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Macroalgae (seaweed) for liquid transportation biofuel production: what is next?

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ABSTRACT

Marine algal biofuel is considered a promising solution for energy and environmental challenges. Macroalgal biomass has the potential for bypassing the shortcoming of first and second generation of biomass from food crop and lignocellulosic sources. In this review, we summarize the findings in this domain in the past two decades with a focus on the process of saccharification and fermentation of macroalgae for transportation biofuels. In general, macroalgae contains high levels of carbohydrates, almost no or comparatively less lignin than in terrestrial plants, which makes it a very promising source for liquid biofuel production via bioconversion. After harvest, macroalgal biomass goes through several process units, including pre-treatment and/or saccharification and fermentation to be converted to biofuel, e.g., bioethanol. We also propose strategies for further studies to realize macroalgae biomass potential for transportation bioenergy production.

Contents

1. Introduction

Macroalgae, technical synonym for 'seaweed', is a collective term referring to a series of non-phylogenetic [117], multi-cellular [7], macroscopic [62] and eukaryotic organisms. The advantages of macroalgae as complementary feedstock from marine source are apparent: 1) it holds by and large equal environmental merits as microalgae has because it is also grown in marine systems; 2) it can be grown under worse water and nutrient conditions and is easier to be harvested [3]; 3) its higher carbohydrate content makes it suitable for bioconversion into fuel molecules such as methane [81], hydrogen [108], ethanol [54], n-butanol [97], 2,3-butanadiol [83], etc. These reasons make macroalgal biomass as 'special issue' [116] or 'untapped resource' [106, 129]. The utilization of macroalgae for biorefinery started from the 17th century for industrial soda and alginate in France and Ireland (then part of Great Britain) [19],and then for iodine extraction with illumination powered by seaweed derived biogas in 1893 by British chemist Edward Curtis, and then for kelp industry in California, USA in World War I due to shortage of potash [90]. In 1910s, Hercules Co. developed advanced high-throughput mechanic harvest for kelp and processed potash, acetone with a scale up to 1.6 million tons [10] and in 1970s, the first period of oil crisis witnessed a two-decade project put forward by US DOE [112] on algae biomass feedstock. Though research effort in the project was mainly on microalgae, the cultivation, engineering and biotechnological manipulation of algal gained tremendous advancements. In 1980s,

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Macrocystis spp. in California was investigated for producing methane via bioconversion [36]. With the booming oil price from late 1990s until the peak in 2008 [114], biofuel as a substitute for fossil fuel, gained drastically rapid growing attention in both academia and industry, However, in the particular case of macroalgal biofuel or biorefinery, research on it was falling behind "biofuel" in general both volumetrically and temporally (Fig. 1). Several national and regional studies being conducted on macroalgae in the 2000s, including ones from United States [106], Netherlands [102], Ireland [15], Denmark [91] and South Korea [24], research on this topic has gained its popularity in recent years. Meanwhile, private investment and research also contribute significantly to the development of the domain. For example, in 2010 Bio Architecture Lab and Statoil started a partnership on converting sugars in off-shore cultivated brown algae into biofuel with engineered microbes, and by 2012 the company ran several operation facilities in Chile [78]. However, in 2014 the company was seeking opportunities for shutting down the production lines because of the marginal competence of processing macroalgae into biofuel rather than selling macroalgae as it is. Their Indian counterpart Sea6 Energy teamed up with Novozyme, aiming at joining technology in enzymology and seaweed cultivation together to exploit the potential of Indian red seaweed [4].

Though it has attracted much attention, research on macroalgae for industrial liquid biofuel production is still in its infancy [119]. One Life Cycle Assessments (LCA) based on open-pond on-land cultivation system have cast doubt on the viability of utilizing macroalgal biomass for biofuel production, especially in terms of net energy consumption in processing, as compared to other feedstocks [25]. Nonetheless, other LCA, which considered off-shore cultivation systems have come to optimistic results [3,106]. For other examples, [Langlois et al. [67]] suggested using offshore wind farm to get the clean and efficient electricity onsite with a few technical improvements can lead to high level production efficiency, and another LCA showed the production of biogas from near shore open pond cultivated macroalgae by co-digestion with agricultural waste produced more valuable bioenergy than conventional techniques [18]. Therefore it is evident that the assessment of macroalgae is very pathway dependent.

Hitherto, the production economics is a main factor restricting the industrialization, since laboratorial or pilot-scale study has shown that the cost over profit ratio in the process has not reached an acceptable level [91]. On the other hand, the social and economic factors are not yet favoring the development of macroalgae feedstock either. Unlike food crops, e.g., corn in United States and sugarcane juice in Brazil and lignocellulosic biomass, e.g., corn stover [55], rice straw [57], wood sawdust [61], flax shives [40], cultivation of marine algae that is huge enough to feed this potential industry is much less widely available [106]. Though estimation has shown that substituting 1% of US road transportation fuel with macroalgal biofuel only requires 0.09% area of Exclusive Economic Zone (EEZ) [106], such potential activity is likely to stay on paper until encouraging policies being put forward. This indicates if the concept of marine algae-based biorefinery is going to be implemented, socio-economic and policy alteration is equally essential as those in technological counterparts [88].

With the increasing popularity on macroalgae, there were several reviews on this topic in recent years [20,26,37,86,117,129,134], each emphasizing on some aspects of the domain. However none of them addressed specifically the use of macroalgae for liquid biofuel. Here we summarize latest advances on liquid biofuel production from macroalgal sources, especially on bioethanol, and focus on the processes of saccharification and fermentation. In addition, the review is also meant to project how the advancement of relevant technology could propel the proceedings in this domain in the near future.

2. Literature summary

The table summarizes studies with the whole process of macroalgal bioethanol production reported in last two decades. It can be seen that the studies are diverse in several aspects including algae species, biomass variety, strain employed for fermentation, and methods and parameters used in steps. (See Table 1)

3. Algae species and biomass type

Till now about more than half of the works focused on one species in brown algae, *Laminaria japonica*, followed by several species in *Sargassum*spp. This is probably because the species has been traditionally consumed and thus extensively cultivated and researched in East Asian countries [82]. In 2014, *Laminaria japonica* accounts for almost half of the production of seaweed in China, which is currently the largest seaweed producing country. On the other hand, the most intensively studies species in red algae and green algae are species within *Gracilaria* spp. and *Ulva* spp., respectively, which are also species with high production annually in Asian countries, including Japan, Indonesia and Philippine. (www.seafoodwatch.org).

In the researches on brown seaweed, attention has been concentrated on utilizing all possible carbohydrate in fermentation. The problem is mainly in the co-utilization of glucose, galactose and mannitol [60], which is a typical problem being tackled also in other related fields [41]. In contrast, in red seaweed, researches have been done by-and-

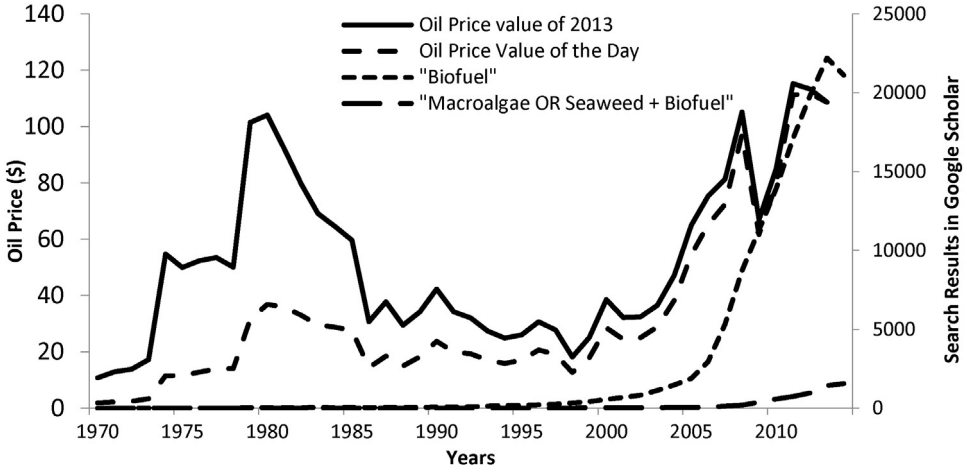

Fig. 1. The comparison of oil prices (in USD), biofuel research and macroalgal biofuel research along years from 1970s to 2014. (Data source for oil price data: inflationdata.com; for publication volume of 'biofuel' and 'macroalgae/seaweed + biofuel': Google scholar by entering the keywords and year accordingly). The oil price reached a peak during oil crisis in 80s, and meanwhile the research volume of biofuel started to take off. From 2000 to 2010, oil price underwent another peak, accompanied by the exponentially increasing number of publication in biofuel. Compared with biofuel in general, macroalgae derived biofuel is still underdeveloped but also gained rapid increases in last decade.

Table 1
Literature summary on macroalgae bioethanol in last two decades.

Algae species[1]	Pre-treatments and/or acid hydrolysis[2]	Enzymatic hydrolysis	Saccharification yield (*w*/*w*)	Fermentation organism	Yield reported	Normalized yield[3]	Reference
Brown Algae							
Laminaria hyperborea	n.a.	n.a.	n.a.	*P. angophorae* (CBS 5830)	0.43 g/g substrate	n.a.	[46]
Laminaria hyperborea	pH 6, 23 °C, 30 min, 25% load (wet base)	Laminarinase 0.1 U/100 g, pH 6, 32 °C, 25% load (wet base)	n.a.	*S. cerevisiae* (Ethanol Red), SSF	0.45% (*v*/*v*)	2.84%	[1]
Alaria crassifolia Kjellman	2% sulfuric acid, 121 °C, 30 min, 25% load	The pellet in acid hydrolysis was subject to 0.5 mL Meicelase, 50 °C, pH 5.5, 120 h. Hydrolysate of both steps were merged.	28.4% glucose and 21.3% galactose	*S. cerevisiae* (IAM 4178)	55.0 g/L	22.0%	[135]
Laminaria japonica	0.1% sulfuric acid, 1.0 h, 121 °C	Cellulase (45 FPU/g) and cellubiase (55 CBU/g), pH 4.8, 50 °C, 2.0% load, 48 h	27.8% glucose	*S. cerevisiae*	0.143 L/kg	11.30%	[35]
Laminaria japonica	100 mMHCl, 121 °C, 15 min, 10% load	Celluclast 1.5 L, Viscozyme L, 1%, pH 5.5, 50 °C, 24 h	8.1% (*w*/*w*)	*E.coli*KO11, SSF	0.4 g ethanol/g sugars	23.0% to 29.0%	[60]
Sargassum sagamianum	Thermal liquefication, 150 °C, 15 MPa, 15 min, 10% load	n.a.	30.1% (*w*/*w*)	*P. Stipitis* (CBS 7126)	0.3–0.35 g ethanol/g sugar	10.0%	[136]
Laminaria digitata	2 M HCl, 30 min, 5% load	0.5 U *Trichoderma* laminarinase, 24 °C	n.a.	*P. angophorae*, SSF	167 mL per kg biomass	13.2%	[2]
Laminaria japonica	n.a.	n.a.	n.a.	*E.coli* (ATCC8739) with synthetic pathway, SSF	4.7%(*v*/*v*)	28.1%	[128]
Saccharina japonica	40 mM Sulfuric Acid, with Termamyl 120 L, 121 °C, 60 min, 10% solid load	*Bacillus sp.* JS-1, 1 g dcw/L. pH 7. 30 °C, 7.5 d	69.1% of total carbohydrate in biomass	*P. angophorae* KCTC 17574, SSF	7.7 g/L	7.7%	[50]
Sargassum spp.	4% sulfuric acid, 115 °C, 90 min, 10% load	Cellulase 50 FPU/g, Cellulase 250 FPU/g, U/g,pH 4.8, 50 °C, 10% load, 100 h	25.50%	*S.cerevisiae*	2.79 g/L	2.79%	[12]
Saccharina japonica	0.06% sulfuric acid, 170 °C, 15 min, 5% load	Cellulase 15 FPU/g-glucan, β -glucosidase 70 pNPGU/g-glucan, pH 4.8, 40 °C, 3% load, 48 h	29.09% glucan	*S. cerevisiae* (DK 410362), SSF	4.90 g/L	14.3%	[70]
L. digitata and S. latissima	72% sulfuric acid, 30 °C, 60 min + 4% sulfuric acid, 120 °c, 40 min	Cellic®CTec2,	n.a	n.a.	n.a.	n.a.	[76]
Saccharina japonica	4% sulfuric acid, 30 min	n.a.	n.a.	n.a.	37.9% oil	n.a.	[22]
Red Algae							
Gracilaria salicornia	2% sulfuric acid, 120 °C, 30 min,	MP BiomedicalsCellulase, 5 g/L, pH 5.0, 26 h,	17.4 g Glucose/kg fresh algae	*E.coli*KO11	79.1 g/kg dry biomass	7.91%	[127]
Kappaphycus alvarezii	900 mM sulfuric acid, 100 °C, 60 min, 5% solid load, repeatedly	None	21.6% after five times	*S. cerevisiae* (NCIM 3523)	95.37%	12.80%	[59]
Kappaphycus alvarezii	200 mM Sulfuric Acid, 130 °C, 15 min, 10% solid load	n.a.	30.5% reducing sugar	*S. cerevisiae*	3.3 g/L	3.30%	[85]
Gelidiumamansii	1.5% sulfuric acid, 140 °C, 15% solid load, 60 min	n.a.	35 g/L Galactose, 8 g/L Glucose	*B. custersii* (KCTC18154P)	27.6 g/L	39.2%	[95]
Kappaphycus alvarezii	1% Sulfuric Acid, ºC, 60 min, 33.3% load (*w*/*w*)	Cellulase 45 FPU/g,	81.62 g/L	*S. cerevisiae* (CBS1782), SSF	65 g/L	19.5%	[43]
Gracilari averrucosa	5.0% sodium hydroxide, 80 °C, 120 min, 5% load	Cellulase 20 FPU/g, β-glucosidase 60 U/g, pH 5.0, 50 °C, 10% load	37.82 g/L	*S. cerevisiae* (HAU strain)	14.89 g/L	14.89%	[65]
Eucheuma cottonii	4% dowax (TM) Dr.-G8, 120 °C, 30 min, 10% load	Cellulase 15 FPU/g, β-glucosidase 52 CBU/g, pH 4.8, 50 °C, 2% load	99.8% glucose	*S. cerevisiae* (YSC2, type II)	Around 75% theoretical yield	42.4%	[119]
Gelidium amansii	4% Sulfuric Acid, 120 °C, 60 min	n.a.	68.58% glucose	n.a.	n.a.	n.a.	[53]
Gelidium amansii	Ionic liquid + AlL, 120 °C, 30 min	n.a.	81% galactose	n.a.	n.a.	n.a.	[75]
Green Algae							
Ulva pertusa Kjellman	150 °C, 15 MPa, 15 min, 10% load	Cellulase 30 FPU/g, pH 4.8, 50 °C, 24 h	98.59% glucose	*S. cerevisiae* (ATCC 24858)	12.4 g/L	12.4%	[23]
Ulva fasciata Delile	n.a.	Viscozyme L, 2%, 5% load, 36 h	184.4 mg/g	*S. cerevisiae* (MTCC No. 180)	0.45 g/g sugar	8.3%	[121]
Chaetomorphalinum	Ball milling	Prehydrolysis, Novozyme 188 and Celluclast 1.5 L, 15 FPU/g, 50 °C, 24 h; SSF, 20 FPU/g, 32 °C, 200 h.	n.a.	*S. cerevisiae* (ATCC 96581), SSF	18 g ethanol/100 g DM	18%	[110]
Ulva lactuca	Sulfuric acid, pH 2, 150 °C, 10 min, 10% load	n.a.	75%-93%	*C. beijerinckii*	40%	40%	[124]
Ulva fasciata Delile	n.a.	n.a.	93.81%	*C. sphaerospermum*	0.47 g/g sugar	n.a.	[122]

Note: 1. To avoid ambiguity by various names of a same species, there are some changes made compared to original article. 2. Pre-treatment column includes any treatment on the biomass after harvest, washing, drying, pulverization, but before, if any, enzymatic hydrolysis. 3. Since various units were used in different studies, to make it clear and comparable, a normalized unit is used in this table. The value in reported yield used the number and unit written by original author and the nominated yield was cited or calculated by authors of the present review, which is in g ethanol/g biomass. In most studies, more than one scenario was conducted, but only the one with highest yield was selected and reported in this table.

large on residues after hydrocolloid extraction [35]. The reason behind this is probably due to the higher price of red algae derived polysaccharides, such as agar [103], that overwhelmed the motivation of utilizing whole biomass as feedstock for biofuel production. It is obvious that ethanol, as a platform and commodity chemical, is lower in price and has several technological obstacles to overcome, such as cell wall material degradation and bioconversion with high efficiency [15], to overcome to be efficiently produced.

4. Pretreatment and saccharification

The tasks of pretreatment and saccharification are consistent, which is to decompose cell wall matrix and degrade such polymeric molecules into fermentable sugars [104]. For this purpose, various physical and chemical treatments have been employed. Meanwhile, high performance anion exchange chromatography (HPAEC) after various acid hydrolysis was found the best method for the quantification of carbohydrate composition in seaweed [76].

The most widely adopted pretreatment is hydrothermal treatment with acid or alkali. In some studies, treatment with dilute acid (<5%) was considered as "pretreatment" [35,45,61], whereas in others it was called "acid hydrolysis" [51,95,118]. This is normally determined by the design of the process, because in some cases such hydrothermal treatment is followed by enzymatic degradation. In the hydrothermal treatment process, the protons in acid are able to interfere the intermolecular hydrogen bonds [56], and thus release cellulose molecules from the amorphous region and partially hydrolyze cellulose molecules in the cell wall [139]. Alkaline treatment can lead to more amorphous regions and thus make cellulose more amenable and accessible by enzyme in later process [87]. Hong et al. [45], suggested that optimum conditions for hydrolysis by dilute sulfuric acid at 150 °C, 60 min of reaction time and optimum fermentation conditions with commercial yeast dosage of 30 wt.% relative to seaweed for 3 days of time. Meanwhile, compared to above mentioned traditional way of pretreatment, gamma irradiation has been shown to cost less time and is more eco-friendly [137].

Under given combination of acidity and temperature, acid also works as catalyst for polysaccharide chain break-down. Taking cellulose as an example, proton from acid interacts with oxygen atom which connects the glycosidic bond, forming a conjugated acidic intermediate. The C–O bond in such intermediate then breaks down with addition of water molecule, liberating a free sugar unit and proton [132]. A complementary mechanism for this is that the proton initially attacks the 4′ carbon atom at one end of the glycosidic bond which has low electron cloud density, then with addition of water, the C–O bond is cleaved and free sugar and proton released [132]. However, in most cases in plant cell wall materials, polysaccharides possess more complicated situations (Fig. 2), as diverse sugar unit, glycosidic bonds, side chain, molecular weight could all lead to different kinetics in glycosidic bonds breakdown [44]. Wei et al. [129] showed the structural information about the polysaccharides present in macroalgae.

Hydrothermal treatment requires only simple equipment and material, but has one major drawback, which is the formation of significant amount of toxins for fermentation, such as furfural, 5-hydroxymethylfurfural (5-HMF) and levulinic acid [79]. The previous two could inhibit activities of enzymes including alcohol dehydrogenase, pyruvate dehydrogenase and aldehyde dehydrogenase, and thus mitigate the glycolysis pathway [5,94]. Weak acids, such as levulinic acid could interfere the ionization equilibrium on plasma membrane and therefore hinder cell growth [94].

A study with application of low concentration (0.3%,*w*/*v*) Tris–HCl showed efficient enzymatic hydrolysis of agar from red macroalgae. [68] The resultant was immediately neutral after hydrolysis and

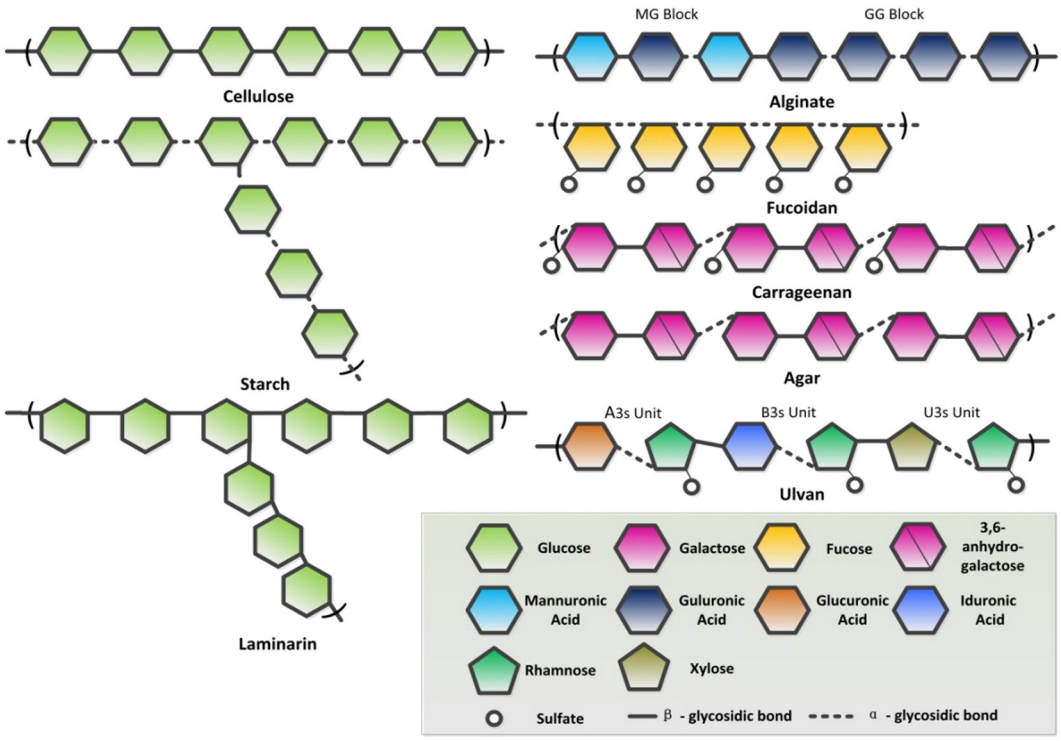

Fig. 2. Structures of polysaccharides in Macroalgae (based on [129]). (1) Cellulose is a chain of β-1,4-linked D-glucose. In plant cell wall, cellulose molecules form supramolecularmicrofibrils of various crystalline types [92]; (2) starch is the storage polysaccharide formed by α-1,4-linked D-glucose backbone and α-1,6 linkages from braches. It has been reported that amylopectin is the mainly present form of starch in green algae [74]; (3) laminarin is a glucan typically present in *Laminaria spp.*, whose backbone is composed of β-1,3-linked D-glucose [101]; (4)alginate is a hetero-polysaccharide in brown seaweed, mainly composed of two repeating units, mannuronic acid and guluronic acid [131]; (5) fucoidan is a sulfated α-1,4-linked fucan present in brown seaweed [71]; (6)carrageenan is a sulfated heteropolysaccharide present mainly in red algae, with galactose and 3,6-anhydro-galactose as repeating units intermittently connected by β-1,4-linkage and α-1,3-linkage [17,98]; (6) agar is a polysaccharide in red algae with a backbone of alternating β-1,4 and α-1,3 linked galactan. [28]; (7) ulvan is a heterogeneous polysaccharide present in green algae with multiple motifs, including monosaccharides of rhamnose, iduronic acid, glucuronic acid and xylose [105]. Since the elucidation of such polysaccharides are still in progress and sometimes debatable, the information here are just generally considered as correct.

therefore neutralization was not needed and less salt was formed. Solid state fermentation-derived cellulose was also found useful for the saccharification of *Ulva Fasciata* which is cellulose rich green seaweed [122]. López Barreiro et al. [73] studied on three brown macroalgae *F. vesiculosus*, *L. saccharina* and *A. esculenta* subjected to hydrothermal liquefaction (HTL) at 350 °C and 15 min and found that, HTL at low heating rates is not useful for high yields of biofuel. [52] investigated the effects of changes in pH, temperature and time in hydrothermal decomposition of sodium alginate and found that hydrothermal decomposition of alginate is better in higher reaction temperature and longer reaction time, but it is responsible for the conversion of few useful compounds to less valuable products. The application of ionic liquid (IL) and acidic IL for hydrolysis of the released polysaccharides from macroalgae *Gelidium amansii* reached 81% galactose and 7% glucose yield in 120 min. at 1200 °C [75].

In a comprehensive study, Schultz-Jensen et al. [110] compared the formation of fermentation inhibitors, including furfural and 5-HMF with several pretreatment methods that have been used in lignocellulosic biofuel industry (hydrothermal, wet oxidation, steam explosion, plasma assisted and ball milling) on *C. linum*. The result showed that ball milling, among all methods employed, produced lowest level of inhibitors while maintaining the yield of ethanol. Tan and Lee [119] used solid catalyst Dowex (TM) Dr.-G8 to pretreat the cellulosic residues from macroalgae *E.cottonii* and found that under the catalyst load of 4%, there was no furfural and 5-HMF detected. Efforts have also been taken in detoxification either before fermentation [85] with activated charcoal or in situ [72] with microorganism innate pathways. In another study, it has been shown that treatment with activated charcoal or overdose of lime could efficiently remove inhibitors, with 5-HMF being reduced up to 75.6% percent [85]. However, the fermentable sugar concentration also saw a decrease of ca. 40%.

It is worthy of notation that from the fermentation perspective, these compounds are inhibitors which are not favored, whereas they could also become desired platform chemical product from a biological source in other purposes [13,21]. Thus, separation of fermentable sugars from such inhibitors could also provide an extra value-added product and can be a potential processing unit to be incorporated in macroalgae biorefinery.

After pretreatment, saccharification is used to degrade polymeric chains into monomeric sugars, which are substrates for subsequent fermentation. Saccharification can be a separate step followed by fermentation (SHF) or can be conducted simultaneously with fermentation (SSF). The degrading agent can be acid, but in most recent cases enzymes have been used for saccharification after acid pretreatment. Since acid is not selective, and the number and variety of glycosidic linkages in the biomass can be different upon all variables of the biomass, it is very difficult to control the optimal parameters for acidic saccharification. As a result, either not all monosaccharides are released or some released monosaccharides are further oxidized into toxins, which have been mentioned above. However, the high prices of enzymes and time required for process, makes acid hydrolysis a better option though there are few limitations such as requirement of nutrients and low yield of glucose. Jeong et al. [53] studied the two step acid saccharification and reached a highest glucose yield of 68.58%.

Enzymatic saccharification is complementary for the shortcomings of acidsaccharification, since enzymes have selectivity on linkages [50]. Nevertheless, the diversity of glycosidic linkages in macroalgal biomass determines that to efficiently degrade most if not all polysaccharides, a cocktail of enzymes is needed. Till now, though many enzymes have been reported of activities on macroalgae polysaccharide, no such commercial cocktail has been available. In most researches summarized above, enzymes employed were mainly glucanase, such as cellulose [35] and laminarinase [111], or commercially available cocktail designed for lignocellulosic biomass such as Celluclast 1.5 L [135] and Viscozyme L [121]. Such commercial enzyme cocktail contain multiple enzyme activities, including cellulase and xylanase. In studies, after efficient pretreatment, enzymatic saccharification can be very efficient on the particular polysaccharides that the enzyme is capable of working on [70]. In another study, enzyme Lactozym, with doses of 2.0 mL per 10 g of seaweed for enzymatic saccharification has reached optimum yield [45].

Simultaneous saccharification and fermentation (SSF) has been widely used in studies from recent years [50,60,70,120], which is also a main-stream technology used in ligonocellulosic biofuel industrial production. Since most enzymes and ethanol producing microorganisms work optimally under similar temperature and pH conditions, the two steps are highly compatible. The main advance of SSF is that sugar released from polysaccharides can be utilized directly instead of being accumulated otherwise, which could compromise the activity of ethanol producer. In an comparative study between SSF and SHF, it has also been shown that real-time usage of saccharification product may have some in situ detoxification effect, as the toxins can be fermented at low concentrations [93]. It should be taken into consideration that although macroalgae cultivation is better option for carbon trapping in ocean [63], the overall production of bioenergy from cultivation is also responsible for carbon emission. Fermentation stage contributes most carbon footprint in the whole bioenergy processing from macroalgae, responsible for 0.046 kg CO2e per MJ; and more than half is due to enzymatic pretreatment process [34].

5. Energy extraction

Currently there are several processing technologies for energy extraction for liquid biofuel from macroalgal feedstock, including bioconversion, thermal liquefaction and pyrolysis. Pyrolysis is the process in which the organic structure is decomposed into the gaseous compounds and carbon rich residue. It is generally used for making bio-crude or bio-oil, where dry biomass of macroalgae needs to be processed under 400 to 600 °C. Pyrolysis can deal with feedstock with high ash content [107]. However, due to the fact that it needs dry feedstock and the high amount of oxygenates present in product, the whole process of pyrolysis is considered to be energy negative [20], which makes pyrolysis a less attractive choice for processing macroalgal biomass (yet microalgae has shown good potential [86].

Thermal liquefaction is similar to a pressurized aqueous pyrolysis [77]. Though it does not need dry feedstock which saves energy in dehydration process, it showed negative results in energy balance when dealing with feedstock with a moisture of higher than 90% [126]. Hydrothermal treatment is a possible solution for macroalgae [29], but high ash content may be a challenging factor since the hydrothermal liquefaction is essentially liquefaction in hot water.

The bioconversion pathway has been outlined for positive energy balance [31] and the products can be more readily used. While there are some discrete researches on fermentation of sugars into other fuel molecules such as butanol [47,96], fatty acid [133] and pinene [111], ethanol bioconversion is considered as benchmark in liquid biofuel from macroalgae. As far as the author is concerned, there are several reasons for this. Firstly, macroalgae has high concentration of carbohydrate and low concentration of oil and lipid [27], which is a typical suitable medium for ethanol production if sugars can be released efficiently. Secondly, compared with other relatively novel high-density molecules, ethanol is easier and more readily incorporated into current transportation infrastructure. Pure ethanol or blend with gasoline has been used in Brazil and USA for years [8]. Last but not least, ethanol is a platform chemical, meaning it is versatile in many chemical synthetic industries other than transportation.

The core issue of ethanol production is to find an ethanol producer that is capable of uptaking and fermenting sugars in hydrolysate, and meanwhile maintaining its robustness under negative conditions. Unlike pretreatment and hydrolysis which are less selective on raw material, fermentation is very species dependent because polysaccharides from different algae species can be degraded into difference kinds of

sugars (Fig. 2). The utilization of these different sugars requires different microorganism strains.

By far most of the attention has been attracted by brown algae. The typical hydrolysate of brown algae contains glucose, galactose, mannose, mannitol and alginate derived oligomers and monomers [60]. Since the most traditional ethanol producer *S. cerevisiae* (Brewer's yeast) is not able to metabolize sugars other than glucose, the normalized ethanol yield could not reach a value higher than 10%. For this reason, efforts were taken in two different ways. On the one hand, other more robust *S. cerevisiae* strains were used. Strain DK 410362 was used to ferment a hydrolysate of *Laminaria japonica* from extremely dilute acid treatment and has yield 14.3% ethanol [70]. Strain IAM 4178 has been used in fermentation of chigaiso (*Alaria crassifalia* Kjellman) hydrolysate and reached a yield of 22.0% [135]. Strain ATCC 8739 with introduction of genes for mannitol metabolism, alginolytic enzyme secretion and alginate derived oligomer uptake was engineered [128]. This strain reached a yield of 28.1%, because of so far broadest substrate utilization capability.

On the other hand, species with natural ability to ferment mannitol were also used. Several species and strains from *Pichiaspp.* were used to ferment mannitol. Results showed that *Pichiaspp.* can reach a yield marginally higher than 10% [50], which is better than native *S. cerevisiae*. In other studies, recombinant strain *E. coli* KO11 was used as ethanol producer [60]. Due to its capability of utilizing mannitol, a yield above 20% was reached.

In red seaweed, hydrolysis of carrageenan and agar led to high amount of galactose and 3,6-anhydro-galactose in the hydrolysate [17]. For this reason, strains with higher galactose metabolism capabilities were used to reach higher yield. For example, Strain NCIM 3523 [59] was used in *Kappaphycus alvarezii*, and over 90% of all reducing sugar was converted after 96 h fermentation. The scale-up in this study went up to 100 L and also gained positive results. In another study from Park et al. [95], continuous batch process with *B. custersii*, which was able to metabolize both glucose and galactose, reached a normalized yield of 39.2%. It has to be mentioned that the unsaturated sugar unit, 3,6-anhydro-galactose has not been reported to be utilized in fermentation so far, as the author is concerned. However, a novel catabolic pathway [138] has been characterized on this sugar unit, and it is possible that in the near future there will be new strains with capability of utilizing this sugar.

In terms of green algae, the main polysaccharide constituent except for glucan is ulvan [105], which is sulfated hetero-polysaccharide with high proportion of rhamnose residue and several other motifs containing uronic acids. Hitherto the fine structure of ulvan has been comprehensively but not fully characterized [66,105]. However, no specific strain aiming at utilizing the sugars released from this polysaccharide has been reported. This may explain why the normalized ethanol yield from *Ulva spp.* has not been over 20%.

Except for hexose, pentose and sugar alcohol, uronic acid also accounts for considerable amount of sugar in macroalgae [117]. To date no reported study on macroalgae has focused on utilizing these acidic sugar units, probably because the presence of two or more redox cofactors and glycerol in bacterial pathway for utilizing acidic sugars. To delicately render such redox system during recombinant strain design has been shown to be challenging [6]. Nevertheless, the pathway for metabolizing galacuronic acid has been characterized in *Hypocrea jecorina* [48]. It can be expected that introducing such pathway into *S. cerevisiae* could lead to more exhaustive usage of biomass from macroalgae.

Macroalgae has potential to provide various kinds of chemical products and byproducts, but nowadays it is generally used for single product such as bioethanol or alginate etc. Efforts to get various products and byproducts from seaweed can result in the cascading valorization of seaweed [125]. However, it will be necessary to take into consideration that, variations in pH, temperature and time can make subtle changes under hydrothermal conditions both on less important products and high value added products [52].

6. What is next?

The research on macroalgal biofuel has gained attention in the last couple of decades, especially in last five years. Worldwide researchers in academia, industry and entrepreneurship have investigated a spectrum of raw material viabilities, cultivation and energy extraction technologies. However, to push forward this futuristic idea and make it widely industrialized, there is still a long way to go.

The main bottleneck is processing economics. With the current low oil price, it is even more difficult to make algal fuel competitive to fossil fuels than several years ago. As far as we are concerned, lowering expenditure and increasing the outcome need to work together to gradually narrow the economic gap. Some of the current ideas for both aspects are outlined in Table 2.

Macroalgae can be cultivated by off-shore, near-shore or on-shore ways, but commercial cultivation of macroalgae needs various types of climatic factors and physiological parameter such as salinity of water, temperature, nutrients etc. Among the three types of macroalgae generally known as red, green and brown, brown algae is the fastest growing plant in the world. Brown macroalgae, also known as kelp, contains 60% of carbohydrates in dry weight [63]. Kerrison et al. [58] discussed various physiological parameters for cultivation of brown macroalgae and suggested recommendation for better growth. It was found that brown macroalgae shows variations in composition in different seasons, e.g.,, highest carbohydrates content in autumn and lowest in winter, impact on concentrations of protein, ash, etc. This can be beneficial for industries for maximizing yields of targeted macroalgae components and minimizing less valuable components [109]. While on-shore cultivation has been shown to be too costly [14,91], off-shore cultivation could be a very promising alternative. However, the production cost including capital cost, operation, maintenance and processing cost of biofuel from macroalgae is found more than market price even in offshore farming [113], because of the procedure of dehydration as macroalgae generally contains considerable amount of water. Researchers on microalgae has started “OMEGA” off-shore cultivation project in collaboration with US navy, which is going to be the world's first natural photobioreactor [140]. In addition, there is still sufficient space for improvement on cultivation techniques. For example, a model of smart mixing system has been recently proposed [38] to better utilize the solar energy per unit marine area. Meanwhile, if the macroalgae cultivation could have some additional environmental benefits, it is likely to win some policy support, e.g.,, subsidies, or could reach collaboration with agricultural and other industrial sectors. For example, ecological research have shown that integration of macroalgae cultivation with e.g.,, shrimp [89], salmon [123] and pearl oyster [99] can remediate eutrophication from coastal areas. In this case, we may expect a new kind of cooperation which could lower the cost for nutrient for macroalgae cultivation and meanwhile lower the cost for aftercare for sea food cultivation. Moreover, similar to the practice in microalgae like what Israeli company ‘Seambiotic’ is doing [16], the cultivation of macroalgae can also make use of exhausted gas from other industries with some pretreatments. All these deeds could amplify the merits of macroalgae as it has already relatively low environmental impacts [25].

On the other hand, the products need to be more valuable than ‘macroalgae as it is’ to really push the R&D activities forward. Though main usage of macroalgae is for human consumption, the commercial interest for using macroalgae to produce other products such as alginate, agar and carrageenan by pharmaceutical and nutraceutical industries is also growing [109]. In European countries, France harvests approximately 30,000 to 50,000 tons of brown macroalgae for hydrocolloid production on a yearly basis [64], but for many countries nowadays the first and foremost approach is to utilize as much biomass as possible to produce fuel. Synthetic biology has shed light on this. Consolidated bioprocessing has been realized with synthetic pathways for glycolytic enzymes and transporters across cell membrane [30]. It is also possible to produce tailor-made enzyme cocktail to expand the scope of

Table 2
Strategies for improving the processing economics of macroalgaebiorefinery.

Lower the expenditure	Increase the outcome
Off-shore cultivation	Broader substrate utilization
More intensified cultivation	Value added by-products
Mitigation of eutrophication	High density molecules
Adaptation of carbon dioxide from industries	

polysaccharide utilized in saccharification, as what has been done on brown algae [9]. Moreover, with ongoing understanding of the natural interaction between algae and its accompanying microorganism community [130], further exploitation of macroalgae and the bacterium can be expected. In fermentation, to uptake and ferment more sugars, researches in lignocellulosic ethanol have proposed two strategies [41]: one using synthetic pathways to amplify traditional ethanol producer with more capabilities; the other using multiple organisms to co-ferment the sugar mixture. To date in the field of macroalgae, the previous idea has been tried [128], whereas the latter remains a blank. A rarely touched approach could also fulfill the task, which is to ferment the hydrolysate with multiple organisms sequentially, e.g.,, *S. cerevisiae* and *E.coli* [39]. In the research of [Kim et al. [60]], this approach was tried and has achieved highest yield among all scenarios.

However, in the current low oil price situation, if only bulk chemical like ethanol is produced, it is still difficult to reach economic competence even with improved substrate utilization capabilities. Therefore, at least in the short term, research efforts should also be distributed on application of macroalgae on advanced food ingredients, pharmaceutical, cosmetics, etc. In addition, another way to increase the value of product is to produce more advanced fuel, e.g.,, aviation fuel. There is great opportunity in this respect given the EU framework which calls for 10% of renewable energy in transportation by 2020 [80] Compared to the current capabilities of battery, biofuel is more likely to foster airline companies to reach such targets.

On top of this, in the era of biorefinery, flexibility of process design should be maintained [33], because the desired type of product could change upon location and market. Considering the fluctuation of biomass in geological distribution, cultivation techniques, growing and harvesting seasons and the part of biomass that is incorporated in bioconversion [2], the case-by-case studies, like ones reviewed in this article may not give holistic guidance to the field, because it is very difficult to duplicate the same scenario from one place to another. In this case, the field needs to introduce more quantitative tools for making the process controllable and results predictable. For example, incorporating metabolic modeling would be a preferable direction [11,84]. In such holistic approach, constraint-based models, such flux balance analysis could be used to calculate the output with given input [69]. The method has successfully been used on 10 L scale fermentation of sugar mixture with *E.coli* [42]. However, to deal with engineered strains and microorganisms grown under odd conditions, more insight into the selection of a more biologically relevant objective function in FBA is needed [100]. In addition, for multiple organism system, the inter-organism relationship and flux exchange has not been fully understood, which makes it difficult to model such co-culture system with flux balance analysis [32].

Macroalgae has potential to provide biomass, but the processes to get desired products from biomass still need to be improved. Among many processes to get energy from biomass of macroalgae, anaerobic digestion process has highest potential to provide the biofuel, in the form of methane [20]. Nevertheless, there is still contradiction in between the anaerobic digestion and gasification about the higher efficiency, but in the case of India, both have been found to be promising methods for bioenergy from biomass [86].

In a nutshell, except for the cultivation issue, which is a unique void for macroalgae industry itself, the other technological proceedings of the field will gain impetus from fundamental research and first and second generations biomass utilization. Issues such as pretreatment with higher efficiency, polysaccharide degradation, co-utilization of hexose and pentose are also typical bottlenecks being tackled in lignocellulosic biofuel production. It is obvious that the third generation biofuel has a lot to inherit from the second, which far more academic and industrial efforts have been devoted in.

Bioenergy from macroalgae, will be better alternatives in terms of fuel requirements for fastest growing economies such as India. In such economies, government promotes small scale industries for economic development and employment generation, but economy is meanwhile growing with many environmental and social problems [49]. From the authors' perspective, the coming years or decade will witness the maturation of macroalgae technologies. With the processing technology and fundamental research going alongside, we can expect this new stream of natural resource really being tapped.

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References

[1] J. Adams, J. Gallagher, I. Donnison, Fermentation study on Saccharina latissima for bioethanol production considering variable pre-treatments, J. Appl. Phycol. 21 (2009) 569–574, http://dx.doi.org/10.1007/s10811-008-9384-7.
[2] J.M.M. Adams, T.A. Toop, I.S. Donnison, J.A. Gallagher, Seasonal variation in Laminaria digitata and its impact on biochemical conversion routes to biofuels, Bioresour. Technol. 102 (2011) 9976–9984, http://dx.doi.org/10.1016/j.biortech.2011.08.032.
[3] D. Aitken, C. Bulboa, A. Godoy-Faundez, J.L. Turrion-Gomez, B. Antizar-Ladislao, Life cycle assessment of macroalgae cultivation and processing for biofuel production, J. Clean. Prod. 75 (2014) 45–56, http://dx.doi.org/10.1016/j.jclepro.2014.03.080.
[4] AlgaeIndustryMagazine.com, Novozymes and Sea6 Energy Team on Seaweed Research[WWW Document] AlgaeIndustryMagazine.com, 2012 (URL http://www.algaeindustrymagazine.com/novozymes-and-sea6-energy-team-on-seaweed-research/ (accessed 11.11.15)).
[5] J.R. Almeida, T. Modig, A. Petersson, B. Hähn-Hägerdal, G. Lidén, M.F. Gorwa-Grauslund, Increased tolerance and conversion of inhibitors in lignocellulosic hydrolysates by *Saccharomyces cerevisiae*, J. Chem. Technol. Biotechnol. 82 (2007) 340–349, http://dx.doi.org/10.1002/jctb.1676.
[6] J.R.M. Almeida, D. Runquist, V. Sànchez i Nogué, G. Lidén, M.F. Gorwa-Grauslund, Stress-related challenges in pentose fermentation to ethanol by the yeast *Saccharomyces cerevisiae*, Biotechnol. J. 6 (2011) 286–299, http://dx.doi.org/10.1002/biot.201000301.
[7] A. Annam Renita, D. Joshua Amarnath, Production of bio-diesel from marine macro algae, Recent Advances in Space Technology Services and Climate Change 2010 (RSTS & CC-2010), IEEE 2010, pp. 430–432, http://dx.doi.org/10.1109/RSTSCC.2010.5712882.
[8] M. Balat, H. Balat, Recent trends in global production and utilization of bio-ethanol fuel, Appl. Energy 86 (2009) 2273–2282, http://dx.doi.org/10.1016/j.apenergy.2009.03.015.
[9] G. Banerjee, S. Car, J.S. Scott-Craig, M.S. Borrusch, N. Aslam, J.D. Walton, Synthetic enzyme mixtures for biomass deconstruction: production and optimization of a core set, Biotechnol. Bioeng. 106 (2010) 707–720, http://dx.doi.org/10.1002/bit.22741.
[10] K.R. Benson, P.F. Rehbock, Oceanographic History: The Pacific and Beyond, University of Washington Press, 2002.
[11] O. Bernard, Hurdles and challenges for modelling and control of microalgae for CO2 mitigation and biofuel production, J. Process Control 21 (2011) 1378–1389, http://dx.doi.org/10.1016/j.jprocont.2011.07.012.
[12] M.G. Borines, R.L. de Leon, J.L. Cuello, Bioethanol production from the macroalgae Sargassum spp, Bioresour. Technol. 138 (2013) 22–29, http://dx.doi.org/10.1016/j.biortech.2013.03.108.
[13] J.J. Bozell, L. Moens, D.C. Elliott, Y. Wang, G.G. Neuenscwander, S.W. Fitzpatrick, R.J. Bilski, J.L. Jarnefeld, Production of levulinic acid and use as a platform chemical for derived products, Resour. Conserv. Recycl. 28 (2000) 227–239, http://dx.doi.org/10.1016/S0921-3449(99)00047-6.
[14] A. Bruhn, J. Dahl, H.B. Nielsen, L. Nikolaisen, M.B. Rasmussen, S. Markager, B. Olesen, C. Arias, P.D. Jensen, Bioenergy potential of Ulva lactuca: biomass yield, methane production and combustion, Bioresour. Technol. 102 (2011) 2595–2604, http://dx.doi.org/10.1016/j.biortech.2010.10.010.
[15] T. Bruton, H. Lyons, Y. Lerat, M. Stanley, M.B. Rasmussen, A review of the potential of marine algae as a source of biofuel in Ireland, Sustain. Energy Irel., Dublin, 2009 88.
[16] T. Bruton, H. Lyons, Y. Lerat, M. Stanley, M.B. Rasmussen, A review of the potential of marine algae as a source of biofuel in Ireland, Sustain. Energy Irel., Dublin, 2009 88.
[17] V.L. Campo, D.F. Kawano, D.B.D. Silva, I. Carvalho, Carrageenans: biological properties, chemical modifications and structural analysis — a review, Carbohydr. Polym. 77 (2009) 167–180, http://dx.doi.org/10.1016/j.carbpol.2009.01.020.

[18] A. Cappelli, E. Gigli, F. Romagnoli, S. Simoni, D. Blumberga, M. Palerno, E. Guerriero, Co-digestion of macroalgae for biogas production: an LCA-based environmental evaluation, Energy Procedia 72 (2015) 3–10, http://dx.doi.org/10.1016/j.egypro.2015.06.002.
[19] V. Chapman, Seaweeds and Their Uses, University of California Press, London, New York, 1980.
[20] H. Chen, D. Zhou, G. Luo, S. Zhang, J. Chen, Macroalgae for biofuels production: progress and perspectives, Renew. Sust. Energ. Rev. 47 (2015) 427–437, http://dx.doi.org/10.1016/j.rser.2015.03.086.
[21] J.N. Chheda, Y. Rom án-Leshkov, J.A. Dumesic, Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono- and poly-saccharides, Green Chem. 9 (2007) 342, http://dx.doi.org/10.1039/b611568c.
[22] J. Choi, J.-W. Choi, D.J. Suh, J.-M. Ha, J.W. Hwang, H.W. Jung, K.-Y. Lee, H.-C. Woo, Production of brown algae pyrolysis oils for liquid biofuels depending on the chemical pretreatment methods, Energy Convers. Manag. 86 (2014) 371–378, http://dx.doi.org/10.1016/j.enconman.2014.04.094.
[23] W.Y. Choi, J.G. Han, C.G. Lee, C.H. Song, J.S. Kim, Y.C. Seo, S.E. Lee, K.H. Jung, D.H. Kang, S.J. Heo, J.S. Cho, H.Y. Lee, Bioethanol production from Ulva pertusa Kjellman by high-temperature liquefaction, Chem. Biochem. Eng. Q. 26 (2012) 15–21.
[24] I.K. Chung, J.H. Oak, J.A. Lee, J.A. Shin, J.G. Kim, K.-S. Park, Installing kelp forests/seaweed beds for mitigation and adaptation against global warming: Korean project overview, ICES J. Mar. Sci. 70 (2013) 1038–1044, http://dx.doi.org/10.1093/icesjms/fss206.
[25] A.F. Clarens, E.P. Resurreccion, M.A. White, L.M. Colosi, Environmental life cycle comparison of algae to other bioenergy feedstocks, Environ. Sci. Technol. 44 (2010) 1813–1819, http://dx.doi.org/10.1021/es902838n.
[26] M. Daroch, S. Geng, G. Wang, Recent advances in liquid biofuel production from algal feedstocks, Appl. Energy 102 (2013) 1371–1381, http://dx.doi.org/10.1016/j.apenergy.2012.07.031.
[27] C. Dawczynski, R. Schubert, G. Jahreis, Amino acids, fatty acids, and dietary fibre in edible seaweed products, Food Chem. 103 (2007) 891–899, http://dx.doi.org/10.1016/j.foodchem.2006.09.041.
[28] M. Duckworth, W. Yaphe, The structure of agar, Carbohydr. Res. 16 (1971) 189–197, http://dx.doi.org/10.1016/S0008-6215(00)86113-3.
[29] D.C. Elliott, P. Biller, A.B. Ross, A.J. Schmidt, S.B. Jones, Hydrothermal liquefaction of biomass: developments from batch to continuous process, Bioresour. Technol. 178 (2014) 147–156, http://dx.doi.org/10.1016/j.biortech.2014.09.132.
[30] M. Enquist-Newman, A.M.E. Faust, D.D. Bravo, C.N.S. Santos, R.M. Raisner, A. Hanel, P. Sarvabhowman, C. Le, D.D. Regitsky, S.R. Cooper, L. Peereboom, A. Clark, Y. Martinez, J. Goldsmith, M.Y. Cho, P.D. Donohoue, L. Luo, B. Lamberson, P. Tamrakar, E.J. Kim, J.L. Villari, A. Gill, S.A. Tripathi, P. Karamchedu, C.J. Paredes, V. Rajgarhia, H.K. Kotlar, R.B. Bailey, D.J. Miller, N.L. Ohler, C. Swimmer, Y. Yoshikuni, Efficient ethanol production from brown macroalgae sugars by a synthetic yeast platform, Nature 505 (2014) 239–243, http://dx.doi.org/10.1038/nature12771.
[31] P. Fasahati, H.C. Woo, J.J. Liu, Industrial-scale bioethanol production from brown algae : effects of pretreatment processes on plant economics, Appl. Energy 139 (2015) 175–187, http://dx.doi.org/10.1016/j.apenergy.2014.11.032.
[32] K. Faust, J. Raes, Microbial interactions: from networks to models, Nat. Rev. Microbiol. 10 (2012) 538–550, http://dx.doi.org/10.1038/nrmicro2832.
[33] S. Fernando, S. Adhikari, C. Chandrapal, N. Murali, Biorefineries: current status, challenges, and future direction, Energy Fuel 20 (2006) 1727–1737, http://dx.doi.org/10.1021/ef060097w.
[34] J.M. Fry, J. Joyce, S. Aumonier, Carbon Footprint of Seaweed as Biofuel, 2012.
[35] L. Ge, P. Wang, H. Mou, Study on saccharification techniques of seaweed wastes for the transformation of ethanol, Renew. Energy 36 (2011) 84–89, http://dx.doi.org/10.1016/j.renene.2010.06.001.
[36] S. Ghosh, D.L. Klass, D.P. Chynoweth, Bioconversion of *Macrocystis Pyrifera* to Methane 791–807, 1981.
[37] C.S. Goh, K.T. Lee, A visionary and conceptual macroalgae-based third-generation bioethanol (TGB) biorefinery in Sabah, Malaysia as an underlay for renewable and sustainable development, Renew. Sust. Energ. Rev. 14 (2010) 842–848, http://dx.doi.org/10.1016/j.rser.2009.10.001.
[38] A. Golberg, A. Liberzon, Modeling of smart mixing regimes to improve marine biorefinery productivity and energy efficiency, Algal Res. 11 (2015) 28–32, http://dx.doi.org/10.1016/j.algal.2015.05.021.
[39] A. Golberg, E. Vitkin, G. Linshiz, S.A. Khan, N.J. Hillson, Z. Yakhini, M.L. Yarmush, Proposed design of distributed macroalgal biorefineries: thermodynamics, bioconversion technology, and sustainability implications for developing economies, Biofuels Bioprod. Biorefin. 8 (2014) 67–82, http://dx.doi.org/10.1002/bbb.1438.
[40] S. González-García, L. Luo, M.T. Moreira, G. Feijoo, G. Huppes, Life cycle assessment of flax shives derived second generation ethanol fueled automobiles in Spain, Renew. Sust. Energ. Rev. 13 (2009) 1922–1933, http://dx.doi.org/10.1016/j.rser.2009.02.003.
[41] S.-J. Ha, Q. Wei, S.R. Kim, J.M. Galazka, J. Cate, Y.-S. Jin, Cofermentation of cellobiose and galactose by an engineered *Saccharomyces cerevisiae* strain, Appl. Environ. Microbiol. 77 (2011) 5822–5825, http://dx.doi.org/10.1128/AEM.05228-11.
[42] T.J. Hanly, M.A. Henson, Dynamic flux balance modeling of microbial co-cultures for efficient batch fermentation of glucose and xylose mixtures, Biotechnol. Bioeng. 108 (2011) 376–385, http://dx.doi.org/10.1002/bit.22954.
[43] P.I. Hargreaves, C.A. Barcelos, A.C.A. da Costa, N. Pereira Jr., Production of ethanol 3G from Kappaphycus alvarezii: evaluation of different process strategies, Bioresour. Technol. 134 (2013) 257–263, http://dx.doi.org/10.1016/j.biortech.2013.02.002.
[44] C. Hoebler, J.L. Barry, A. David, J. Delort-Laval, Rapid acid hydrolysis of plant cell wall polysaccharides and simplified quantitative determination of their neutral monosaccharides by gas–liquid chromatography, J. Agric. Food Chem. 37 (1989) 360–367, http://dx.doi.org/10.1021/jf00086a020.
[45] I.K. Hong, H. Jeon, S.B. Lee, Comparison of red, brown and green seaweeds on enzymatic saccharification process, J. Ind. Eng. Chem. 20 (2014) 2687–2691, http://dx.doi.org/10.1016/j.jiec.2013.10.056.
[46] S.J. Horn, I.M. Aasen, K. Østgaard, Ethanol production from seaweed extract, J. Ind. Microbiol. Biotechnol. 25 (2000) 249–254, http://dx.doi.org/10.1038/sj.jim.7000065.
[47] M.H. Huesemann, L.-J. Kuo, L. Urquhart, G.A. Gill, G. Roesijadi, Acetone–butanol fermentation of marine macroalgae, Bioresour. Technol. 108 (2012) 305–309, http://dx.doi.org/10.1016/j.biortech.2011.12.148.
[48] E.H. Huisjes, M.A.H. Luttik, M.J.H. Almering, M.M.M. Bisschops, D.H.N. Dang, M. Kleerebezem, R. Siezen, A.J.A. van Maris, J.T. Pronk, Toward pectin fermentation by *Saccharomyces cerevisiae*: expression of the first two steps of a bacterial pathway for D-galacturonate metabolism, J. Biotechnol. 162 (2012) 303–310, http://dx.doi.org/10.1016/j.jbiotec.2012.10.003.
[49] K.N. Ingle, K. Harada, C.N. Wei, K. Minamoto, A. Ueda, Policy framework for formulating environmental management strategy for sustainable development of tanneries in India, Environ. Health Prev. Med. 16 (2011) 123–128, http://dx.doi.org/10.1007/s12199-010-0168-8.
[50] J.-S. Jang, Y. Cho, G.-T. Jeong, S.-K. Kim, Optimization of saccharification and ethanol production by simultaneous saccharification and fermentation (SSF) from seaweed, Saccharina japonica, Bioprocess Biosyst. Eng. 35 (2012) 11–18, http://dx.doi.org/10.1007/s00449-011-0611-2.
[51] S.S. Jang, Y. Shirai, M. Uchida, M. Wakisaka, Production of mono sugar from acid hydrolysis of seaweed, Afr. J. Biotechnol. (2014)http://dx.doi.org/10.4314/ajb.v11i8.
[52] W. Jeon, C. Ban, G. Park, T. Yu, J. Suh, H. Chul, D. Heui, Catalytic hydrothermal conversion of macroalgae-derived alginate: effect of pH on production of furfural and valuable organic acids under subcritical water conditions, J. Mol. Catal. A Chem. 399 (2015) 106–113, http://dx.doi.org/10.1016/j.molcata.2015.01.011.
[53] T.S. Jeong, Y.S. Kim, K.K. Oh, Two-stage acid saccharification of fractionated Gelidium amansii minimizing the sugar decomposition, Bioresour. Technol. 102 (2011) 10529–10534, http://dx.doi.org/10.1016/j.biortech.2011.09.017.
[54] R.P. John, G.S. Anisha, K.M. Nampoothiri, A. Pandey, Micro and macroalgal biomass: a renewable source for bioethanol, Bioresour. Technol. 102 (2011) 186–193, http://dx.doi.org/10.1016/j.biortech.2010.06.139.
[55] K. Kadam, J. McMillan, Availability of corn stover as a sustainable feedstock for bioethanol production, Bioresour. Technol. (2003).
[56] K. Kamide, K. Okajima, K. Kowsaka, Dissolution of natural cellulose into aqueous alkali solution: role of super-molecular structure of cellulose, Polym. J. 24 (1992) 71–86, http://dx.doi.org/10.1295/polymj.24.71.
[57] K. Karimi, G. Emtiazi, M.J. Taherzadeh, Ethanol production from dilute-acid pretreated rice straw by simultaneous saccharification and fermentation with Mucor indicus, Rhizopus oryzae, and, Enzym. Microb. Technol. (2006).
[58] P.D. Kerrison, M.S. Stanley, M.D. Edwards, K.D. Black, A.D. Hughes, The cultivation of European kelp for bioenergy: site and species selection, Biomass Bioenergy 80 (2015) 229–242, http://dx.doi.org/10.1016/j.biombioe.2015.04.035.
[59] Y. Khambhaty, K. Mody, M.R. Gandhi, S. Thampy, P. Maiti, H. Brahmbhatt, K. Eswaran, P.K. Ghosh, Kappaphycus alvarezii as a source of bioethanol, Bioresour. Technol. 103 (2012) 180–185, http://dx.doi.org/10.1016/j.biortech.2011.10.015.
[60] N.-J. Kim, H. Li, K. Jung, H.N. Chang, P.C. Lee, Ethanol production from marine algal hydrolysates using *Escherichia coli* KO11, Bioresour. Technol. 102 (2011) 7466–7469, http://dx.doi.org/10.1016/j.biortech.2011.04.071.
[61] T. Kim, C. Choi, K. Oh, Bioconversion of sawdust into ethanol using dilute sulfuric acid-assisted continuous twin screw-driven reactor pretreatment and fed-batch simultaneous, Bioresour. Technol. (2013).
[62] H. Klöser, M.L. Quartino, C. Wiencke, Distribution of macroalgae and macroalgal communities in gradients of physical conditions in Potter Cove, King George Island, Antarctica, Hydrobiologia 333 (1996) 1–17, http://dx.doi.org/10.1007/BF00020959.
[63] S. Kraan, Mass-cultivation of carbohydrate rich macroalgae, a possible solution for sustainable biofuel production, Mitig. Adapt. Strateg. Glob. Chang. 18 (2013) 27–46, http://dx.doi.org/10.1007/s11027-010-9275-5.
[64] S. Kraan, Algal polysaccharides, novel applications and outlook, Carbohydrates - Compr. Stud. Glycobiol. Glycotechnol. 2012, pp. 489–532, http://dx.doi.org/10.5772/51572.
[65] S. Kumar, R. Gupta, G. Kumar, D. Sahoo, R.C. Kuhad, Bioethanol production from *Gracilaria verrucosa*, a red alga, in a biorefinery approach, Bioresour. Technol. 135 (2013) 150–156, http://dx.doi.org/10.1016/j.biortech.2012.10.120.
[66] M. Lahaye, A. Robic, Structure and functional properties of ulvan, a polysaccharide from green seaweeds, Biomacromolecules 8 (2007) 1765–1774, http://dx.doi.org/10.1021/bm061185q.
[67] J. Langlois, J.-F. Sassi, G. Jard, J.-P. Steyer, J.-P. Delgenes, A. Hélias, Life cycle assessment of biomethane from offshore-cultivated seaweed, Biofuels Bioprod. Biorefin. 6 (2012) 387–404, http://dx.doi.org/10.1002/bbb.1330.
[68] C.H. Lee, E.J. Yun, H.T. Kim, I.-G. Choi, K.H. Kim, Saccharification of agar using hydrothermal pretreatment and enzymes supplemented with agarolytic β-galactosidase, Process Biochem. 50 (2015) 1629–1633, http://dx.doi.org/10.1016/j.procbio.2015.06.017.
[69] J.M. Lee, E.P. Gianchandani, J.A. Papin, Flux balance analysis in the era of metabolomics, Brief. Bioinform. 7 (2006) 140–150, http://dx.doi.org/10.1093/bib/bbl007.
[70] J.Y. Lee, P. Li, J.Y. Lee, H.J. Ryu, K.K. Oh, Ethanol production from Saccharina japonica using an optimized extremely low acid pretreatment followed by simultaneous saccharification and fermentation, Bioresour. Technol. 127 (2013) 119–125, http://dx.doi.org/10.1016/j.biortech.2012.09.122.
[71] B. Li, F. Lu, X. Wei, R. Zhao, Fucoidan: structure and bioactivity, Molecules (2008).

[72] Z.L. Liu, J. Moon, B.J. Andersh, P.J. Slininger, S. Weber, Multiple gene-mediated NAD(P)H-dependent aldehyde reduction is a mechanism of in situ detoxification of furfural and 5-hydroxymethylfurfural by *Saccharomyces cerevisiae*, Appl. Microbiol. Biotechnol. 81 (2008) 743–753, http://dx.doi.org/10.1007/s00253-008-1702-0.

[73] D. López Barreiro, M. Beck, U. Hornung, F. Ronsse, A. Kruse, W. Prins, Suitability of hydrothermal liquefaction as a conversion route to produce biofuels from macroalgae, Algal Res. 11 (2015) 234–241, http://dx.doi.org/10.1016/j.algal.2015.06.023.

[74] P. MacArtain, C.I.R. Gill, M. Brooks, R. Campbell, I.R. Rowland, Nutritional value of edible seaweeds, Nutr. Rev. 65 (2008) 535–543, http://dx.doi.org/10.1111/j.1753-4887.2007.tb00278.x.

[75] L.B. Malihan, G.M. Nisola, N. Mittal, J.G. Seo, W.-J. Chung, Blended ionic liquid systems for macroalgae pretreatment, Renew. Energy 66 (2014) 596–604, http://dx.doi.org/10.1016/j.renene.2014.01.003.

[76] D. Manns, A.L. Deutschle, B. Saake, A.S. Meyer, Methodology for quantitative determination of the carbohydrate composition of brown seaweeds (Laminariaceae), RSC Adv. 4 (2014) 25736–25746, http://dx.doi.org/10.1039/c4ra03537b.

[77] A. Marcilla, L. Catalá, J.C. García-Quesada, F.J. Valdés, M.R. Hernández, A review of thermochemical conversion of microalgae, Renew. Sust. Energ. Rev. 27 (2013) 11–19, http://dx.doi.org/10.1016/j.rser.2013.06.032.

[78] Marketwired, Statoil & Bio Architecture Lab Partner to Commercialize Macroalgae-to-Ethanol Process in Norway[WWW Document] Marketwired, 2010 (URL http://www.marketwired.com/press-release/statoil-bio-architecture-lab-partner-commercialize-macroalgae-ethanol-process-norway-1319351.htm (accessed 11.9.15)).

[79] C. Martín, M. Galbe, C.F. Wahlbom, B. Hahn-Hägerdal, L.J. Jönsson, Ethanol production from enzymatic hydrolysates of sugarcane bagasse using recombinant xylose-utilising *Saccharomyces cerevisiae*, Enzym. Microb. Technol. 31 (2002) 274–282, http://dx.doi.org/10.1016/S0141-0229(02)00112-6.

[80] B.V. Mathiesen, H. Lund, P. Nørgaard, Integrated transport and renewable energy systems, Util. Policy 16 (2008) 107–116, http://dx.doi.org/10.1016/j.jup.2007.11.007.

[81] T. Matsui, Y. Koike, Methane fermentation of a mixture of seaweed and milk at a pilot-scale plant, J. Biosci. Bioeng. 110 (2010) 558–563, http://dx.doi.org/10.1016/j.jbiosc.2010.06.011.

[82] I. Mazarrasa, Y.S. Olsen, E. Mayol, N. Marbà, C.M. Duarte, Global unbalance in seaweed production, research effort and biotechnology markets, Biotechnol. Adv. 32 (2014) 1028–1036, http://dx.doi.org/10.1016/j.biotechadv.2014.05.002.

[83] S. Mazumdar, J. Lee, M.-K. Oh, Microbial production of 2,3 butanediol from seaweed hydrolysate using metabolically engineered *Escherichia coli*, Bioresour. Technol. 136 (2013) 329–336, http://dx.doi.org/10.1016/j.biortech.2013.03.013.

[84] A.L. Meadows, R. Karnik, H. Lam, S. Forestell, B. Snedecor, Application of dynamic flux balance analysis to an industrial *Escherichia coli* fermentation, Metab. Eng. 12 (2010) 150–160, http://dx.doi.org/10.1016/j.ymben.2009.07.006.

[85] M. Meinita, J.-Y. Kang, G.-T. Jeong, H. Koo, S. Park, Y.-K. Hong, Bioethanol production from the acid hydrolysate of the carrageenophyte Kappaphycus alvarezii (cottonii), J. Appl. Phycol. 24 (2012) 857–862, http://dx.doi.org/10.1007/s10811-011-9705-0.

[86] J.J. Milledge, B. Smith, P.W. Dyer, P. Harvey, Macroalgae-derived biofuel: a review of methods of energy extraction from seaweed biomass, Energies 7 (2014) 7194–7222, http://dx.doi.org/10.3390/en7117194 (19961073).

[87] A. Mittal, R. Katahira, M.E. Himmel, D.K. Johnson, Effects of alkaline or liquid-ammonia treatment on crystalline cellulose: changes in crystalline structure and effects on enzymatic digestibility, Biotechnol. Biofuels 4 (2011) 41, http://dx.doi.org/10.1186/1754-6834-4-41.

[88] R. Möller, D. Clayton, Micro- and macro-algae: utility for industrial applications, outputs from the EPOBIO project, CNAP University of York York UK, 2007http://dx.doi.org/10.1037/11474-008.

[89] S. Nelson, E. Glenn, J. Conn, D. Moore, Cultivation of Gracilaria parvispora (Rhodophyta) in shrimp-farm effluent ditches and floating cages in Hawaii: a two-phase polyculture system, Aquaculture (2001).

[90] P. Neushul, Seaweed for war: California's World War I kelp industry, Technol. Cult. (1989) 561–583.

[91] L. Nikolaisen, P.D. Jensen, K.S. Bech, Energy Production from Marine Biomass (Ulva lactuca), 2008 1–72.

[92] A.C. O'Sullivan, Cellulose: the structure slowly unravels, Cellulose 4 (1997) 173–207, http://dx.doi.org/10.1023/A:1018431705579.

[93] K. Öhgren, R. Bura, G. Lesnicki, J. Saddler, G. Zacchi, A comparison between simultaneous saccharification and fermentation and separate hydrolysis and fermentation using steam-pretreated corn stover, Process Biochem. 42 (2007) 834–839, http://dx.doi.org/10.1016/j.procbio.2007.02.003.

[94] E. Palmqvist, B. Hahn-Hägerdal, Fermentation of lignocellulosic hydrolysates. I: inhibition and detoxification, Bioresour. Technol. 74 (2000) 17–24, http://dx.doi.org/10.1016/S0960-8524(99)00160-1.

[95] J.-H. Park, J.-Y. Hong, H.C. Jang, S.G. Oh, S.-H. Kim, J.-J. Yoon, Y.J. Kim, Use of Gelidium amansii as a promising resource for bioethanol: a practical approach for continuous dilute-acid hydrolysis and fermentation, Bioresour. Technol. 108 (2012) 83–88, http://dx.doi.org/10.1016/j.biortech.2011.12.065.

[96] T. Potts, J. Du, M. Paul, The production of butanol from Jamaica bay macro algae, 31 (2012) 29–36.

[97] T. Potts, J. Du, M. Paul, P. May, R. Beitle, J. Hestekin, The production of butanol from Jamaica bay macro algae, Environmental Progress and Sustainable Energy 2012, pp. 29–36, http://dx.doi.org/10.1002/ep.10606.

[98] V.D. Prajapati, P.M. Maheriya, G.K. Jani, H.K. Solanki, Carrageenan: a natural seaweed polysaccharide and its applications, Carbohydr. Polym. 105 (2014) 97–112, http://dx.doi.org/10.1016/j.carbpol.2014.01.067.

[99] P. Qian, C. Wu, M. Wu, Y. Xie, Integrated cultivation of the red alga Kappaphycus alvarezii and the pearl oyster Pinctada martensi, Aquaculture (1996).

[100] K. Raman, N. Chandra, Flux balance analysis of biological systems: applications and challenges, Brief. Bioinform. 10 (2009) 435–449, http://dx.doi.org/10.1093/bib/bbp011.

[101] S.M. Read, G. Currie, A. Bacic, Analysis of the structural heterogeneity of laminarin by electrospray-ionisation-mass spectrometry, Carbohydr. Res. (1996).

[102] E. Reith, E. Deurwaarder, K. Hemmes, Bio-Offshore: Grootschalige Teelt van Zeewieren in Combinatie met Offshore Windparken in de Noordzee, 2005.

[103] N. Rhein-Knudsen, M.T. Ale, A.S. Meyer, Seaweed hydrocolloid production: an update on enzyme assisted extraction and modification technologies, Mar. Drugs 13 (2015) 3340–3359, http://dx.doi.org/10.3390/md13063340.

[104] R. Rinaldi, F. Schüth, Acid hydrolysis of cellulose as the entry point into biorefinery schemes, ChemSusChem 2 (2009) 1096–1107, http://dx.doi.org/10.1002/cssc.200900188.

[105] A. Robic, C. Rondeau-Mouro, J.F. Sassi, Y. Lerat, M. Lahaye, Structure and interactions of ulvan in the cell wall of the marine green algae *Ulva rotundata* (Ulvales, Chlorophyceae), Carbohydr. Polym. 77 (2009) 206–216, http://dx.doi.org/10.1016/j.carbpol.2008.12.023.

[106] G. Roesijadi, S.B. Jones, Y. Zhu, Macroalgae as a biomass feedstock : a preliminary analysis, Analysis (2010) 1–50.

[107] A.B. Ross, J.M. Jones, M.L. Kubacki, T. Bridgeman, Classification of macroalgae as fuel and its thermochemical behaviour, Bioresour. Technol. 99 (2008) 6494–6504, http://dx.doi.org/10.1016/j.biortech.2007.11.036.

[108] C. Sambusiti, M. Bellucci, A. Zabaniotou, L. Beneduce, F. Monlau, Algae as promising feedstocks for fermentative biohydrogen production according to a biorefinery approach: a comprehensive review, Renew. Sust. Energ. Rev. 44 (2015) 20–36, http://dx.doi.org/10.1016/j.rser.2014.12.013.

[109] P. Schiener, K.D. Black, M.S. Stanley, D.H. Green, The seasonal variation in the chemical composition of the kelp species Laminaria digitata, Laminaria hyperborea, Saccharina latissima and *Alaria esculenta*, J. Appl. Phycol. 27 (2014) 363–373, http://dx.doi.org/10.1007/s10811-014-0327-1.

[110] N. Schultz-Jensen, A. Thygesen, F. Leipold, S.T. Thomsen, C. Roslander, H. Lilholt, A.B. Bjerre, Pretreatment of the macroalgae *Chaetomorpha linum* for the production of bioethanol — comparison of five pretreatment technologies, Bioresour. Technol. 140 (2013) 36–42, http://dx.doi.org/10.1016/j.biortech.2013.04.060.

[111] C. Scullin, V. Stavila, A. Skarstad, J.D. Keasling, B.a. Simmons, S. Singh, Optimization of renewable pinene production from the conversion of macroalgae Saccharina latissima, Bioresour. Technol. 184 (2015) 415–420, http://dx.doi.org/10.1016/j.biortech.2014.09.105.

[112] J. Sheehan, T. Dunahay, J. Benemann, P. Roessler, A look back at the U.S. Department of Energy's aquatic species program — biodiesel from algae office of fuels development, Natl. Renew. Energy Lab. 328 (1998) 1–328, http://dx.doi.org/10.2172/15003040.

[113] M. Song, H. Duc Pham, J. Seon, H. Chul Woo, Marine brown algae: a conundrum answer for sustainable biofuels production, Renew. Sust. Energ. Rev. 50 (2015) 782–792, http://dx.doi.org/10.1016/j.rser.2015.05.021.

[114] D. Sornette, R. Woodard, W.-X. Zhou, The 2006–2008 oil bubble: evidence of speculation, and prediction, Phys. A 388 (2009) 1571–1576, http://dx.doi.org/10.1016/j.physa.2009.01.011.

[116] R.Y. Surampalli, T.C. Zhang, R.D. Tyagi, Special issue: algae as biofuel, Water Environ. Res. 86 (2014) 2255-2255.

[117] M. Suutari, E. Leskinen, K. Fagerstedt, J. Kuparinen, P. Kuuppo, J. Blomster, Macroalgae in biofuel production, Phycol. Res. 63 (2015) 1–18, http://dx.doi.org/10.1111/pre.12078.

[118] I.S. Tan, M.K. Lam, K.T. Lee, Hydrolysis of macroalgae using heterogeneous catalyst for bioethanol production, Carbohydr. Polym. 94 (2013) 561–566, http://dx.doi.org/10.1016/j.carbpol.2013.01.042.

[119] I.S. Tan, K.T. Lee, Solid acid catalysts pretreatment and enzymatic hydrolysis of macroalgae cellulosic residue for the production of bioethanol, Carbohydr. Polym. 124 (2015) 311–321.

[120] I.S. Tan, K.T. Lee, Enzymatic hydrolysis and fermentation of seaweed solid wastes for bioethanol production: an optimization study, Energy 78 (2014) 53–62, http://dx.doi.org/10.1016/j.energy.2014.04.080.

[121] N. Trivedi, V. Gupta, C.R.K. Reddy, B. Jha, Enzymatic hydrolysis and production of bioethanol from common macrophytic green alga Ulva fasciata Delile, Bioresour. Technol. 150 (2013) 106–112, http://dx.doi.org/10.1016/j.biortech.2013.09.103.

[122] N. Trivedi, C.R.K. Reddy, R. Radulovich, B. Jha, Solid state fermentation (SSF)-derived cellulase for saccharification of the green seaweed Ulva for bioethanol production, Algal Res. 9 (2015) 48–54, http://dx.doi.org/10.1016/j.algal.2015.02.025.

[123] M. Troell, C. Halling, A. Nilsson, Integrated marine cultivation of Gracilaria chilensis (Gracilariales, Rhodophyta) and salmon cages for reduced environmental impact and increased economic, Aquaculture (1997).

[124] H. van der Wal, B.L.H.M. Sperber, B. Houweling-Tan, R.R.C. Bakker, W. Brandenburg, A.M. López-Contreras, Production of acetone, butanol, and ethanol from biomass of the green seaweed Ulva lactuca, Bioresour. Technol. 128 (2013) 431–437, http://dx.doi.org/10.1016/j.biortech.2012.10.094.

[125] J.W. van Hal, W.J.J.J.J. Huijgen, A.M.M. López-Contreras, Opportunities and challenges for seaweed in the biobased economy, Trends Biotechnol. 32 (2014) 231–233, http://dx.doi.org/10.1016/j.tibtech.2014.02.007.

[126] D.R. Vardon, B.K. Sharma, G.V. Blazina, K. Rajagopalan, T.J. Strathmann, Thermochemical conversion of raw and defatted algal biomass via hydrothermal liquefaction and slow pyrolysis, Bioresour. Technol. 109 (2012) 178–187, http://dx.doi.org/10.1016/j.biortech.2012.01.008.

[127] X. Wang, X. Liu, G. Wang, Two-stage hydrolysis of invasive algal feedstock for ethanol FermentationF, J. Integr. Plant Biol. 53 (2011) 246–252, http://dx.doi.org/10.1111/j.1744-7909.2010.01024.x.

[128] A.J. Wargacki, E. Leonard, M.N. Win, D.D. Regitsky, C.N.S. Santos, P.B. Kim, S.R. Cooper, R.M. Raisner, A. Herman, A.B. Sivitz, A. Lakshmanaswamy, Y. Kashiyama, D. Baker, Y. Yoshikuni, An engineered microbial platform for direct biofuel production from brown macroalgae, Science 335 (2012) 308–313, http://dx.doi.org/10.1126/science.1214547 (80-.).
[129] N. Wei, J. Quarterman, Y.-S.S. Jin, Marine macroalgae: an untapped resource for producing fuels and chemicals, Trends Biotechnol. 31 (2013) 70–77, http://dx.doi.org/10.1016/j.tibtech.2012.10.009.
[130] T. Wichard, Exploring bacteria-induced growth and morphogenesis in the green macroalga order Ulvales (Chlorophyta), Front. Plant Sci. 6 (2015) 86, http://dx.doi.org/10.3389/fpls.2015.00086.
[131] T.Y. Wong, L.A. Preston, N.L. Schiller, ALGINATE LYASE: review of major sources and enzyme characteristics, structure–function analysis, biological roles, and applications, Annu. Rev. Microbiol. 54 (2000) 289–340, http://dx.doi.org/10.1146/annurev.micro.54.1.289.
[132] Q. Xiang, Y.Y. Lee, P.O. Pettersson, R.W. Torget, Heterogeneous aspects of acid hydrolysis of α-cellulose, Appl. Biochem. Biotechnol. 105–108 (2003) 505–514.
[133] X. Xu, J.Y. Kim, H.U. Cho, Bioconversion of volatile fatty acids from macroalgae fermentation into microbial lipids by oleaginous yeast, 264 (2015) 735–743.
[134] M. Yanagisawa, S. Kawai, K. Murata, Strategies for the production of high concentrations of bioethanol from seaweeds: production of high concentrations of bioethanol from seaweeds, Bioengineered 4 (2013) 224–235, http://dx.doi.org/10.4161/bioe.23396.
[135] M. Yanagisawa, K. Nakamura, O. Ariga, K. Nakasaki, Production of high concentrations of bioethanol from seaweeds that contain easily hydrolyzable polysaccharides, Process Biochem. (2011).
[136] J.H. Yeon, S.E. Lee, W.Y. Choi, D.H. Kang, H.Y. Lee, K.H. Jung, Repeated-batch operation of surface-aerated fermentor for bioethanol production from the hydrolysate of seaweed Sargassum sagamianum, J. Microbiol. Biotechnol. 21 (2011) 323–331, http://dx.doi.org/10.4014/jmb.1010.10057.
[137] M. Yoon, J.I. Choi, J.W. Lee, D.H. Park, Improvement of saccharification process for bioethanol production from Undaria sp. by gamma irradiation, Radiat. Phys. Chem. 81 (2012) 999–1002, http://dx.doi.org/10.1016/j.radphyschem.2011.11.035.
[138] E.J. Yun, S. Lee, H.T. Kim, J.G. Pelton, S. Kim, H.-J. Ko, I.-G. Choi, K.H. Kim, The novel catabolic pathway of 3,6-anhydro-L-galactose, the main component of red macroalgae, in a marine bacterium, Environ. Microbiol. 17 (2015) 1677–1688, http://dx.doi.org/10.1111/1462-2920.12607.
[139] H. Zhao, J. Kwak, Z. Conradzhang, H. Brown, B. Arey, J. Holladay, Studying cellulose fiber structure by SEM, XRD, NMR and acid hydrolysis, Carbohydr. Polym. 68 (2007) 235–241, http://dx.doi.org/10.1016/j.carbpol.2006.12.013.
[140] J.R. Ziolkowska, L. Simon, Recent developments and prospects for algae-based fuels in the US, Renew. Sust. Energ. Rev. 29 (2014) 847–853, http://dx.doi.org/10.1016/j.rser.2013.09.021.