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# Microwave Assisted Acid Hydrolysis of Brown Seaweed *Ascophyllum nodosum* for Bioethanol Production and Characterization of Alga Residue

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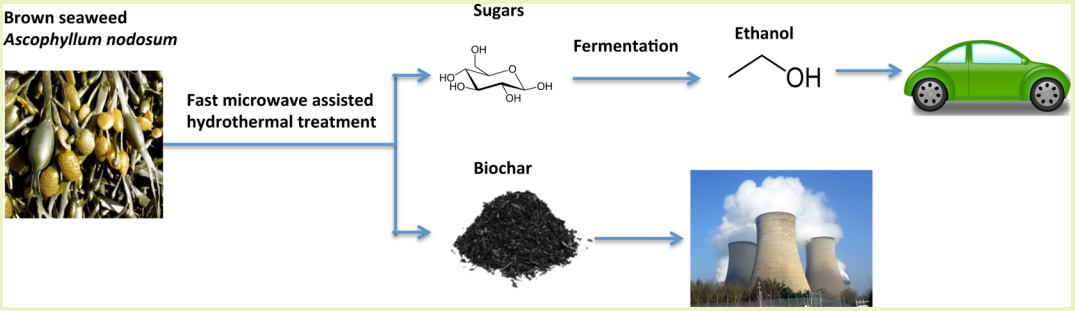


**ABSTRACT:** For the first time, brown seaweed *Ascophyllum nodosum* was studied as a feedstock for the production of bioethanol. Saccharification was carried out by microwave assisted acid hydrolysis. The optimal condition was 0.4 M $H_2SO_4$, 3.13% (w/v) of biomass concentration, reaction temperature at 150 °C for 1 min, resulting in 127 mg/g monosaccharides of seaweed being released. The hydrolysates solution was concentrated and fermented directly without further detoxification. The concentration of furfural, hydroxymethyfufural and phenolic in the fermentation medium were 0.00, 0.01 and 1.8 g/L, respectively. An ethanol concentration of 5.57 g/L and a conversion efficiency of 60.7% (based on glucose, galactose and mannose) were achieved. More than 50% energy yield of alga residue was recovered after hydrolysis, and the energy densification ranged from 1.4 to 1.7, with HHVs from about 19−24 MJ/kg. The findings of this study demonstrated that microwave heating is a fast and efficient way to produce sugars and biochar in one simple process. And *Ascophyllum nodosum* can be potentially used as a feedstock for bioethanol and biochar production.

**KEYWORDS:** *Ascophyllum nodosum, Microwave assisted hydrolysis, Monosaccharide, Bioethanol, Biochar*

## INTRODUCTION

The rapid growth in population, energy consumption and global environmental concerns has encouraged the development of sustainable, renewable and efficient biofuels as alternatives of conventional fossil fuels.[1] Bioethanol is one of those biofuels, which has been widely accepted as the most promising replacement of gasoline to act as a transport fuel.[2] Bioethanol can be divided into three generations according to the biomass used. The first generation bioethanol is produced from edible feedstock like starch, corn and sugarcane. Therefore, ethanol production from these resources was blamed to affect food supply.[3] Second generation bioethanol is produced from agricultural waste, mainly lignocellulosic biomass like wood, wheat straw and sugarcane bagasse. However, lignin within the biomass makes it difficult to degrade to fermentable sugar,[4] so pretreatment is necessary, which will increase energy consumption.[5] Seaweed, an abundant and carbon-neutral renewable resource, is classified as third generation biomass for ethanol production. It is lignin free, does not compete with conventional agricultural land and grows fast.[6] Moreover, the high carbohydrate content of seaweed makes it a good candidate for fuels.[7] The interest of using seaweed as potential biomass for ethanol production has been increasing recently. Various seaweed species such as red seaweed *Palmaria palmate*,[8] *Gelidiella acerosa*,[9] *Eucheuma cottonii*,[10] *Gracilaria* sp.,[6,11] brown seaweed *Saccharina japonica*,[12,13] *Undaria pinnatifida*,[14] green seaweed *Ulva intestinalis* and *Rhizoclonium riparium*[15] have been investigated.

Bioethanol production from seaweed involves four major operations including pretreatment, hydrolysis, fermentation and distillation.[2] Acid hydrothermal treatment is probably the most widely used pretreatment method to increase the digestibility of biomass.[12] Enzyme hydrolysis is a time-consuming process, so simultaneous saccharification and fermentation (SSF) was introduced and reported to have higher ethanol yield than separate hydrolysis and fermentation (SHF).[4,16] Only a few reports are about bioethanol production directly using the hydrolysate from dilute acid hydrothermal treatment with out further detoxification.[8,15] Although it is more likely that the byproduct generated during the acid hydrolysis process may inhibit cell wall and fermentation,[17,18] it is still worth investigating due to its low cost and high reaction rate.[8]

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Recently, it has been reported that microwave heating presents a potentially faster, more efficient and selective method for the thermal treatment of biomass.[19,20] Brown seaweed *Ascophyllum nodosum* grows in abundance is widespread along the coast of the United Kingdom. Around 32 000 t of *Ascophyllum nodosum* is harvested per year for the production of alginates, fertilizers and for the manufacture of seaweed meal for animal and human consumption.[21]

This study combines microwave heating and sulfuric acid to perform a fast hydrolysis of *Ascophyllum nodosum*. Variables such as temperature, time, acid concentration and biomass loading were optimized to obtain highest monosaccharide yield. Then the hydrolysate was further explored for bioethanol production without detoxification. Moreover, the biomass residue after hydrolysis was also analyzed and its potential to be used as biochar fuels was also evaluated.

## MATERIALS AND METHODS

**Raw Materials and Chemicals.** *Ascophyllum nodosum* was obtained from Bod Ayre Products Ltd., Shetland, UK, in October 2011. The fresh seaweed was dried by microwave heating and grounded. A sieve selected different particle size and <1 mm seaweed was used for the hydrolysis process.

Concentrated sulfuric acid (~98%) and ethanol were obtained from Fisher Scientific UK Ltd. Barium hydroxide, sodium acetate, standard D-glucose, D-galactose, D-mannose, D-xylose, L-rhamnose, L-fucose, D-galacturonic acid, D-glucuronic acid, gallic acid, furfural and hydroxymethyfufural were purchased from Sigma-Aldrich UK Ltd. All reagents were of analytical grade.

**Chemical Composition Analysis.** The crude seaweed was analyzed to determine moisture, protein, ash, lipid, phenolic and carbohydrate content (Table 1). The moisture content was determined by drying the seaweed samples in an oven at 105 °C until a constant weight was obtained. Protein content was calculated by converting the nitrogen content, determined by micro-Kjeldahl method (6.25*N). The lipids from seaweed powder were extracted in a Soxhlet extractor using hexane.[22] The phenolic content was measured by extracting the seaweed powder with 80% ethanol and the extract was measured by the Folin−Ciocalteu (FCR) method using gallic acid as reference. Ash content was determined by heating the samples at 600 °C for 4 h. Carbohydrate content was determined by acid hydrolysis. The seaweed powder was initially treated by 2 M trifluoroacetic acid (TFA) for 2 h at 121 °C, then residual seaweed was treated by 72% sulfuric acid for 4 h at room temperature, followed by dilute acid (diluted down to 3.2% sulfuric acid) for 4 h at 120 °C. The sugar content was measured by a phenol−$H_2SO_4$ method[23] using fucose as the standard.

**Microwave Assisted Hydrolysis Procedure.** The microwave assisted hydrolysis process was investigated by varying different process parameters: different acid concentration (0.01−0.4 M), temperature (120−180 °C), biomass loading (solid/liquid ratio: 0.6%−6%, w/v) and reaction time (0−30 min). The dried seaweed powder was subjected to different concentration of acidic solution in a standard CEM Discover microwave reaction tube (35 mL). The sample was subsequently inserted into the microwave and irradiated under dynamic mode to enable the system to achieve the desired temperature. Temperature and pressure were recorded during this process using the microwave pressure head and the inbuilt IR sensor. After irradiation, the suspensions were centrifuged to separate the residual alga, which was washed with distilled water and dried at 80 °C until constant weight. The liquid was neutralized by saturated $Ba(OH)_2$ and then freeze-dried for further use.

**Bioethanol Fermentation.** *Saccharomyces cerevisiae* ATCC no. 200062 was used for fermentation. The yeasts were cultured in ATCC medium (yeast extract 10.0 g/L, bacto-peptone 20.0 g/L, glucose 20.0 g/L) until the $OD_{600}$ reached 0.5. Two g of freeze-dried hydrolysates was dissolved in 10 mL of distilled water, 0.25 mL of 2 M sodium acetate and 2 mL of 10× ATCC medium no glucose (100 g/L yeast extract, 200 g/L bacto-peptone) was added and the mixture was sterilized at 121 °C for 30 min. Then 2 mL of prepared yeasts was added and the final volume was made up to 20 mL with sterile water. The sample was then incubated in a shaking incubator at 37 °C with a shaking speed of 130 rpm for a total time of 72 h. Samples were withdrawn at different time intervals and were centrifuged at 3000 rpm for 10 min. The supernatant obtained after centrifugation was then analyzed for bioethanol and residual sugar content. Fermentation was done in duplicate.

**Analytical Method.** The quantification of monosaccharides of liquid hydrolysates was done by high-performance anion-exchange chromatography (HPAEC) on a Dionex Carbopac PA-10 column with integrated amperometry detection. The monosaccharides were quantified by using external calibration with an equimolar mixture of nine monosaccharide standards (arabinose, fucose, galactose, galacturonic acid, glucose, glucuronic acid, mannose, rhamnose and xylose).

The quantification of furfural and hydroxymethyfufural in the fermentation medium were done by high-performance liquid chromatography (HPLC) on an ACE C18 column (250 × 4.6 mm) with an evaporative light scattering detector (ELSD). The mobile phase was mixture of MeCN and $H_2O$ (1:3). The flow rate was 0.8 mL/min, and analyses were performed at 30 °C.

Elemental analysis of carbon, hydrogen and nitrogen contents of the seaweed residue was performed using an Exeter Analytical (Warwick, UK) CE440 Elemental Analyzer (calibrated against acetanilide with S-benzyl-thioronium chloride internal standard). The calorific value of the seaweed residue was determined by a Parr 6200 calorimeter, made by Scientific & Medical Products Ltd., UK.

Bioethanol concentration was analyzed by gas chromatography (HP 6890 series, Hewlett-Packard. Inc., USA) using a flame ionization detector (FID) with a Stabilwax column (Crossbond Carbowax polyethylene glycol; length, 30 m; inner diameter, 0.25 mm; film thickness, 0.25 um). The following operating conditions were used: detector temperature of 225 °C; injector temperature of 225 °C; oven temperature was increasing from 100 (2.0 min) to 175 °C at 10 °C/min. Helium was used as the carrier gas and 1-propanol was used as internal standard.

At least three samples were used in all analytical determinations, and data are presented as the mean of three replicates.

## RESULTS AND DISCUSSION

**General Compositional Analysis of Raw Material.** Table 1 shows the compositions of *Ascophyllum nodosum* used in this study. The carbohydrate content of this seaweed was 44.66% (w/w), which is within the range (40−60%) reported for brown seaweed.[4,14,24] However, it is lower than the carbohydrate content (50−70%) of most red seaweed reported.[2,11,15] Wu et al.[11] and Jang et al.[4]reported even higher content of carbohydrate 76.67% in *Gracilaria* sp. and 74.4% in *Gelidum amansii*, respectively. The differences in the chemical compositions of seaweed have been demonstrated to depend on species, maturity and various environmental factors such as water temperature, light and salinity.[25,26] The other compo-

**Table 1. Composition of Brown Seaweed *Ascophyllum nodosum***

| component | composition % (w/w) |
|---|---|
| carbohydrate | 44.66 ± 2.1 |
| protein | 5.24 ± 0.22 |
| lipid | 2.99 ± 0.07 |
| ash | 18.61 ± 0.89 |
| moisture | 13.48 ± 0.32 |
| phenolic | 1.4 ± 0.21 |
| others | 13.62 |


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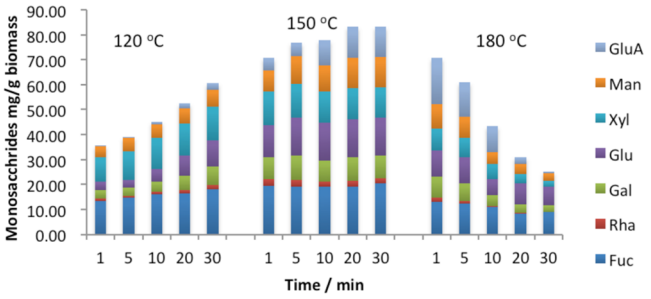


**Figure 1.** Effects of temperature on the monosaccharides yield (reaction conditions: 0.1 M $H_2SO_4$, biomass loading 3.13%).

nents were protein 5.24%, lipid 2.99%, ash 18.61%, moisture 13.48%, phenolic 1.4% and others 13.62%, respectively.

**Hydrolysis of *Ascophyllum nodosum*.** The *Ascophyllum nodosum* was hydrolyzed under various conditions.

**Effect of the Reaction Temperature.** The effect of reaction temperature is shown in Figure 1. It can be seen that the temperature had a significant effect on the hydrolysis process and the optimal temperature for high monosaccharide yield was 150 °C, where 70−85 mg/g seaweed of monosaccharides can be produced. Figure 1 also shows that fucose and mannose could be obtained efficiently at 120 °C; however, other sugars like galactose, glucose, xylose and glucuronic acid required a higher temperature. The monosaccharide yield decreased at 180 °C, especially with longer holding time. This is probably because the secondary reactions of monosaccharides to other chemicals such as HMF or levulinic acid[27] were more prevalent at this elevated temperature. Therefore, 150 °C was chosen as the optimum hydrolysis temperature for this study.

As the hydrolysis process was conducted at temperatures from 120 to 180 °C, which is within the range of hydrothermal carbonization temperature,[28] seaweed residue was also characterized as potential biochar for fuel. Table 2 shows the effect of temperature on biochar properties. It can be seen that compared with raw seaweed, carbon content was dramatically increased and it also increased with process temperature. As a result, the higher heating values of biochar were much higher than the feedstock (13.73 MJ/kg), ranging between 19.36 and 23.26 MJ/kg, about a 40−70% increase in energy density. This increase is comparable or even higher than the reported data. For example, Liu et al. reported 34−66% and 32−55% energy density increase of coconut fiber and Eucalyptus leaves, at 200−375 °C,[29] and Xu et al. reported increase 10−44% of macroalgae at 180−200 °C.[30]

To determine the efficiency of the hydrothermal carbonization process, energy densification and energy yield were also studied. As defined by Yan et al., the energy densification was determined by energy content of biochar divided by the energy content of raw feedstock, while the energy yield was defined as the char mass yield multiplied by the energy densification ratio.[31] As shown in Table 2, energy densification increased with temperature, from a low value of 1.41 at 120 °C to a high value of 1.69 at 180 °C. This value is comparable with hydrocarbons derived from food waste (1.82), mixed municipal waste stream (1.73) and anaerobic digestion waste (1.5), which were treated at 250 °C for 20 h.[32] However, although better solid fuels can be obtained at higher temperature, the overall energy yield was decreasing with temperature due to the decreasing of mass yield.

**Effect of the Acid Concentration.** To investigate the effect of acid concentration on the release of monosaccharides, *Ascophyllum nodosum* was hydrolyzed under various sulfuric acid concentrations (0.01−0.4 M) at 150 °C. According to Figure 2, the yield of monosaccharide increased dramatically with acid concentration. In addition, the monosaccharide yield increased with holding time when acid concentration was lower than 0.2 M; however, it began to decrease with longer holding time when acid concentration was 0.2−0.4 M. This indicated that high acid concentration with longer reaction time would result in degradation of sugars and formation of byproduct, which has also been reported by other researchers.[33,34] The optimal acid concentration for higher monosaccharide yield was 0.4 M, 5 min, 136 mg/g seaweed of monosaccharides. 0.4 M $H_2SO_4$ was also reported in the literature as the optimal concentration for hydrolyzing seaweed biomass.[8,15,24] So, 0.4 M $H_2SO_4$ was chosen as the optimum hydrolysis concentration for this study.

As shown in Table 3, carbon content of biochar increased with acid concentration and the higher heating values ranged 19.17−23.30 MJ/kg. The higher heating values of biochar are strongly dependent on the original feedstock. The biochar derived from food waste,[32] wheat straw,[35] sewage sludge[36] and pine sawdust[37] were reported to have HHVs of 29.1, 19.0, 14.74 and 25.42 MJ/kg, respectively. Energy densification also increases with acid concentration, from a low value of 1.40 of $H_2O$ to a high value of 1.70 with 0.4 M $H_2SO_4$. Mass yield recovered decreased with acid concentration, however, the efficient carbonization with acid still makes high energy yields.

**Effect of the Biomass Concentration.** Figure 3a shows the effect of different biomass concentrations on the hydrolysis process. As expected, lower biomass concentration resulted in higher monosaccharide yield, 176.18 mg/g seaweed of monosaccharide. This is probably because, in the low biomass concentration system, seaweed particles were better distributed, and better contact with water makes the hydrolysis more efficient. However, when under these conditions the actual monosaccharide concentration is considered (Figure 3b), 0.63% biomass ratio was quite low, which means more energy will be consumed during concentration process afterward. Therefore, 3.13% was chosen as the best biomass concentration considering both monosaccharide yield and concentration.

**Table 2. Effect of Temperature on Biochar Properties[a]**

| sample | % C | % H | % N | HHV[b] (MJ/kg) | ED[c] | mass yield % | EY[d] % |
|---|---|---|---|---|---|---|---|
| raw seaweed | 36.26 | 4.86 | 0.84 | 13.73 | | | |
| 120 °C | 48.66 | 5.35 | 1.75 | 19.36 | 1.41 | 40.13 | 56.58 |
| 150 °C | 51.08 | 5.11 | 1.31 | 19.72 | 1.44 | 34.53 | 49.72 |
| 180 °C | 58.82 | 5.46 | 0.81 | 23.26 | 1.69 | 26.62 | 44.99 |

[a]Reaction conditions: 0.1 M $H_2SO_4$, 30 min, biomass loading 3.13%. [b]Higher heating value. [c]ED (energy densification) = $HHV_{sample}/HHV_{seaweed}$. [d]EY (energy yield) = HHV biochar × biochar yield/$HHV_{seaweed}$.



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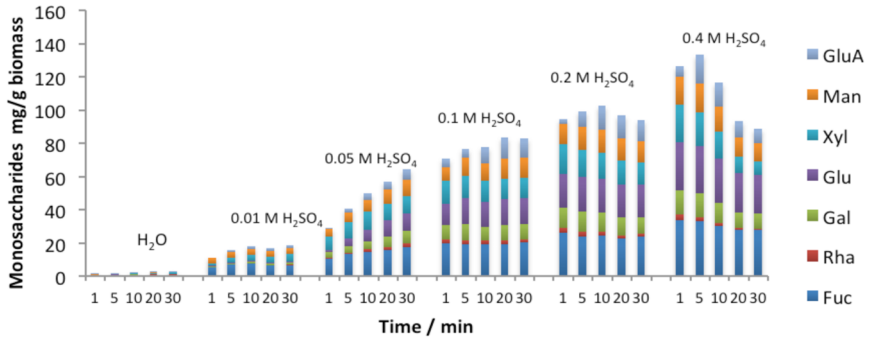


**Figure 2.** Effects of acid concentration on the monosaccharides yield (reaction conditions: MW 150 °C, biomass loading 3.13%).

**Table 3. Effect of Acid Concentration on Biochar Properties**

| sample | % C | % H | % N | HHV (MJ/kg) | ED | mass yield % | EY % |
|---|---|---|---|---|---|---|---|
| raw seaweed | 36.26 | 4.86 | 0.84 | 13.73 | | | |
| $H_2O$ | 47.77 | 5.64 | 1.86 | 19.17 | 1.40 | 39.07 | 54.70 |
| 0.1 M $H_2SO_4$ | 51.08 | 5.11 | 1.31 | 19.72 | 1.44 | 34.53 | 49.72 |
| 0.2 M $H_2SO_4$ | 56.69 | 5.39 | 0.82 | 23.01 | 1.67 | 33.56 | 56.24 |
| 0.4 M $H_2SO_4$ | 57.24 | 5.32 | 0.82 | 23.30 | 1.70 | 32.16 | 54.67 |

Reaction conditions: MW 150 °C, 30 min, biomass loading 3.13%.

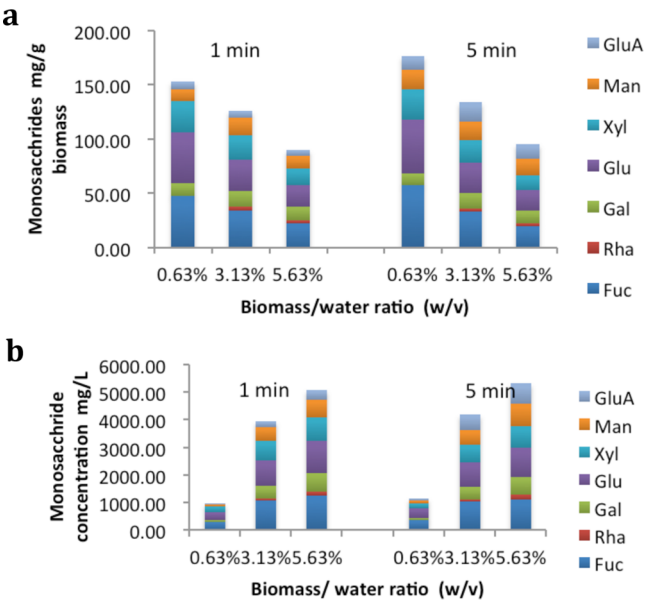


**Figure 3.** Effects of biomass concentration on the monosaccharides yield (a) monosaccharides yield (b) monosaccharides concentration of liquid (reaction conditions: MW 150 °C, 0.4 M $H_2SO_4$).

Figure 3 also shows that although monosaccharide yield and concentration of 5 min holding time was slightly higher than 1 min holding time, the increase was mainly from glucuronic acid, which is not available for ethanol fermentation with currently available methodology.[38] Thus, 1 min holding time was chosen for the hydrolysis process, which is much shorter than literature using conventional heating for hours.[8,9,15,33,39−41]

**Table 5. Byproduct Compounds Contained in Initial Fermentation Medium**

| byproduct | concentration (g/L) |
|---|---|
| phenolic | 1.82 |
| HMF | 0.01 |
| furfural | not detected |

Table 4 shows the effect of biomass ratio on biochar properties. It reveals that carbon content of biochar decreased with increasing biomass concentration and the higher heating values were ranging between 24.21 and 22.52 MJ/kg. The energy densification also decreased with biomass concentration, from a high value of 1.76 of 0.63% to a low value of 1.64 of 5.63%. Neither mass yield nor energy yield recovered varies significantly within the range studied.

From these results, it could be concluded that the optimum condition for hydrolyzing *Ascophyllum nodosum* is 0.4 M $H_2SO_4$, 3.13% (w/v) of biomass concentration, reaction temperature at 150 °C for 1 min, resulting in 127 mg/g monosaccharides of seaweed. The seaweed residue obtained under the above reaction condition has a higher heating value of 22.93 MJ/kg, the energy densification is 1.67 and energy yield recovered is 55.49%.

**Fermentation.** The hydrolysate solution obtained was freeze-dried and then dissolved at a concentration of 100 g/L

**Table 4. Effect of Biomass Loading on Biochar Properties[a]**

| sample | % C | % H | % N | HHV (MJ/kg) | ED | mass yield % | EY % |
|---|---|---|---|---|---|---|---|
| raw seaweed | 36.26 | 4.86 | 0.84 | 13.73 | | | |
| 0.63% | 53.89 | 5.67 | 1.01 | 24.21 | 1.76 | 33.66 | 59.24 |
| 3.13% | 54.05 | 5.70 | 1.60 | 22.93 | 1.67 | 33.23 | 55.49 |
| 5.63% | 52.71 | 5.36 | 1.21 | 22.52 | 1.64 | 35.21 | 57.74 |

[a]Reaction conditions: MW 150 °C, 0.4 M $H_2SO_4$, 1 min.



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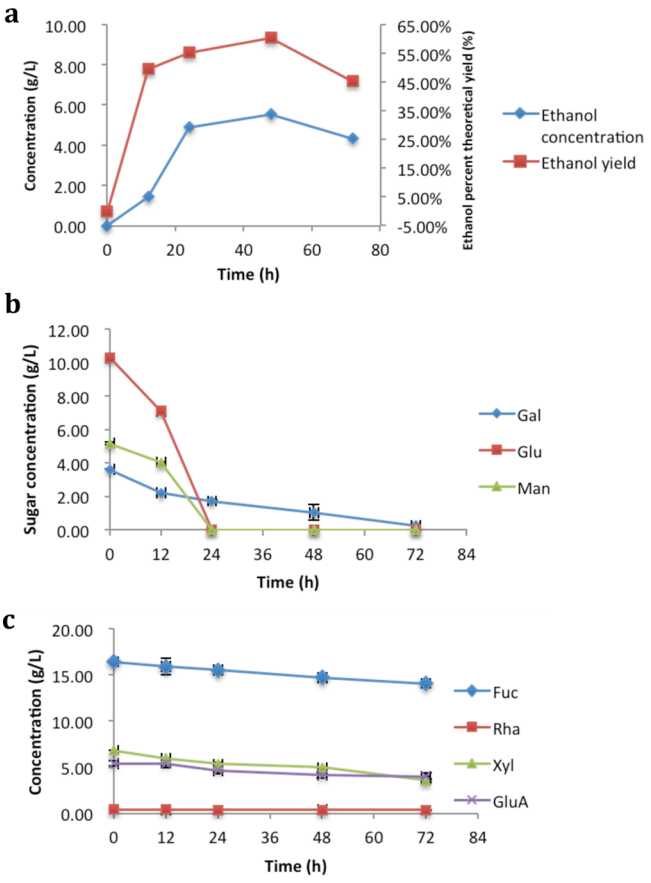


**Figure 4.** Ethanol production (a) and changes in sugar content (b) mostly consumed sugar (c) less consumed sugar.

for fermentation. As the fermentation inhibitors might be generated during the hydrolysis process, furfural (FF), hydroxymethyfufural (HMF) and phenolic concentrations of the initial fermentation medium were analyzed (Table 5). FF is degraded from pentose sugars whereas HMF is a degradation compound from hexose sugars, and their toxicity depend on the concentration in the fermentation medium.[42] As shown in Table 5, there was no FF detected and the concentration of HMF was only 0.01 g/L, which indicated that fast microwave heating could minimize the degradation of sugars. Phenolic compounds can also inhibit the fermentation process, as they partition into biological membranes and cause loss of integrity, thereby affecting their ability to serve as selective barriers and enzyme matrices.[43] Although seaweed is well-known to contain no or little lignin, according to the compositional analysis of our seaweed sample, there is 1.4% phenolic content present. Therefore, the phenolic content in the fermentation medium was estimated by the Folin−Ciocalteu (FCR) method using gallic acid as reference, it is about 1.8 g/L. However, the specific phenolic molecule is unknown. Among the phenolics, 4-hydroxybenzoic acid was reported to have no significant effect on either growth or ethanol productivity with 2 g/L concentration;[44] however, 4-hydroxycinnamic acid and ferulic acid severely inhibited ethanol productivity at low concentrations in *S. cerevisiae*.[45] Therefore, to minimize the inhibition from phenolic, a pre-extraction of phenolic might be useful.

Figure 4a shows that ethanol concentration increased significantly in 24 h and continued to increase until 48 h. The decline in ethanol production after 48 h of fermentation

**Table 6. Comparison of Saccharification and Ethanol Production from Various Seaweed Species**

| seaweed species | hydrolysis method | sugar released | fermentation conditions | ethanol yields | references |
|---|---|---|---|---|---|
| *Gracilaria tenuistipitata* (red seaweed) | 4% biomass loading (w/v) in 0.1 M HCl at 95 °C for 15 h | NA | *S. cerevisiae* TISTR (10%, v/v) 30 °C, 120 rpm, 18 h | 0.004 g/g reducing sugar (0.9%) | 15 |
| *Kappaphycus alvarezii* (red seaweed) | 10% biomass loading (w/v) in 0.2% (w/v) $H_2SO_4$, 130 °C, 15 min | 305 mg/g (including 256 mg galactose) | commercial brewer's yeast 30 °C, 120 rpm, 72 h | 0.21g/g galactose (41%) | 39 |
| *Palmaria palmate* (red seaweed) | 10% biomass loading (w/v) in 0.4 M $H_2SO_4$ at 125 °C for 25 min | 218.4 mg/g (including 27 mg glucose, 127.6 mg galactose) | commercial brewer's yeast (1.5 g/L) 30 °C, 130 rpm, 72 h | 17.3 mg/g seaweed | 8 |
| *Ascophyllum nodosum* (brown seaweed) | 3.13% biomass loading (w/v) in 0.4 M $H_2SO_4$ at 150 °C for 1 min | 127 mg/g (including 15 mg galactose, 29 mg glucose, 23 mg mannose) | *S. cerevisiae* ATCC (10%, v/v) 37 °C, 130 rpm, 72 h | 20.9 mg/g seaweed 0.31g/g glucose + mannose + galactose (60.7%) | this work |



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might be attributed to consumption of accumulated ethanol by the organism.[46] The maximum ethanol concentration was 5.57 g/L, 60.7% theoretical yield and 20.8 mg/g seaweed. This is higher than those that also used acid hydrolysate for fermentation (Table 6).[8,15,39] Chirapart et al. obtained an ethanol yield of 4.5 mg/g sugar (0.9% theoretical yield) of *Gracilaria tenuistipitata*, Mutripah et al. reported to have 15.7 mg/g seaweed of ethanol from *Palmaria palmata* whereas Meinita et al. obtained 41% theoretical ethanol yield from *Kappaphycus alvarezii*. This also indicated that fast microwave heating could decrease the formation of byproducts, which severely inhibit the fermentation process. Brown seaweed has not been previously studied for ethanol production using hydrolysate from acid treatment directly.

Figure 4b,c reveals that glucose, galactose and mannose were the three major sugars that were consumed, whereas the concentrations of fucose, xylose, rhamnose and glucuronic acid just had slight decreases. It has been reported widely that glucose and galactose can be consumed by *S. cerevisiae*,[8,10,11] and according to this work, *S. cerevisiae* also can consume mannose. *S. cerevisiae* cannot ferment xylose directly; however, recent research demonstrated that metabolic engineering of *S. cerevisiae* could result in strains capable of efficiently producing ethanol from xylose.[47,48] Compared with the high content of fermentable sugars (e.g., glucose, galactose) in red seaweed, the carbohydrate composition in brown seaweed is more complex. Little information is available on fermenting fucose, rhamnose and glucuronic acid to ethanol. Recently, Wargacki et al. discovered an engineered microbial platform that can metabolize alginate polysaccharides.[49] And Hwang et al. investigated the possibility of fermenting the fucose, rhamnose and glucuronic acid into lactic acid by *Lactobacillus* strains.[50] It is reported that at least 4% of ethanol concentration is necessary for the reduction of energy consumption during the distillation step.[4,51] However, the ethanol concentration in this study was about 0.7% (v/v, 7.06 mL/L); therefore, more investigation needs to be done to optimize the ethanol production.

## CONCLUSIONS

In conclusion, brown seaweed *Ascophyllum nodosum* was successfully used as a potential feedstock for bioethanol production. Microwave assisted hydrothermal treatment provided a fast and efficient saccharification with minimal inhibitors that ensured the fermentability. A total of 127 mg/g monosaccharides of seaweed were released in 1 min holding time and 20.8 mg/g ethanol of seaweed was obtained. The ethanol concentration and conversion efficiency were 5.57 g/L and 60.7% (based on glucose, galactose and mannose) respectively, which was comparatively higher than those also used hydrolytes from hydrothermal treatment. In addition, more than 50% weight of alga residue was recovered after hydrolysis, and the energy densification ranged from 1.4 to 1.7, with HHVs from about 19−24 MJ/kg, which can also be potentially used as solid fuel.

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### Author Contributions

The paper was written through contributions of all authors. All authors have given approval to the final version of the paper.

### Notes

The authors declare no competing financial interest.

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