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ORIGINAL ARTICLE

Steam gasification of marine biomass and its biochars for hydrogen-rich gas production

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Abstract

In this study, steam gasifications of a kind of marine biomass, i.e., *Zostera marina* (eelgrass), and the biochars derived from pyrolysis of it were carried out for the biohydrogen production in a fixed-bed reactor. The effects of reaction temperature and water injection rate on the hydrogen production were investigated. In order to understand the effect of sea salts attached on the surface of eelgrass for the hydrogen production, the eelgrass washed by water (washed-eelgrass) was also used as the feedstock. It was observed that hydrogen productions from the gasification of washed-eelgrass as well as its biochar were higher than those of raw eelgrass and its biochar, indicating that the impurities of raw eelgrass had a negative effect on the hydrogen production. The biochar derived from the pyrolysis of washed eelgrass at 550 °C had the largest amount of hydrogen yield at the gasification temperature of 850 °C with a water injection rate of 0.15 g/min. It was found that both the hydrogen production and reaction rates were enhanced by mixing washed-eelgrass biochar obtained at 350 °C with the calcined seashells at a weight ratio of 1 to 2, especially at the gasification temperature of 650 °C. Meanwhile, in the presence of the calcined seashell, CO_2 content decreased sharply whereas the hydrogen yield had no obvious increase.

Keywords Pyrolysis · Steam gasification · Marine biomass · Biochar · Biohydrogen

1 Introduction

Traditional fossil fuels have played a dominant role in modern society by supplying more than 80% of global energy demand [1]. However, the emission of a large amount of carbon dioxide (CO_2) gas from the application of them leads to serious climate change. To solve this problem, various renewable energy resources such as biomass, wind, and geothermal energy have been considered to replace the traditional fossil energy. As a second energy resource, hydrogen has gained great attention since it has the highest energy density with a calorific value of 122 MJ kg^{-1}, about 2.75 times higher than other hydrocarbon fuels [2, 3]. Moreover, the product of hydrogen combustion is only water without the emission of any carbon and sulfur byproducts. However, as a secondary form of energy like electricity, hydrogen has to be artificially produced from some processes such as the splitting of water and steam reforming of natural gas, coal, and oil. Currently, the industrial-scale hydrogen production has been dominated by fossil fuels with the most important process of steam reforming [4]. In order to achieve the renewable and sustainable hydrogen production, biomass has been considered the ideal primary source in the steam reforming process to replace the fossil fuels for the hydrogen production [5]. Hydrogen can be produced from biomass via either thermochemical or biological routes [6–9]. In particular, almost all biomass can be used as the carbon resources in the steam reforming process for the generation of hydrogen-rich gas. Pyrolysis and

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gasification are two main thermochemical routes for the biomass conversion. In the inert gas atmosphere, fast pyrolysis can produce a large amount of bio-oil from biomass while slow pyrolysis can produce a large amount of biochar [10]. Like the coal-char, biochar can be reformed by steam to produce hydrogen-rich gas product [11]. Thus, it is important to investigate the steam gasification of various biochars from various biomass for the production of hydrogen.

To date, most of the researches have been focusing on the steam gasification of various land-based biomass such as edible crops (i.e., sugar cane, wheat, grains, and sugar beet, etc.) and non-food plant biomass [10, 12]. Recently, marine biomass (e.g., seagrass and seaweed) are gaining considerable interest as a feedstock for sustainable hydrogen production since they have fast growth rate, high mass productivity per area, large amounts of simple carbohydrates, and no competition with food demand [13, 14]. Especially, for those countries with large coastal areas, marine biomass should have great potential for the production of biofuels including biohydrogen [15]. For instance, algae (microalgae) has been applied for methane and biodiesel productions [1, 13, 14]. However, other marine biomass resources such as seagrass and seaweed are still needed to be investigated for the production of syngas by the steam gasification process [16]. In particular, a large amount of alkali and alkaline earth metal (AAEM) contained in the marine biomass could serve as the self-catalysts to enhance the gasification rate [17–21]. Besides such a self-catalytic effect, the addition of some AAEM-containing materials from wastes such as calcined seashells with high content of calcium species could be used as the CO_2 sorbent as well as catalysts to produce hydrogen-rich gas from the steam gasification of biomass by enhancing the water-gas shift reaction [22–27]. For instance, in our previous work, the calcined scallop shell which mainly contained CaO with porous structure showed the good catalytic effect on the steam reforming of the volatiles and tar derived from biomass to syngas [28].

As non-woody biomass, marine biomass always has the characteristics of high moisture content, low density, and low carbon content, which could result in low syngas production from the steam gasification process. Therefore, it is necessary to investigate the feasibility of utilizing the marine biomass source for biohydrogen production by the steam gasification. *Zostera marina* is one of the marine biomasses known by the common names of eelgrass and sea wrack, and widely grows in the Northern Hemisphere [29]. In Aomori Prefecture, north region of Japan, which is surrounded by the sea from three sides (Fig. S1), there are a large amount of eelgrass growing in the shallow seashores. In this study, eelgrass was chosen as the marine biomass feedstock to produce biohydrogen-rich gas by the steam gasification process. The objectives were to investigate the feasibility of utilizing the eelgrass and its biochar derived from the pyrolysis process for the production of biohydrogen via the steam gasification. The steam gasification conditions were optimized. Besides, one kind of small parasitic seashell waste obtained from aquaculture was calcined and utilized as a CO_2 sorbent as well as the catalyst for enhancing hydrogen production in the steam gasification process. It is expected to provide a way to effectively apply the wasted marine biomass together with the wastes from aquaculture for the production of biohydrogen.

2 Experimental

2.1 Materials

Eelgrass obtained from Mutsu Bay of Aomori prefecture, Japan (Fig. S1) was chosen as the marine biomass sample in this study. Considering the effect of the sea salts during the pyrolysis and gasification processes of eelgrass, raw eelgrass (RE) and washed-eelgrass (WE) were prepared separately. The RE sample was used directly for the pyrolysis and steam gasification experiments without washing while the WE sample was washed by the freshwater for several times to remove out the sea salts on the surface of the eelgrass. In addition, in order to investigate the effect of pyrolysis temperature on the physical and chemical structure of biochar derived from the eelgrass, different biochars were prepared by pyrolyzing the eelgrass at different final pyrolysis temperatures (350–550 °C) for 2 h with a slow heating rate of 10 °C/min. The obtained biochars derived from the washed-eelgrass are named as WEC-350, WEC-450, and WEC-550, respectively, and those derived from the raw eelgrass are named as REC-350, REC-450, and REC-550, respectively. All the biomass samples were cut and sieved into a size of $0 < d_p < 1$ mm and dried in the oven at 105 °C for 24 h before storage for further usage. Meanwhile, the biochar samples were sieved into the same size range. The remaining moisture was analyzed by using the MX50 moisture content analyzer (AND, Japan). It was found that the moisture contents of dried RE and WE were 3.82 wt% and 8.72 wt%, respectively. The Vario El cube elemental analyzer was used for ultimate analyses. The compositions of biomass ash were analyzed by an XRF equipment (Energy-Dispersive X-ray Spectrometer, EDX-800HS, Shimadzu) after calcination at 800 °C for 2 h in air. Tables 1 and 2 show the elemental analysis and XRF analysis results of eelgrass and its char samples derived from the pyrolysis at different temperatures. Herein, all the ash samples for XRF analysis were prepared by calcinating RE and WE and their chars in the muffle furnace at 800 °C for 2 h. However, the char samples were collected from the pyrolysis process.

2.2 Catalyst preparation

The concept of using CaO as a catalyst as well as a CO_2 sorbent to enhance hydrogen production has currently gained

Table 1 Ultimate analysis results of eelgrass and its char samples obtained from different pyrolysis temperatures

Ultimate analysis (wt%, d. a. f. basis[a])					
	N	C	H	S	O[b]
Eelgrass	1.4	32.6	4.5	0.5	61.0
RE-350char	1.8	39.5	2.7	0.5	55.5
RE-450char	1.4	37.3	1.8	0.7	58.8
RE-550char	1.4	39.1	1.0	0.7	57.8
WE-350char	2.7	54.5	4.0	0.1	38.7
WE-450char	2.3	53.6	2.4	0.7	41.0
WE-550char	2.5	60.8	1.8	0.4	34.5

[a] Dry and ash-free

[b] By difference

wide attention due to its cheapness and abundance [25, 26, 30]. In this study, one kind of small parasitic seashell discarded in the northern region of Japan, which is mainly composed of calcium species, was chosen as the CaO source. The seashell was firstly calcinated at a temperature of 900 °C in a muffle furnace for 2 h, so that $CaCO_3$, the main component of the seashell, was decomposed into CaO. Once the calcination step was finished, the calcined seashell (CS) was stored in a closed container to prevent carbonation again and humidification. The CS was ground to the fine powder before physically mixing with the biochar samples. The main compositions of CS are shown in Table 3 based on the XRF analysis.

2.3 Experimental setup and conditions

Figure 1 illustrates the setup for the biomass pyrolysis as well as the steam gasification, in which a down-flow fixed-bed reactor with an internal diameter of 18 mm and a length of 350 mm was used. For each run, a single biomass sample or a mixed sample was introduced into a sample holder made by the stainless steel mesh, which was then put in the center of the reactor. The reactor was heated up to the desired temperature from room temperature with a heating rate of 10 °C/min and held at that temperature during the pyrolysis and steam gasification processes. All the reactions were conducted at the atmospheric pressure. For the steam gasification, deionized water was initially introduced into a steam generator (250 °C) using a peristaltic pump and then carried to the reactor by argon gas with a flow rate of 50 cm^3/min. The produced gases were passed through two cooling baths at around 0 °C and a dry cylinder with $CaCl_2$ particles and analyzed using an online gas chromatograph (Agilent 7890B GC System) per 8 min or collected using a gasbag. For different experiments, different sample mass and reaction time were applied. For the steam gasification of the biochar, 0.5 g of the biochar was used for each run. For the steam gasification of the eelgrass samples, 1.0 g of the sample was used. When the online gas chromatography system was used to analyze the instantaneous gas production rate, longer reaction time was applied to obtain a more complete gas production trend during the reaction. Meanwhile, in the case of using the gas bag, the generated gas was collected in 120 min.

Table 2 Main compositions of ash in eelgrass and its char samples obtained from different pyrolysis temperatures

XRF Analysis (wt%)						
	Ca	K	Na	Si	Cl	Other
Original RE	15.2	22.0	12.1	0.9	43.9	5.9
RE ash	6.0	13.3	25.2	1.3	47.8	6.4
RE-350char ash	7.2	15.4	19.9	1.2	50.5	5.8
RE-450char ash	5.7	15.0	22.9	1.0	50.0	5.4
RE-550char ash	5.8	13.9	24.7	1.0	48.9	5.7
Original WE	14.0	21.5	13.9	0.8	43.8	6.0
WE ash	21.3	15.3	16.4	1.5	32.1	13.4
WE-350char ash	65.4	3.2	3.0	3.6	3.8	21.0
WE-450char ash	63.8	3.0	3.9	3.3	4.4	21.6
WE-550char ash	65.3	3.9	3.3	3.3	4.9	19.3

Table 3 XRF analysis results of calcined seashells (CS)

XRF analysis (wt%)				
	Ca	K	Mg	Other
CS	94.7	0.3	2.4	2.6

3 Results and discussion

3.1 Pyrolysis of eelgrass

Figure 2a and b show the gas yields and mass balances respectively for the pyrolysis of RE and WE at 350 °C, 450 °C, and 550 °C. From Fig. 2a, one can see that the gas production of both samples increased with the pyrolysis temperature, and higher gas production was obtained from WE at the same condition. However, it should be noted that CO_2 was the main product in the gas phase during the pyrolysis process. Figure 2b shows the mass balances of the products from the pyrolysis process. Herein, since the liquid product was difficult to be collected, its mass was calculated by the difference method based on mass balance after weighting the solid residues and analyzing gaseous products by GC. One can see that the largest amount of solids (including biochar and ash) was achieved at the pyrolysis temperature of 350 °C for both cases, and more solids were obtained from the pyrolysis of RE. In

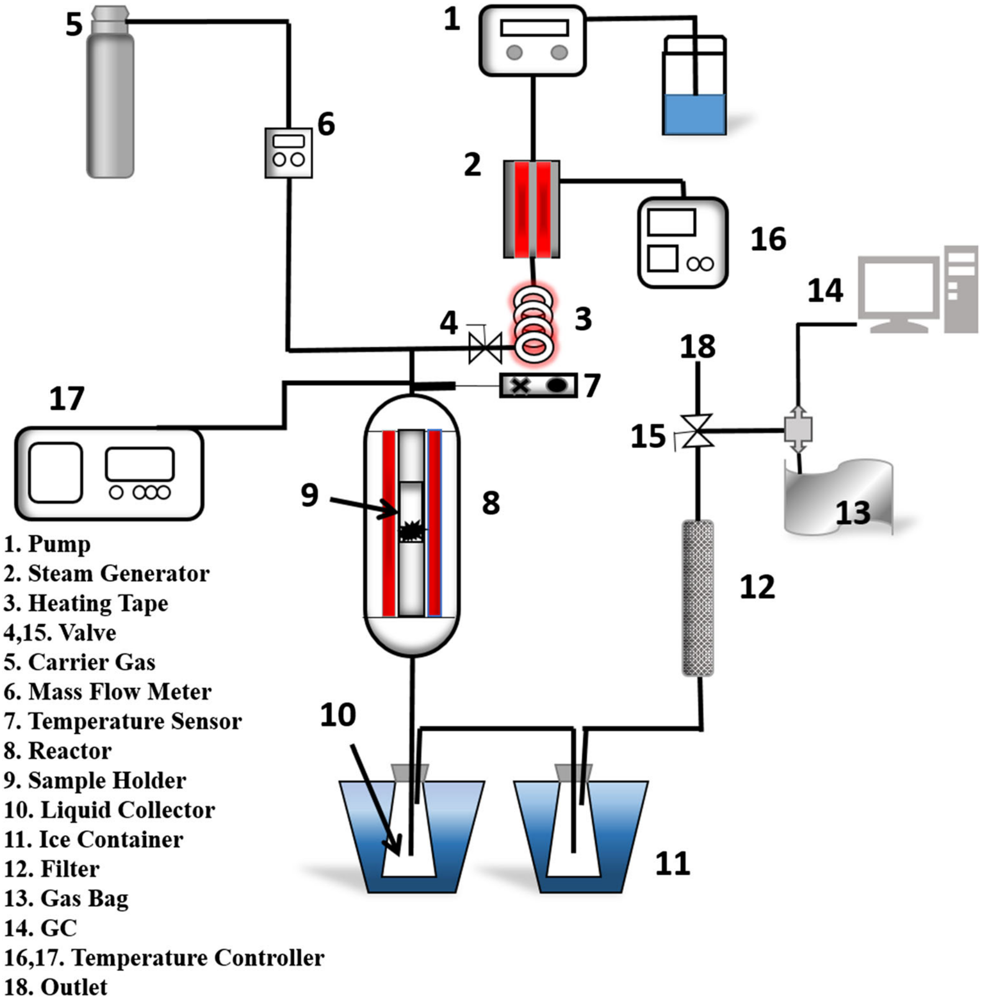

Fig. 1 Schematic diagram of a fixed-bed reactor for pyrolysis as well as steam gasification

general, the pyrolysis behavior of biomass is always strongly affected by the mineral content contained in the biomass, especially the AAEM component content [31–41]. As shown in Table 2, the RE contained more alkaline metal species of K and Na as well as Cl due to the sea salts attached on the surface of the biomass but the WE contained more calcium species and lower alkaline metal species as well as Cl species. It should be noted that these elements should exist in the intrinsic structure of WE, which could play a more important role in the biomass pyrolysis than the attached sea salts, and the existence of Cl species could hinder the catalytic performance [31, 42, 43]. Thus, the larger content of solid products from the pyrolysis of RE might be attributed to the high content of impurities (sea salts) covered on the surface of biomass, which could hinder the reactivity of biomass. It is found that approximately 2 wt% sea salts on the RE was washed out in this study. Moreover, the thermalgravimetric analysis (TGA) was conducted by heating the samples from ambient temperature to 900 °C in air atmosphere with a heating rate of 10 °C/min and hold at the terminal temperature for 2 h. As shown in Fig. S2, it can be seen that the weight decreasing trends of RE and WE were almost identical but the final remaining ash amount decreased approximately 2 wt% more for the WE, which should be also attributed to the washing of RE.

3.2 Steam gasification of eelgrass

In gasification reactions, the gasifying agent has significant influences on the quantity and quality of product gas. Air, oxygen, and steam as well as mixtures of these can be generally utilized as the gasifying agent. However, among these gasifying agents, steam gasification is more favorable for hydrogen-rich gas production since steam can provide hydrogen and is able to promote the water-gas shift reaction. Thus, in order to obtain high content of hydrogen from gasification of eelgrass, steam was chosen as the gasifying agent in this study. Firstly, the steam gasifications of RE and WE at different temperatures which ranged from 600 to 800 °C for 2 h with a water injection rate of 0.05 g/min were compared. As shown in Fig. 3a, the total gas yield from the steam gasification of WE was higher than that from that of RE at each gasification temperature, suggesting that the removal of

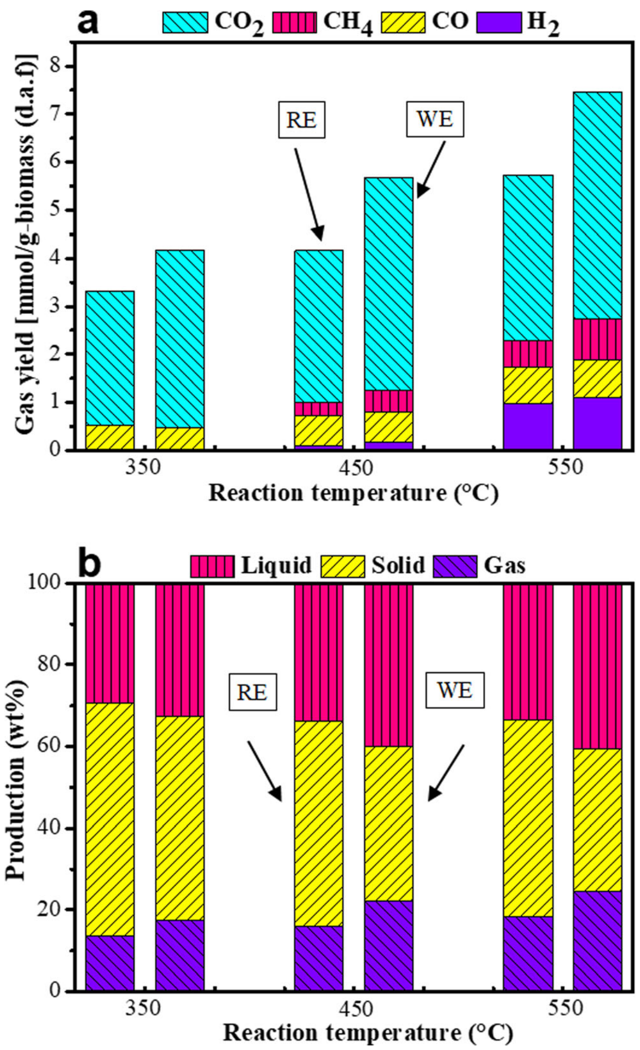

Fig. 2 Gas yields (**a**) and mass balances (**b**) in the pyrolysis of RE and WE at 350, 450, and 550 °C

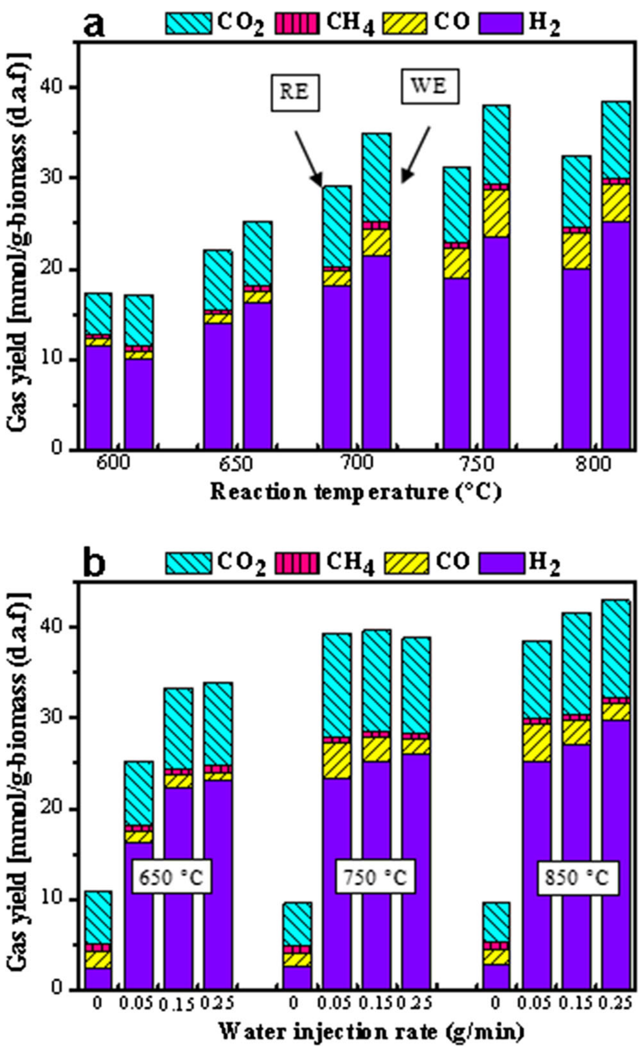

Fig. 3 **a** Gas yields from the steam gasifications of WE and RE at different temperatures for 2 h with a water injection rate of 0.05 g/min; **b** gas yield from gasification of WE at different water injection rates with different gasification temperatures

inorganic compounds from the marine biomass was also beneficial for the steam gasification. Herein, the sea salts covered on the surface of RE with a large amount of Cl species might not only inhibit the mass and heat transfer during the pyrolysis and gasification processes but also decrease the self-catalytic effect. As stated above, more AAEM species, especially Ca, K, and Na, existed in the intrinsic structure of WE (Table 2), which could enhance the steam reforming of tar as well as char due to the high self-catalytic activity [44]. In addition, although the moisture content of WE is higher than that of RE, as shown in Fig. S3, it can be seen from the thermogravity analysis (TGA) result that the water in the WE can be evaporated at 200 °C and the further decomposition rate of WE is higher than that of RE. Since the steam gasification of WE showed better results at different temperatures than that of RE, WE was chosen as the biomass feedstock for further study.

To increase the biohydrogen production, it is important to control the steam amount in the gasification process since it can promote water-gas shift (WGS) reaction ($H_2O + CO \rightarrow CO_2 + H_2$) [45]. Therefore, the effect of water injection rate on the steam gasification was investigated. As shown in Fig. 3b, compared with the case in the absence of steam (pyrolysis), with the introduction of steam, gas yields (especially for H_2 and CO_2 yields) increased significantly. However, as the water injection rate was increased to some extent, the gas yield increase rate became slow, and the excess introduction of steam could result in a decrease of the gas yield since the excess steam could not react with the biomass and/or generated tar but dilute the reaction environments. Furthermore, excessive steam could lead to the local temperature drop on the surface of biomass, and in this case, the reaction rates of the steam reforming as well as water-gas shift (WGS) could be reduced to some extent. Thus, in this study, the water injection rate of 0.15 g/min was determined as the optimum condition to conduct further study.

3.3 Steam gasification of biochars

In general, when biomass is introduced into a gasifier, the pyrolysis will occur at a relatively low temperature so that tar is generated from the biomass, and then the steam gasification of the remained char will occur at a relatively high temperature. As such, the generated tar could cover the remained char to hinder the char gasification. In order to solve this problem and improve the whole efficiency, it is suggested to separate the pyrolysis and char gasification processes [45]. Thus, in this study, the gasifications of various biochars derived from the pyrolysis of RE and WE at different temperatures (i.e., the biochars: REC-350, REC-450, and REC-550 and WEC-350, WEC-450, WEC-550) at three different temperatures (650, 750, and 850 °C) with a water injection rate of 0.15 g/min were performed. Figure 4 presents the gas productions for the steam gasifications of the biochars derived from RE (a) and WE (b). It can be observed that the gas yield increased with the increasing of final temperature since the steam gasification is endothermic reaction. Although the highest gas productions for either WEC-550 or REC-550 biochars were at 850 °C, these two kinds of biochars showed low reactivity at lower temperatures. In our previous study [45], it is also found that the biochar obtained from woody biomass at a lower pyrolysis temperature also showed a higher reactivity. Herein, the biochar from the marine biomass also exhibited the similar results. Moreover, the gas yields obtained from the steam gasification of WEC were higher than those obtained from REC. As shown in Table 1, much more carbon content contained in the WEC, which should play a significant role in the gasification reaction since the higher carbon content of WEC can result in higher gas yield theoretically. Furthermore, as shown in Table 2, higher total AAEM compound contents including Ca, K, and Na but less Cl species existed in the WEC samples than those in REC samples. As stated above, the AAEM species, especially those intrinsic AAEM compounds, have high self-catalytic effect on the steam gasification but the Cl species could hinder the gasification rate [46, 47]. Thus, more AAEM species in the char matrix of WEC resulted in higher gasification efficiency. As shown in Fig. 4b, since the biochar of WEC-350 had higher reactivity at either low or high temperatures, it was selected for the further study.

In our previous study [28], it is found that the calcined scallop shells exhibited high catalytic activity during the biomass gasification since the alkaline species of CaO in it can not only enhance the reforming reaction but also serve as an absorber for the generated CO_2, which can enhance the WGS reaction during the reaction period. In this study, the calcined parasitic seashell (CS) was also mixed with WEC-350 to investigate the catalytic effect of CS on the gasification. As shown in Fig. 4c, the hydrogen gas production increased obviously in the presence of CS, and simultaneously the detected CO_2 content decreased sharply at the steam gasification temperature of 650 °C. Moreover, in the presence of CS, the CO yield was also decreased, indicating that more generated CO from the gasification was converted to

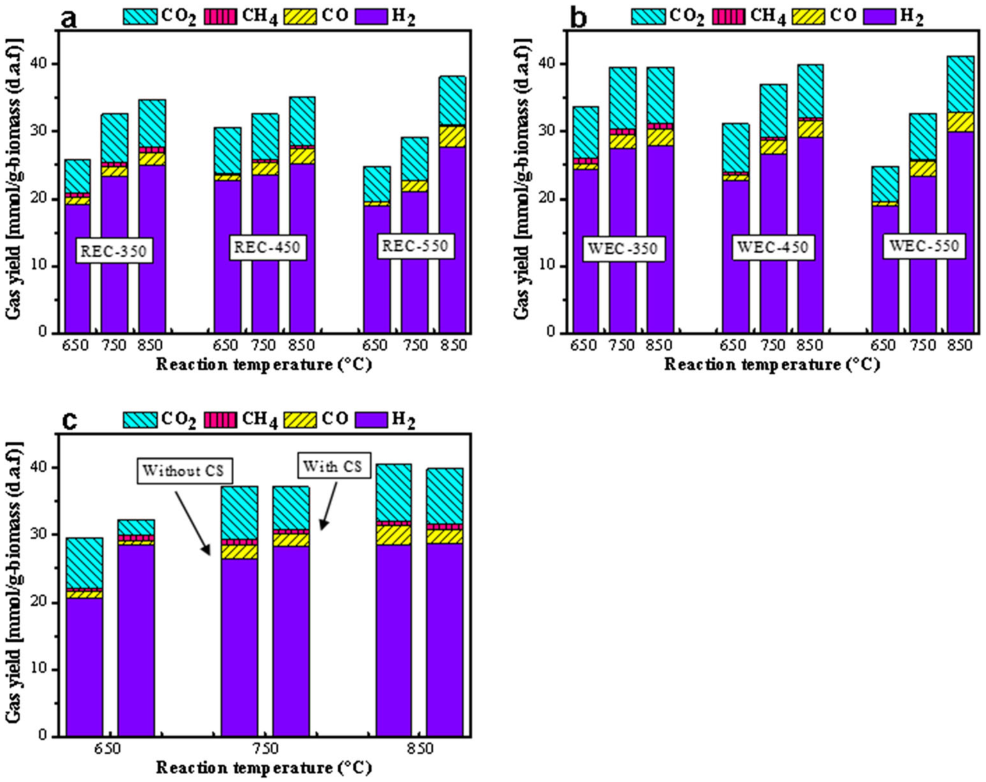

Fig. 4 Steam gasification of biochars from RE (**a**) and WE (**b**) at three different temperatures of 650 °C, 750 °C, and 850 °C with a water injection rate of 0.15 g/min; **c** steam gasifications of WEC-350 with and without CS addition at the reaction temperatures of 650 °C, 750 °C, and 850 °C with a water injection rate of 0.15 g/min

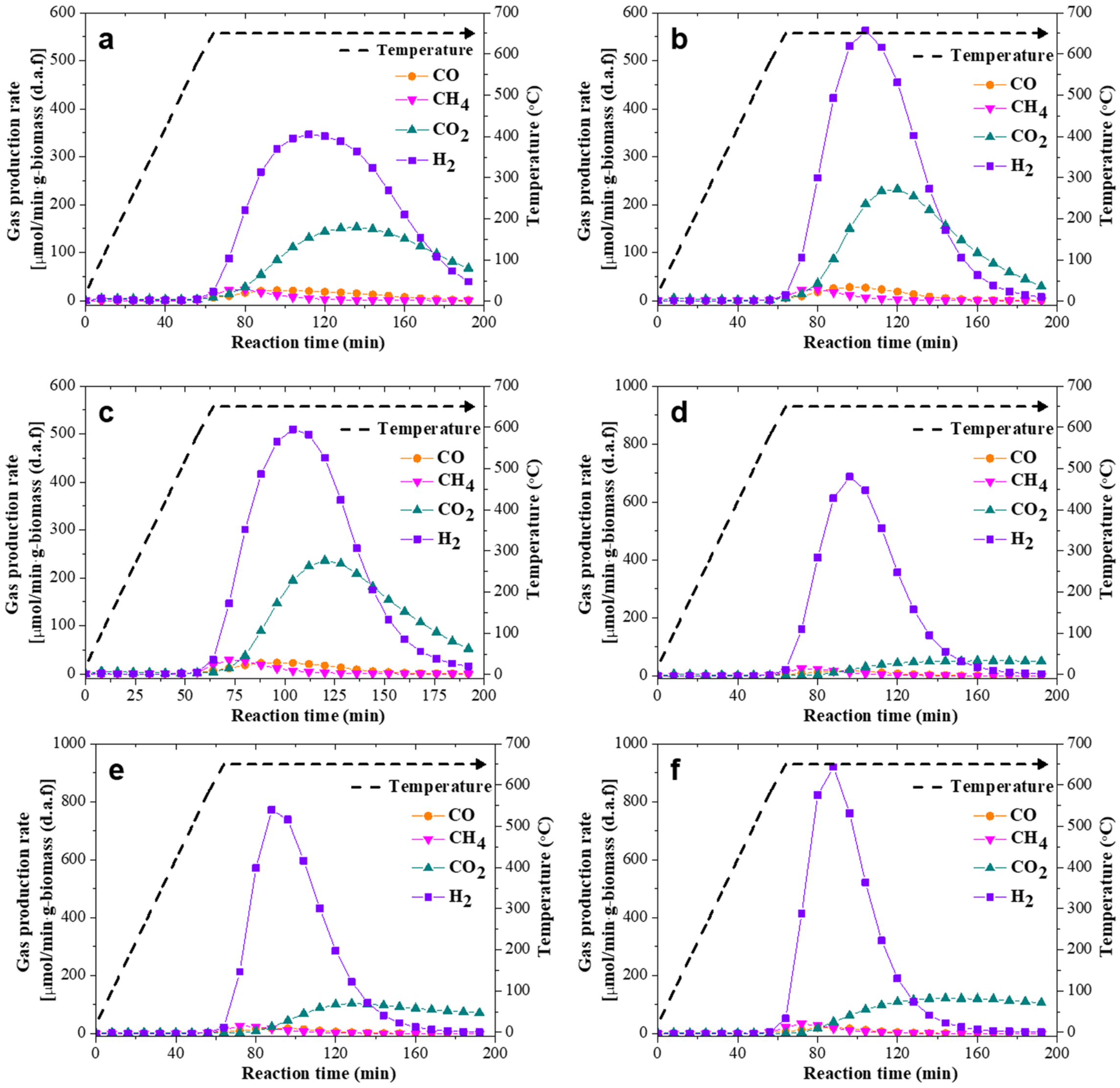

Fig. 5 Effect of water injection rate on the gasification of WEC-350 at 650 °C in the absence of CS: **a** 0.05 g/min; **b** 0.10 g/min; **c** 0.15 g/min. Effect of water injection rate on the gasification of WEC-350 at 650 °C in the presence of CS: **d** 0.05 g/min; **e** 0.10 g/min; **f** 0.15 g/min

CO_2 and H_2 by the WGS reaction with the assistance of CS. On the other hand, no obvious increase in hydrogen yield was observed at a higher temperature than 650 °C. It is probably related to the decomposition temperature of $CaCO_3$ (around 800 °C). CS absorbed the produced CO_2 during the gasification process and converted CaO to $CaCO_3$, but after the temperature was increased to around 800 °C, $CaCO_3$ might be decomposed and released CO_2 again, which affected the gasification reactions. Thus, the reaction temperature should be lower than 800 °C to obtain a positive CO_2 adsorption effect of CS on hydrogen production. Herein, although the total gas amount was not affected significantly by the addition of CS, the composition of the gases, especially the concentration of H_2, increased in the presence of CS. In addition, it should be noted that a high content of Ca species existed as the intrinsic AAEM compound in the biochar matrix, which could play a more important role in the catalytic steam gasification of biochar than the mixed CaO species.

Figure 5 shows the stream-on-time tests on the steam gasifications of WEC-350 at 650 °C in the absence and presence of CS with different water injection rates of 0.05, 0.10, and 0.15 g/min. It is obvious that the H_2 yield peaks were achieved faster and the stream-on-time CO_2 yields at any temperatures and water injection rates were much lower than those in the absence of CS, indicating the catalytic activity and CO_2 adsorption effect of CS. Herein the steam reforming reaction and water-gas shift reaction were promoted by adding calcined seashells during the gasification of WEC-350. After CO and H_2 were produced from the steam reforming reaction, CO would continue to react with steam to produce CO_2 and H_2 since the water-gas shift reaction was promoted by calcined seashells. The produced CO_2 was absorbed by calcined seashells, which was also the reason why the total oxygen and carbon contents in the syngas reduced. Moreover, one can see that the detected CO_2 decreased slowly in the presence of CS (Fig. 5e, f), indicating that the absorbed CO_2 on CS was slowly released at the end of the steam gasification.

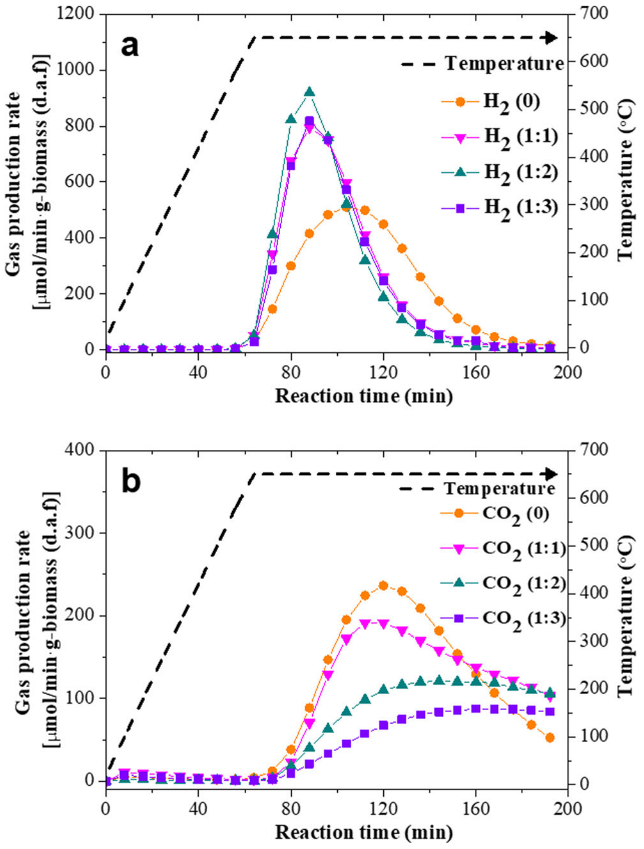

Fig. 6 Effect of the mixing ratio between WEC-350 and CS (WEC-350: CS) on the steam gasification at 650 °C with a water injection rate of 0.15 g/min. **a** H_2 gas production rate; **b** CO_2 gas production rate

In order to investigate the effect of the addition amount of CS during the steam gasification of WEC-350, the WEC-350 was physically mixed with CS by different weight ratios (1:0, 1:1, 1:2, 1:3) before gasified at 650 °C with a water injection rate of 0.15 g/min. As shown in Fig. 6a, at any weight mixing ratios, the H_2 yield reached the peak much faster than that without CS, and the H_2 production rates were also much higher at the early reaction stage, indicating that the reaction rates were also enhanced by using the CS catalyst. However, the addition of the excessive amount of CS resulted in a little decrease of the H_2 production rate, possibly caused by the hindrance of the mass transfers of steam and generated gases. Meanwhile, as shown in Fig. 6b, detected CO_2 yield was decreased obviously with the increase of CS addition amount, also indicating the CO_2 adsorption effect by CS. Thus, it can be concluded that the CS could effectively enhance hydrogen production and absorb CO_2 during the gasification reaction.

4 Conclusions

In this study, a kind of wasted marine biomass, eelgrass, and its biochars derived from pyrolysis of it at different temperatures were gasified by steam for the hydrogen-rich gas production. Meanwhile, a kind of small discarded parasitic seashell was calcined to serve as the catalysts to enhance the hydrogen production rate. The effects of key factors, i.e., reaction temperature, water injection rate, and catalyst mixing amount, on the steam gasification performance were investigated. Based on the experimental results, the following conclusions were obtained:

1) Liquid and solid products were the major productions from the pyrolysis process. The gas yield from the pyrolysis of washed eelgrass (WE) was higher than that from raw eelgrass (RE). But CO_2 was the main gas product in the gas phase.
2) The hydrogen-rich gas yield (especially H_2 and CO_2 yields) obtained from the steam gasification of WE was higher than that from RE. The sea salts including Cl species covering on the surface of RE had a negative effect on the gasification performance. Higher gasification temperature and larger water injection rate were found to be beneficial for hydrogen production. However, too high temperature as well as too high steam amount had no obvious effects on the increase of gas yield.
3) The biochars derived from the pyrolysis of eelgrass showed high reactivity and high hydrogen-rich gas yield in the steam gasification process. Especially, the biochar obtained at the pyrolysis temperature of 350 °C had high reactivity at either low or high gasification temperatures. To further improve the hydrogen yield, the calcined seashell (CS) was mixed with the WEC-350 and used for the steam gasification. It was found that the CS not only enhanced H_2 yield and production rate but also served as an absorber for the generating of CO_2, especially at the steam gasification temperature of 650 °C. The H_2 gas yield from the steam gasification of WEC-350 at 650 °C was almost the same as that at 850 °C with the assistance of CS.

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