



## Recent advancement on hydrogen production from macroalgae via supercritical water gasification

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### ABSTRACT

Hydrogen, one of the green energy resources, has attracted much attention since it can be produced from biomass with zero net CO<sub>2</sub> emissions. Supercritical water gasification (SCWG) is an emerging technology for hydrogen production from macroalgae. It enables the elimination of the costly feedstock-drying step. However, a comprehensive review of hydrogen production from macroalgae via SCWG is still limited. Therefore, this article highlights the potential application of SCWG for hydrogen production from macroalgae as an alternative energy source. Firstly, the SCWG of macroalgae, including the fundamental process of SCWG, non-catalytic and catalytic SCWG of macroalgae, are comprehensively reviewed. The critical strategies on SCWG for hydrogen production from macroalgae are also presented. Finally, this paper also highlights the main challenges and future prospective in implementing SCWG of macroalgae for hydrogen production. The overall findings provide new insights for the future guideline related to suitable and highly effective hydrogen production from macroalgae.

### 1. Introduction

Nowadays, it is undeniable that most of the energy used for daily needs such as electricity, transport, and industry comes from non-renewable fuels. The endless dependency on fossil fuels causes two main drawbacks, i) severe environmental damage owing to the emissions of air polluting matters, and ii) unsustainability for a more extended period. Therefore, developing environmentally benign energy sources to renew and sustainably alter fossil fuel society is vital for environmental and human health. Hydrogen has been envisaged as an emerging clean energy carrier that reduces environmental pollution and minimizes fossil fuel dependency. Besides, since hydrogen combustion

generates only water vapor as a by-product, hydrogen is considered a clean energy fuel (Sharma and Ghoshal, 2015; Ratna Frida Susanti et al., 2014b). Hydrogen can be a worthwhile chemical for various industrial purposes, such as ammonia and methanol manufacturing (Kalamaras and Efstathiou, 2013; Pandey et al., 2019).

Currently, hydrogen is generated chiefly using fossil resources such as crude oil and natural gas by reforming. Natural gas is the primary source of hydrogen production by steam methane reforming method (Akbari-Emadabadi et al., 2017). However, natural gas has a high depletion rate and cost (Pandey et al., 2019). Biomass is considered one of the best renewable sources of hydrogen production to maintain sustainable demand and its cost. Furthermore, producing hydrogen from

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biomass as a renewable resource has attracted much attention since it can be generated with zero net CO<sub>2</sub> emission, unlike fossil resources.

Several approaches have been evolved to produce hydrogen from biomass via either thermochemical or biological processes. Hydrogen production via the biological route can be accomplished through anaerobic fermentation. Even though the biological hydrogen productions are less energy-intensive and more environmentally friendly than the thermochemical route, the biological way is not feasible for large-scale production due to the low hydrogen yield. Hence, the thermochemical way is the most mature technology to produce hydrogen from biomass (Holladay et al., 2009). One of the thermochemical conversions of biomass to generate hydrogen is supercritical water gasification (SCWG). Principally, SCWG utilizes the specific properties of water as solvent mainly due to its lower dielectric constant compared to liquid water and alcohols. SCWG technology is suitable for converting macroalgae into hydrogen since this biomass contains high moisture (Matsumura et al., 2005). The dielectric constant of water and the ionic product drop drastically at the close critical point. This condition makes the water a non-polar-like solvent with the ability to dissolve the organic matter and gases (Samamulya et al., 2017a).

There have been a number of reviews regarding hydrogen production from biomass (i.e., Arregi et al., 2018; Lee et al., 2021; Liu et al., 2019; Pandey et al., 2019; Parthasarathy and Narayanan, 2014; Shahbaz et al., 2020). However, most of them focused on a more general thermochemical process of biomass to hydrogen production. Moreover, several paper reviews on SCWG of biomass also have been reported (De Blasio and Järvinen, 2017; Okolie et al., 2019; Rodriguez Correa and Kruse, 2018). Nevertheless, all reviews focused on general biomass, not specific to macroalgae for hydrogen production. To the best of our knowledge, a comprehensive review on hydrogen production from macroalgae via SCWG has yet to be reported. Macroalga is prospective to be used as feedstock to produce hydrogen since it has a higher growth rate than terrestrial plants. Moreover, macroalgae can be grown using seawater, significantly reducing the pressure on available freshwater. Freshwater is a finite resource and should be used for growing food rather than energy crops. Thus, this review aims to provide a comprehensive overview to understand the emerging technology of SCWG to convert macroalgae into hydrogen as the future energy carrier. We also cover the characteristic of macroalgae concerning SCWG target products. Various recent researches and applications of SCWG, both catalytic and non-catalytic, are compared. Furthermore, the critical strategies to generate optimum hydrogen-rich syngas from SCWG of macroalgae are presented. This study also elaborates the fundamental process, reaction network, the yield of hydrogen production to be the reference for the latest developments in implementing SCWG using macroalgae as the feedstock. Lastly, the main challenges and future prospective in implementing SCWG of macroalgae for hydrogen-rich gas are also highlighted.

## 2. Characteristics of macroalgae

Macroalgae are fast-growing multicellular autotrophs that can be classified into three main groups based on their photosynthetic pigments: (1) red algae (Rhodophyceae, Chla, and phycobilins), (2) brown algae (Phaeophyceae, Chla, and Chlc), and (3) green algae (Chlorophyceae, Chla, and Chlb) (Polat and Ozogul, 2008; Sudhakar et al., 2018). Macroalgae can store and produce adequate carbon resources required for a biorefinery by utilizing inorganic carbon (Gao and McKinley, 1994). Marine macroalgae have great potential as biofuel feedstock and have grabbed attention worldwide since they do not compete with other land and freshwater crops. Moreover, macroalgae have rapid growth rates, high polysaccharide content, high ability to mitigate atmospheric CO<sub>2</sub>, high biomass yield (3.3–11.3 kg wet weight m<sup>-2</sup> year<sup>-1</sup>), promoting green fuel for green earth, and so forth (Bayu et al., 2021; Kim et al., 2013).

Macroalgae are dissimilar from terrestrial plants based on their

chemical composition. In contrast with terrestrial plants, macroalgae contain high contents of water (90%-fresh weight), carbohydrates (25–50%-dry weight), protein (7–15%-dry weight), and low lipid contents (1–5%-dry weight). These chemical compositions of macroalgae vary depending on the species (Fig. 1). Additionally, macroalgal biochemical contents are affected by the harvesting period as well as the environmental growth. Compared to terrestrial biomass, the main carbohydrate fraction in macroalgae is a hydrocolloid (10–40%) (Yazdani et al., 2015). Further, macroalgae contain less cellulose, hemicellulose, and lignin as much as 2–10%, 9%, ~3%-dry weight, respectively (Kraan, 2012).

Apart from that, the proximate and elemental compositions of macroalgae are also significantly different from terrestrial biomass. The contents of carbon, hydrogen, and oxygen of macroalgae are lower than those of land-based plants. Meanwhile, macroalgae have higher contents of nitrogen and sulfur than terrestrial plants. Moreover, the ash contents in marine macroalgae are generally higher than corresponding values for lignocellulosic biomass since macroalgae contain high-level minerals, especially calcium and magnesium (Bayu et al., 2021). In contrast, the heating value of various macroalgae is much lower than that of energy crops or any other lignocellulosic biomass. Furthermore, macroalgae have higher metal and halogens contents than terrestrial plants (Ghadiryfar et al., 2016). The proximate and ultimate analyses of various macroalgae in comparison to the terrestrial plants are presented in Table 1.

## 3. SCWG of macroalgae

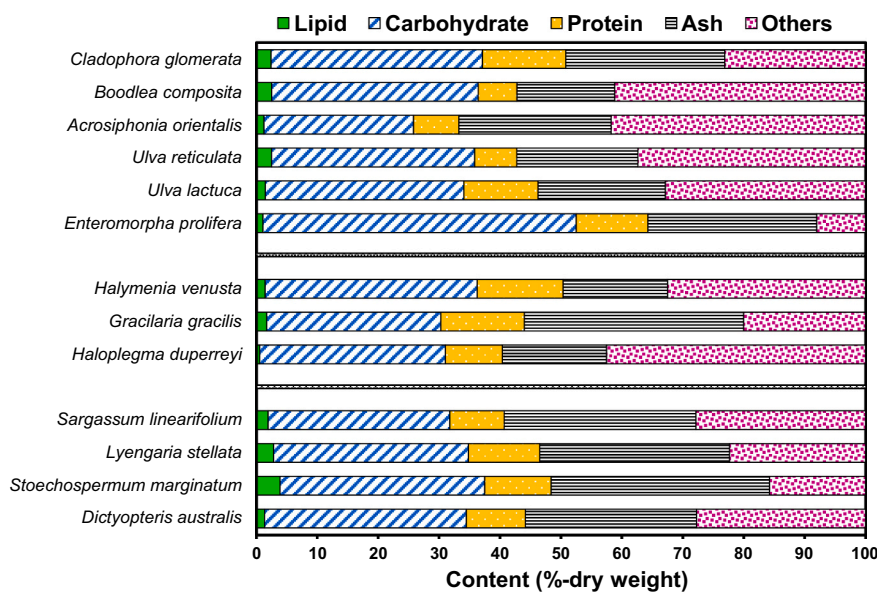
### 3.1. The fundamental process of SCWG

A supercritical state of water can be found when water reaches its critical point of temperature ( $T_c \geq 374$  °C) and pressure ( $P_c \geq 22.1$  MPa). In SCWG, the water can act as a solvent with high diffusivity, mass transfer capability, and dissolving power (Fan et al., 2018). Physicochemical properties of water, such as viscosity, density, ion product, thermal conductivity, dielectric constant, dissolution performance, and diffusion coefficient under this state, are remarkably dissimilar from either the liquid phase or the gas phase. Thus, it enables rapid reaction and a homogeneous environment for the gasification of liquid and gas systems without phase boundaries (Cao et al., 2018).

Temperature increment can cause a change in water viscosity. According to Guo et al. (2010), the water viscosity at the critical point is around  $2.98 \times 10^{-5}$  Pa s, providing a good diffusion coefficient and creating an excellent reaction system for high reaction rates. Additionally, the density of water under supercritical conditions is much lower than that of its liquid. Moreover, an increase in water temperature can reduce the dielectric constant of water significantly from about 80 (at standard temperature and pressure) to around 5 (at a critical point). The decrement of the dielectric constant of water under supercritical conditions allows water to operate likewise to nonpolar compounds, thus making it a suitable solvent for nonpolar organic compounds.

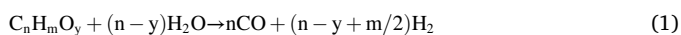
Nevertheless, when water temperature exceeds the critical point, the ionic product diminishes with increasing temperature, making the free radical reaction dominant (Bröll et al., 1999). From this viewpoint, supercritical water empowers the solvation potential for most organic compounds and gases (Japas and Franck, 1985; Kritzer, 2004; Savage, 1999). Hence, SCWG is a reassuring method that has attracted significant attention for hydrogen-rich gas generation. The fundamental steps for SCWG of macroalgae are shown in Fig. 2.

In general, SCWG is represented in several chemical reaction steps, including steam reforming, water-gas shift, and methanation reactions, as shown in Eqs. (1)–(4) (Leong et al., 2021; Rodriguez Correa and Kruse, 2018). Under supercritical conditions, the organic compounds will decompose to generate carbon monoxide (CO) and hydrogen (Reaction (1)). Further, produced CO can react with water to generate CO<sub>2</sub> and H<sub>2</sub>, called water-gas shift reaction (Reaction (2)). The reaction



**Fig. 1.** Chemical composition of three major groups of macroalgae: brown (below), red (middle), and green macroalgae (up). The values are varied depending on the harvesting period and environmental growth (Source of data: Lee et al. (2020); Pourkarimi et al. (2019)). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

equilibrium (2) is favorably moved to the right side due to the system's large amount of water, confirming that water is an essential reactant for both the water-gas shift reaction and biomass hydrolysis. According to the Le Châtelier principle, reactions (1) and (2) are favored at high dilution since both reactions consume water. Therefore, under the low concentration of feedstock conditions (such as 1 wt%), hydrogen is also possibly generated at relatively low temperatures (Ratna Frida Susanti et al., 2014b). Due to the endothermic nature of biomass decomposition during SCWG reaction, the formation of hydrogen is preferred at temperatures remarkably beyond the critical point of water. According to Yan et al. (2006), carbon dioxide and methane gases are thermodynamically chosen at higher biomass loading and lower temperature.



The reaction of SCWG offers many advantages over conventional thermochemical process methods, including (1) that the gasification takes place in supercritical water. Thus the energy required for the drying step can be eliminated (Farobie et al., 2017); (2) utilization of water as a reaction medium, avoiding costly solvents, and improving practical applications (Guo et al., 2010); (3) no mass transfer constrain, making the SCWG process take place very rapidly and completely (Kritzer and Dinjus, 2001); (4) better heat transfer characteristics in the reaction process than those in liquid and gas (Loppinet-Serani et al., 2008); (5) high reaction rate (Kruse et al., 2007); and (6) that good flowability can reduce the yield of coke, prolonging the catalyst life (Kruse and Gawlik, 2003; Matsumura et al., 2005).

Several combinations and applications of SCWG reactors suitable for various types of biomass have been addressed in the literature (Matsumura et al., 2005). These SCWG reactors generally can be classified into two categories, namely batch and continuous flow reactor.

### 3.1.1. SCWG in a batch reactor

In principle, the vessel applied in a batch reactor for a chemical reaction does not have feed and effusive streams. Lee et al. (2021) reported

that batch reactors are generally restricted to fundamental studies investigating the gasification efficiency of both model compound and actual biomass. Moreover, the batch reactor is favored to investigate the distribution for various feedstock materials and product yield (Matsumura et al., 2005).

Fig. 3 shows the typical batch reactor configuration for the SCWG process. All experimental studies about SCWG of macroalgae have been conducted in a batch reactor (Cherad et al., 2014, 2013; Deniz et al., 2015; Duan et al., 2018b; Graz et al., 2016; Norouzi et al., 2017; Onwudili et al., 2013; Safari et al., 2016; Schumacher et al., 2011). Generally, two materials (i.e., Inconel and diamond anvil cell (DAC)) are commonly used in the batch reactor of SCWG of macroalgae. DAC-type reactors made up of micro-hollow insured with a press machine typically are made of diamond, enabling operating conditions at extreme temperature and pressure, approximately 400–800 °C and 20–3000 MPa, respectively (Smith and Fang, 2009). It was reported by Reddy et al. (2014) that a DAC-type batch reactor could be operated under rapid heating and cooling conditions by using micro-electric heaters.

Even though a batch reactor enables to examine the product yield during the SCWG process, this reactor has several shortcomings, namely (i) it takes time to heat the feedstock to reach the desired temperature, (ii) the conversion may occur at undefined temperatures once the gasification rate is more significant than heating rate, (iii) the pressure is sometimes uncontrollable, and (iv) the actual reaction time may be unaccounted (Azadi and Farnood, 2011; Matsumura et al., 2005).

### 3.1.2. SCWG in a continuous reactor

The SCWG continuous flow reactor was developed to enhance hydrogen-rich syngas production. The typical continuous flow reactor of SCWG is presented in Fig. 4. This continuous flow reactor is extensively applied to examine the effects of operating conditions for biomass gasification in SCWG (Farobie et al., 2017; Samanmulya et al., 2017b). The continuous flow reactor has advantages that include (i) gasification reactions at high temperatures and pressures occur in short residence time, (ii) operating parameters can be controlled easily, (iii) elucidation of the reaction kinetics can be calculated more precisely than the batch reactor, and (iv) the heat can be recovered efficiently (Amrullah and Matsumura, 2018; Yong and Matsumura, 2013).

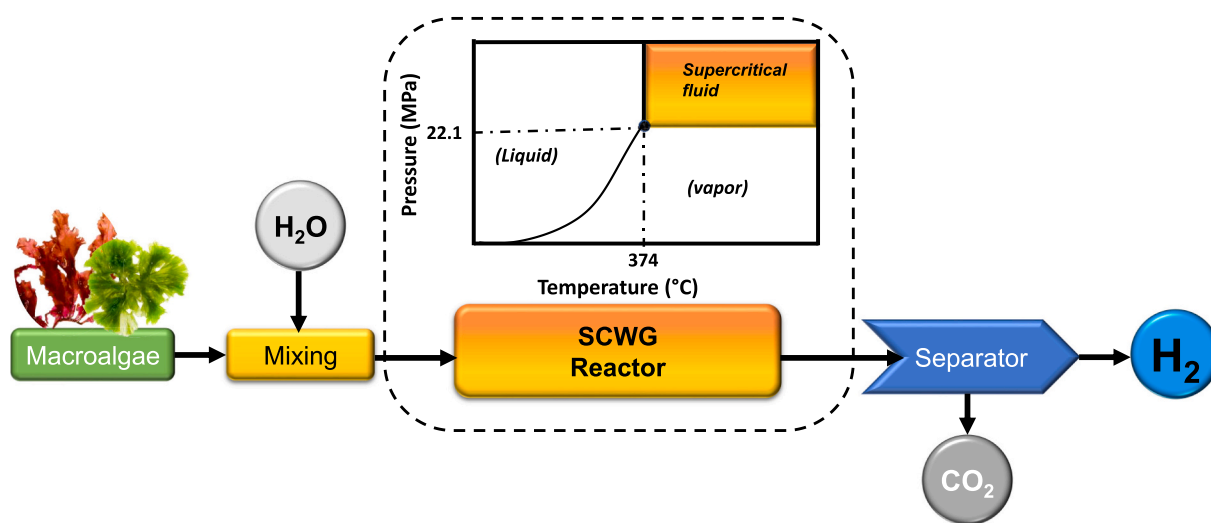
Nevertheless, converting the SCWG reactor mode from batch to continuous is frequently challenging because of various factors,

**Table 1**  
The proximate and ultimate analyses of various macroalgae in comparison to the terrestrial plants.

Macroalgae		Proximate analysis				Elemental analysis					HHV <sup>c</sup> (MJ kg <sup>-1</sup> )	Ref.
Group	Strain	Moisture (wt%)	Ash (wt%)	Volatile matter	Fixed carbon	C (wt %)	H (wt %)	O (wt %)	N (wt %)	S (wt %)		
Brown macroalgae	<i>Chorda filum</i>	13.1	11.61	52.2	24.9	39.1	4.7	37.2	1.4	1.6	15.6	(Ross et al., 2008)
	<i>Fucus serratus</i>	11.4	23.4	45.5	24.2	33.5	4.8	34.4	2.4	1.3	16.7	(Ross et al., 2008)
	<i>Fucus vesiculosus</i>	12.3	22.8	51.4	23.8	32.9	4.8	35.6	2.5	2.4	15.0	(Ross et al., 2008)
	<i>Laminaria digitata</i>	13.7	25.8	53.4	25.3	31.6	4.9	34.2	0.9	2.4	17.6	(Ross et al., 2008)
	<i>Laminaria japonica</i>	6.1	29.0	58.0	9.7	35.2	5.5	40.5	1.4	0.5	13.0	(Choi et al., 2015)
	<i>Laminaria hyperborea</i>	12.4	18.0	53.5	21.5	35.0	5.3	35.1	1.1	2.1	16.5	(Ross et al., 2008)
	<i>Macrocystis pyrifera</i>	8.0	38.4	42.4	33.4	27.3	4.1	34.8	2.0	1.9	16.0	(Ross et al., 2008)
	<i>Saccharina japonica</i>	6.9	20.2	68.8	4.1	32.9	6.2	60.0	0.9	–	12.1	(Kim et al., 2012)
	<i>Sargassum natans</i>	10.5	29.1	48.9	11.6	25.9	5.6	24.2	3.6	1.2	8.7	(Parsa et al., 2018)
	Red macroalgae	<i>Gracilaria gracilis</i>	5.9	36.0	53.1	10.9	31.5	5.9	17.5	2.9	2.0	11.7
<i>Euclima cottonii</i>		7.3	22.5	53.6	16.6	48.6	6.9	42.3	1.4	0.8	12.3	(Saeed et al., 2020)
<i>Enteromorpha clathrata</i>		10.1	21.2	57.9	10.7	32.7	4.9	24.7	4.4	2.0	12.0	(Pourkarimi et al., 2019)
Green macroalgae	<i>Enteromorpha prolifera</i>	9.8	12.5	68.8	8.9	32.9	4.7	57.5	2.5	2.4	12.4	(Zhao et al., 2013)
	<i>Cladophora glomerata</i>	4.4	26.1	44.8	29.1	31.3	5.0	30.7	4.9	2.0	13.7	(Parsa et al., 2018)
Terrestrial plants												
	Coconut frond	11.28	2.31	91.81	5.88	44.83	6.16	48.22	0.79	–	18.15	(da Silva et al., 2019)
	Coconut shell	4.42	1.05	91.03	7.92	58.33	14.33	24.65	1.32	1.37	28.85	(Mohamed Noor et al., 2019)
	Sawdust	8.00	0.40	87.60	12.00	50.10	6.20	43.70	0.02	0.04	20.4	(Masnadi et al., 2014)
	Switchgrass	6.00	6.30	76.90	16.80	47.90	6.20	45.00	0.80	0.10	19.60	(Masnadi et al., 2014)
	Forest residue	7.32	0.20	79.80	20.00	53.16	6.25	40.00	0.30	0.09	19.50	(Vamvuka et al., 2003)
	Empty fruit bunches	7.95	5.36	83.86	10.78	49.07	6.48	38.29	0.70	<0.10	19.35	(Abdullah and Gerhauser, 2008)
	Corn cob	9.70	1.20	80.60	18.20	43.60	5.80	48.60	0.70	1.30	16.90	(Azeez et al., 2010)
	Jatropha residue	4.95	0.76	81.00	11.39	46.39	6.55	42.53	0.53	–	19.39	(Murata et al., 2016)
	Wood chip	9.80	0.30	86.20	0.53	51.70	6.20	41.80	0.30	–	20.7	(Cao et al., 2011b)

Note: <sup>c</sup>HHV: Higher heating value.

“–”: not available.



**Fig. 2.** The fundamental process of supercritical water gasification of macroalgae.



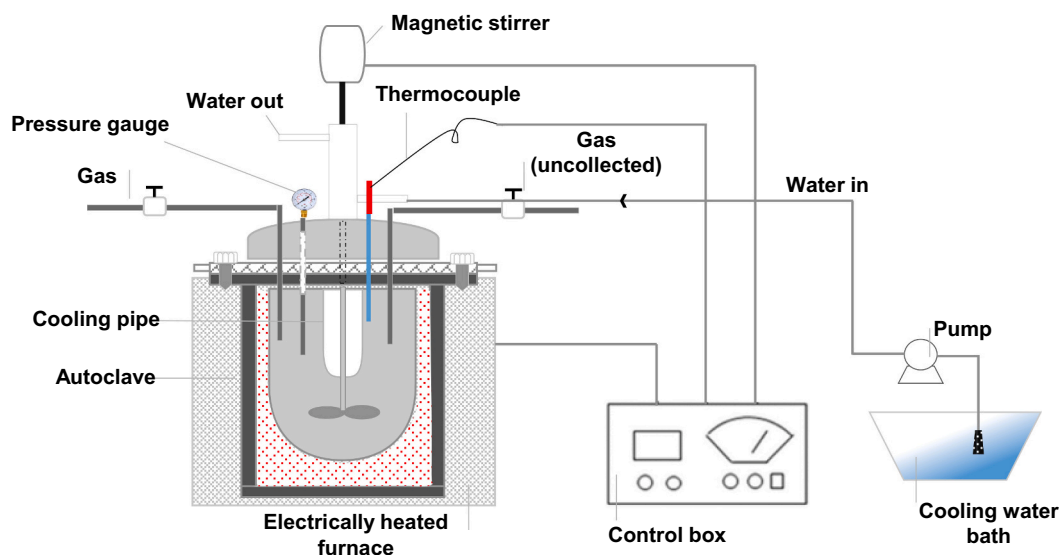


Fig. 3. Schematic diagram of typical batch reactor configuration.

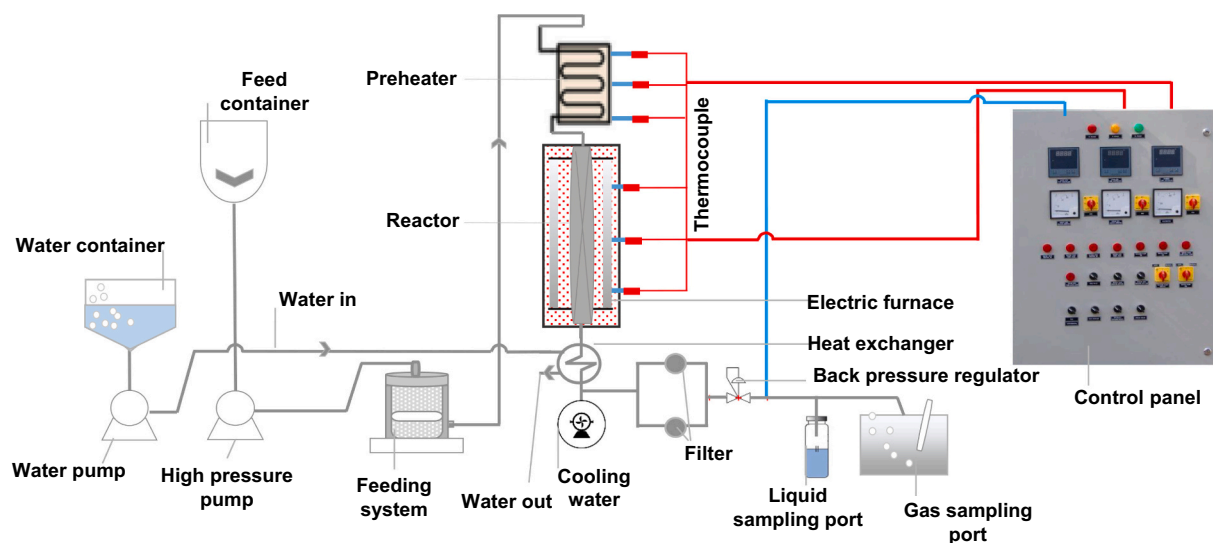


Fig. 4. Schematic diagram of typical continuous flow SCWG reactor.

including the need for feedstock preheating and acceptable feedstock concentrations (Cherad et al., 2014). The critical issue in an SCWG continuous flow reactor for solid biomass is reactor plugging because of insoluble solid feedstock and char formation. Extensive works have been implemented to establish different specific designs of SCWG reactors to suppress char formation, especially by using tubular reactor (Lu et al., 2008; Matsumura and Minowa, 2004). In a semi-pilot scale study using TU Delft/Gensos tubular reactor, Yakaboylu et al. (2018) reported no blocking for SCWG of dry starch (feedstock loading of 4.4 wt%) at 600 °C, and the carbon gasification efficiency as high as 73.9% was achieved. After shutting down the reactor, slight char and oil production quantities were obtained as much as 2.3 wt% and 10.4 wt%, respectively (Yakaboylu et al., 2018). Moreover, in a continuous-mode pilot-scale reactor of “VERENA,” plugging and char formations were prevented by implementing a rapid heating process and employing a tubular flow reactor.

### 3.2. Non-catalytic SCWG of macroalgae

SCWG can be conducted either by a non-catalytic process at higher

operating temperatures or by a catalytic process at lower operating temperatures. Several studies have been performed to decompose macroalgae via non-catalytic SCWG, as presented in Table 2. Schumacher et al. (2011) had examined SCWG of several macroalgae species, i.e., *Laminaria digitata*, *Alaria esculenta*, *Fucus serratus*, and *Bifurcaria bifurcate* at 500 °C using a batch reactor. They found that the char productions from gasification of macroalgae were significantly lower than those from gasification of protein and lignocellulosic-containing biomass. The gaseous components from SCWG of macroalgae contain primarily H<sub>2</sub>, followed by CO<sub>2</sub>, CH<sub>4</sub>, and a trace amount of CO in the range of 32–42; 30–45; 15–27; and < 1% v/v, respectively. Of all investigated macroalgae, a maximum gas yield was found in SCWG of *Bifurcaria bifurcate* at 504 g/kg seaweed. Meanwhile, the gas yields from SCWG of other macroalgae were approximately 315–379 g/kg seaweed. Intriguingly, the enhanced gas generation during the SCWG of macroalgae was observed, which may be attributed to the inorganic salt contents of macroalgae that could act as a catalyst. Moreover, the aqueous phases consist primarily of glycolic, formic, acetic acids, and phenols.

Deniz et al. (2015) have studied the non-catalytic hydrothermal gasification of *Posidonia oceanica* by varying temperatures (300–600 °C)

**Table 2**  
Hydrogen production from non-catalytic SCWG of macroalgae.

Group	Macroalgae species	Feedstock loading (wt%)	Temperature (°C)	Pressure (MPa)	H <sub>2</sub> production (mol/kg feedstock)	Ref.	
Brown macroalgae	<i>Alaria esculenta</i>	5	500	30.2	13.20	(Schumacher et al., 2011)	
	<i>Bifurcaria bifurcata</i>	5	500	30.4	16.00	(Schumacher et al., 2011)	
	<i>Fucus serratus</i>	5	500	30.3	14.25	(Schumacher et al., 2011)	
	<i>Laminaria digitata</i>	5	500	30.4	11.80	(Schumacher et al., 2011)	
	<i>Alaria esculenta</i>	6.66	500	23.6–28.1	3.30	(Cherad et al., 2013)	
	<i>Laminaria digitata</i>	6.66	500	23.6–28.1	3.57	(Cherad et al., 2013)	
	<i>Laminaria hyperborea</i>	6.66	500	23.6–28.1	3.70	(Cherad et al., 2013)	
	<i>Saccharina latissima</i>	6.66	500	23.6–28.1	4.23	(Cherad et al., 2013)	
	Green macroalgae	<i>Posidonia oceanica</i>	8	600	44.2	10.37	(Deniz et al., 2015)
		<i>Ulva rotundata</i>	7	550	23.7	2.70	(Graz et al., 2016)
<i>Enteromorpha intestinalis</i>		1	500	23.6–28.1	5.25	(Norouzi et al., 2017)	

and biomass loading (0.04–0.12 g/mL). These authors reported that the gaseous product distributions and gasification efficiency were comprehensively affected by the concentration of biomass and reaction temperature. The gasification and hydrogen yield could be enhanced by increasing temperature and decreasing biomass loading via supporting the water-gas shift and steam reforming reaction rates. The gaseous components from hydrothermal gasification of *Posidonia oceanica* are mainly hydrogen of 10.37 and methane of 6.34 mol/kg feedstock, observed at 600 °C and biomass concentration of 0.08 g/mL (Deniz et al., 2015).

Graz et al. (2016) reported that the non-catalytic SCWG of *Ulva* sp. generated a gas fraction of 23% v/v H<sub>2</sub> and 17% v/v CH<sub>4</sub> at 550 °C and 23.7 MPa. It was found that by a rising the biomass concentration from 7 to 16.4 wt%, hydrogen yields reduced from 2.7 to 1.8 mol/kg. It confirms that high algae concentration is unfavorable for H<sub>2</sub> formation. Meanwhile, an increase in temperature from 400 °C to 550 °C (a constant feedstock loading of 16.4 wt%) improved the H<sub>2</sub> production from 0.1 to 1.8 mol/kg. Moreover, the SCWG of *Ulva* sp. generated a trace amount of solid residue primarily composed of carbon (20 wt%), salts (KCl, NaCl, CaSO<sub>4</sub>), SiO<sub>2</sub>, and CaCO<sub>3</sub>.

**Table 3**  
Hydrogen production from catalytic SCWG of macroalgae.

Group	Macroalgae species	Feedstock loading (wt%)	Temperature (°C)	Pressure (MPa)	Catalyst	H <sub>2</sub> production (mol/kg feedstock)	Ref.
Brown macroalgae	<i>Laminaria hyperborea</i>	6.66	500	–	1.5 M NaOH	16.27	(Cherad et al., 2014)
	<i>Saccharina latissima</i>	5	500	36	1.67 M NaOH	15.10	(Onwudili et al., 2013)
	<i>Saccharina latissima</i>	5	500	36	1.67 M NaOH+ 5% Ni/Al <sub>2</sub> O <sub>3</sub>	14.2	(Onwudili et al., 2013)
	<i>Saccharina latissima</i>	5	500	36	5% Ni/Al <sub>2</sub> O <sub>3</sub>	5.2	(Onwudili et al., 2013)
	<i>Alaria esculenta</i>	6.66	500	23.6–28.1	5% Ru/Al <sub>2</sub> O <sub>3</sub>	7.80	(Cherad et al., 2013)
	<i>Laminaria digitata</i>	6.66	500	23.6–28.1	5% Ru/Al <sub>2</sub> O <sub>3</sub>	7.90	(Cherad et al., 2013)
	<i>Laminaria hyperborea</i>	6.66	500	23.6–28.1	5% Ru/Al <sub>2</sub> O <sub>3</sub>	8.50	(Cherad et al., 2013)
	<i>Saccharina latissima</i>	6.66	500	23.6–28.1	5% Ru/Al <sub>2</sub> O <sub>3</sub>	10.20	(Cherad et al., 2013)
	<i>Laminaria hyperborea</i>	6.66	500	–	5% Ni/Al <sub>2</sub> O <sub>3</sub>	6.19	(Cherad et al., 2014)
	<i>Laminaria hyperborea</i>	6.66	500	–	5% Ru/Al <sub>2</sub> O <sub>3</sub>	7.68	(Cherad et al., 2014)
Green macroalgae	<i>Enteromorpha intestinalis</i>	1	440	23.7	12% Ni-6% Fe on γ-Al <sub>2</sub> O <sub>3</sub>	8.70	(Norouzi et al., 2017)
	<i>Enteromorpha intestinalis</i>	1	440	23.7	0.5% Ru-12% Ni-6% Fe on γ-Al <sub>2</sub> O <sub>3</sub>	9.93	(Norouzi et al., 2017)
	<i>Enteromorpha intestinalis</i>	1	440	23.7	1% Ru-12% Ni-6% Fe on γ-Al <sub>2</sub> O <sub>3</sub>	10.49	(Norouzi et al., 2017)
	<i>Enteromorpha intestinalis</i>	1	440	23.7	1.5% Ru-12% Ni-6% Fe on γ-Al <sub>2</sub> O <sub>3</sub>	10.86	(Norouzi et al., 2017)
	<i>Enteromorpha intestinalis</i>	1	440	23.7	2% Ru-12% Ni-6% Fe on γ-Al <sub>2</sub> O <sub>3</sub>	12.28	(Norouzi et al., 2017)

It is worthwhile to note that the study about a correlation between the organic matter composition of macroalgae and hydrogen yield is still limited. Onwudili et al. (2013) reported that the carbohydrate-rich macroalgae *S. latissimi* produced more hydrogen gas than the two algae species of *C. vulgaris* and *S. platensis*. This finding is in good agreement with the previous study of Kruse et al. (2007) who found that carbohydrate-rich biomass is more suitable for hydrogen production under SCWG than lipid and protein. Kruse et al., (2007) assumed that the protein could suppress the gas yield through the mechanism of radical scavenger inhibition since it generates the nitrogen cyclic organic compounds via the Maillard reaction.

### 3.3. Catalytic SCWG of macroalgae

Since SCWG reactions have high activation energies, the catalyst is an essential factor in enhancing hydrogen production efficiency in the SCWG process of macroalgae. Guan et al. reported that SCWG could be performed using low operating temperatures (i.e., 350–500 °C) by employing catalysts during the SCWG process for hydrogen production (Guan et al., 2012b). In general, the catalysts for SCWG reaction are

classified into homogeneous (alkali-based) and heterogeneous (Ni-based and noble metal-based). Moreover, a unique algal hydro char catalyst has been used due to inorganic compound content and good porosity (Safari et al., 2016). Overall, most catalysts enable increased hydrogen production by decreasing the CO yields via the water-gas shift reaction (Lee et al., 2021). Several studies on catalytic production of hydrogen from SCWG of macroalgae are presented in Table 3.

### 3.3.1. Alkali-based homogenous catalysts

Several alkali-based homogeneous catalysts commonly used for SCWG of real and model biomass compounds include KOH,  $\text{KHCO}_3$ ,  $\text{K}_2\text{CO}_3$ , NaOH,  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ , LiOH, and  $\text{Ca}(\text{OH})_2$ . These catalysts can enhance hydrogen production by accelerating the water-gas shift reaction and improving the breakage of C—C bonds. The degradation mechanism of biomass in the presence of an alkali catalyst has been proposed by García Jarana et al. (2008), who conducted SCWG of industrial organic waste. They assumed that the presence of an alkali-based homogeneous catalyst could enhance the decomposition of biomass into organic acid intermediate compounds, which are subsequently decomposed into  $\text{H}_2$  and  $\text{CO}_2$ .

Moreover, alkali-based homogeneous catalysts could reduce the char/tar formation. There are two possibilities on how the alkali-based homogeneous catalyst could reduce the char/tar formation. First, alkali-based catalysts have roles in accelerating the biomass decomposition into intermediate compounds, e.g., formate and acetate salts that suppress polymerization reaction towards tar/char generation (Onwudili et al., 2013). Second, the alkali hydroxides can generate the OH ions, which can neutralize the organic acid molecules serving as the intermediates' polymerization for char formation (Hu et al., 2020). It was reported by Xu et al., (2019) that the alkali-based homogeneous catalysts have shown better catalytic performance on selectivity and enhancing hydrogen yield over heterogeneous catalysts. Furthermore, according to Onwudili et al. (2013), the alkali-based homogeneous catalysts could promote ammonia from nitrogen-containing feedstock, applicable for recycling nutrients. Furthermore, the alkali-based homogeneous catalysts could provide OH radicals acting as a ring-breaking stimulant for aromatic synthesis, increasing gasification efficiency for SCWG of algae.

Study about the use of alkali-based homogeneous catalysts for SCWG of macroalgae is still limited, as shown in Table 3. Cherad et al. (2014) compared catalytic and non-catalytic SCWG of *Laminaria hyperborea* in a batch reactor. They found that hydrogen product for gasification of *Laminaria hyperborea* using a catalyst of NaOH was approximately three times higher (16.27 mol  $\text{H}_2$ /kg feedstock) than non-catalytic SCWG (5.18 mol  $\text{H}_2$ /kg feedstock). It could be associated with the fact that sodium hydroxide has a crucial role in taking carbon dioxide, accelerating biomass decomposition into intermediate compounds, and enhancing the water gas shift reaction. Moreover, the product gas of NaOH-catalyzed gasification of *Laminaria hyperborea* primarily contains  $\text{H}_2$  and  $\text{CH}_4$  with trace amounts of hydrocarbons (C2-C4), generating a higher recovery of energy (82.9%) compared to non-catalytic SCWG (52.4%).

Onwudili et al. (2013) have investigated SCWG of microalgae (*Spirulina plantensis* and *Chlorella vulgaris*) and macroalgae (*Saccharina latissimi*) at 36 MPa and 500 °C with and without the catalysts' addition of NaOH and Ni— $\text{Al}_2\text{O}_3$  for 30 min in a batch reactor. It was reported that whenever sodium hydroxide was used, the water-soluble compounds were the predominant products. Therefore, the hydrogen fraction was three times higher due to  $\text{CO}_2$  absorption and further transformation to sodium carbonate. Moreover, they found that the tar yields were suppressed by up to 71% in the presence of NaOH since alkali catalyzes the decomposition of biomass into intermediate compounds, including acetate and methanoate salts. The preferable formation of these intermediates can reduce the reaction pathway of polymerization towards increased char/tar generation during the hydrothermal gasification process. The gas composition mainly contains carbon dioxide with the

use of Ni catalyst or without catalyst addition.

Meanwhile, the main components of  $\text{H}_2$  and  $\text{CH}_4$  were quickly produced when NaOH was employed. All feedstock reached maximum gasification efficiency in the omnipresence of NaOH. Among algae investigated, *Saccharina latissimi* demonstrated a maximum yield of hydrogen gas (15.1 mol/kg) and the highest gasification efficiency (92.6%) in the presence of NaOH than other algae owing to its more excellent content of carbohydrates. Nevertheless, the hydrogen gas product was reduced to 14.2 mol/kg if the SCWG of *Saccharina latissimi* was conducted with the assistance of NaOH and Ni— $\text{Al}_2\text{O}_3$ .

Even though utilization of alkali-based homogeneous catalysts can reduce the operating temperature and suppress the char formation during SCWG, this process has a drawback as the readjustment of the catalyst is challenging. In this context, the supplementary expenditure for the supply of new catalysts and the treatment of alkali catalyst waste produced from the SCWG process is highly required (Okolie et al., 2019). These difficulties have driven most researchers to use heterogeneous catalysts to achieve high selectivity towards hydrogen production and similar catalytic activity.

### 3.3.2. Heterogeneous catalysts

Heterogeneous catalysts have superiority over alkali-based homogeneous catalysts in terms of reusability, high selectivity, and being environmentally friendly. Hence, investigating the role of heterogeneous catalysts on SCWG reaction has been attracting researchers worldwide. Ni-based and noble metal-based heterogeneous catalysts are active to cleave C—C and C—O bonds and water gas shift reaction, generally resulting in the good catalytic performances of algae gasification (Azadi et al., 2012). Fig. 5 shows the reaction pathway for the Ni-catalyzed supercritical water gasification of biomass. As shown, carbohydrates are initially dehydrogenated on the metal surface, generating intermediates before C—C or C—O bonds cleavage.

Further, intermediate compounds are decomposed via C—C bond cleavage to result in syngas, which undergoes a water-gas shift reaction to generate hydrogen and carbon dioxide. Further reaction of hydrogen with CO and  $\text{CO}_2$  generates alkanes and water through methanation and Fischer-Tropsch reactions (Cortright et al., 2002). Additionally, side reactions of undesirable alkanes formation could occur from the cleavage of C—O bonds followed by hydrogenation reaction, generating an intermediate compound of alcohols. Furthermore, catalytic dehydration catalyzed by protons in the aqueous solution or Brønsted acid sites on catalyst surfaces should affect the selectivity of products. Another pathway to generate undesirable alkanes is through the intermediate compound of organic acids. The intermediates are generated by metal-catalyzed dehydrogenation reactions followed by carbon rearrangement. Carbon atoms of organic acids that are not bonded to oxygen atoms generally produce alkanes. Even though nickel catalyst has high activity for catalyzing the C—C bond cleavage and water-gas shift reaction, the selective production of hydrogen under SCWG conditions is challenging.

However, Ni-based catalysts have still been widely used to date since they are relatively inexpensive and can be tuned for their activity and selectivity in combination with other metals. Similar to homogeneous catalysts, heterogeneous catalysts can also suppress coke formation and improve the gasification of fractionous intermediates such as ethylbenzene and phenol. The most effective catalyst is commonly based on noble metals such as rhodium (Rh) and ruthenium (Ru) because they are selective for the hydrogenation of CO and  $\text{CO}_2$  (Xu et al., 2019). The catalytic mechanism of Ru during the SCWG process has been proposed by Guo et al. (2010) in which they assumed that oxygenated compounds containing hydroxyl groups are adsorbed to the catalytic Ru surface predominantly through one or more oxygen atoms. Initially, the biomass is subjected to dehydrogenation on the catalyst surface, followed by subsequent cleavage of C—C or C—O bonds. The C—C bonds cleavage leads to syngas, which undergoes a water-gas shift reaction to produce hydrogen and carbon dioxide. Meanwhile, the C—O bonds cleavage

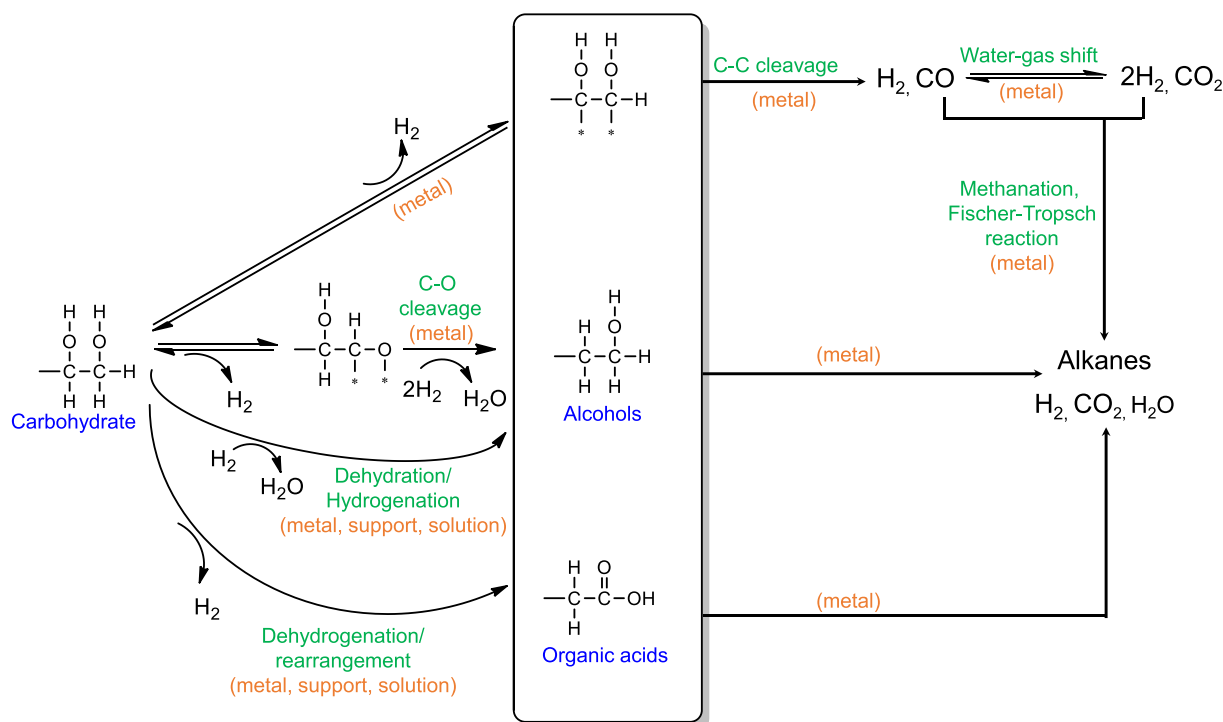


Fig. 5. Proposed reaction networks for hydrogen production by reactions of oxygenated carbohydrates with water adapted from Cortright et al., (2002) (\*represents a surface metal site).

generates organic acids and alcohols. Although Rh and Ru catalysts have good selectivity and high activity, their application to the industrial scale is limited by their high production cost.

Physical characteristics of the catalyst, such as particle size and surface area, play a crucial function in the reaction of SCWG of algae. Norouzi et al. (2017) reported that the catalysts having smaller metal particle sizes with higher dispersion rates generally exhibit good catalytic activity. Apart from that, the load of catalysts also plays a significant role in influencing both gas yield and compositions. For instance, hydrogen yield increased from 9.93 to 12.28 mol/kg algae, increasing the loading amount of Ru-catalyst from 0.5% to 2%, while methane yields slightly decreased.

To date, there are several studies limited on the utilization of heterogeneous catalysts in the SCWG of macroalgae. Cherad et al. (2013) investigated the SCWG of four species of macroalgae, namely *Laminaria digitata*, *Alaria esculenta*, *Laminaria hyperborea*, and *Saccharina latissima* using Ru/Al<sub>2</sub>O<sub>3</sub> catalyst at 500 °C and 36 MPa using a batch reactor. They observed that hydrogen with C<sub>1</sub>-C<sub>4</sub> gases yields increased by 30% in the existence of Ru/Al<sub>2</sub>O<sub>3</sub> for all four species of macroalgae compared with non-catalytic SCWG. Additionally, the gasification efficiency of the non-catalytic SCWG of *S. latissima* (57.78%) significantly increased when Ru/Al<sub>2</sub>O<sub>3</sub> was used as a catalyst (91.69%). The hydrogen yields of four macroalgae species are higher (7.75, 7.85, 8.50, and 10.20 mol H<sub>2</sub>/kg algae for *Alaria esculenta*, *Laminaria digitata*, *Laminaria hyperborea*, and *Saccharina latissima*, respectively) compared with those reported for microalgae of *Nannochloropsis* sp. (3.2 mol/kg). The water resulting from the SCWG of macroalgae could be directly utilized to cultivate green microalgae *Chlorella vulgaris*, confirming the appropriateness of nutrient recycling from macroalgae gasification within an algal biorefinery context.

A year later, the same researchers have conducted a comparative study of catalytic and non-catalytic SCWG of *Laminaria hyperborea* under various factors (catalyst loading, reaction temperature, feed concentration, and time) in a batch reactor (Cherad et al., 2014). They observed that catalysts could increase the yield of hydrogen from 5.18 mol H<sub>2</sub>/kg algae (non-catalytic SCWG) to 6.19 mol H<sub>2</sub>/kg algae (Ni/

Al<sub>2</sub>O<sub>3</sub>-catalyzed SCWG) and 7.68 mol H<sub>2</sub>/kg algae (Ru/Al<sub>2</sub>O<sub>3</sub>-catalyzed SCWG). The methane yield was found more than doubled when using Ru/Al<sub>2</sub>O<sub>3</sub> (8.95 mol/kg algae) compared to non-catalytic SCWG of (3.30 mol/kg algae), confirming that Ru/Al<sub>2</sub>O<sub>3</sub> has better selectivity to enhance methane yield than Ni/Al<sub>2</sub>O<sub>3</sub>. However, an increase in ruthenium loading from 5 to 20 wt% had no significant influence on methane yields.

Norouzi et al. (2017) investigated the gasification of *Enteromorpha intestinalis* in supercritical water. They employed a bimetallic catalyst of Ni and Fe impregnated on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, either with or without Ru as a promoter. Fe-Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> gave a higher total gas yield than non-catalytic reaction (17.72 and 30.16 mmol/g of *E. intestinalis*, respectively). The hydrogen and total gas yields for the promoted catalysts with 0.5–2 wt% of Ru were enhanced by factors of 1.22 and 1.15, respectively. Among those catalysts, 2% Ru-12% Ni-6% Fe on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has the smallest particle size and best dispersion, leading to more efficiency for sustainable production of gaseous products. Meanwhile, the water-gas shift reaction is also enhanced, resulting in higher hydrogen yield. Moreover, the highest selectivity of 0.74 was also found in the SCWG of *E. intestinalis* with 2% Ru-12% Ni-6% Fe on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. However, increasing the concentration of Ru caused a slight decrease in the methane yield due to Ru's restraining role in the methanation reaction.

Besides the alkali-based homogeneous and metal-based heterogeneous catalysts, metal oxides are also gaining more attention to be utilized as catalysts for SCWG of biomass. However, the utilization of this metal oxide catalysts for SCWG of macroalgae has not been studied well. Hence, some studies with model compounds and other biomass are presented here. Seif et al. (2016) examined hydrogen production via SCWG of industrial waste streams using three transition metal oxide catalysts (MnO<sub>2</sub>, CuO, and Co<sub>3</sub>O<sub>4</sub>). They observed that the catalytic activity of metal oxide catalysts for hydrogen production is as follows: Co<sub>3</sub>O<sub>4</sub> > CuO > MnO<sub>2</sub>. Furthermore, Cao et al. (2020) investigated 14 common metal oxides (ZnO, TiO<sub>2</sub>, SnO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, WO<sub>3</sub>, MoO<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, CuO, ZrO<sub>2</sub>, Co<sub>2</sub>O<sub>3</sub>) on SCWG of black liquor. They found that all tested metal oxides enhanced the gasification efficiency, and the highest H<sub>2</sub> yield of 21.67 and 21.03 mol/kg was obtained



with  $\text{Co}_2\text{O}_3$  and  $\text{ZnO}$  as the catalysts. Moreover, the use of metal oxide as the support of metal catalysts during SCWG also have been widely used. Lu et al. (2013) reported that catalyst support with metal oxides has good selectivity and good durability in SCWG of glucose. Besides, it could improve hydrogen yield during SCWG of glucose. They found that catalytic activity for hydrogen production is in the following order:  $\text{CeO}_2/\text{Al}_2\text{O}_3 > \text{La}_2\text{O}_3/\text{Al}_2\text{O}_3 > \text{MgO}/\text{Al}_2\text{O}_3 > \text{Al}_2\text{O}_3 > \text{ZrO}_2/\text{Al}_2\text{O}_3$ . Meanwhile, the sequence of hydrogen selectivity is as follows:  $\text{CeO}_2/\text{Al}_2\text{O}_3 > \text{La}_2\text{O}_3/\text{Al}_2\text{O}_3 > \text{ZrO}_2/\text{Al}_2\text{O}_3 > \text{Al}_2\text{O}_3 > \text{MgO}/\text{Al}_2\text{O}_3$ . Moreover, they reported that the  $\text{CeO}_2/\text{Al}_2\text{O}_3$  support has the good ability as a carbon remover on the catalyst surface, probably owing to its high oxygen storage capacity and oxygen mobility. In another study using lignin as a feedstock, Kang et al. (2016a, 2016b) found that the sequence of catalytic activity of Ni-based catalysts is as follows  $\text{Ni}/\text{Al}_2\text{O}_3 > \text{Ni}/\text{TiO}_2 > \text{Ni}/\text{AC} > \text{Ni}/\text{ZrO}_2 > \text{Ni}/\text{MgO}$ . In a recent publication, the catalytic activity of La promoted  $\text{Ni}/\text{Al}_2\text{O}_3$  in hydrogen production via SCWG of food waste dropped by 31 and 65% in the 2nd and 3rd runs, respectively. It could be attributed to the loss of active sites due to the cracking of the catalyst surface and the deactivation of the catalyst by fouling or carbon deposition. Generally, the previous findings reveal that the metal oxide enhances the hydrogen yield, especially with a single run. Nevertheless, the continued use of a catalyst will reduce the stability and activity of the catalyst.

### 3.4. Comparison of SCWG of macroalgae and other biomass

Several studies reported that the hydrogen yield from SCWG of macroalgae is much higher than that of microalgae and other lignocellulosic biomass. Table 4 shows the compilation of literature related to the SCWG using macroalgae and other biomass for comparison purposes. Schumacher et al. (2011) found that the hydrogen yields obtained from SCWG of several species of macroalgae (*Laminaria digitata*, *Alaria esculenta*, *Fucus serratus*, and *Bifurcaria bifurcata*) are in the range of 11.80 to 16.00 mol  $\text{H}_2$ /kg algae. Meanwhile, their research group reported that SCWG of different kinds of agricultural wastes (tobacco stalk, corn stalk, cotton stalk, sunflower stalk, corncob, oreganum stalk, chromium-tanned waste, and vegetable-tanned waste) could generate hydrogen yields in the range of 4.18–8.30 mol  $\text{H}_2$ /kg biomass (Yanik et al., 2007).

For the case of SCWG of microalgae, Jiao et al. (2017) found that the maximum hydrogen yields of 5.97, 5.1, 4.0, and 2.7 mol  $\text{H}_2$ /kg biomass were achieved for SCWG of *C. pyrenoidosa*, *Nannochloropsis* sp., *Schizochytrium limacinum*, and *S. platensis*, respectively. Furthermore, Zhang et al. (2019) reported that the hydrogen yield of merely 2.92 mol  $\text{H}_2$ /kg feedstock was obtained for non-catalytic SCWG of microalgae *Microcystin* sp. They assumed that the low hydrogen yield could be attributed to high protein content in microalgae which can inhibit the free radical chain reactions for the gas generation. In another study by Samiee-Zafarghandi et al. (2019) using *Chlorella* PTCC6010, the hydrogen yield of merely 1.7 mol  $\text{H}_2$ /kg feedstock could be generated at 405 °C and 30 min in the presence of graphene-support nanocatalyst.

As shown in Table 4, the hydrogen yield obtained from the SCWG of terrestrial plant-derived biomass is in the range of 0.3 to 7.6 mol  $\text{H}_2$ /kg feedstock. Kang et al. (2016b) examined the SCWG of canola meal, wheat straw, and timothy grass at 450–650 °C, 26 MPa, and 50 min reaction time. They found that the significant yields of hydrogen of 3.36, 2.08, and 1.83 mol  $\text{H}_2$ /kg biomass were achieved in the presence of  $\text{K}_2\text{CO}_3$  catalyst for canola meal, wheat straw, and timothy grass, respectively. These hydrogen yields are comparable with the study reported by Nanda et al. (2016a) who obtained the hydrogen yields of 3.3, 4.8, 3.5, 3.5, 3.7, and 4.5 mol  $\text{H}_2$ /kg biomass for SCWG of banana peel, coconut shell, orange peel, pineapple peel, sugarcane, and bagasse, respectively in the presence of  $\text{NaOH}/\text{K}_2\text{CO}_3$  catalyst. Recently, Okolie et al. (2020) found that the hydrogen yield of as much as 7.6 mol  $\text{H}_2$ /kg biomass was achieved in SCWG of soybean straw with the addition of 3 wt% KOH as a catalyst.

**Table 4**

The compilation of literature related to the SCWG using macroalgae and other biomass.

Biomass type	Name of feedstock	Operating conditions	Maximum $\text{H}_2$ yield (mol/kg-dry feedstock)	Ref.
Macroalgae	<i>Alaria esculenta</i>	Feedstock loading 5 wt %, 500 °C, 30.2 MPa, no catalyst	13.2	(Schumacher et al., 2011)
	<i>Bifurcaria bifurcata</i>	Feedstock loading 5 wt %, 500 °C, 30.4 MPa, no catalyst	16	(Schumacher et al., 2011)
	<i>Fucus serratus</i>	Feedstock loading 5 wt %, 500 °C, 30.3 MPa, no catalyst	14.25	(Schumacher et al., 2011)
	<i>Laminaria digitata</i>	Feedstock loading 5 wt %, 500 °C, 30.4 MPa, no catalyst	11.8	(Schumacher et al., 2011)
	<i>Laminaria hyperborea</i>	Feedstock loading 6.66 wt%, 500 °C, 1.5 M NaOH catalyst	16.27	(Cherad et al., 2014)
	<i>Posidonia oceanica</i>	Feedstock loading 8 wt %, 600 °C, 44.2 MPa, no catalyst	10.37	(Deniz et al., 2015)
	<i>Enteromorpha intestinalis</i>	Feedstock loading 1 wt %, 400 °C, 23.7 MPa, 2% Ru-12% Ni-6% Fe on $\gamma$ - $\text{Al}_2\text{O}_3$ catalyst	12.28	(Norouzi et al., 2017)
Microalgae	<i>C. pyrenoidosa</i>	Feedstock loading 50 wt %, 430 °C, 60 min, 5% Ru/C catalyst	5.97	(Jiao et al., 2017)
	<i>Nannochloropsis</i> sp.	Feedstock loading 50 wt %, 430 °C, 60 min, 5% Pd/C catalyst	5.1	(Jiao et al., 2017)
	<i>Schizochytrium limacinum</i>	Feedstock loading 50 wt %, 430 °C, 60 min, 5% Pd/C catalyst	4.0	(Jiao et al., 2017)
	<i>S. platensis</i>	Feedstock loading 50 wt %, 430 °C, 60 min, 5% Pd/C catalyst	2.7	(Jiao et al., 2017)
	<i>C. pyrenoidosa</i>	550 °C, 49 MPa, 60 min, 20 wt% Ru/C catalyst	3.17	(Duan et al., 2018a)
	<i>Microcystin</i> sp	Feedstock loading 96.15 wt%, 500 °C, no catalyst	2.92	(Zhang et al., 2019)
	<i>Chlorella vulgaris</i>	Feedstock loading 1.5 wt %, 550 °C, 30 MPa, no catalyst	9.34	(Fozer et al., 2019)

(continued on next page)

Table 4 (continued)

Biomass type	Name of feedstock	Operating conditions	Maximum H <sub>2</sub> yield (mol/kg-dry feedstock)	Ref.
Terrestrial plants	<i>Chlorella</i> PTCC6010	Feedstock loading 1.4 wt %, 405 °C, 30 min, graphene-support nanocatalyst (0.4 g/g)	1.7	(Samiee-Zafarghandi et al., 2019)
	Canola meal	Feedstock loading 0.65 g biomass, 5 mass ratio of water to biomass, 450–650 °C, 26 MPa, 50 min, K <sub>2</sub> CO <sub>3</sub> catalyst	3.4	(Kang et al., 2016b)
	Wheat straw	Feedstock loading 0.65 g biomass, 5 mass ratio of water to biomass, 450–650 °C, 26 MPa, 50 min, K <sub>2</sub> CO <sub>3</sub> catalyst	2.1	(Kang et al., 2016b)
	Timothy grass	Feedstock loading 0.65 g biomass, 5 mass ratio of water to biomass, 450 to 650 °C, 26 MPa, 50 min, K <sub>2</sub> CO <sub>3</sub> catalyst	1.8	(Kang et al., 2016b)
	Banana peel	Feedstock loading 16.7–32.1%, 400–600 °C, 24 MPa, 15–45 min, NaOH/K <sub>2</sub> CO <sub>3</sub> catalyst	3.3	(Nanda et al., 2016a)
	Coconut shell	Feedstock loading 16.7–32.1%, 400–600 °C, 24 MPa, 15–45 min, NaOH/K <sub>2</sub> CO <sub>3</sub> catalyst	4.8	(Nanda et al., 2016a)
	Orange peel	Feedstock loading 16.7–32.1%, 400–600 °C, 24 MPa, 15–45 min, NaOH/K <sub>2</sub> CO <sub>3</sub> catalyst	3.5	(Nanda et al., 2016a)
	Pineapple peel	Feedstock loading 16.7–32.1%, 400–600 °C, 24 MPa, 15–45 min, NaOH/K <sub>2</sub> CO <sub>3</sub> catalyst	3.5	(Nanda et al., 2016a)
	Sugarcane	Feedstock loading 16.7–32.1%,	3.7	(Nanda et al., 2016a)

Table 4 (continued)

Biomass type	Name of feedstock	Operating conditions	Maximum H <sub>2</sub> yield (mol/kg-dry feedstock)	Ref.
	Bagasse	400–600 °C, 24 MPa, 15–45 min, NaOH/K <sub>2</sub> CO <sub>3</sub> catalyst	4.5	(Nanda et al., 2016a)
		Feedstock loading 16.7–32.1%, 400–600 °C, 24 MPa, 15–45 min, NaOH/K <sub>2</sub> CO <sub>3</sub> catalyst		
	Beech sawdust	Feedstock loading 15 wt %, 400 °C, 30 MPa, 16 h, no catalyst	0.6, 1.2, and 0.7 for Inconel-625, SS, and ceramic reactor	(Castello et al., 2017)
		Feedstock loading 10–25%, 300–550 °C, 22 MPa, 15–60 min, 30 wt% catalyst	3.3, 2.7, and 2 for KOH, NaOH, and Na <sub>2</sub> CO <sub>3</sub> , respectively	(Nanda et al., 2017)
	Wheat straw	Feedstock loading 20–35 wt%, 300–550 °C, 22 MPa, 40–70 min, 5 wt% catalyst	3, 4.2, and 5.1 for no catalyst, Ru/Al <sub>2</sub> O <sub>3</sub> , and Ni/Si-Al <sub>2</sub> O <sub>3</sub> , respectively	(Nanda et al., 2018)
		Feedstock loading 9.1%, 300–600 °C, 22–25 MPa, 60 min	4.2 for raw biomass; 11.1, 8.8, and 8 for Ni, Ru, and Fe impregnated biomass, respectively	(Kumar and Reddy, 2019)
	Banana pseudostem	Feedstock loading 9.1%, 300–600 °C, 22–25 MPa, 60 min	6.6 and 7.6 for no catalyst and KOH, respectively	(Okolie et al., 2020)
		Feedstock loading 9.1–16.7%, 300–500 °C, 22–25 MPa, 30–60 min, 3 wt% catalyst		

In general, the previous findings show that SCWG of macroalgae has superiority in terms of high hydrogen yield compared to microalgae and other lignocellulosic biomass. Two plausible reasons can explain why the hydrogen yield obtained from SCWG of macroalgae is considerably higher than that of lignocellulosic biomass and microalgae: (i) macroalgae have high carbohydrate content and (ii) the gasification of macroalgae is enhanced owing to its significant amounts of inorganic salts.

#### 4. Critical strategies on SCWG for hydrogen production

As aforementioned above, the primary chemical reactions that occurred during SCWG, such as methanation and water-gas shift reaction, are reversible. Hence, critical strategies by optimizing the reaction conditions to generate maximum hydrogen yield during SCWG are needed. The main operating parameters during SCWG affecting hydrogen yield, including temperature, reaction time, and feedstock concentration, are thoroughly discussed in this section.

#### 4.1. Effect of temperature

As aforementioned above, the primary chemical reactions that occurred during SCWG include methanation and water-gas shift reaction. Promdej and Matsumura (2011) investigated SCWG of glucose at 25 MPa and temperature range 300–460 °C in a continuous flow reactor to clearly understand the temperature effect on the SCWG reaction mechanism. They categorized the hydrothermal glucose decomposition mechanisms in sub- and supercritical water into ionic and radical reactions depending on reaction rate and temperature. Under sub-critical conditions, glucose decomposition was dominated by ionic mechanisms, whereas free radical mechanisms are favored under supercritical conditions. Furthermore, Kruse and Dinjus (2007) reported that increasing temperature above the critical point of water reduced the density and ionic product, and the mechanisms proceeded as the radical reaction. In another study by Guo et al. (2010), the results indicated that temperature had a significant role in the shift of reaction mechanisms from ionic reaction to free radical reaction during SCWG of biomass, which has advantageous on enhancing the fuel gas productions. From these findings, it can be confirmed that increasing reaction temperature beyond the critical point could promote the free radical reaction, and thus improving gasification efficiency and gaseous products.

From a thermodynamical point of view, the decomposition of biomass composed of complex bonding molecules favors a high amount of energy. The main chemical reactions during SCWG are endothermic. Hence, achieving the equilibrium reaction to produce hydrogen and carbon dioxide requires high external energy. The elevated reaction temperature is necessary to proceed the reaction equilibrium forward to promote hydrogen generation. Therefore, the production of hydrogen prevails over methane formation at high reaction temperatures. A lot of reports related to SCWG of the model compound as well as real biomass

give consent to this fact (Acelas et al., 2014; Guan et al., 2012a; Nurcahyani et al., 2020; Samanmulya et al., 2017a; Sheikhdavoodi et al., 2015; Sinag et al., 2012; Ratna F. Susanti et al., 2014a; Yoshida et al., 2004). Matsumura et al. (2005) reported that high-temperature gasification ranges are more convenient for a high hydrogen production yield. In a similar route, Gadhe and Gupta (2007) observed the increasing hydrogen gas yield from 0.2 to 1.3 mol/mol methanol as the temperature increased from 500 to 700 °C during methanol gasification at 27.6 MPa. Furthermore, Jin et al. (2010a) reported that increasing temperature from 550 to 650 °C could increase the hydrogen yield from 4.42 to 8.94 mol/mol glucose for SCWG of glucose at 25 MPa. However, the calculation using Gibbs free energy minimization and Peng-Robinson equation state of the equilibrium gas yield indicated that hydrogen yield tends to be nearly constant after 650 °C for SCWG of glucose 650 °C (Susanti et al., 2014a, 2014b).

Fig. 6 (a) shows the effect of temperature on hydrogen yield during SCWG of macroalgae. Overall, the yield is significantly lifted with an increase in temperature. Cherad et al. (2014) noted that the yield of hydrogen during SCWG of *L. hyperborea* was recorded by 3.96 mol H<sub>2</sub>/kg algae at 400 °C (experimental conditions: 30 min holding time with 20% Ru/Al<sub>2</sub>O<sub>3</sub>), while it increased by almost double at 550 °C, i.e., 7.57 mol H<sub>2</sub>/kg algae. A similar finding by Deniz et al. (2015) found that the hydrogen yield increased sharply from 0.09 to 10.37 mol H<sub>2</sub>/kg algae as the temperature increased from 300 to 600 °C in the SCWG of *P. oceanica*. Moreover, Graz et al. (2016) also investigated the effect of temperature on SCWG of *Ulva* sp. within a short residence time of 7 min. They found that the hydrogen yields were raised from 0.13 to 1.8 mol H<sub>2</sub>/kg algae by rising temperature from 400 to 550 °C at 16.4 wt% and 23–25 MPa. In agreement with these results, Norouzi et al. (2017) examined that hydrogen production from SCWG of *E. intestinalis* in a batch reaction increased more than double from 1.89 to 4.12 mol H<sub>2</sub>/kg

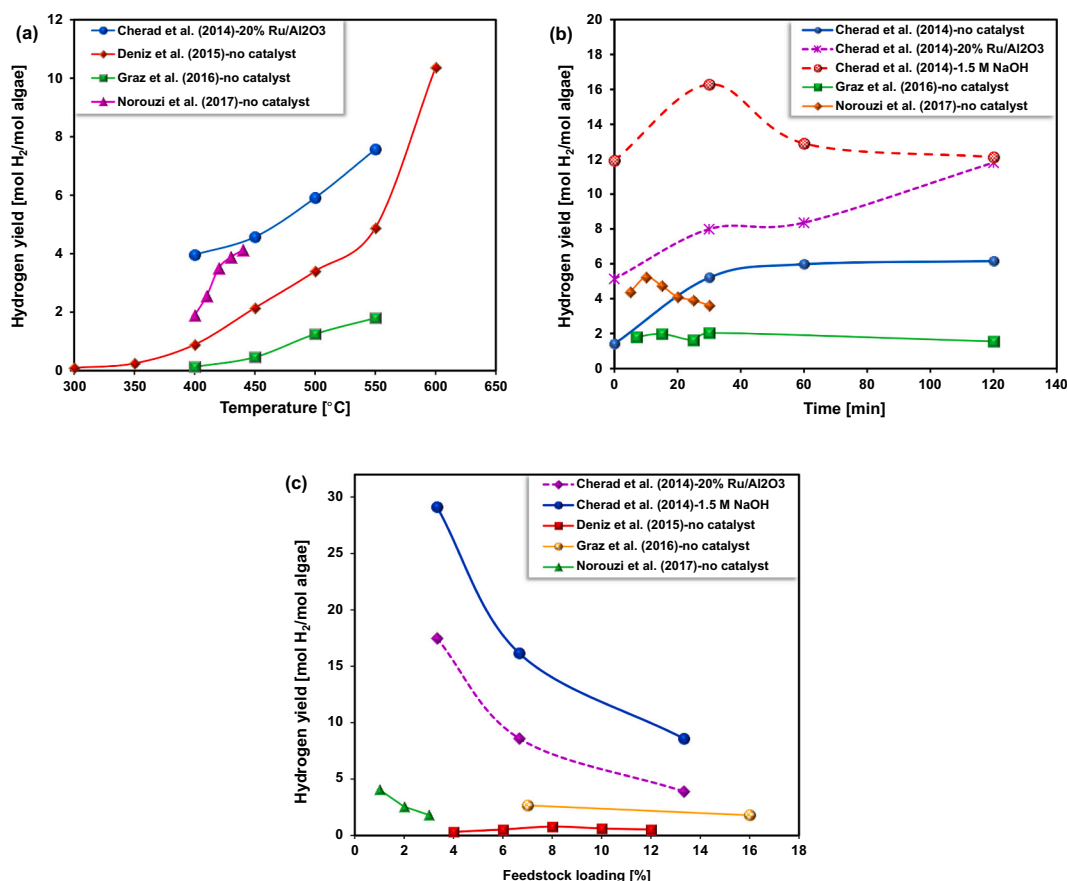


Fig. 6. Effect of (a) temperature, (b) time, and (c) feedstock loading on hydrogen yield during SCWG of macroalgae.

algae as the temperature increased from 400 to 440 °C with *E. intestinalis* loading of 0.06 g and water loading of 6 g. Therefore, a high reaction temperature increases the gasification efficiency and hydrogen-rich syngas production from macroalgae.

#### 4.2. Effect of reaction time

Reaction time is another critical affecting parameter on SCWG of macroalgae that significantly affects the composition and the yield of product gas. From the SCWG reactor configuration point of view, the reaction time can be defined in two different ways. In the batch reactor, reaction time is referred to the time or duration for which the reactants stay inside the reaction (Williams and Onwudili, 2005). Meanwhile, reaction time for the continuous reactor is determined by dividing the reactor volume by the flow rate of feedstock at a specific temperature and pressure (Yong and Matsumura, 2012).

In general, the increment of reaction times enhanced gasification efficiency and hydrogen production (Castello et al., 2013; Guo et al., 2007, 2010; Ibrahim and Akilli, 2019; Susanti et al., 2010; Xu et al., 2012). It is due to the long reaction times could improve the thermal cracking reactions (Chen et al., 2003). At a short reaction time, hydrothermal liquefaction is mainly occurred (Nanda et al., 2019). On the other hand, the gasification and free radical mechanisms decomposing the intermediate compounds to generate the gases are favored at a long reaction time (Yong and Matsumura, 2013). Overall, several researches reported that hydrogen yield and gasification efficiency increased with reaction time (Castello et al., 2013; Louw et al., 2016; Osada et al., 2012). It can be explained because a longer reaction time could enhance the biomass decomposition and water-gas shift reaction to produce H<sub>2</sub> and CO<sub>2</sub>. However, prolonging reaction time beyond the optimum condition may cause a drop in hydrogen yield due to methanation reactions that consume hydrogen.

Several published papers related to SCWG of macroalgae give countenance to this fact. The influence of reaction time on the yield of hydrogen during SCWG of macroalgae is presented in Fig. 6 (b). Cherad et al. (2013) investigated the effect of reaction time on the non-catalytic SCWG of *L. hyperborea* at 500 °C. They reported that the yields of hydrogen and methane were increased as the hold time increased in non-catalytic reactions. However, no significant change in hydrogen yield was discovered as the time was raised double from 30 to 60 min. At a longer reaction time of 120 min, the hydrogen yields from Ru/Al<sub>2</sub>O<sub>3</sub>-catalyzed SCWG of *L. hyperborean* were increased approximately from 8.36 to 11.8 mol H<sub>2</sub>/kg *L. hyperborean*. The highest hydrogen yield was found as much as 16.27 mol H<sub>2</sub>/kg algae in Ru/Al<sub>2</sub>O<sub>3</sub>-catalyzed SCWG of *L. hyperborean* at a reaction time of 30 min. Nevertheless, the yield of hydrogen decreases by increasing the reaction time to 120 min due to the consumption of hydrogen in the methanation reactions.

In the SCWG of *Ulva* sp. macroalgae, Graz et al. (2016) reported that a short time of 7 min is sufficient to obtain a reasonable gasification rate of algae. The hydrogen yields were raised from 1.80 to 1.98 mol H<sub>2</sub>/kg algae by prolonging the reaction time from 7 to 15 min at 23–25 MPa and became relatively steady. Herein, A long reaction time of SCWG should be considered only to enhance methane production. Having similar findings, Norouzi et al. (2017) observed that during SCWG of *E. intestinalis*, the hydrogen yield was increased to some extent with the increase of reaction time from 5 to 10 min, and reached the maximum value at 5.25 mol/kg *E. intestinalis*. Still, no significant increase in hydrogen yield was observed after that. Meanwhile, the production of methane was increased gradually from 5 to 30 min while hydrogen and carbon monoxide are consumed by methanation.

#### 4.3. Effect of feedstock concentration

The concentration of feedstock is another factor that undoubtedly influences the yield of hydrogen and gasification efficiency. In general, lower feedstock loading mainly leads to higher hydrogen yield and

gasification efficiency, though effluent recovery and high pumping costs are needed for low feed concentrations (Chakinala et al., 2010; Cherad et al., 2014). A high feedstock concentration leads to pumping issues of the SCWG process in the continuous reactor due to plugging problems. Susanti et al. (2012) reported that SCWG experiments could not be conducted well to gasify glucose with a concentration beyond 20 wt% due to reactor plugging. One possibility to circumvent this problem is using a fluidized bed reactor, as suggested by several researchers (Jin et al., 2010b; Lu et al., 2008; Matsumura and Minowa, 2004).

Under SCWG conditions, water has dual functions as both reaction medium and reactant. The reaction routes during SCWG (steam reforming, hydrolysis, and water-gas shift reactions) generally lead to the main product of hydrogen (Okolie et al., 2019). In high feedstock loading, lack of water can suppress the steam reforming and water-gas shift reactions, potentially reducing hydrogen yields. On the other hand, in low feedstock loading, the excess water can shift the water-gas shift reaction forward, leading to increased hydrogen yield. Furthermore, the excess water can change the methanation reactions backward, decreasing the yield of methane. Steam reforming reaction is the reaction of water with biomass to generate hydrogen and CO. Besides, a water-gas shift reaction allows water to react with CO to generate hydrogen and CO<sub>2</sub>. Hence, a low feedstock loading in SCWG should favor both reactions to enhance hydrogen yield. This fundamental aspect is proven by previous findings on SCWG of model compounds and actual biomass (C. Cao et al., 2011a; Chakinala et al., 2010; Hao et al., 2003; Kipçak and Akgün, 2012; Nanda et al., 2016b, 2018; Rashidi and Tavasoli, 2015; Su et al., 2020).

The effect of feedstock loading for SCWG of macroalgae is presented in Fig. 6 (c). Overall, the increase in macroalgae concentrations leads to a decrease in the yields of hydrogen. Cherad et al. (2013) investigated the effect of feedstock concentration on gasification of *L. hyperborea* using 1.5 M NaOH and 20 wt% Ru/Al<sub>2</sub>O<sub>3</sub> catalysts at a temperature of 500 °C. They found that hydrogen yields sharply decreased from 17.48 to 8.61 mol H<sub>2</sub>/kg algae when the feed concentration increased from 3.33 to 6.66 wt% for Ru/Al<sub>2</sub>O<sub>3</sub>-catalyzed SCWG of *L. hyperborea*. Furthermore, increasing the feed loading to 13.33 wt% resulted in a significant reduction in hydrogen yield to 3.91 mol H<sub>2</sub>/kg algae. Deniz et al. (2015) found similar findings, who observed that the yield of hydrogen reduced from 0.79 to 0.53 mol H<sub>2</sub>/kg algae as the amount of biomass loading increased from 0.08 to 0.12 g/mL during SCWG of *P. oceanica* at 400 °C. In another study by Graz et al. (2016), when the concentration of *Ulva* sp. was raised from 7 to 16.4 wt%, the yields of hydrogen notably reduced from 2.7 to 1.8 mol H<sub>2</sub>/kg algae at 550 °C and 7 min reaction time. Hydrogen yields from SCWG of *E. intestinalis* macroalgae also showed a similar trend. Hydrogen yield decreased dramatically from 4.07 to 2.55 mol H<sub>2</sub>/kg algae by increasing the loading of *E. intestinalis* from 1 wt% to 2 wt% (Norouzi et al., 2017). Overall, these findings pointed out that increased macroalgae concentrations suppressed steam reforming and water-gas shift reactions, reducing the gaseous products' hydrogen yields.

## 5. Challenges and future perspective

SCWG is a promising and environmentally benign technology that enables the decomposition of macroalgae to produce hydrogen-rich syngas within a short reaction time. However, there are still many challenges in implementing macroalgae hydrogen production, both small- and large-scale operations. Several main challenges of SCWG for hydrogen production from macroalgae include:

### (1) Energy efficiency issue

As mentioned previously, high exterior energy to increase the reaction temperature for hydrogen production is required owing to the endothermic nature of SCWG. The energy needed to reach the high temperature will directly influence the overall energy efficiency of the



SCWG process. Therefore, efficient energy recovery equipment is unavoidable to optimize and enhance the energy efficiency of the SCWG process. The high-efficiency heat exchangers are necessary to recover the heat for water heating to achieve efficient hydrothermal decomposition. In addition, to increase energy efficiency, utilization of non-conventional energy sources may be more enjoyable. Nevertheless, using a heat exchanger with a low heating rate to preheat the feedstock can increase the char and tar formation. The heat exchanger used in SCWG was performed by Karlsruhe Institute of Technology in VERENA pilot plant design to circumvent the energy efficiency problem (Boukiss et al., 2007; Ibrahim and Akilli, 2019).

- (2) The high operating cost for high-temperature and high-pressure processes

High-temperature and high-pressure operations to undergo the SCWG process require advanced compatible materials such as alloy-type materials that are pretty costly. Previous researchers have proposed non-conventional heating sources such as solar to reduce the cost of the SCWG process (Chen et al., 2010; Xiao et al., 2013). Lu et al. (2011) reported the technical and economic evaluations of solar energy for SCWG, and they summarized that it is a promising technology for hydrogen production.

- (3) Plugging and char formation

Plugging and char formation are pivotal problems during the SCWG process (Adar et al., 2017). The plugging is mainly due to the incomplete gasification process and the lower solubility of inorganic salts under SCW conditions (Bermejo and Cocero, 2006; Kruse, 2008). Char formation can be suppressed by employing higher heating rates or heating biomass rapidly (Hendry et al., 2011). Moreover, char also can be reduced by using organic acid as a radical scavenger agent in SCWG, as reported by Matsumura and co-workers (Changsuwan et al., 2020; Matsumura et al., 2018). The pioneering work of circumventing the reactor plugging problems was conducted by Matsumura and Minowa by employing a fluidized bed reactor (Matsumura and Minowa, 2004).

- (4) Corrosion of the reactor material

Another technical challenge of SCWG for macroalgae is the corrosion of the reactor material (Kritzer, 2004). Alloy-type reactors are generally made of Ni-based materials that react with feedstock and water to generate undesirable products (Lee and Ihm, 2009; Park and Tomiyasu, 2003). Moreover, extreme conditions such as high temperatures and chemicals mainly cause decay. There are several possibilities to overcome this problem, including employing crustal encapsulation and filament winding to protect the layer of the reactor (Wei et al., 2013) and a cooling strategy to avoid the condition of high temperature and density that causes high corrosive rates (Vadillo et al., 2013). Moreover, Pinkard et al. (2019) pointed out several main approaches to mitigate corrosion: flow control, the use of corrosion-resistant materials, and the optimization of operating conditions.

Future studies that are interesting to be conducted to overcome the challenges as mentioned above for SCWG of macroalgae include:

- (1) Integrating the SCWG in the biorefinery concept of macroalgae. For example, the macroalgae residues are re-used after extracting high-value compounds used for hydrogen production via SCWG. From the CO<sub>2</sub>-footprint perspective, combining SCWG with a supercritical turbine or with additional anaerobic digestion looks promising.
- (2) The development of a reactor with a proficient system to recover the heat from the effluent for macroalgae heating.
- (3) The suppression of char formation via fast heating, the particular concentration of feedstock, mixture modification as well as

employing organic acid radical scavenger for SCWG of macroalgae.

- (4) The development of low-cost yet environmentally benign catalysts that can decrease reaction temperatures and promote hydrogen production.
- (5) The enhancement of hydrogen yield and gasification efficiency via optimizing the operating conditions (temperature, pressure, feedstock concentration, and residence time) and the investigation of the biomass components interaction (among several species of macroalgae and macroalgae with other biomass mixtures).
- (6) There is also a need for detailed techno-economic and life cycle analyses of developed processes.

## 6. Conclusion

This article highlights an insight into the potential of macroalgae for hydrogen production via SCWG. The literature review indicated that either the non-catalytic or catalytic process could perform SCWG of macroalgae. The literature review also revealed that the factors affecting the SCWG of macroalgae, including temperature, reaction time, and macroalgae concentration, are the key to realizing the complete gasification of macroalgae. Even though SCWG is a promising technology for hydrogen production from macroalgae, technical hurdles are not yet solved entirely, and several challenges have severely hampered its scale-up. Several approaches to counterbalance the challenges have been proposed in this article.

## 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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