the reaction pressure should be relatively low. Nanda et al. (2019) assessed the gasification effect in detail and proposed the suitable reaction pressure range of 22–30 MPa.

3.3.2.3. Reactant concentration. Excessive reactant concentration reduces the contact area between reactant and supercritical water. The low-molecular-weight decomposition products of coke formed by biomass pyrolysis weaken the mass transfer with supercritical water due to the increase in reactant concentration, which hinders the steam reforming reaction and consequently leads to the reduction of carbon gasification rate. Intermediates production is also amplified with high reactant concentration. The rate of tar and coke polymerization is higher than that of tar and coke decomposition. The increase of tar and coke formation may cause blockage of the reactor (Okolie et al., 2019; Sharma, 2019).

Ortiz et al. (2015) gasified glycerol (1.0 L/h) to produce hydrogen at 600 °C and 24 MPa. When the mass fraction of glycerol increased from 5% to 30%, the yield and volume fraction of hydrogen decreased while the volume fraction of methane increased. Guo et al. (2012) studied the effect of substrate concentration on the gasification reaction of alkali lignin in supercritical water and found that with the increase in reactant concentration, both gasification rate and carbon gasification rate showed a downward trend. Nanda et al. (2015) studied the supercritical water gasification of fructose. When the mass fraction increased from 4% to 10%, the carbon gasification rate decreased from 88% to 76%. However, high-concentration gasification can increase the treatment capacity of sewage sludge and enhance the competitiveness of supercritical water treatment technology (Okolie et al., 2019). Therefore, robust gasification of high-concentration biomass for high hydrogen yield is the direction for future development.

*3.3.2.4. Reaction time.* When the reaction rate is limited, prolonging the reaction time is beneficial to complete reaction (Martin-Sanchez et al., 2017). Guan et al. (2016) studied the effect of reaction time on phenol gasification at 450, 500, and 550 °C. It was found that the unit

yields of  $CO_2$ ,  $H_2$ ,  $CH_4$ , and other components increased rapidly at the beginning of the reaction and then tended to remain stable and unchanged after a period of time. The trend of carbon gasification rate was consistent with that of gas components. In order to reduce the energy consumption and improve the production efficiency, it is necessary to select the appropriate reaction time and avoid the prolonged time during which the gasification efficiency cannot be significantly improved.

### 4. Challenges and prospects of hydrogen production from biomass gasification

Thermochemical conversion of biomass waste for hydrogen production is a promising approach to relieve the worldwide crisis of energy shortage and achieve sustainable biomass valorization. At present, a key step for its development and application is to explore cost-effective catalysts that increase H2 production, reduce gasification temperature, and promote tar cracking. During the modification of catalysts, synergistic effects occurred between the impregnated metals and the precursor catalysts, which can be characterized by improving the dispersion of metals, alleviating the carbon deposition on the surface of catalysts, or improving the sintering resistance of catalysts. These features should warrant more research efforts in the development and design of catalysts. According to the recent reports, although the activity and selectivity of the catalysts have been significantly improved, the stability and recyclability of the catalysts remain a big challenge in future scaled-up applications. New ways for catalyst preparation (e.g., supercritical fluid deposition technology (Ju et al., 2018b) and modification methods (e.g., composite catalyst carrier (El-Emam and Ozcan, 2019)) are expected to further improve the catalyst activity and stability.

Since carbonization will inevitably increase the cost of raw materials, the carbon yield is a key indicator for biomass steam gasification. At present, the research on hydrogen production from biochar gasification is rather limited. If high-efficiency catalysts can be explored to effectively achieve carbon gasification at relatively low temperature, it will significantly promote the feasibility and competitiveness of hydrogen production from biomass gasification. In addition, high-quality syngas from biochar-based hydrogen production also has wide applications and simple preparation process. Although hydrogen production from biomass steam gasification attains high content of H2 (generally 40%-60%) and high calorific value of syngas, tar is generated as a byproduct along with gasification process. Such produced hydrocarbon mixture can be further utilized and converted into valuable syngas via tar reforming. Future research on developing green and sustainable technologies for tar treatment is of decisive significance for biomass gasification to become a commercially competitive route for hydrogen production.

Besides, the process of biomass supercritical water gasification for hydrogen production expects further improvement. High-temperature reaction environment incurs intensive energy consumption, corrosion issues, and tar as by-products, which need to be minimized. In order to fully manoeuvre the reaction process of biomass, further studies on reaction mechanisms, reaction thermodynamics, and reaction kinetics demand concerted and cross-disciplinary efforts, from small molecules to large molecules, from simple to complex, clarifying and controlling the reaction pathways of all intermediates.

Moreover, emerging data processing methods are expected to be involved in the future studies on hydrogen production from biomass gasification, such as meta-analysis, bibliometric analysis, and machine learning methods. Such techniques that integrate and analyze the collected information from different reports will be helpful in exploring the significance and relationships of various operating parameters on the gasification systems (e.g., reaction time, reactant concentration, operating pressure, temperature, steam-to-biomass ratio, and biomass characteristics). Moreover, the implementation of large-scale biomass

gasification still remains challenging in many aspects, such as temporal variation and spatial heterogeneity in waste biomass sources and supply chain. It is crucial to generate a holistic understanding to improve the existing policies on waste management and foster circular economy via expanded collaboration among different stakeholders. Environmental sustainability assessment and techno-economic analysis are still limited in the current literature. Therefore, future work on biomass gasification is expected to address the environmental sustainability, elucidate the overall carbon footprint and energy flow, and assess the availability and impact of resource consumption in large-scale manufacturing processes.

#### 5. Conclusions

Biomass is a renewable and clean energy source, which has great potential to replace fossil fuels for hydrogen production. The hydrogen yield in the gaseous product is determined by the process conditions of biomass gasification. Temperature and steam flow are important operation parameters, which need to be optimized by comprehensive consideration of economy and gasification efficiency. The choice of materials also has a critical influence on the gasification efficacy. High metal content in ash is often more conducive to the production of hydrogen-rich syngas. The design of catalysts can significantly improve the gasification reaction. Their stability and activity are important concerns for industrial applications, which need to be further articulated and tailored through future research efforts. Although some breakthroughs and innovations have been made for biomass hydrogen production on the basis of existing technologies, it still requires more scientific advances to render it economically competitive and environmentally benign for large-scale industrial production. For biomass hydrogen production, the urgent issues are to realize the controllability and scalability of production process, improve the reaction rate and efficiency, save the production costs, and accelerate the industrialization process. In summary, to broaden the applicability of biomass gasification technology, future research efforts are expected to focus on cost-effective catalyst, tar treatment, condition optimization, material and energy flow analysis, sustainability assessment, techno-economic analysis, and large-scale implementation involving diverse state-of-theart techniques. In the long run, biomass hydrogen production is the technology which has the brightest future in response to the increasing societal demand for green and sustainable chemical and energy industries.

#### CRediT authorship contribution statement

Leichang Cao: Data curation, Writing - original draft, Visualization. Iris K.M. Yu: Data curation, Writing - original draft, Visualization. Xinni Xiong: Conceptualization, Resources, Supervision, Investigation, Writing - review & editing, Project administration, Funding acquisition, Data curation, Writing - original draft, Visualization. Shicheng Zhang: Conceptualization, Methodology, Validation, Writing - review & editing. James H. Clark: Conceptualization, Methodology, Validation, Writing - review & editing. Yun Hau Ng: Conceptualization, Methodology, Validation, Writing - review & editing. Yun Hau Ng: Conceptualization, Methodology, Validation, Writing - review & editing. Jin Shang: Conceptualization, Methodology, Validation, Writing - review & editing. Yong Sik Ok: Conceptualization, Methodology, Validation, Writing - review & editing.

#### Declaration of competing interest

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

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