

Developments in seaweed biorefinery research: A comprehensive review

Ravi S. Baghel*

Biological Oceanography Division,
CSIR-National Institute of Oceanography,
Dona Paula, Goa, India-403004

*Corresponding author

Email: rsbaghel@nio.org; ravisingh501@gmail.com

Phone: +91 8322450295, Fax: +91 8322450606

Abstract

The seaweed biorefinery is the analog of a petroleum refinery to produce a wide variety of chemicals and fuels using the technological invention from seaweed biomass in a sustainable manner. It is expected to be a game-changer in marine bio-economy developments. During the last decade, it has emerged as one of the most focused area in seaweed research and development. This comprehensive review describes the origin of the seaweed biorefinery concept and developments to date. The various integrated biorefinery approaches are presented with the key process developed for valorizing green, red, and brown algal biomass along with the prepared bio-products. The advantages of the biorefining process, such as the value addition of biomass, environmental benefits, and sustainability of fuel from seaweed biomass, are highlighted in the present article. The role of integrated biorefinery in the growth of the marine bio-economy is also described. Further, major challenges for the commercial implementation and possible solutions are discussed. Finally, a multistage cascade bioprocessing model is proposed for fresh seaweed biomass valorization at a commercial scale.

Keywords: Bio-economy, Integrated biorefinery, Bioproducts, Seaweed, Sustainability, Environment

1. Introduction

The global demand for food, feed, chemicals, and energy increases along with the world population. Now the world is looking toward exploring the ocean's potential to fulfill these requirements, as land resources cannot be explored to an extent. Simultaneously, seaweeds (macroalgae) are gaining significant attention as they pose unique characteristics like worldwide occurrence, huge availability, and high production rate using advanced cultivation technologies. Moreover, seaweed farming does not require fertile land as it grows in the ocean. Agricultural inputs such as fertilizers, pesticides, and irrigation are also not needed compared to traditional crops [1]. From prehistoric times, certain seaweeds have been utilized in many countries, including Costa Rica, Japan, China, and Egypt, as a human diet [2]. The red seaweed *Porphyra*, commonly known as Nori, is rich in proteins and vitamins and thus used to prepare sushi, especially in Japan, South Korea, the United States, and the United Kingdom [3,4]. For many years, seaweed biomass has been mainly used for the industrial production of hydrocolloids such as agar, agarose, carrageenan, and alginate [5]. Based on sourced hydrocolloids, seaweeds are divided into three major groups. Seaweeds that contain agar are known as agarophytes; carrageenan-yielding seaweeds are called carrageenophytes, while seaweed species used to extract alginate are grouped as alginophytes [6]. In 2015, about 120,000 tons of hydrocolloids were produced globally [7]. After hydrocolloids, seaweed biostimulants are majorly used in the agricultural sector as a fertilizer and soil conditioner. The vast diversity of algal taxa and its rich chemical composition provides ample opportunities for this valuable resource's bio-prospection. Seaweed harvesting was estimated at 35.8 million tons' fresh weight (FW) in 2019 [8]. Farmed seaweeds represented 97.2%, and the remaining part came from the wild collection [8]. Further, a special session was organized in the 75th UN assembly to release the seaweed manifesto for boosting global seaweed production and its utilization for a sustainable future.

In the last decade, seaweeds have also been widely studied for diverse applications such as the production of fuels, proteins, lipids, cellulose, various chemicals [9,10], and electricity [11]. Other than these, green materials from plants and seaweeds are reported to have innovative applications. For example, plant and seaweed extracts showed the potential to act as metal corrosion inhibitors due to the presence of heteroatoms and/or pi electrons. Corrosion is the biggest threat to metals as it damages the metals and their chemical and mechanical properties; thus, synthetic corrosion inhibitors are used to protect metals from corrosion as they are known to have good corrosion inhibition efficiencies [12]. However, at the same time, they are not considered sustainable and environmentally friendly. So attention turned towards the search for plant-based green materials as corrosion inhibitors. In recent years, much research has been published on biomaterials from different plants [12-16] and extracts

from seaweeds [17-20] used as metal corrosion inhibitors in different environmental conditions. Graphene oxide nanosheets [21] and polymer-based aerogels preparation [22] are the applied applications of seaweed-based biomaterials. Fuel and chemical production other than hydrocolloids from seaweed biomass remains challenging, considering economic feasibility and sustainability. The scope for seaweed cultivation expansion and the biomass potential for producing food, feed, chemicals, and fuels turn attention to seaweed integrated biorefinery research [23,24]. The biorefinery is analogous to a petroleum refinery [25], wherein seaweed biomass is converted into a variety of value-added commodity chemicals and fuels using sustainable approaches [26]. Currently, seaweed integrated biorefinery (macroalgal biorefinery) is an interesting and important area of research.

The chemical engineering components such as chemical, mechanical, biological, biochemical, thermal, and microbial treatments, either alone or in combination, have developed an opportunity for sustainable and economical conversion of biomass into value-added products and bioenergy. The integrated biorefinery approach has the potential to solve economic and environmental concerns by producing multiple co-products and minimizing the effluent discharge. With innovations in chemical engineering, several integrated biorefining processes for red [10,29], and green [24,30] seaweeds have developed. With this background, this review article comprises the various aspects of seaweed integrated biorefinery to understand the present scenario and to give a better insight for future research and developments. The origin of the seaweed integrated biorefinery concept and developments to date are presented. The various integrated biorefinery approaches are explained using key processes for red, brown, and green seaweeds. Biorefining processes are compared with traditional processes regarding products produced, biomass conversion rates, material efficiencies, and biomass value-addition. The E factor, the valuable measure of the environmental acceptability of chemical processes, was also calculated and compared with the traditional process. The various strategies used for economic bioethanol production from seaweed biomass are described. Further challenges for commercial implementation of these processes and possible solutions are discussed. At last, based on the findings, a multistage cascade bioprocessing model is proposed for the sustainable utilization of fresh seaweed biomass.

2. Seaweed composition and seaweed based products

The data on the proximate composition of any organism provides insights into its possible utilization. Seaweed, being aquatic organisms, contain huge amounts of water in their bodies ranging from 63-96%, while the rest are made up of organic matter and minerals. The water content in seaweeds widely varies with species and depends on the thallus architecture (Table 1). The dry mass of seaweeds

is composed of total lipid 0.6-4%, protein 3-50%, total carbohydrate 22-62%, and ash 12-46% on dry weight (DW) (Table 1). The chemical compositions of seaweeds also vary from one group to another.

Table 1 Proximate composition of different group of seaweeds

Seaweed Type	Water (% FW)	Lipid (% DW)	Protein (% DW)	Carbohydrate (% DW)	Ash (%DW)
Green	74-87 [31]	1.3-4.0 [33,34]	7-33 [36]	33-58 [35]	12-37 [34,38]
Red	70-96 [31,32]	0.6-2.8 [34,35]	5-50 [36,37]	31-62 [35]	12-46 [34,38]
Brown	63-91 [31,32]	1-2.5 [35]	3-22 [35]	22-43 [10,35]	27-39 [39]

Due to the rich chemical composition and huge component diversity among red, green, and brown seaweeds, they produce several biochemicals with commercial applications in various sectors such as food, feed, textile, nutraceutical, and pharmaceuticals (Fig. 1). For example, the seaweed carbohydrates differ much from those of terrestrial plants [40]. Cellulose is present in all seaweeds, and the rest of the carbohydrates vary with groups. The carbohydrate in green seaweeds is composed of various polysaccharides such as ulvan, starch, mannan, and monosaccharides like glucose, mannose, rhamnose, xylose, galactose, uronic acid, and glucuronic acid. The red seaweed carbohydrate consists of polysaccharides of agar/carrageenan, cellulose, and monosaccharides containing glucose and galactose. Brown seaweed contained polysaccharides such as laminarin, alginate, mannitol, fucoidan, cellulose, and various monosaccharides such as glucose, galactose, xylose, uronic acid, glucuronic acid, fucose, mannuronic acid, and guluronic acid. The high level of variations observed in the chemical composition of different seaweeds is owing to their geographical distribution, environmental factors including nutrients, and finally on, genetic material [41-43]. Seaweeds are rich sources of natural pigments such as chlorophyll a and b (green seaweeds), phycobiliproteins R-phycoerythrin and R-Phycocyanin (red seaweeds), and xanthophylls (brown seaweeds). Apart from this, seaweeds are also known to have vitamins and polyunsaturated fatty acids (PUFAs). The wide range of chemical component diversity makes them promising biomass for producing food, feed, chemicals, and bio-energy using integrated biorefinery approaches.

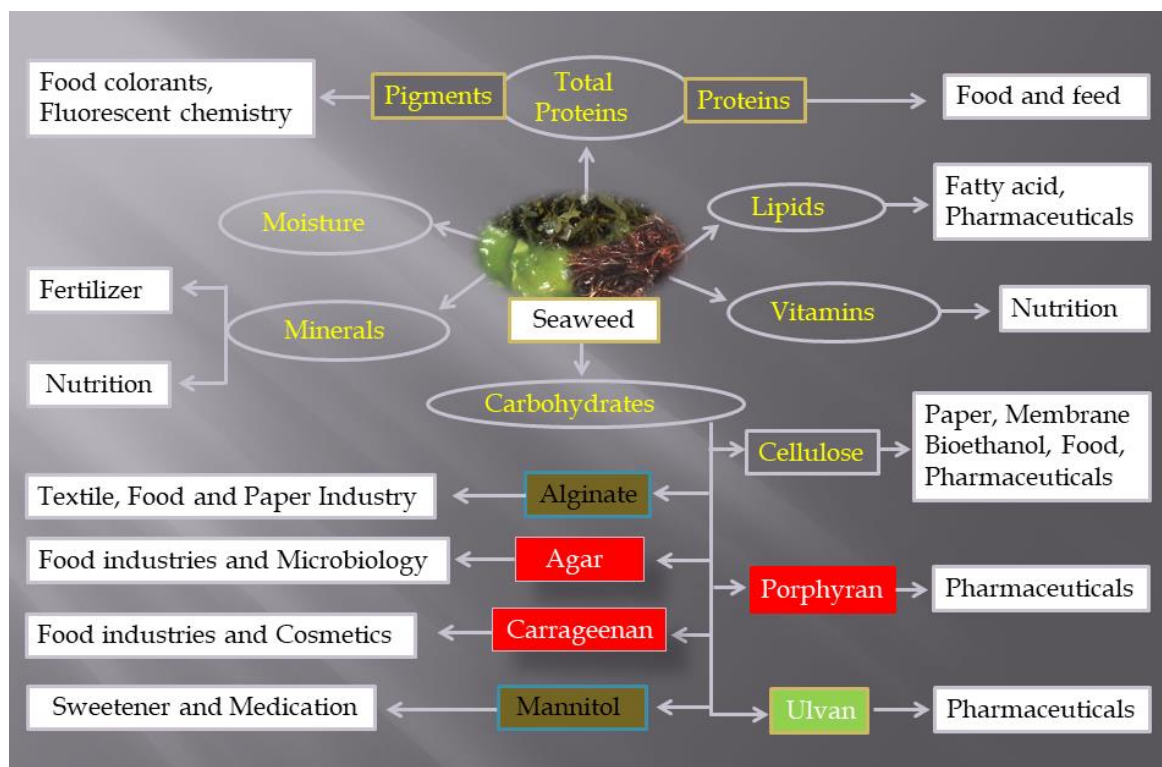


Figure 1 Seaweed-based natural products and their major applications

3. Origin of seaweed integrated biorefinery concept

In the late 1960s, Dr. Howard A. Wilcox proposed the seaweed biomass (Kelp) potential for bioenergy production. Due to the oil crisis in the 1970s, the U.S. Navy was working to find alternative fuel sources to fulfill the demands. During the late 1970s and 1980s, extensive research was carried out in the United States to produce gas using anaerobic digestion of seaweed biomass [44-46]. Similarly, during the 1980s in Europe, research was done on biogas production from *Ulva* and *Gracilaria* biomass [47-49]. Several studies explored the potential of green seaweeds *Ulva*, *Cladophora*, and *Chaetomorpha*, brown seaweeds *Macrocystis pyrifera*, *Sargassum*, *Laminaria*, and *Ascophyllum*, and red seaweed *Gracilaria* for the production of the methane with yields ranged from 0.021 to 0.480 m³ kg⁻¹ VSa in different temperature and hydraulic retention time [50]. Later, Horn et al. [51] produced ethanol from brown seaweed *Laminaria hyperborean*. Subsequently, extensive research was carried out to explore the potential of several seaweed species for bioethanol production. Various treatments, such as acidic hydrolysis, enzymatic hydrolysis, and thermal liquefaction, either alone or in combination, were used to produce reducing sugar and fermented to produce ethanol [52]. However, most research focused only on preparing single products, bioethanol or biogas from seaweed biomass. Thus bioenergy production remains uneconomical and non-sustainable from seaweed biomass compared to other traditional biofuel sources. Further, increasing global demands for food,

feed, and commodity chemicals and the need for gainful algal biomass processing in an environment-friendly manner have developed toward integrated seaweed biorefinery research [27]. In 2005, an integrated process for producing liquid fertilizer and carrageenan from fresh seaweed *Kappaphycus alvarezii* was developed [53]. Subsequently, several reports have been published by the energy research center for the Netherlands (ECN), indicating the possibilities for producing value-added chemicals and fuels from seaweed biomass in biorefinery approaches [54-57]. It was also assumed that the production of chemicals and energy in the integrated biorefinery approach enhances economic feasibility and reduces the environmental impacts of the process [54]. Further, various research reports on the chemical compositions of seaweed biomass strengthened the possibilities of their utilization in a biorefinery manner. Afterward, several research articles were published describing the process for the recovery/production of several products from red, green, and brown seaweed biomass.

3. Developments in seaweed integrated biorefinery research

The seaweed integrated biorefinery research got momentum in the early last decade and developed a significant attraction to researchers in the mid of decade and continued further (Fig. 2). The member of all three groups, green, red, and brown seaweed, has been widely explored for their potential for producing chemical and fuels around the globe. Fifty-nine papers covering 59 different seaweed species have been published, reporting the recovery of a minimum of two products and a maximum of 7 products using integrated biorefining approaches from 2012-2022 (Fig. 3). A total of 255 products were developed with an average of 4.32 products per species, much higher than traditional processing with an expected outcome of 1 product per species. At the same time, 53 different products were accounted excluding the repeating products (the same product from different species) (Fig. 3). Overall, a maximum of 24 algal species were investigated for the production of ethanol, 21 for hydrocolloids, 20 for biogas, 19 for biochar/hydrochar, 14 for bio-crude oil, and 10 for natural colorants along with other co-products (Fig. 3). In red seaweeds, 18 research papers covering the 14 seaweed species extracted a maximum number of 7 products from a species (Table 2). A 28 research articles explored the potential of 27 brown seaweed species for a maximum of 5-6 products recovery (Table 3). Among the green seaweeds, 17 papers have reported exploring 15 species to recover a minimum of two products and a maximum of 6 products from a species (Table 4).

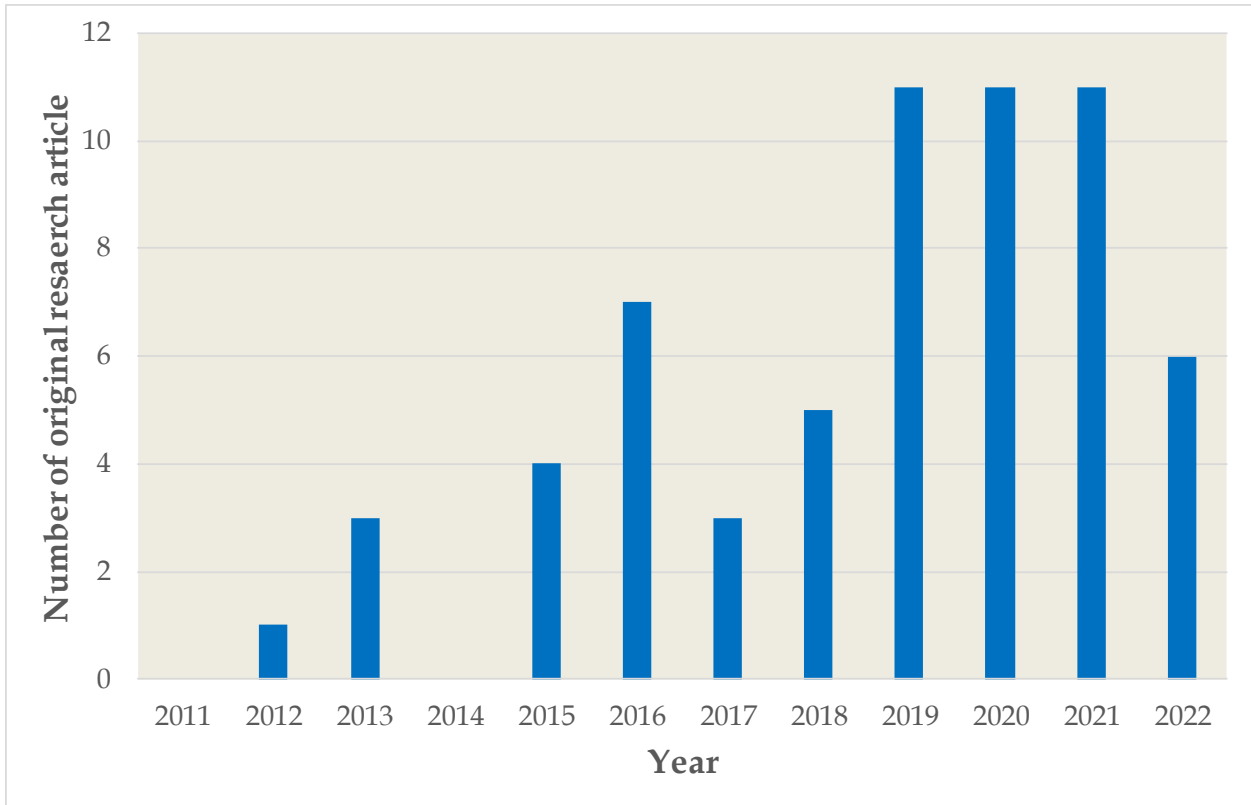


Figure 2 Year-wise original research article published on seaweed biorefinery during 2011-2022

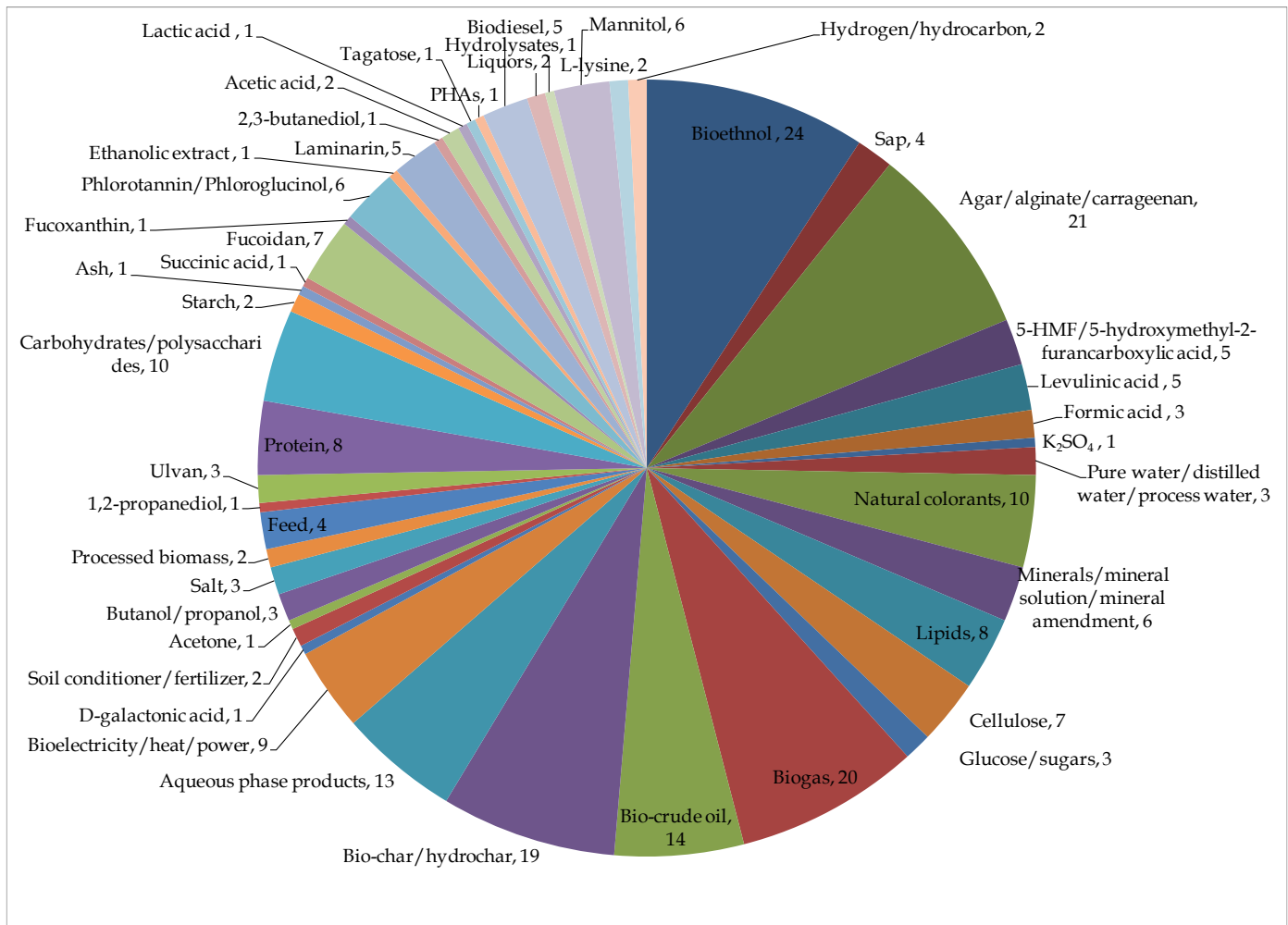


Figure 3 Distribution of the products prepared from different seaweed species using integrated biorefining approaches

Table 2 Red seaweeds based integrated biorefinery processes reported (2011-2022), techniques/treatments used, and various developed products

S. No.	Species	Techniques/treatments	Products	Ref.
1	<i>Kappaphycus alvarezii</i>	Mechanical treatment, acidic hydrolysis and fermentation	Sap and bioethanol	[58]
2	<i>Gracilaria verrucosa</i>	Alkali extraction, acidic hydrolysis and fermentation	Agar and bioethanol	[59]
3	<i>Kappaphycus alvarezii</i>	Mechanical treatment, acid catalysis, and acidic treatment	5-hydroxymethyl furfural (HMF), levulinic acid (LA), formic acid (FA), K ₂ SO ₄ , and pure water	[60]
4	<i>Gelidiella acerosa</i> , <i>Gracilaria dura</i> , <i>Gelidium pusillum</i>	Mechanical treatment, aqueous extraction, organic solvent extraction, alkali and acid treatment	R-phycoerythrin, R-phyococyanin mineral solution, lipids, agar, and cellulose/bioethanol	[27]
5	<i>Gracilaria corticata</i>	Mechanical treatment, aqueous extraction, organic solvent extraction, enzymatic hydrolysis, and fermentation	R-phycoerythrin, R-phyococyanin, mineral solution, lipids, agar, bioethanol, and soil conditioner	[61]
6	<i>Kappaphycus alvarezii</i>	Alkali extraction, enzymatic hydrolysis, and fermentation	Carrageenan and glucose	[62]
7	<i>Chondrus crispus</i> , <i>Solieria chordalis</i>	Hydrothermal liquefaction	Bio-crude oil, bio-char, gas, and aqueous phase products	[28]
8	<i>Solieria filiformis</i>	Enzymatic hydrolysis, organic extraction, aqueous extraction	Water-soluble extract, lipid, and carrageenan	[63]

9	<i>Gracilaria lemaneiformis</i>	Acidic and hydrothermal treatment	Levulinic acid and algae hydrochar	[64]
10	<i>Kappaphycus alvarezii</i>	Acid hydrolysis, enzymatic hydrolysis, and fermentation	Carrageenan and biethanol	[65]
11	<i>Hydropuntia dentata</i>	Acidic hydrolysis, simultaneous saccharification and fermentation (SSF), microbial fuel cells (MFCs)	Bioethanol and bioelectricity	[66]
12	<i>Gracilaria tenuistipitata</i>	Mechanical treatment, aqueous extraction, and alkali extraction	R-phycoerythrin and agar	[67]
13	<i>Gelidium amansii</i>	Acidic hydrolysis and biocatalysis	D-galactonic acid and 5-hydroxymethyl-2-furancarboxylic acid	[68]
14	<i>Gracilaria manilaensis</i> , <i>Kappaphycus alvarezii</i>	Alkali treatment, enzymatic hydrolysis, and fermentation	Agar, carrageenan, and bioethanol	[69]
15	<i>Gelidium sesquipedale</i>	Autohydrolysis and enzymatic hydrolysis	Agar, liquor, and glucose	[70]
16	<i>Gelidium sesquipedale</i>	Autohydrolysis, acid hydrolysis, and isomerization	Agar and tagatose	[71]
17	<i>Gracilaria spp.</i>	Acid hydrolysis, fermentation, and anaerobic digestion	Bioethanol and biogas	[72]
18	<i>Gracilaria gracilis</i>	Buffer extraction, microwave assisted non-catalysed (water only), acid catalysed (H ₂ SO ₄), and metal cation catalysed (PbII and AlIII) extarction	Pigments, acetic acid, formic acid, lactic acid levulinic acid, and 5-hydroxymethylfurfura l (5-HMF)	[73]

Table 3 Brown seaweeds based integrated biorefinery processes reported (2011-2022), techniques/treatments used, and various developed products

S. No.	Species	Techniques/treatments	Products	Ref.
1	<i>Laminaria digitata</i>	Enzymatic hydrolysis and fermentation	Succinic acid, methane, and feed	[74]
2	<i>Ascophyllum nodosum</i>	Thermal treatment, alcoholic extraction, acid, and alkali treatments	Fucoidan, alginate, sugars, and biochar	[75]
3	<i>Sargassum muticum</i>	Mechanical treatment, alcoholic extraction, and autohydrolysis	Fucoanthin, fucoidan, phlorotannin, salt, ethanol extracts, and saccharidic	[76]
4	<i>Laminaria japonica</i>	Fermentation, esterification, hydrogenation	Ethanol, propanol, butanol	[77]
5	<i>Ascophyllum nodosum</i> , <i>Fucus ceranoides</i> , <i>Fucus vesiculosus</i> , <i>Himanthalia elongata</i> , <i>Laminaria digitata</i> , <i>Laminaria hyperborea</i> , <i>Pelvetia canaliculata</i> , <i>Sargassum muticum</i>	Hydrothermal liquefaction (HTL)	Bio-crude oil, bio-char, gas, and aqueous phase products	[28]
6	<i>Saccharina japonica</i>	Pretreatment, enzymatic hydrolysis, and fermentation	Bioethanol and protein	[78]
7	<i>Fucus serratus</i> , <i>Fucus vesiculosus</i> , <i>Ascophyllum nodosum</i> , <i>Laminaria digitata</i> , <i>Laminaria saccharina</i>	Ethanol extraction, alkali extraction, and fermentation	Biogas and bioproducts	[79]
8	<i>Sargassum muticum</i>	Non isothermal autohydrolysis	Alginate, fucoidan/phloroglucinol	[80]
9	<i>Durvillaea potatorum</i>	Acid treatment, alkali extraction	Alginate, fucoidan, and laminarin	[81]
10	Kelp	Genetically engineered microbe, hydrolysis, and fermentation	Bioethanol, 2,3-butanediol, and lycopene	[82]

11	<i>Sargassum vulgare</i>	Acidic hydrolysis, simultaneous saccharification and fermentation (SSF), microbial fuel cells (MFCs)	Bioethanol and bioelectricity	[66]
12	<i>Saccharina japonica</i>	Poly-generation pyrolysis	Hydrocarbon fuel, heat, and power	[83]
13	<i>Sargassum tenerrimum</i>	Mechanical treatment, alkali treatment, and acidic treatment	Sap, alginate, protein, and cellulose	[10]
14	<i>Carpophyllum flexuosum</i> , <i>Carpophyllum plumosum</i> , <i>Ecklonia radiata</i> , <i>Undaria pinnatifida</i>	Ethanolic extraction, aqueous and alkali extraction	Pigments, manitol, phlorotannins, alginate, carbohydrate	[84]
15	<i>Saccharina japonica</i>	Hydrothermal liquefaction	Heat, hydrogen, and power	[85]
16	<i>Sargassum sp.</i>	Hydrothermal pretreatment (HTP) and anaerobic digestion (AD)	Biogas, fertilizer	[86]
17	<i>Nizimuddinina zanardini</i>	Chemical treatments, hydrolysis, and fermentation	Mannitol, protein, minerals, alginate, bioethanol, and electricity	[87]
18	<i>Durvillaea Antarctica</i> , <i>Laminaria digitata</i>	Mechanical treatment, chemical treatments, enzymatic hydrolysis, and fermentation	Sodium alginate and L-lysine	[88]
19	<i>Sargassum muticum</i>	Mechanical treatment, autohydrolysis, chemical treatments, and anaerobic digestion	Sap, calcium alginate, biogas, and mineral amendment	[89]
20	<i>Sargassum muticum</i>	Microwave hydrothermal treatment, acid hydrolysis and fermentation	Liquor and bioethanol	[90]
21	<i>Laminaria digitata</i> , <i>Fucus vesiculosus</i> , <i>Saccharina latissima</i>	Water extraction, filtration, and acid extraction	Laminarin, Fucoidan, and feed supplement	[91]

22	<i>Sargassum spp.</i>	Acid hydrolysis, fermentation, and anaerobic digestion	Bioethanol and biogas	[72]
23	<i>Sargassum spp.</i>	Water extraction, ethanoic precipitation, solvent extraction, and acid-catalyzed transesterification	Polysaccharide and biodiesel	[92]
24	<i>Ascophyllum nodosum</i>	Ethanol extraction, acid extraction, microwave assisted non-catalysed (water only), acid catalysed (H ₂ SO ₄), and metal cation catalysed (PbII and AlIII) extraction	Laminarin, mannitol, alginate, acetic acid, formic acid, and levulinic acid	[73]
25	<i>Undaria pinnatifida waste</i>	Microwave-assisted hot water extraction	Proteins and fucoidan	[93]
26	<i>Laminaria digitata</i>	Microwave-assisted hydrothermal carbonization	Hydrochar, levulinic acid, and 5-hydroxymethylfurfural (5-HMF)	[29]
27	<i>Padina tetrastromatica</i>	Hydrothermal liquefaction	Bio-oil and biochar	[94]
28	<i>Padina tetrastromatica, Sargassum swartzii</i>	Acid and enzyme hydrolysis, solvent extraction, and transesterification	Bioethanol and biodiesel	[95]

Table 4 Green seaweeds integrated biorefinery processes reported (2011-2022), techniques/ treatments used and various developed products

S. No.	Species	Techniques/ treatments	Products	Ref.
1	<i>Ulva lactuca</i>	Pre-treatment, enzymatic saccharification, and fermentation	Acetone, butanol, and ethanol	[96]
2	<i>Chaetomorpha linum</i>	Thermochemical hydrolysis, enzymatic hydrolysis, and fermentation	Bioethanol and biogas	[97]
3	<i>Ulva ohnoi</i> , <i>Ulva tepida</i>	Aqueous washing and drying	Salt and processed biomass	[98]
4	<i>Ulva lactuca</i>	Thermal and enzymatic hydrolysis, and fermentation	Animal feed, acetone, butanol, bioethanol and 1,2-propanediol	[99]
5	<i>Ulva fasciata</i>	Mechanical grinding, thermal and chemical extraction, and fermentation	Mineral rich liquid extract (MRLE), lipid, ulvan and cellulose/bioethanol	[24]
6	<i>Ulva ohnoi</i>	Aqueous, thermal, and chemical extraction	Salt, ulvan and protein enriched residual mass	[100]
7	<i>Ulva lactuca</i>	Mechanical pressing and crushing, heat treatment, organic solvent extraction, alkali extraction, and chemical extraction	Sap, lipid, ulvan, protein, and cellulose	[101]

8	<i>Ulva intestinalis</i> , <i>Ulva lactuca</i> , <i>Rhizoclonium riparium</i>	Hydrothermal liquefaction (HTL)	Bio-crude oil, bio-char, bio-gas, and aqueous phase products	[28]
9	<i>Ulva lactuca</i>	Osmotic shock, enzymatic hydrolysis, pulsed electric field, and high shear homogenization	Proteins and carbohydrates	[102]
10	<i>Ulva lactuca</i>	Aqueous, thermal, chemical extraction, and anaerobic fermentation	Sap, ulvan, protein, and methane	[103]
11	<i>Ulva ohnoi</i>	PEF treatment coupled with mechanical press	Starch, proteins, and ash	[104]
12	<i>Ulva fasciata</i>	Acidic hydrolysis, simultaneous saccharification and fermentation (SSF), and microbial fuel cells (MFCs)	Bioethanol and bioelectricity	[66]
13	<i>Ulva ohnoi</i>	Homogenization, solvent extraction, acid extraction, and alkali extraction	Salt, starch, lipid, ulvan, protein, and cellulose	[105]
14	<i>Ulva</i> sp.	Subcritical water hydrolysis	Protein, 5-hydroxymethylfurfural (5-HMF), hydrochar, and bioethanol	[106]
15	Sea lettuce	Hydrothermal carbonization	Hydrochar and process water	[107]
16	<i>Ulva</i> sp.	Hydrothermal processing	Monosaccharides, polyhydroxyalkanoates, and hydrochar	[108]

17	<i>Ulva sp.</i>	Hydrothermal processing, fermentation	and	Protein, ethanol, water, and electricity	hydrochar, distilled	[109]
18	<i>Ulva spp.</i>	Acid fermentation, anaerobic digestion	hydrolysis, and	Bioethanol and biogas		[72]
19	<i>Ulva spp.</i> <i>Cladophora spp.</i>	Water extraction, ethanoic solvent extraction, acid-catalyzed transesterification	precipitation, and	Polysaccharide and biodiesel		[92]
20	<i>Ulva lactuca</i>	Homogenization, solvent extraction, acid extraction, and extraction	acid and alkali	Starch, lipid, and cellulose	ulvan,	[30]
21	<i>Ulva lactuca</i>	Soxhlet accelerated extraction, hydrothermal treatment, acid hydrolysis	extraction, solvent	Liquors and hydrolysates		[110]

4. Seaweed biorefinery approaches and Key processes

Two types of biorefinery approaches have been developed for seaweed biomass processing: primary and secondary. The primary level biorefining approach is used to segregate the biomass components in their native state or a little bit modified, such as extraction of lipids, proteins, cellulose, minerals, carbohydrates, agar, alginate, and carrageenan. This type of approach mostly uses mechanical, chemical, and water treatments. The second level of biorefining approaches is used to convert whole algal biomass directly into final or end products like the production of bioethanol, biogas, bio-butane, bio-oil, bio-char, acids, etc. This type of approach use treatments like hydrolysis, fermentation, anaerobic digestion, pyrolysis, and hydrothermal liquefaction. The primary-level biorefinery approaches are advantageous over the secondary-level approach. They provide high-value products with a higher rate of biomass utilization, and extracted products have further opportunities for modification, derivatization, and use as per requirements. The key process, along with the products developed for red, brown, and green seaweeds, is described in detail under subheadings.

4.1. Biorefining of red seaweeds

The red seaweed species belonging to the carrageenophytes and agarophytes have been widely studied to produce various products using integrated biorefinery processes (Table 2). The first patented integrated process was the extraction of sap and carrageenan from *K. alvarezii* [53]. The fresh *K. alvarezii* biomass was crushed using grinder-cum-mixer to prepare a slurry. The slurry was subjected to filtration using a muslin cloth/filter press to separate the sap (rich in trace elements, plant growth regulators, soluble protein, and carbohydrates) and residual granules. The prepared sap had the potential as liquid fertilizer, and granular mass was used to prepare refined carrageenan using $\text{Ca}(\text{OH})_2$ treatment at 107 °C for 1 h followed by alcohol precipitation and filtering and drying. The processing of 1 ton of fresh biomass in an integrated manner was computed to yield 750 L of sap and 30 kg of refined carrageenan. The developed process substantially enhanced biomass value and minimized the space and time needed for the drying of biomass required in conventional carrageenan extraction methods. Khambhaty et al. [58] reported an integrated process for producing ethanol and seaweed sap from fresh *K. alvarezii* biomass. The sap was expelled from biomass in the first step, and residual biomass was saccharified using 0.9 N H_2SO_4 at 100 °C. A 30% (w/w) reducing sugar yield was obtained in a 16 kg granules processing batch, and an 80% conversion efficiency of sugars to ethanol was obtained in fermentation using *Saccharomyces cerevisiae*. Further, E10 gasoline made from seaweed-based ethanol was used in a petrol vehicle test run. Based on the report, 750 liters of sap and 6.7 kg of ethanol could be produced from a ton of fresh biomass processing. Mondal et al. [60] extracted sap and granules from *K. alvarezii*. The granules were used to prepare various products such

as 5-hydroxymethyl furfural (HMF) (18%), levulinic acid (LA) (5.6%), formic acid (FA) (2%), and K_2SO_4 (27%). HMF was derived from carrageenan through a reaction with $Mg(HSO_4)_2$ acid catalyst. Reddy et al. [111] patented an advanced integral process for extracting as many as five products: liquid fertilizer, natural colorant, lipid, carrageenan, and cellulose from fresh *K. alvarezii* and *Sarconema scinaoides* biomass. In brief, fresh *K. alvarezii/S. scinaoides* biomass was homogenized in phosphate buffer using a mixer grinder. The supernatant and residual granules were separated using centrifugation. The natural colorants R-phycoerythrin (R-PE) and R-phycocyanin (R-PC) were precipitated from the supernatant using 30% ammonium sulfate. The residue obtained from the first step was then used to recover total lipid through solvents (chloroform and methanol, 1:2) extraction. The residues leftover from lipid extraction were used as raw material for carrageenan extraction. The residual material was treated with 8% KOH for 2 h at 72 °C, followed by muslin cloth filtration. The alkali-treated material was added with water, neutralized with HCl, and subjected to cooking at 80 °C for 45 min. The cooked material was homogenized and centrifuged at 7000 rpm for 3 min to separate the aqueous extract and residues. Carrageenan was precipitated from the supernatant using isopropanol, and cellulose was extracted from the residual pellet. R-PE and R-PC's yields were reported in the range of 56–242 and 40–539 $\mu\text{g gm}^{-1}$ FW, while lipid, carrageenan, and cellulose yields were 0.66–1.08, 30–36, and 2.6–3.2% on DW. Apart from this, bio-crude oil, bio-char, gas, and aqueous phase products were prepared from *Chondrus crispus* and *Solieria chordalis* using hydrothermal liquefaction [28]. The HTL was done at 350 °C with a heating rate of $\sim 30 \text{ K min}^{-1}$ in a reactor. The yields of bio-crude, gas, aqueous phase products, and bio-char ranged from 6–8, 13–14, 5–33, and 39–51% of dry biomass, respectively. The aqueous phase product contained water-soluble light organics, ammonia, and phosphates. The water-soluble extract, lipid, and carrageenan were extracted from *Solieria filiformis* cultivated sequentially in an integrated multi-trophic aquaculture (IMTA) system [63].

In the account of agarophytic seaweeds, *Gracilaria verrucosa* red seaweed biomass has been used to produce agar and bioethanol sequentially [59]. Initially, $\sim 27\text{--}33\%$ agar was extracted, and residual biomass was enzymatically hydrolyzed and fermented using *Saccharomyces cerevisiae* to get bioethanol. Briefly dried biomass was treated with 5% NaOH solution for 2 h at 80 °C, followed by water washing and neutralizing treated biomass with 1.5% H_2SO_4 . The treated biomass was boiled for 90 min with distilled water, and the filtrate obtained was used to prepare agar using freeze-thaw, followed by drying at 60 °C. The research projected that the processing of 1000 kg of dry biomass in a sequential manner could yield 38 kg of bioethanol in addition to 250 kg of agar. The high water content in seaweed biomass is a recurrent problem and one of the key bottlenecks for sustainable use

as it increases transportation and dewatering treatment costs. To counter this issue and maximize biomass utilization, Baghel et al. [27] developed an integrated process for recovering as many as five products: crude pigments, mineral solution, lipids, agar, and cellulose/ethanol from fresh agarophytic seaweed biomass. The process was tested with the three seaweed species: *Gelidiella acerosa*, *Gelidium pusillum*, and *Gracilaria dura*. The research suggests that processing a ton of agar-bearing fresh biomass could yield 0.3–0.7 kg of R-phycoerythrin (R-PE), 0.1–0.3 kg of R-phycoerythrin (R-PC), 3.1–3.6 kiloliters of the mineral solution, 1.2–4.8 kg of lipids, 28.4–94.4 kg of agar, 4.4–41.9 kg of cellulose/1.8–17.4 kg of ethanol. Later on, a process reported for the 100 gm fresh *Gracilaria corticata* biomass enables the recovery of as many as six products: phycobiliproteins ($292 \pm 7 \mu\text{g gm}^{-1}$ FW), mineral solution (318 ml), lipids (1.41%), agar (22.45%), bioethanol (2.89%), and soil conditioner (12.39%) on DW with zero solid effluent discharge [61] (Fig. 4). In brief, in the first step, aqueous extract rich in pigments and minerals was prepared from fresh *G. corticata* biomass. A concentrated pigment mixture and mineral-rich water were separated using ultra-membrane filtration (UMF). The mineral-rich water was reused to prepare an aqueous extract from two batches of fresh biomass. The dried residual mass left from the first step was used to extract lipids using the solvent chloroform-methanol (1:2 v/v). The solvents were recovered and reused. The residual mass left after lipid extraction was dried and cooked with distilled water for agar extraction. The dried residue was mixed with distilled water, cooked at 120 °C for 1.5 h, and homogenized using a grinder. The homogenized material was centrifuged to separate agar containing aqueous phase and cellulose-rich residual pulp. Agar was recovered from the aqueous phase using the freeze-thaw method. The residual pulp that remained from agar extraction was dried and enzymatically hydrolyzed to get reducing sugar. Further hydrolysates were fermented to ethanol using the yeast *Saccharomyces cerevisiae*. The residual pulp yielded 12.72% bioethanol, and the process was free from acid and alkali application.

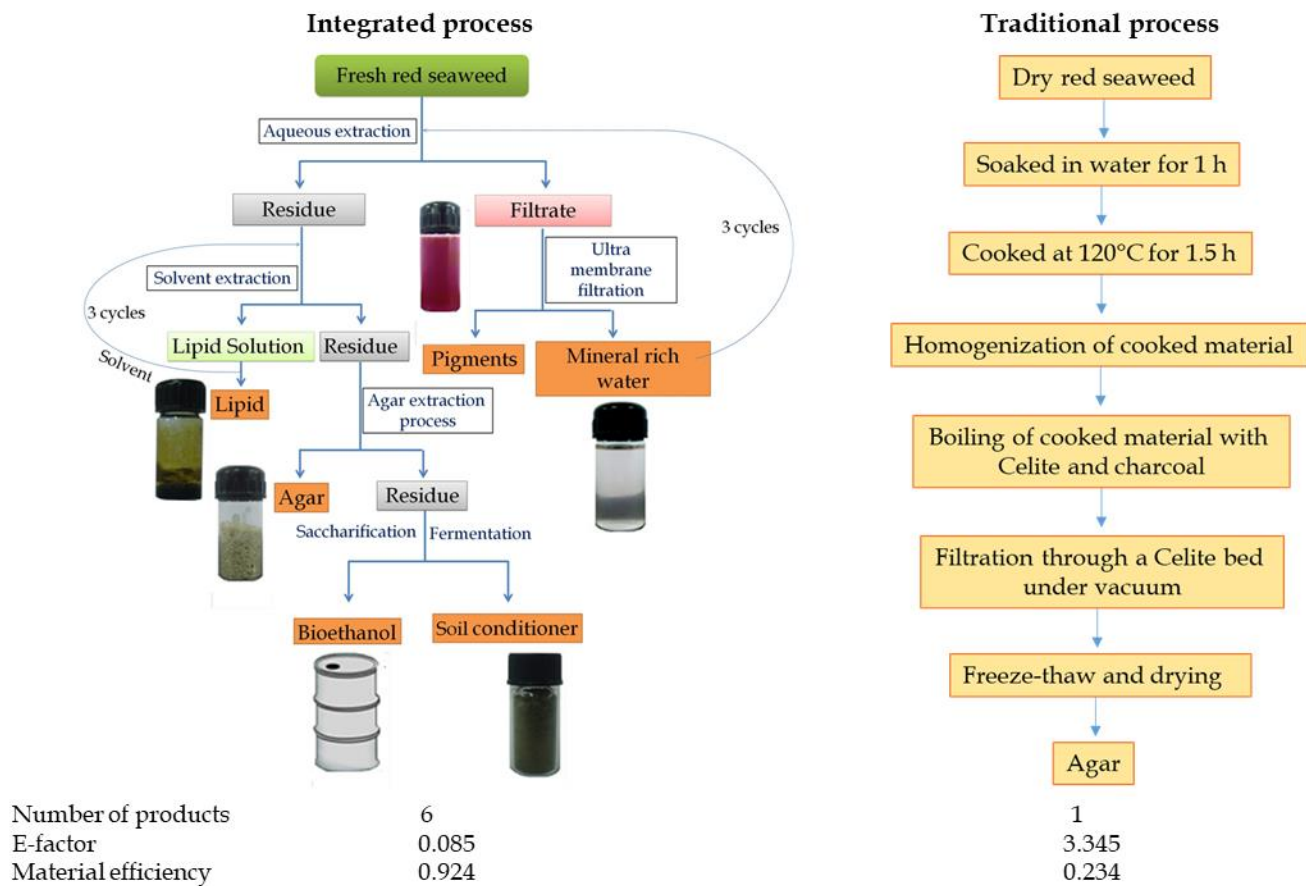


Figure 4 Comparison between integrated biorefining process and traditional agar extraction process from red seaweed. Modified and adapted from Baghel et al. [61]

Recently *Gelidium sesquipedale* biomass was valorized to produce agar, liquor, and glucose using autohydrolysis and enzymatic hydrolysis approaches [70]. Agar and tagatose from the same seaweed species using autohydrolysis, acid hydrolysis, and isomerization were also reported [71]. More recently, several products such as pigments, acetic acid, formic acid, lactic acid, levulinic acid, and 5-hydroxymethylfurfural (5-HMF) were prepared from *Gracilaria gracilis* biomass using different treatments such as buffer extraction, microwave-assisted non-catalyzed (water only), acid-catalyzed (H_2SO_4), and metal cation catalyzed (PbII and AlIII) extractions [73].

4.2. Biorefining of brown seaweeds

Brown seaweeds consist of commercially exploited genera, such as *Ascophyllum*, *Laminaria*, *Macrocystis*, *Durvillaea*, *Ecklonia*, and *Sargassum*, which were commercially exploited for alginate production. The *Laminaria* genus species are major alginate sources in temperate waters. In contrast, species belonging to the *Sargassum* genera are the primary source of alginate in India and other tropical countries. The other products reported from brown seaweeds are fucoidan, mannitol, cellulose, and

biostimulants. The brown seaweeds have been reported to form golden tide in the Gulf of Mexico [112] and Africa, Antigua, and the southern Caribbean [113], which can also be effectively utilized to produce various valuable bioproducts. Similar to red seaweed, two types of biorefining processing are used to valorize the brown seaweed biomass 1) segregation into its components and 2) conversion of biomass into the end/final products by acid/enzymatic hydrolysis/fermentation/hydrothermal treatment (Table 3). In biorefining cascade valorization, Yuan et al. [75] prepared fucoidan (14.09%), alginate (18.24%), sugars (10.87%), and biochar (21.44%) from *Ascophyllum nodosum* dry biomass with biomass to a product conversion rate of 64.6%. Similarly, *Sargassum muticum* biomass was valorized in the biorefinery concept to fractionate the carotenoid, phenolic, and fucoidan [76]. Also, *Sargassum muticum* biomass was used to prepare as many as three products: alginate, fucoidan/phloroglucinol, with 65% product recovery [80]. Zhang et al. [84] reported a sequential process for the recovery of bioproducts such as pigments (3.4-9.8%), mannitol (22.2–30.7%), phlorotannins (0.1–5.1%), other carbohydrates (12.2–18.5%), and alginates (5.2–15.5%) on DW from 4 brown seaweeds *Carpophyllum flexuosum*, *Carpophyllum plumosum*, *Ecklonia radiata*, and *Undaria pinnatifida*. The biomass to biomaterial conversion rate was between 77.7-82.1%, which includes 13.5-19.5% of seaweed residues. Baghel et al. [10] reported a biorefining process for sustainable utilization of fresh brown algal biomass (*Sargassum*) in 1 kg batch to produce sap (541.33 ± 5.50 mL), alginic acid (32 ± 1.5 gm), protein concentrate (3.8 ± 0.2 gm), cellulose (10 ± 0.5 gm), and salt (115 ± 5 gm). The process has several advantages over traditional ones in terms of a high biomass-to-products conversation rate of 93%, lesser chemical inputs, and minimal effluent discharge (Fig. 5). Similarly, six products, mannitol, protein, minerals, alginate, bioethanol, and electricity, were prepared from *Nizimuddiniana zanardini* biomass using chemical treatments, hydrolysis, and fermentation [87]. In the first step, the seaweed slurry was subjected to hot water extraction for 1 h at 120 °C in a reactor. The filtrate and filter cake were separated by using a vacuum belt filter. Mannitol, protein, and minerals were purified from the filtrate. In the second step, the filter cake was hydrolyzed using cellulase enzyme, and the glucose-containing liquid phase and the solid were separated. The liquid phase was fermented to ethanol using the *Zymomonas mobilis* microorganism, and solids were used to prepare alginate. In the end, the remaining solids were used to produce electricity using a turbogenerator. Further, Tedesco et al. [73] prepared several bioproducts, such as laminarin, mannitol, and alginate, along with the acids like acetic acid, formic acid, and levulinic acid from *Ascophyllum nodosum* biomass. Recently *Undaria pinnatifida* waste was valorized to get proteins and fucoidan using microwave-assisted hot water extraction [93].

In the second type of processing, brown seaweeds *Laminaria digitata* have been fermented to get various products such as succinic acid, methane, and feed [74], ethanol, 2,3-butanediol, and lycopene from Kelp [82]. Subsequently, biogas and fertilizer were produced from *Sargassum* biomass using hydrothermal pretreatment following anaerobic digestion [86], and bioethanol and biogas using acid hydrolysis, fermentation, and anaerobic digestion [72]. Apart from these, brown seaweed biomass was also subjected to hydrothermal liquefaction wherein bio-crude oil, a bio-char, gas, and aqueous phase products were produced from several seaweeds such as *Ascophyllum nodosum*, *Fucus ceranoides*, *Fucus vesiculosus*, *Himanthalia elongata*, *Laminaria digitata*, *Laminaria hyperborea*, *Pelvetia canaliculata*, *Sargassum muticum* [28], and bio-oil and biochar produced from *Padina tetrastromatica* [94]. Also, hydrochar, levulinic acid, and 5-hydroxymethylfurfural were produced from *Laminaria digitata* with microwave-assisted hydrothermal carbonization (HTC) [29]. The HTC of *L. digitata* was carried out in a microwave at low temperatures (160, 180, and 200 °C) and 1, 2, and 4% H₂SO₄ concentrations. The 200 °C temperature and 4% H₂SO₄ concentration were found to optimum yield 12.5% levulinic acid and 5.8% 5-hydroxymethylfurfural in the process liquor, along with the 15.9% hydrochar having a heating value of 25.5 MJ/kg volatile solids which were comparable to lignite coal. A total of 84% of carbon was recovered from seaweed biomass. For the key processes presented in table 3, the biomass-to-product conversion rate ranged from 43.57% to 93%. This is much higher than the traditional use of alginophytic seaweed biomass to prepare single-product alginate (10-30% DW). Among the biorefining approaches, the first one, the segregation of brown seaweed biomass into its components, including major product alginate, is preferable at the present level of alginate seaweed biomass production as alginate has huge market demand with continuous growth.

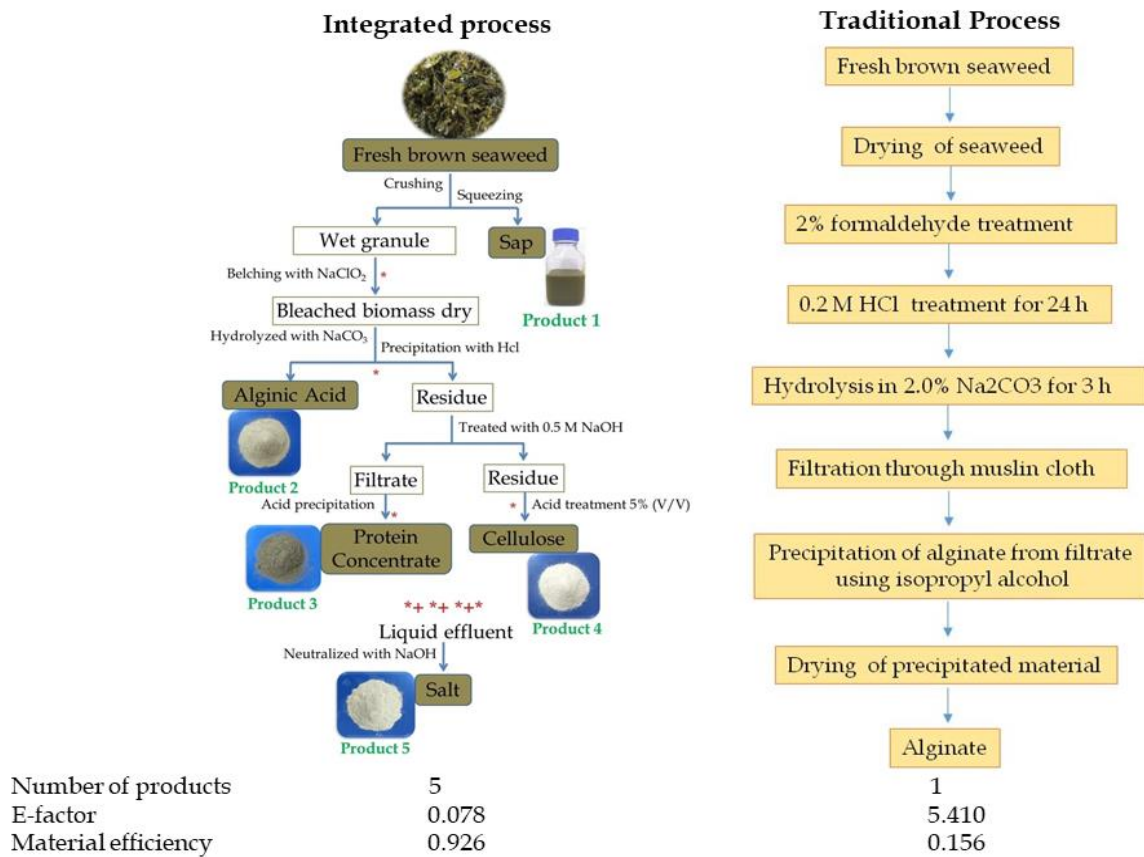


Figure 5 Comparison between integrated biorefining process and traditional alginate extraction process from brown seaweed. Modified and adapted from Baghel et al. [10]

4.3. Biorefining of green seaweeds

The present study reviewed 21 research articles (2011-2022) on the biorefining of green seaweeds (Table 4). Like red and brown seaweed biomass processing, both biorefining approaches (component fractionation and acid/enzymatic hydrolysis/fermentation/hydrothermal liquefaction) and additionally subcritical hydrolysis were used. Biorefining of green seaweed biomass was initiated with the production of fermentative products. Initially, acetone, butanol, and ethanol were prepared from *Ulva lactuca* biomass [96]. Freeze-dried milled *Ulva lactuca* was given alkali and acid treatments. Over 90% of sugars were solubilized by hot-water treatment and hydrolysis using commercial cellulases. Acetone, butanol, and ethanol (ABE) were produced from hydrolysate fermentation using two microorganisms *Clostridium acetobutylicum* and *Clostridium beijerinckii*. Subsequently, Yahmed et al. [97] successfully produced bioethanol and biogas from *Chaetomorpha linum*. In the first step, *C. linum* biomass was given three pretreatments: acidic, neutral, and alkali. Among the treatments, alkali pretreatment (3% NaOH) was found best in thallus disintegration, biomass recovery, and enzymatic digestibility. The *C. linum* feedstock was hydrolyzed using cellulase enzyme produced from the

fermentation of *Aspergillus awamori* yielded fermentable sugar of 0.22 ± 0.02 g/g dry substrate. The reducing sugar was fermented into bioethanol with a yield of 0.093 g/g pretreated algae using the microbe *Saccharomyces cerevisiae*. The liquid effluents and solid residues left from the bioethanol production were subjected to an anaerobic digester to produce methane with a yield of 0.26 ± 0.045 L/gVS. Similarly, Bikker et al. [99] prepared five products: animal feed, acetone, butanol, ethanol, and 1,2-propanediol from *Ulva lactuca* biomass. Out of 21 articles included in this study, eight dealt with the fractionation of biomass into its components. Very first, salt (29-36%) and processed biomass were prepared from *Ulva ohnoi* and *Ulva tepida* [98]. Later Trivedi et al. [24] prepared the four products mineral-rich liquid extract (MRLE) (26%), lipid (3%), ulvan (25%), and cellulose (11%) on DW from *Ulva fasciata* biomass, and 66% of biomass was recovered as products. In brief fresh *U. fasciata* biomass was homogenized in water using a mixer grinder and centrifuged to separate minerals-rich supernatant and residues. Lipid was extracted using solvents from residues left from mineral extractions. The residues that remained after lipid extraction was used to extract ulvan by cooking it with water for 2 h at 90 °C, and the cooked material was mixed and filtered through a muslin cloth. The filtrate was precipitated with 2–2.5 volumes of chilled isopropyl alcohol to get ulvan. Further, cellulose-rich residues obtained from muslin cloth filtration were used as a raw material for cellulose extraction, and extracted cellulose was hydrolyzed using cellulase enzyme and fermented to ethanol using the *Saccharomyces cerevisiae*.

Also, salt, ulvan, and protein-enriched residual mass were prepared from *Ulva ohnoi* [100]. Later *Ulva lactuca* biomass was valorized to recover five products sap, lipid, ulvan, protein, and cellulose [101]. Recently, Prabhu et al. [105] reported a biorefining process for the recovery of 6 products 45.42% salts, 3.67 % starch, 3.81% lipids, 13.88% ulvan, 14.83 % proteins, and 8.70% cellulose with biomass to products conversion of $90.31 \pm 1.94\%$ (Fig. 6). Apart from these Raikova et al. [28] produced multiple bioproducts such as bio-crude oil (15-30%), a bio-char (23-38%), bio-gas (12-14%), and aqueous phase products (11-25%) from *Ulva intestinalis*, *Ulva lactuca*, and *Rhizoclonium riparium* biomass using hydrothermal liquefaction process (350 °C; ca. ~ 30 K min⁻¹). Further, Polikovskiy et al. [106] prepared four products protein (5.8%), 5-HMF (0.52%), hydrochar (21.1%), and bioethanol (4.67%) from *Ulva* biomass using subcritical water hydrolysis. Recently, *Ulva spp.* was investigated to prepare five products protein, hydrochar, ethanol, distilled water, and electricity employing the hydrothermal processing and fermentation approach [109] and also bioethanol and biogas prepared by integrating three treatments acid hydrolysis, fermentation, and anaerobic digestion [72]. More recently, Andrade et al. [103] produced liquors and hydrolysates from *Ulva lactuca* biomass. Unlike red and brown seaweeds, no such high-value marketable products are obtained from

green seaweed biomass; thus, the selection of the biorefinery approach depends on the products required.

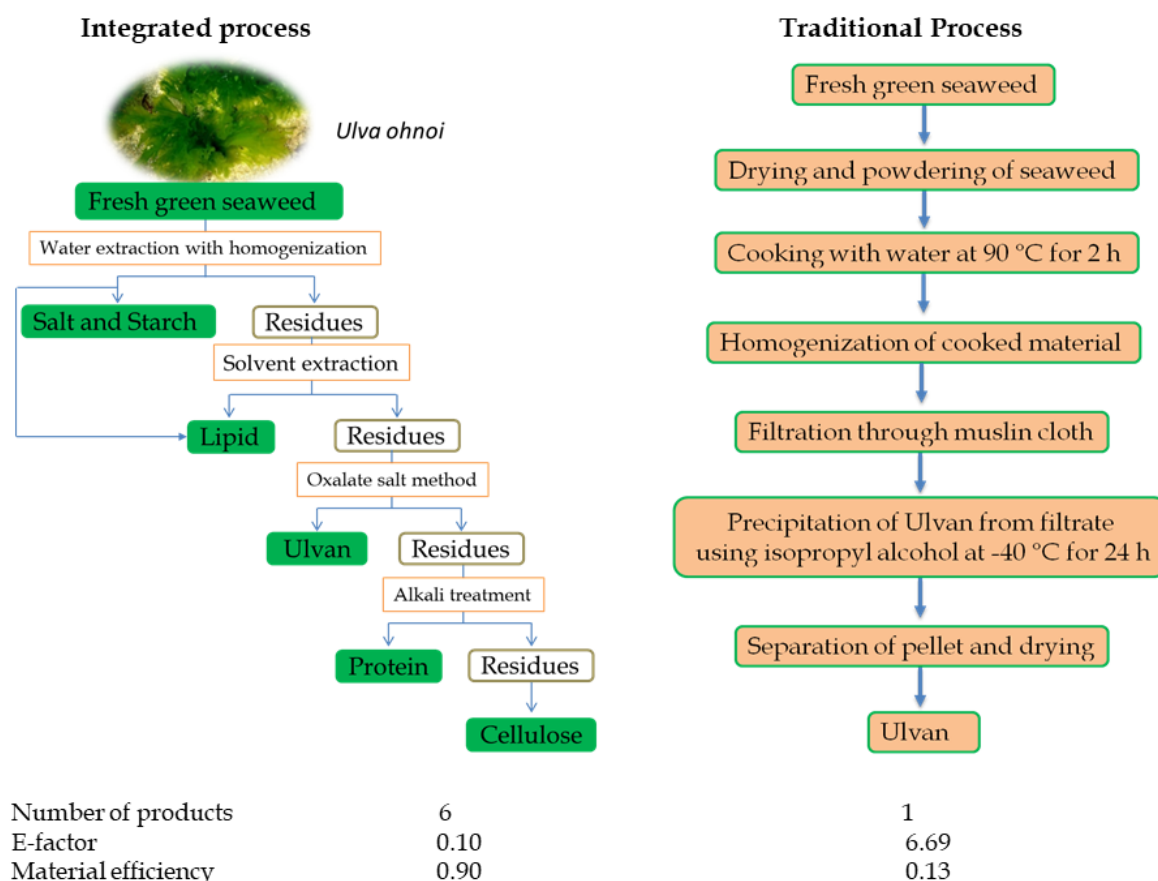


Figure 6 Comparison between integrated biorefining process [105] and traditional ulvan extraction process form green seaweed

Biotechnological advances in seaweed biorefinery

While considering seaweed biomass for bioethanol production, only the cellulose fraction (1.5–34% DW) of biomass is easily hydrolyzed and fermented among the carbohydrates [23]. The conversion of major sulfated polysaccharides fraction (10-50%) of seaweed biomass into fermentable sugar remains challenging; thus, engineered microbes have been designed to overcome this challenge as biotechnological advancement. Four reports are available: two dealt with engineered yeast and two with engineered bacteria. Initially, metabolically modified, alginate-assimilating, pit-forming bacterium, *Sphingomonas* sp. A1 (strain A1) was developed [114]. Designed ethanologenic recombinant strain A1 was able to convert brown seaweed polysaccharide alginate into ethanol. Later on, yeast-based (*Saccharomyces cerevisiae*) engineered microbial platforms were developed for bioethanol production [115,116]. The synthetic yeast platforms were capable of hydrolysis and

fermenting brown seaweed sugars into bioethanol. Recently, the *Vibrio* sp. dhg genetic toolbox was designed to demonstrate its ability to rapidly produce ethanol, 2,3-butanediol, and lycopene from brown macroalgae sugar mixture with high productivity and yields [82]. However, scaling up these processes for commercial production from a technological point of view and ensuring economic feasibility are the major bottlenecks, as alginate has a much higher value than bioethanol. Thus, surplus seaweed biomass production is needed to use these strategies for commercial bioethanol production.

5. Advantages of seaweed biorefining approaches

The seaweed biorefining process includes various benefits, such as adding value to biomass, ensuring sustainable biofuel production, and environmental benefits over traditional seaweed processing. The benefits are depicted in detail in the following sections.

5.1. Value addition of biomass and marine bio-economy

Currently, advanced processes with sustainable biomass utilization are given importance while developing new technologies for achieving sustainable economic growth and development in the marine bio-economy. Seaweeds are considered a prominent ocean component to contribute to it, and it could be possible with increased biomass production and sustainable utilization. Basically, single-fraction seaweed hydrocolloids such as agar sourced from agarophytic seaweeds, alginate from alginophytes, and carrageenan extracted from carrageenophytes are the major commercial component of seaweed biomass. Agar content range from 9-25% on DW is the commercially utilized fraction from agar-bearing seaweeds [117,118]. Alginophytic and carrageenophytic seaweeds constitute about 10-30% alginate [10] and up to 50% of carrageenan, respectively, by DW of biomass, depending on the species that is the only commercially used fraction. The integrated biorefining processes help to produce several coproducts along with hydrocolloids and ensure biomass value addition. For example, Eswaran et al. [53] patented a process for the sequential production of sap liquid fertilizer and carrageenan from fresh seaweed *K. alvarezii*. The sap has been proven to improve the yields of various crops and vegetables. India-based Aquagri Processing Pvt. Ltd, Delhi, is successfully using this technology for the commercial production of sap and carrageenan. The overall estimated revenues for one ton of fresh biomass processing in an integrated manner were US\$ 853.5, 3.2 fold higher than the single product refined carrageenan production (266.34 US\$) from the same quantity of biomass (Table 5). Also, the proof of concepts of integrated biorefining process has been reported for agar, and alginate seaweed biomass showed a clear advantage to increase the biomass utilization and revenues over the traditional processing. For red seaweed, an integrated process was reported for the valorization of agar-producing seaweeds *Gracilaria corticata* yielded agar with five co-products (Fig.4). Thus, the biomass

utilization rate was increased to 92% compared to biomass processing for the recovery of single-product agar (23%) [61]. The material efficiency calculated as per equations 1, 2, and 3 [119] for integrated process 0.921 was much higher than 0.23, material efficiency calculated for biomass processing for recovery of single product agar. Also, the products produced from one-ton fresh biomass were found to have an estimated market value of US\$ 1051 against the 336 US\$ from single product agar extraction, resulting in three-fold value addition of biomass (Table 5).

Among the brown seaweeds, processing a ton of fresh alginate-yielding *Sargassum* biomass yielded as many as five commercial products with a 93% biomass utilization rate [10]. This process showed its superiority and future scope over the existing process for alginate extraction, which ends in single product alginate with 15.6% biomass utilization (Depending on species). The material efficiency (0.926) for the integrated process was much improved compared to the traditional process (0.156) used for alginate extraction (Fig. 5). Further, one-ton wet biomass processing in the integrated biorefinery concept is estimated to substantially increase revenues to US\$ 799 from US\$ 237 [10] (Table 5). In green seaweeds, *Ulva fasciata* biomass was valorized in an integrated manner to recover four commercially important fractions with a 66% biomass utilization rate with a material efficiency of 0.66 compared with the single product Ulvan recovery (26%) with 0.26 material efficiency [24]. Also, from the green seaweed, *Ulva ohnoi* revenue was estimated between US\$ 1.56 and US\$ 3.93 kg⁻¹ of dry biomass upon integrated processing [105]. Based on the examples mentioned above of integrated processing for different seaweeds and their material efficacy data, the integrated biorefining process significantly increases the biomass utilization rates and helps to 2-3-fold value addition of seaweed biomass. Balina et al. [120] analyzed the role of the biorefinery concept on the ground of bioeconomy principles and, through a SWOT analysis, concluded that biorefinery has the potential for the development of a sustainable bioeconomy. More recently, Trivedi et al. [121] also highlighted the importance of the biorefining process in marine bioeconomy developments. Thus, the commercialization of proof of concepts biorefineries will undoubtedly form the basis for the marine bioeconomy and its development.

$$E \text{ Factor} = \frac{\text{Mass of wastes}}{\text{Mass of products}} \quad (1)$$

Material efficiency can be calculated as equation 2 and 3

$$\text{Material efficiency} = \frac{1}{1+E \text{ Factor}} \quad (2)$$

$$= \frac{\text{Mass of products}}{\text{mass of products}+\text{mass of wastes}} \quad (3)$$

Table 5 Comparison of revenues from one tone fresh seaweed biomass processing using integrated biorefinery approach and traditional processing (single product extraction)

Seaweed species	Cost of tone of fresh biomass (US\$)	Integrated biorefinery			Tradition processing	
		Product (quantity)	Product value (US\$)	Revenues (US\$)	Product (quantity)	Revenues (US\$)
Carrageenan seaweed, values are adjusted from Eswaran et al. [53]						
		Sap (700 L)	0.87/L	609		
<i>Kappaphycus alvarezii</i>	62.75 (0.0627/kg)	Carrageenan (30 kg)			Carrageenan (32.68 Kg)	266.34
			8.15/Kg	244.5		
Total	62.7			853.5		266.34
Agar seaweed, values are adjusted from Baghel et al. [61]						
<i>Gracilaria corticata</i>		Liquid fertilizer (600 L)	1/L	600		
		Natural colorants (292 gm)	225/Kg	65		
		Lipid (1.72 kg)	---	---		
	75 (0.075/kg)	Agar (27.3 Kg)	12/Kg	327.6	Agar (28 Kg)	336
		Bioethanol (4.44 L)	0.64/L	2.66		
		Soil conditioner (15.1 kg)	3.7/Kg	55.8		
Total	75			1051.06		336
Alginate seaweed, values are adjusted from Baghel et al. [10]						
<i>Sargassum tenerrimum</i>		Sap (540 L)	0.63/L	340.2		
	62.77 (0.0627)	Alginate (32 Kg)	12.55/Kg	401.6	Alginate (18.87 Kg)	236.88
		Protein concentrate (3.80 Kg)	2.51/Kg	9.3		
		Cellulose (10 Kg)	1.25/Kg	12.5		
		Salt (115 Kg)	0.31/Kg	35.05		
Total	62.77			798.65		236.88

5.2. Environmental benefits

The environmental impact is the key factor in deciding the sustainability of processing technology and is thus given importance for achieving sustainable economic growth and development in the world. The E-factor plays a vital role in deciding the effect of the process on the environment. E-factor provides the impetus for developing a cleaner and more sustainable process. The integrated biorefining approaches increase biomass utilization rates and minimize effluent discharges. The E-factor for the selected key integrated biorefining process was calculated according to equation 1 and compared with the E-factor of the traditional single-product extraction process to analyze the environmental impacts. For example, among the red seaweeds, an integrated process for the valorization of *Gracilaria corticata* was selected and evaluated for its environmental impacts. The integrated process recorded a lower E-factor of 0.085 (Fig. 4) compared to the E-factor of 3.345 of the single product (agar) extraction process, indicating the superiority of the integrated biorefining process over the traditional single product extraction process in the context of positive environmental impacts [61]. Among the brown seaweed valorization process, the integrated process reported for *Sargassum* biomass to have a lower E-factor of 0.078 (Fig. 5) while compared to the E-factor (5.41) of the traditional process of alginate extraction [10]. For the green seaweeds, an integrated process reported for the disintegration of *Ulva ohnoi* biomass into six commercial extracts recorded a lower E-factor (0.10) while compared with E factor (6.69) from the single product Ulvan extraction method (Fig.6). Overall, E-factors' data indicate the greenness and superiority of integrated biorefining processes over traditional extraction processes. Other than E-factor, life cycle assessment (LCA) is one of the crucial scientific analyses that help to understand the impacts of any bioprocess on the environment and human health. To date, few LCA analysis has been reported for the seaweed cultivation and production of either bioethanol or biogas from seaweed biomass [122-125]. The LCA analysis for integrated seaweed biorefining process is very rare. Seghetta et al. [126] reported the LCA of the macroalgal biorefinery process that produced ethanol, proteins, and fertilizers. They concluded that the macroalgal biorefineries could play an essential role in the regenerative circular economy through environmental restoration and climate mitigation. Recently LCA analysis [109] reported for co-production of protein and bioethanol, electricity, and water from *Ulva* biomass and found the lowest environmental impacts compared to alternative production strategies. More recently, Fasahati et al. [127] reported the LCA for producing bioenergy from seaweed biomass via three different biological conversion pathways, 1) sugar, (2) volatile fatty acids, and (3) methane pathway. The analysis suggests that the sugar pathway for ethanol production via fermentation is the best alternative for bioenergy production with lower lifecycle outcomes GWP = 106 kg CO₂ eq. Per dry ton seaweed compared with the volatile fatty acid

pathway (GWP = 398 kg CO₂ eq. per dry ton seaweed) and methane platforms (GWP = 279 kg CO₂ eq. per dry ton seaweed).

5.3. Ensuring the economical bioethanol production

Among the renewable fuels, bioethanol is the most common and widely used transport biofuel worldwide. Starch and cellulose from plants, crops, and agricultural waste are the preferred sources for bioethanol production. Bioethanol production was 17,436 Million Gallons in 2020 [128]. The United States and Brazil are top producers using corn and sugarcane as raw materials [128]. However, long-term bioethanol production from food crops remains questionable due to the increasing food demands and the world population. These are land-based crops, and many highly populated countries like south Asian countries have limited scope to divert such food crops for energy production. Later the attention turned to producing bioethanol from non-food feedstock's lignocellulosic biomass as an alternative to first-generation biofuels. The presence of high lignin and hemicellulose content over the cellulose in lignocellulosic biomass has become a major challenge in the depolymerization process. Further, depolymerization of such biomass requires several chemical pre-treatments [129] that make the process expensive and non-eco-friendly. Thus, the goal for the production of bioethanol from lignocellulosic biomass did not meet the expectation. In parallel, seaweed biomass also gained attention as raw material for third-generation bioethanol production. Seaweeds are known to have a high growth rate without any agricultural inputs. Apart from that, the ocean has huge potential for sea cultivation of seaweeds compared to the cultivation of land-based biomass. Initially, Horn et al. [51] succeeded in producing bioethanol from *Laminaria hyperborean* brown seaweed. Later several seaweed species were investigated to explore their potential for bioethanol production. Among green seaweeds, *Ulva reticulata* [130], *Ulva fasciata* [131]; red seaweeds *Chondracanthus tenellus* [132], *Gelidium amansii* [133], and brown seaweeds *Sargassum sagamianum* [134] *Saccharina latissima* [135], *Undaria pinnatifida* [132] were studied for ethanol productions.

To produce bioethanol, acidic, and enzymatic treatments are used for hydrolysis, followed by fermentation (Fig. 7). Despite the research developments on biofuel production from seaweed biomass, it remains uneconomical due to fewer yields and high capital costs per unit of fuel production (Fig. 7). Seaweeds contain carbohydrates in the range of 22-62% of their dry weights, and other parts constitute proteins, lipids, and minerals. Only cellulose fraction is easily hydrolyzed and fermented among the carbohydrates, while depolymerization of major sulfated polysaccharides fraction into fermentable sugar is challenging. For a while, an engineered microbial platform was developed for bioethanol production using alginate [114] and whole alginophytic biomass [115, 116] to maximize the use of carbohydrate fractions. Further, the superstructure process-based volatile fatty acid platform was designed to produce

mixed alcohols and mixed organic acids from *Saccharina japonica* biomass. The results suggest that the biofuel could be produced economically from seaweed with a minimum ethanol selling price of 1.17 US\$/gal. The break-even price of ethanol produced from different seaweed species was also analyzed using techno-economic analysis (TEA), which ranged between 1.17-5.86 US\$/gal (Table 6). Seaweed hydrocolloids such as alginate, agar, and carrageenan are high-value products with a well-established global market [27]. Thus, the sustainability of long-term bioethanol production from such hydrocolloids has remained questionable. Bioethanol production from these hydrocolloid fractions could be sustainable only in the case of surplus seaweed biomass production. However, bioethanol production from seaweed biomass as a co-product may sustain for longer as residual waste remaining after extraction of high-value components (- minerals, hydrocolloids, and proteins) is reported to have a significant amount of cellulose. The approach for multiple product output may provide sustainability and economic viability to bioethanol production compared to that focused solely on fuel production. Thus, high-value co-products must be produced to improve the economics of seaweed bioethanol production. Further, the attention has shifted towards bioethanol production from selectively seaweed cellulose fraction in biorefinery approaches. Subsequently, many investigators reported bioethanol production along with other by-products from seaweed biomass for a different group of seaweeds. For example, in green seaweeds, *Ulva lactuca* [96], *Ulva fasciata* [24]; in red seaweeds, *K. alvarezii* [58], *Gracilaria verrucosa* [59], and in brown seaweed *Saccharina japonica* [78] were studied for ethanol productions with co-products. The cellulose extracted as a by-product from 3 different agar-producing seaweeds was hydrolyzed and fermented to produce bioethanol [27]. Moreover, 12.72% of bioethanol was produced from the residual mass of *Gracilaria corticata* (Fig. 7) [61]. Biorefinery approaches used to extract economically important chemicals along with bioethanol sounds more sustainable and economical. This sustainability and economic viability operated by three major factors 1) Pre-extraction of components other than cellulose increases the concentration of cellulose in residual mass 2) As residual mass is reduced significantly over the initial biomass, thus needs fewer inputs and unit operations for bioethanol production and, 3) the additional bio-products could therefore potentially compensate the costs incurred in bioethanol production.

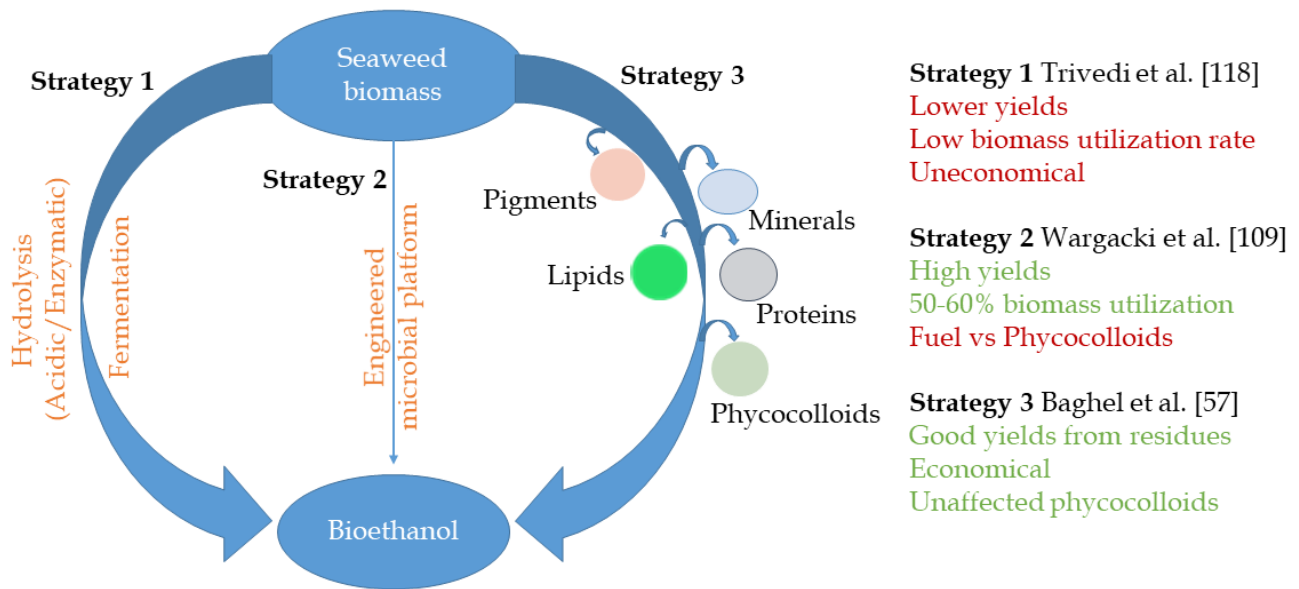


Figure 7 Various strategies used for bioethanol production from seaweed biomass. Adapted from Baghel et al. [23]

Table 6 Literature on industrial scale bioethanol production from seaweeds and breakeven price analyzed using techno-economic analysis (TEA)

Seaweed	Treatments	Breakeven price of ethanol	References
<i>Laminaria japonica</i>	Hydrolysis and fermentation	2.2 US\$/gal	[136]
Seaweed sp.	Hydrolysis and fermentation	5.86 US\$/gal	[137]
<i>Laminaria species</i>	Hot water wash pre-treatment, Saccharification and fermentation	2.08 US\$/gal	[138]
Brown algae	Anaerobic digestion and hydrogenation	1.24 US\$/gal	[139]
Brown algae	Anaerobic digestion, hydrogenation and Pervaporation	1.06 US\$/gal	[1]
<i>Saccharina japonica</i>	Anaerobic digestion/volatile fatty acid route	1.17 US\$/gal	[140]
<i>Saccharina japonica</i>	Enzymatic hydrolysis and fermentation	1.36-2.11 US\$/gal	[141]
<i>Laminaria japonica</i>	Engineered microbial platform	< 1.38 US\$/gal	[127]

6. Applications of seaweed biorefinery materials and future trends

The products prepared from seaweed biorefineries have potential applications in the food, feed, chemicals, and biofuel sectors [142]. For example, seaweed-based sap/minerals are the preferred biostimulants for agricultural applications capturing one-third of the global market and significantly boosting the agriculture sector [143,144]. The seaweed extract market is predicted to reach a value of 894 million euros by the end of 2022 [145]. Seaweed-based proteins as byproducts from biorefinery known to have all essential amino acids could be used as an alternative to traditional sources to fulfill the increasing global demands [146,10,101]. Generally, seaweeds contain low lipid content, but their polyunsaturated fatty acid (PUFA) fraction has often been higher when compared with terrestrial vegetables [33]. The nutritionally important PUFA content ranged from 10–70% of total FAs in seaweed lipids. According to the IndustryARC site, in 2020, the Global PUFA Market was estimated at US\$ 5.3 billion and predicted to grow at a CAGR of 7.7% during 2021-2022 (<https://www.industryarc.com/Research/Pufa-In-Global-Market-Research-509561>, accessed on 17 August 2022). Furthermore, there is a need to fill the gap between the supply and the rapidly increasing PUFAs demands [147]. Thus, lipids extracted from seaweed biomass as a byproduct using the integrated biorefinery could be an additional source for food additives in the nutraceutical industry. Another common component, cellulose, can be used as a feedstock for bioethanol production or cellulose-derived products such as microcellulose, nanocellulose, carboxymethyl cellulose, and bioplastics [23]. The major fraction of green seaweed *Ulva*, a water-soluble sulfated polysaccharide ulvan, may be used in food, pharmaceutical, and agricultural applications [148]. The hydrocolloid agar, carrageenan, and alginate prepared from red and brown seaweeds have excellent gelling, stabilizing, and emulsifying characteristics and high viscosity properties, making them highly commercial and significant in the global hydrocolloid market [5]. These hydrocolloids are used as gelation and thickening agents in food, cosmetics, pharmaceuticals, biotechnological uses, textile, printing, and paper coating. The Global seaweed hydrocolloids market will reach 180K Metric Tons with a value of US\$ 2.3 Billion by 2024 (Industry Experts, Inc, <https://industry-experts.com/>, accessed on 17 August 2022). The products such as ethanol, bio-oil, and biogas, prepared from hydrolysis, fermentation, and anaerobic digestion, have potential in bioenergy and industrial applications, and acids and fine chemicals are useful in chemical industries. Overall, seaweed biorefinery materials will have massive requirements in the future to fulfill the ever-growing world population demands.

7. Challenges in commercial implementation and possible solutions

Although several seaweed biorefining processes have been reported, many challenges still need to be addressed to translate them commercially. Among them, four major ones are 1) Lack of

trustability: basically, most of the proof of concepts developed for the biorefining process are laboratory scale (with a small amount of biomass), and the process needs to be scaled up to a certain level to attract the interest of seaweed industries and new investments. Small-scale research could not answer questions such as certainty of the production process, yields of products in commercial-scale processing, and economic feasibility of the process, which are the key factor for commercial implementation of any bioprocess. Further large-scale production of bulk commodity chemicals has not yet been demonstrated, which is required to achieve commodity markets [149]. This challenge could be triggered by scaling up the biorefining process on a pilot scale which could provide information about the overall sustainability of the process to attract the industries. 2) High transportation cost for fresh biomass: The fresh biomass-based biorefining process has clear advantages such as the easy release of components, less fresh water requirement, and low energy inputs over the dry biomass-based biorefining process. However, the high transportation cost of fresh biomass is the major challenge that must be addressed. Thus, small units can be established in coastal areas to spell out the sap from biomass that includes soluble components such as minerals, protein, and carbohydrates, substantially reducing the mass and transportation cost (Section 10). 3) The higher ash content (12-46%) in seaweed biomass is also a big challenge in the commercial implementation of thermochemical-based biorefineries. The ash content could be minimized in seaweed biomass by the extraction of sap for agricultural applications from fresh biomass prior to thermochemical conversion, as a considerable amount of minerals are released from biomass in sap. Extracting sap from wet biomass also helps reduce the moisture from biomass. 4) Non-Availability of adequate biomass is another major challenge as growth in biomass production is less, especially in the Indian subcontinent; most of the biomass is collected from wild stock, which also decreases gradually, which poses a big barrier to establishing new seaweed processing industries. A major initiative is needed to develop germplasm for potential seaweed species and explore the coastal sites to expand seaweed cultivation. Further mechanized/artificially seaweed farming techniques to maximize seaweed supply around the year at affordable costs are highly needed.

8. Proposed multistage cascade bioprocessing model for fresh seaweed biomass

Based on research experience on seaweed biorefinery and literature reviewed to tackle challenges towards the commercialization of the seaweed biorefining process, a multistage cascade bioprocessing model is proposed (Fig. 8) to utilize existing industrial infrastructure for sustainable utilization of existing seaweed biomass. Instead of complete processing of whole seaweed biomass in a single industry or setting up the new complete infrastructure at a single site, it can be processed in part by dividing into three individual processing units with existing industries involved in the

production of individual products such as hydrocolloids, agriculture biostimulants, cellulose, proteins, and bioethanol. Since transporting seaweed biomass in fresh condition from a cultivation site to a processing site is a costly and challenging task thus, small processing unit 1 could be established in coastal areas that could extract the sap and residues from biomass. Sap can be subjected to ultrafiltration to separate the permeate (rich in pigments and soluble proteins and carbohydrates) and filtrate rich in minerals. Further filtrate could be concentrated using RO technology to get concentrated minerals solution for agriculture use and fresh water for drinking applications. Removing minerals and soluble fractions from residual biomass would densify the other components, such as hydrocolloids and cellulose, and reduce biomass by 40-50%, lowering the transportation cost. The dried residues left from processing unit 1 could be supplied to the existing industries (Processing unit 2) working for hydrocolloid production. After removing hydrocolloids, the cellulose-rich residual biomass could be supplied to (Processing unit 3) industries involved in cellulose extraction or those producing bioethanol based on requirements and demands.

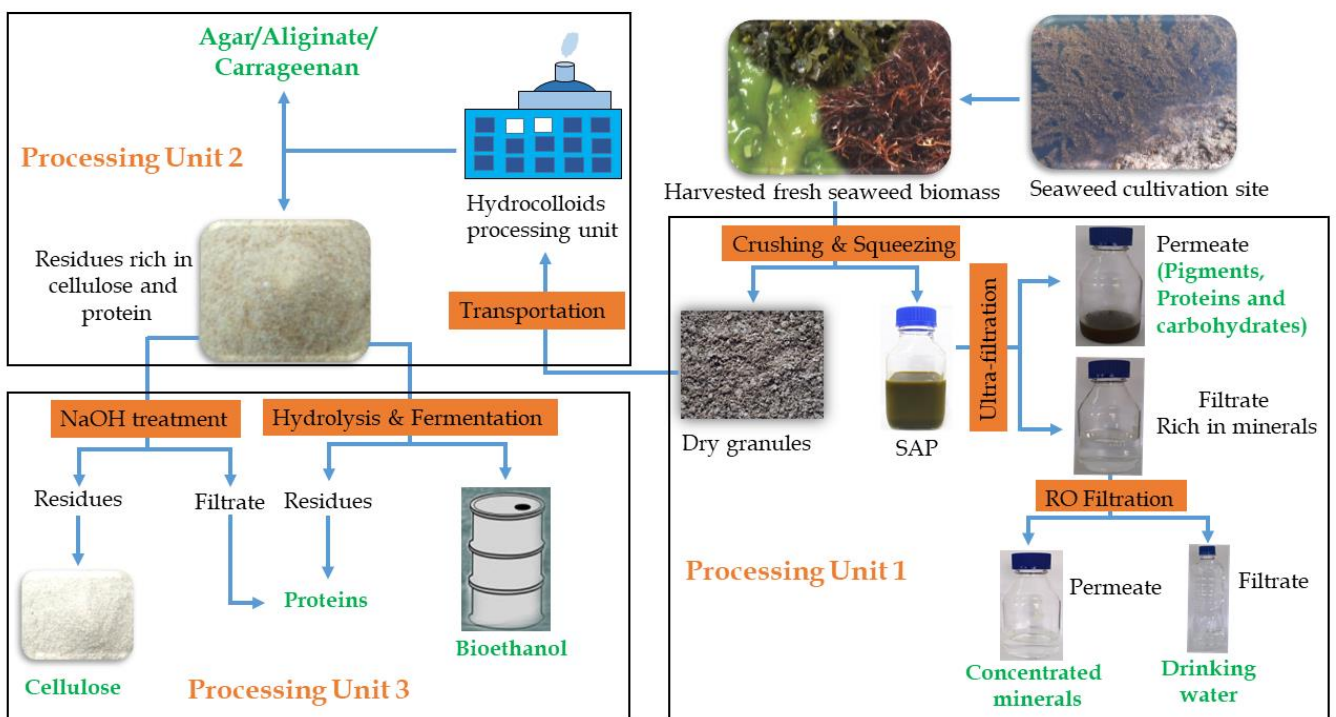


Figure 8 Proposed multistage cascade bioprocessing model for red, green and brown seaweed biomass sustainable processing and products development

9. Conclusions

Research on biogas production from seaweed biomass began long ago in the 1960s and 1970s, and bioethanol in the late 1990s but mostly followed a single-product strategy. The last decade has given a new dimension to seaweed processing research by diverting the single product production strategy to multiple-component extraction from seaweed biomass. Based on a detailed review of various research papers published on seaweed biorefinery, it can be inferred that 1) Biorefining approaches were developed on a laboratory scale for all three green, red, and brown groups of seaweeds. 2) Integrated biorefinery processes show superiority over the traditional ones by adding value to biomass, maximizing biomass utilization, increasing revenues, and environmental benefits such as minimal effluent discharges and lower E-factor. 3) At the present level of red and brown seaweed biomass production, the process dealing with the fractionation of biomass components along with the recovery of major commercial products (Agar/carrageenan/alginate) has higher efficiency in translating commercial-scale over to those converting/degrading major commercial products into end products such as various acids, fuels. 4) Green seaweed biomass can be converted using any strategy depending on the product of interest, as their polysaccharides have not yet stabilized the market. 5) The biorefining processes allows economic bioethanol production as a co-product from seaweed biomass using selective cellulose fraction. 6) There is a need to overcome several challenges, such as the availability of adequate biomass (in the Indian subcontinent), commercial-level processes, economic feasibility, and market for byproducts to translate the lab-scale biorefining approaches to commercial scale and attract the industries.

Declaration of Competing Interest

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

Acknowledgement

The financial support received from OLP-2005 is gratefully acknowledged. RSB thankful to the Director, CSIR-NIO (CSIR-National Institute of Oceanography) for extending the facilities. This is CSIR-NIO's contribution reference number XXXX.

References

- [1] P. Fasahati, J.J. Liu, Economic, energy, and environmental impacts of alcohol dehydration technology on biofuel production from brown algae, *Energy*, 93 (2015) 2321-2336, <https://doi.org/10.1016/j.energy.2015.10.123>.

- [2] T.D. Dillehay, C. Ramírez, M. Pino, M.B. Collins, J. Rossen, J.D. Pino-Navarro, Monte Verde: seaweed, food, medicine, and the peopling of South America, *Science* 320 (2008) 784-786, <https://doi.org/10.1126/science.1156533>.
- [3] J.E. Merrill, Development of nori markets in the western world, *J. Appl. Phycol.* 5 (2) (1993) 149-154, <https://doi.org/10.1007/BF00004010>.
- [4] R.L. Chapman, Algae: the world's most important "plants"—an introduction, *Mitig. Adapt. Strateg. Glob. Chang.* 18 (2013) 5-12, <https://doi.org/10.1007/s11027-010-9255-9>.
- [5] R.S. Baghel, V.A. Mantri, C.R.K. Reddy, A new wave of research interest in marine macroalgae for chemicals and fuels: Challenges and potentials, *Fuels, Chemicals and Materials from the Oceans and Aquatic Sources* (2017) 43-63, <https://doi.org/10.1002/9781119117193.ch3>.
- [6] D.J. McHugh, Worldwide distribution of commercial resources of seaweeds including *Gelidium*, In *International workshop on Gelidium*, (1991) 19-29, Springer, Dordrecht.
- [7] H. Porse, B. Rudolph, The seaweed hydrocolloid industry: 2016 updates, requirements, and outlook, *J. Appl. Phycol.* 29 (2017) 2187-2200, <https://doi.org/10.1007/s10811-017-1144-0>.
- [8] J. Cai, A. Lovatelli, J. Aguilar-Manjarrez, L. Cornish, L. Dabbadie, A. Desrochers, S. Diffey, E. Garrido Gamarro, J. Geehan, A. Hurtado, D. Lucente, Seaweeds and microalgae: an overview for unlocking their potential in global aquaculture development, *FAO Fisheries and Aquaculture Circular* (2021) 1229.
- [9] C.O. Okoli, T.A. Adams II, B. Brigljević, J.J. Liu, Design and economic analysis of a macroalgae-to-butanol process via a thermochemical route, *Energy Convers. Manag.* 123 (2016) 410-422, <https://doi.org/10.1016/j.enconman.2016.06.054>.
- [10] R.S. Baghel, P. Suthar, T.K. Gajaria, S. Bhattacharya, A. Anil, C.R.K. Reddy, Seaweed biorefinery: A sustainable process for valorising the biomass of brown seaweed, *J. Clean. Prod.* 263 (2020) 121359, <https://doi.org/10.1016/j.jclepro.2020.121359>.
- [11] P. Fasahati, C.M. Saffron, H.C. Woo, J.J. Liu, Potential of brown algae for sustainable electricity production through anaerobic digestion, *Energy Convers. Manag.* 135 (2017) 297-307, <https://doi.org/10.1016/j.enconman.2016.12.084>.
- [12] M. Ramezanzadeh, G. Bahlakeh, B. Ramezanzadeh, Study of the synergistic effect of *Mangifera indica* leaves extract and zinc ions on the mild steel corrosion inhibition in simulated seawater: computational and electrochemical studies, *J. Mol. Liq.* 292 (2019) 111387, <https://doi.org/10.1016/j.molliq.2019.111387>.
- [13] M. Ramezanzadeh, G. Bahlakeh, B. Ramezanzadeh, Construction of an epoxy composite with excellent thermal/mechanical properties using graphene oxide nanosheets reduced/functionalized by *Tamarindus indica* extract/zinc ions; detailed experimental and DFT-D computer modeling explorations, *Results Phys.* 19 (2020) 103400, <https://doi.org/10.1016/j.rinp.2020.103400>.
- [14] M. Ramezanzadeh, G. Bahlakeh, Z. Sanaei, B. Ramezanzadeh, Corrosion inhibition of mild steel in 1 M HCl solution by ethanolic extract of eco-friendly *Mangifera indica* (mango) leaves: electrochemical, molecular dynamics, Monte Carlo and ab initio study, *Appl. Surf. Sci.* 463 (2019) 1058-1077, <https://doi.org/10.1016/j.apsusc.2018.09.029>.

- [15] M. Ramezanzadeh, G. Bahlakeh, B. Ramezanzadeh, Z. Sanaei, Adsorption mechanism and synergistic corrosion-inhibiting effect between the green Nettle leaves extract and Zn²⁺ cations on carbon steel, *Ind. Eng. Chem. Res.* 77 (2019) 323-343 <https://doi.org/10.1016/j.jiec.2019.04.056>.
- [16] M. Ramezanzadeh, G. Bahlakeh, Z. Sanaei, B. Ramezanzadeh, Studying the *Urtica dioica* leaves extract inhibition effect on the mild steel corrosion in 1 M HCl solution: Complementary experimental, ab initio quantum mechanics, Monte Carlo and molecular dynamics studies, *J. Mol. Liq.* 272 (2018) 120-136, <https://doi.org/10.1016/j.molliq.2018.09.059>.
- [17] S. Kokilaramani, A. Rajasekar, M.S. AlSalhi, S. Devanesan, Characterization of methanolic extract of seaweeds as environmentally benign corrosion inhibitors for mild steel corrosion in sodium chloride environment, *J. Mol. Liq.* 340 (2021) 117011, <https://doi.org/10.1016/j.molliq.2021.117011>.
- [18] I. Nadi, Z. Belattmania, B. Sabour, A. Reani, A. Sahibed-Dine, C. Jama, F. Bentiss, *Sargassum muticum* extract based on alginate biopolymer as a new efficient biological corrosion inhibitor for carbon steel in hydrochloric acid pickling environment: Gravimetric, electrochemical and surface studies, *Int. J. Biol. Macromol.* 141 (2019) 137-149, <https://doi.org/10.1016/j.ijbiomac.2019.08.253>.
- [19] M. Krishnan, H. Subramanian, H.U. Dahms, V. Sivanandham, P. Seeni, S. Gopalan, A. Mahalingam, A.J. Rathinam, Biogenic corrosion inhibitor on mild steel protection in concentrated HCl medium, *Sci. Rep.* 8(1) (2018) 1-16, <https://doi.org/10.1038/s41598-018-20718-1>.
- [20] M.A. Deyab, Inhibition activity of Seaweed extract for mild carbon steel corrosion in saline formation water, *Desalination* 384 (2016) 60-67, <https://doi.org/10.1016/j.desal.2016.02.001>.
- [21] M. Sharma, D. Mondal, A.K. Das, K. Prasad, Production of partially reduced graphene oxide nanosheets using a seaweed sap, *RSC Adv.* 4(110) (2014) 64583-64588, <https://doi.org/10.1039/C4RA13149E>.
- [22] L. Berglund, T. Nissila, D. Sivaraman, S. Komulainen, V.V. Telkki, K. Oksman, Seaweed-derived alginate–cellulose nanofiber aerogel for insulation applications, *ACS Appl. Mater. Interfaces*, 13(29) (2021) 34899-34909, <https://doi.org/10.1021/acsami.1c07954>.
- [23] R.S. Baghel, C.R.K. Reddy, R.P. Singh, Seaweed-based cellulose: Applications, and future perspectives, *Carbohydr. Polym.* 267 (2021) 118241, <https://doi.org/10.1016/j.carbpol.2021.118241>.
- [24] N. Trivedi, R.S. Baghel, J. Bothwell, V. Gupta, C.R.K. Reddy, A.M. Lali, B. Jha, An integrated process for the extraction of fuel and chemicals from marine macroalgal biomass, *Sci. Rep.* 6 (2016) 3072, <https://doi.org/10.1038/srep30728>.
- [25] T. Chaturvedi, A.I. Torres, G. Stephanopoulos, M.H. Thomsen, J.E. Schmidt, 2020. Developing process designs for biorefineries—definitions, categories, and unit operations, *Energies*, 13 (2020) 1493, <https://doi.org/10.3390/en13061493>.
- [26] R. Salami, M. Kordi, P. Bolouri, N. Delangiz, B. Asgari Lajayer, Algae-based biorefinery as a sustainable renewable resource, *Circular Economy and Sustainability* 1 (2021) 1349-1365, <https://doi.org/10.1007/s43615-021-00088-z>.

- [27] R.S. Baghel, N. Trivedi, V. Gupta, A. Neori, C.R.K. Reddy, A. Lali, B. Jha, Biorefining of marine macroalgal biomass for production of biofuel and commodity chemicals, *Green Chem.* 17 (2015) 2436–2443, <https://doi.org/10.1039/C4GC02532F>.
- [28] S. Raikova, C.D. Le, T.A. Beacham, R.W. Jenkins, M.J. Allen, C.J. Chuck, Towards a marine biorefinery through the hydrothermal liquefaction of macroalgae native to the United Kingdom, *Biomass Bioenergy* 107 (2017) 244-253, <https://doi.org/10.1016/j.biombioe.2017.10.010>.
- [29] C. Deng, R. Lin, X. Kang, B. Wu, X. Ning, D. Wall, J.D. Murphy, Co-production of hydrochar, levulinic acid and value-added chemicals by microwave-assisted hydrothermal carbonization of seaweed, *Chem. Eng. J.* 441 (2022) 135915, <https://doi.org/10.1016/j.cej.2022.135915>.
- [30] M. Gomaa, A.A. Al-Badaani, A.F. Hifney, M.S. Adam, Utilization of cellulose and ulvan from the green seaweed *Ulva lactuca* in the development of composite edible films with natural antioxidant properties. *J. Appl. Phycol.* (2022) 1-12, <https://doi.org/10.1007/s10811-022-02786-z>.
- [31] J. Olsson, G.B. Toth, E. Albers, Biochemical composition of red, green and brown seaweeds on the Swedish west coast, *J. Appl. Phycol.* 32(5) (2020) 3305-3317, <https://doi.org/10.1007/s10811-020-02145-w>.
- [32] F. Ahmad, M.R. Sulaiman, W. Saimon, C.F. Yee, P. Matanjun, 2016. Proximate compositions and total phenolic contents of selected edible seaweed from Semporna, Sabah, Malaysia, *Borneo Sci.* 31 (2012) 85–96.
- [33] P. Kumari, M. Kumar, V. Gupta, C.R.K. Reddy, B. Jha, Tropical marine macroalgae as potential sources of nutritionally important PUFAs, *Food Chem.* 120(3) (2010) 749-757, <https://doi.org/10.1016/j.foodchem.2009.11.006>.
- [34] K. Rohani-Ghadikolaie, E. Abdulalian, W.K. Ng, Evaluation of the proximate, fatty acid and mineral composition of representative green, brown and red seaweeds from the Persian Gulf of Iran as potential food and feed resources, *J. Food Sci. Technol.* 49 (2012) 774-780, <https://doi.org/10.1007/s13197-010-0220-0>.
- [35] M. Kumar, P. Kumari, N. Trivedi, M.K. Shukla, V. Gupta, C.R.K. Reddy, B. Jha, Minerals, PUFAs and antioxidant properties of some tropical seaweeds from Saurashtra coast of India, *J. Appl. Phycol.* 23 (2011) 797–810, <https://doi.org/10.1007/s10811-010-9578-7>.
- [36] P.A. Harnedy, R.J. FitzGerald, Bioactive proteins, peptides, and amino acids from macroalgae 1, *J. Phycol.* 47 (2011) 218-232, <https://doi.org/10.1111/j.1529-8817.2011.00969.x>.
- [37] V. Gressler, N.S. Yokoya, M.T. Fujii, P. Colepicolo, J. Mancini Filho, R.P. Torres, E. Pinto, Lipid, fatty acid, protein, amino acid and ash contents in four Brazilian red algae species, *Food Chem.* 120 (2010) 585-590, <https://doi.org/10.1016/j.foodchem.2009.10.028>.
- [38] P. Matanjun, S. Mohamed, N.M. Mustapha, K. Muhammad, Nutrient content of tropical edible seaweeds, *Eucheuma cottonii*, *Caulerpa lentillifera* and *Sargassum polycystum*, *J. Appl. Phycol.* 21 (2009) 75-80, <https://doi.org/10.1007/s10811-008-9326-4>.
- [39] M. Tabarsa, M Rezaei, Z. Ramezanpour, J. Robert Waaland, R. Rabiei, Fatty acids, amino acids, mineral contents, and proximate composition of some brown seaweeds 1, *J. Phycol.* 48 (2012) 285-292, <https://doi.org/10.1111/j.1529-8817.2012.01122.x>.

- [40] S. Arasaki, T. Arasaki, *Vegetables from the sea*. Japan Publication International Tokyo (1983) 196.
- [41] Y.E. Rodríguez-Montesinos, D.L. Arvizu-Higuera, G. Hernández-Carmona, M. Muñoz-Ochoa, J.I. Murillo-Álvarez, Seasonal variation of the agar quality and chemical composition of *Gracilaria veleroae* and *Gracilaria vermiculophylla* (Rhodophyceae, Gracilariaceae) from Baja California Sur, Mexico, *Phycol. Res.* 61 (2013) 116-123, <https://doi.org/10.1111/pre.12008>.
- [42] H.M. Khairy, S.M. El-Shafay, Seasonal variations in the biochemical composition of some common seaweed species from the coast of Abu Qir Bay, Alexandria, Egypt, *Oceanologia* 55 (2013) 435-452, <https://doi.org/10.5697/oc.55-2.435>.
- [43] J.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, <https://doi.org/10.1016/j.biortech.2011.08.032>.
- [44] D.L. Klass, *Energy from biomass and wastes: 1979 update* (No. CONF-800129-5). Institute of Gas Technology, Chicago, IL, (1979).
- [45] A.M. Tompkins, A.J. Bryce, Marine Biomass Program, final report April 1981-April 1984 (No. PB-85-100691/XAD), General Electric Co., Philadelphia, PA (USA), Advanced Energy Programs Dept. (1984).
- [46] A.N. Tompkins, Marine biomass program annual report, 1982 (No. PB-84-104660), General Electric Co., Philadelphia, PA (USA), Advanced Energy Programs Dept. (1983).
- [47] U. Croatto, R. Energetiche, Exploitation of lagoon macro-algae for biogas production, *Solar Energy R&D in the European Community*, (1981), <https://doi.org/10.1007/978-94-009-8560-5>.
- [48] K. Wagener, Mariculture on land—a system for biofuel farming in coastal deserts, *Biomass* 1(2) (1981) 145-158, [https://doi.org/10.1016/0144-4565\(81\)90022-6](https://doi.org/10.1016/0144-4565(81)90022-6).
- [49] P.A. Moss, D.O. Hall, Biomass for energy in Europe, *International Journal of Solar Energy* 1(4) (1982) 239-261, <https://doi.org/10.1080/01425918208909890>.
- [50] V.N. Gunaseelan, Anaerobic digestion of biomass for methane production: a review, *Biomass Bioenergy* 13(1-2) (1997) 83-114, [https://doi.org/10.1016/S0961-9534\(97\)00020-2](https://doi.org/10.1016/S0961-9534(97)00020-2).
- [51] S.J. Horn, I.M. Aasen, K. Østgaard, Ethanol production from seaweed extract, *J. Ind. Microbiol. Biotechnol.* 25 (2000) 249-254, <https://doi.org/10.1038/sj.jim.7000065>.
- [52] N. Trivedi, V. Gupta, C.R.K. Reddy, B. Jha, Marine macroalgal biomass as a renewable source of bioethanol, *Marine bioenergy: trends and developments*, CRC Publisher, Taylor and Francis Group, USA, (2015) 197-216, <https://doi.org/10.1201/b18494-16>.
- [53] K. Eswaran, P.K. Ghosh, A.K. Siddhanta, J.S. Patolia, C. Periyasamy, A.S. Mehta, K.H. Mody, B.K. Ramavat, K. Prasad, M.R. Rajyaguru, C.R.K. Reddy, Integrated method for production of carrageenan and liquid fertilizer from fresh seaweeds, U.S. Patent 6,893,479 (2005).
- [54] J.H. Reith, W. Huijgen, J.W. van Hal, J. Lenstra, *Seaweed potential in the Netherlands*, Petten: ECN (2009).

- [55] J. Lenstra, H. Reith, J.W. van Hal, Economic perspectives of seaweed, In Presented at the 4th International Algae Congress 1 (2010) 2.
- [56] J.W. van Hal, J. Lenstra, H. Reith, A.M.L. Contreras, Seaweed biorefinery: towards third generation biobased commodities, *Alg'n Chem* (2011).
- [57] J.W. van Hal, 2012, Seaweed Biorefinery: towards third generation biobased fuels and chemicals, In European Algae Biomass Conference, London (2012) 25-26.
- [58] Y. Khambhaty, K.H. Mody, M.R. Gandhi, S. Thampy, P. Maiti, H. Brahmabhatt, K. Eswaran, P.K. Ghosh, *Kappaphycus alvarezii* as a source of bioethanol, *Bioresour. Technol.* 103 (2012) 180-185, <https://doi.org/10.1016/j.biortech.2011.10.015>.
- [59] 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, <https://doi.org/10.1016/j.biortech.2012.10.120>.
- [60] D. Mondal, M. Sharma, P. Maiti, K. Prasad, R. Meena, A.K. Siddhanta, P. Bhatt, S. Ijardar, V.P., Mohandas, A. Ghosh, K. Eswaran, Fuel intermediates, agricultural nutrients and pure water from *Kappaphycus alvarezii* seaweed, *RSC Adv.* 3 (2013) 17989-17997, <https://doi.org/10.1039/C3RA42919A>.
- [61] R.S. Baghel, N. Trivedi, C.R.K. Reddy, A simple process for recovery of a stream of products from marine macroalgal biomass, *Bioresour. Technol.* 203 (2016) 160-165, <https://doi.org/10.1016/j.biortech.2015.12.051>.
- [62] F. Masarin, F.R.P. Cedeno, E.G.S. Chavez, L.E. De Oliveira, V.C. Gelli, R. Monti, Chemical analysis and biorefinery of red algae *Kappaphycus alvarezii* for efficient production of glucose from residue of carrageenan extraction process, *Biotechnol. Biofuels* 9 (2016) 1-12, <https://doi.org/10.1186/s13068-016-0535-9>.
- [63] A. Peñuela, D. Robledo, N. Bourgougnon, G. Bedoux, E. Hernández-Núñez, Y. Freile-Peigrín, Environmentally friendly valorization of *Solieria filiformis* (Gigartinales, Rhodophyta) from IMTA using a biorefinery concept, *Mar. Drugs* 16 (2018) 487, <https://doi.org/10.3390/md16120487>.
- [64] L. Cao, K.M. Iris, D.W. Cho, D. Wang, D.C. Tsang, S. Zhang, S. Ding, L. Wang, Y.S. Ok, Microwave-assisted low-temperature hydrothermal treatment of red seaweed (*Gracilaria lemaneiformis*) for production of levulinic acid and algae hydrochar, *Bioresour. Technol.* 273 (2019) 251-258. <https://doi.org/10.1016/j.biortech.2018.11.013>.
- [65] M.D.N. Meinita, B. Marhaeni, G.T. Jeong, Y.K. Hong, Sequential acid and enzymatic hydrolysis of carrageenan solid waste for bioethanol production: a biorefinery approach, *J. Appl. Phycol.* 31 (2019) 2507-2515, <https://doi.org/10.1007/s10811-019-1755-8>.
- [66] F. Offei, M. Mensah, F. Kemausuor, A. Thygesen, A biorefinery approach to bioethanol and bioelectricity co-production from tropical seaweeds, *J. Appl. Phycol.* 31 (2019) 3899-3913, <https://doi.org/10.1007/s10811-019-01887-6>.
- [67] P. Zhao, X. Wang, J. Niu, L. He, W. Gu, X. Xie, M. Wu, G. Wang, Agar extraction and purification of R-phycoerythrin from *Gracilaria tenuistipitata*, and subsequent wastewater treatment by *Ulva prolifera*, *Algal Res.* 47 (2020) 101862, <https://doi.org/10.1016/j.algal.2020.101862>.

- [68] P. Liu, J. Xie, H. Tan, F. Zhou, L. Zou, J. Ouyang, Valorization of *Gelidium amansii* for dual production of D-galactonic acid and 5-hydroxymethyl-2-furancarboxylic acid by chemo-biological approach, *Microb. Cell Factories* 19 (2020) 1-9, <https://doi.org/10.1186/s12934-020-01357-6>.
- [69] M.J. Hessami, A. Salleh, S.M. Phang, Bioethanol a by-product of agar and carrageenan production industry from the tropical red seaweeds, *Gracilaria manilaensis* and *Kappaphycus alvarezii*, *Iran. J. Fish. Sci.*, 19 (2020) 942-960, <https://doi.org/10.22092/IJFS.2018.117104>.
- [70] J.S. Gomes-Dias, A. Romani, J.A. Teixeira, C.M. Rocha, Valorization of seaweed carbohydrates: Autohydrolysis as a selective and sustainable pretreatment, *ACS Sustain. Chem. Eng.* 8(46) (2020) 17143-17153, <https://doi.org/10.1021/acssuschemeng.0c05396>.
- [71] S.L. Baptista, A. Romani, C. Oliveira, S. Ferreira, C.M. Rocha, L. Domingues, Galactose to tagatose isomerization by the L-arabinose isomerase from *Bacillus subtilis*: A biorefinery approach for *Gelidium sesquipedale* valorization, *LWT*, 151 (2021) 112199, <https://doi.org/10.1016/j.lwt.2021.112199>.
- [72] A.E.F. Abomohra, M.E. El-Hefnawy, Q. Wang, J., Huang, L. Li, J. Tang, S. Mohammed, Sequential bioethanol and biogas production coupled with heavy metal removal using dry seaweeds: Towards enhanced economic feasibility. *J. Clean. Prod.* 316 (2021) 128341, <https://doi.org/10.1016/j.jclepro.2021.128341>.
- [73] S. Tedesco, G. Hurst, E. Randviir, M. Francavilla, A comparative investigation of non-catalysed versus catalysed microwave-assisted hydrolysis of common North and South European seaweeds to produce biochemicals. *Algal Res.* 60 (2021) 102489, <https://doi.org/10.1016/j.algal.2021.102489>.
- [74] M. Alvarado-Morales, I.B. Gunnarsson, I.A. Fotidis, E. Vasilakou, G., Lyberatos, I. Angelidaki, *Laminaria digitata* as a potential carbon source for succinic acid and bioenergy production in a biorefinery perspective, *Algal Res.* 9 (2015) 126-132, <https://doi.org/10.1016/j.algal.2015.03.008>.
- [75] Y. Yuan, D.J. Macquarrie, Microwave assisted step-by-step process for the production of fucoidan, alginate sodium, sugars and biochar from *Ascophyllum nodosum* through a biorefinery concept, *Bioresour. Technol.* 198 (2015) 819-827, <https://doi.org/10.1016/j.biortech.2015.09.090>.
- [76] E.M. Balboa, A. Moure, H. Domínguez, Valorization of *Sargassum muticum* biomass according to the biorefinery concept, *Mar. Drugs* 13 (2015) 3745-3760, <https://doi.org/10.3390/md13063745>.
- [77] P. Fasahati, J.J. Liu, Application of MixAlco® processes for mixed alcohol production from brown algae: Economic, energy, and carbon footprint assessments, *Fuel Process. Technol.* 144 (2016) 262-273, <https://doi.org/10.1016/j.fuproc.2016.01.008>.
- [78] R. Dickson, J.H. Ryu, J.J. Liu, Optimal plant design for integrated biorefinery producing bioethanol and protein from *Saccharina japonica*: A superstructure-based approach, *Energy* 164 (2018) 1257-1270, <https://doi.org/10.1016/j.energy.2018.09.007>.
- [79] S. Tedesco, S. Daniels, Optimisation of biogas generation from brown seaweed residues: Compositional and geographical parameters affecting the viability of a biorefinery concept, *Appl. Energy* 228 (2018) 712-723, <https://doi.org/10.1016/j.apenergy.2018.06.120>.

- [80] N. Flórez-Fernández, H. Domínguez, M.D. Advances in the biorefinery of *Sargassum muticum*: Valorisation of the alginate fractions, *Ind. Crops Prod.* 138 (2019) 111483, <https://doi.org/10.1016/j.indcrop.2019.111483>.
- [81] R.E. Abraham, P. Su, M. Puri, C.L. Raston, W. Zhang, Optimisation of biorefinery production of alginate, fucoidan and laminarin from brown seaweed *Durvillaea potatorum*, *Algal Res.* 38 (2019) 101389, <https://doi.org/10.1016/j.algal.2018.101389>.
- [82] H.G. Lim, D.H. Kwak, S. Park, S. Woo, J.S. Yang, C.W. Kang, B. Kim, M.H. Noh, S.W. Seo, G.Y. Jung, *Vibrio sp.* dhg as a platform for the biorefinery of brown macroalgae, *Nat. Commun.* 10 (2019) 1-9, <https://doi.org/10.1038/s41467-019-10371-1>.
- [83]. Brigljević, J.J. Liu, H. Lim, Comprehensive feasibility assessment of a poly-generation process integrating fast pyrolysis of *S. japonica* and the Rankine cycle, *Appl. Energy*, 254 (2019) 113704, <https://doi.org/10.1016/j.apenergy.2019.113704>.
- [84] R. Zhang, A.K. Yuen, R. de Nys, A.F. Masters, T. Maschmeyer, Step by step extraction of bioactives from the brown seaweeds, *Carpophyllum flexuosum*, *Carpophyllum plumosum*, *Ecklonia radiata* and *Undaria pinnatifida*. *Algal Res.* 52 (2020) 102092, <https://doi.org/10.1016/j.algal.2020.102092>.
- [85] H. Niaz, B. Brigljevic, Y.B. Park, H.C. Woo, J.J. Liu, Comprehensive feasibility assessment of combined heat, hydrogen, and power production via hydrothermal liquefaction of *Saccharina japonica*, *ACS Sustain. Chem. Eng.* 8(22) (2020) 8305-8317, <https://doi.org/10.1021/acssuschemeng.0c01951>.
- [86] T.M. Thompson, P. Ramin, I. Udugama, B.R. Young, K.V. Gernaey, S. Baroutian, Techno-economic and environmental impact assessment of biogas production and fertiliser recovery from pelagic *Sargassum*: A biorefinery concept for Barbados, *Energy Convers. Manag.* 245 (2021) 114605, [10.1016/j.enconman.2021.114605](https://doi.org/10.1016/j.enconman.2021.114605).
- [87] F. Nazemi, K. Karimi, J.F. Denayer, M. Shafiei, Techno-economic aspects of different process approaches based on brown macroalgae feedstock: A step toward commercialization of seaweed-based biorefineries, *Algal Res.* 58 (2021) 102366, <https://doi.org/10.1016/j.algal.2021.102366>.
- [88] S.L. Hoffmann, M. Kohlstedt, L. Jungmann, M. Hutter, I. Poblete-Castro, J. Becker, C Wittmann, Cascaded valorization of brown seaweed to produce L-lysine and value-added products using *Corynebacterium glutamicum* streamlined by systems metabolic engineering. *Metab. Eng.* 67 (2021) 293-307, <https://doi.org/10.1016/j.ymben.2021.07.010>.
- [89] N. Flórez-Fernández, M. Illera, M. Sánchez z, P. Lodeiro, M.D. Torres, M.E. López-Mosquera, M. Soto, M.S. de Vicente, H. Dominguez, Integrated valorization of *Sargassum muticum* in biorefineries, *Chem. Eng. J.* 404 (2021) 125635, <https://doi.org/10.1016/j.cej.2020.125635>.
- [90] P.G. del Río, G. Pablo, B. Gullón, A. Pérez-Pérez, A. Romaní, G. Garrote, Microwave hydrothermal processing of the invasive macroalgae *Sargassum muticum* within a green biorefinery scheme, *Bioresour. Technol.*, 340 (2021) 125733, <https://doi.org/10.1016/j.biortech.2021.125733>.
- [91] X. Zhang, M. Thomsen, Techno-economic and environmental assessment of novel biorefinery designs for sequential extraction of high-value biomolecules from brown macroalgae *Laminaria*

- digitata*, *Fucus vesiculosus*, and *Saccharina latissima*, *Algal Res.* 60 (2021) 102499, <https://doi.org/10.1016/j.algal.2021.102499>.
- [92] K. Ruangrit, S. Chaipoot, R. Phongphisutthinant, K. Duangjan, K. Phinyo, I. Jeerapan, J. Pekkoh, S. Srinuanpan, 2021. A successful biorefinery approach of macroalgal biomass as a promising sustainable source to produce bioactive nutraceutical and biodiesel, *Biomass Convers. Biorefin.* (2021) 1-11, <https://doi.org/10.1007/s13399-021-01310-6>.
- [93] C. Sasaki, S. Tamura, M. Suzuki, K. Etomi, N. Nii, J. Hayashi, K. Kanemaru, Continuous microwave-assisted step-by-step extraction of bioactive water-soluble materials and fucoidan from brown seaweed *Undaria pinnatifida* waste, *Biomass Convers. Biorefin.* (2022) 1-10, <https://doi.org/10.1007/s13399-022-03035-6>.
- [94] E. Vimali, S. Gunaseelan, V.C. Devi, S. Mothil, M. Arumugam, B. Ashokkumar, I.M.G. Moorthy, A. Pugazhendhi, P. Varalakshmi, Comparative study of different catalysts mediated FAME conversion from macroalga *Padina tetrastromatica* biomass and hydrothermal liquefaction facilitated bio-oil production, *Chemosphere* 292 (2022) 133485, <https://doi.org/10.1016/j.chemosphere.2021.133485>.
- [95] N. Jeyakumar, A.T. Hoang, S. Nižetić, D. Balasubramanian, S. Kamaraj, P.L. Pandian, R. Sirohi, P.Q.V. Nguyen, X.P. Nguyen, Experimental investigation on simultaneous production of bioethanol and biodiesel from macro-algae, *Fuel* 329 (2022) 125362, <https://doi.org/10.1016/j.fuel.2022.125362>.
- [96] H. van der Wal, B.L. Sperber, B. Houweling-Tan, R.R. 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, <https://doi.org/10.1016/j.biortech.2012.10.094>.
- [97] N.B. Yahmed, M.A. Jmel, M.B. Alaya, H. Bouallagui, M.N. Marzouki, I. Smaali, A biorefinery concept using the green macroalgae *Chaetomorpha linum* for the coproduction of bioethanol and biogas, *Energy Convers. Manag.* 119 (2016) 257-265, <https://doi.org/10.1016/j.enconman.2016.04.046>.
- [98] M. Magnusson, C. Carl, L. Mata, R. de Nys, N.A. Paul, Seaweed salt from *Ulva*: a novel first step in a cascading biorefinery model, *Algal Res.* 16 (2016) 308-316, <https://doi.org/10.1016/j.algal.2016.03.018>.
- [99] P. Bikker, M.M. van Krimpen, P. van Wikselaar, B. Houweling-Tan, N. Scaccia, J.W. van Hal, W.J. Huijgen, J.W. Cone, A.M. López-Contreras, Biorefinery of the green seaweed *Ulva lactuca* to produce animal feed, chemicals and biofuels, *J. Appl. Phycol.* 28 (2016) 3511-3525, <https://doi.org/10.1007/s10811-016-0842-3>.
- [100] C.R. Glasson, I.M. Sims, S.M. Carnachan, R. de Nys, M. Magnusson, A cascading biorefinery process targeting sulfated polysaccharides (ulvan) from *Ulva ohnoi*, *Algal Res.* 27 (2017) 383-391, <https://doi.org/10.1016/j.algal.2017.07.001>.
- [101] T.K. Gajaria, P. Suthar, R.S. Baghel, N.B. Balar, P. Sharnagat, V.A. Mantri, C.R.K. Reddy, Integration of protein extraction with a stream of byproducts from marine macroalgae: a model forms the basis for marine bioeconomy, *Bioresour. Technol.* 243 (2017) 867-873, <https://doi.org/10.1016/j.biortech.2017.06.149>.

- [102] P.R. Postma, O. Cerezo-Chinarro, R.J. Akkerman, G. Olivieri, R.H. Wijffels, W.A. Brandenburg, M.H. Eppink, M.H., Biorefinery of the macroalgae *Ulva lactuca*: extraction of proteins and carbohydrates by mild disintegration, *J. Appl. Phycol.* 30 (2018) 1281-1293, <https://doi.org/10.1007/s10811-017-1319-8>.
- [103] A. Mhatre, S. Gore, A. Mhatre, N. Trivedi, M. Sharma, R. Pandit, A. Anil, A. Lali, Effect of multiple product extractions on bio-methane potential of marine macrophytic green alga *Ulva lactuca*, *Renew. Energy* 132 (2019) 742-751, <https://doi.org/10.1016/j.renene.2018.08.012>.
- [104] M.S. Prabhu, K. Levkov, Y.D. Livney, A. Israel, A. Golberg, High-voltage pulsed electric field preprocessing enhances extraction of starch, proteins, and ash from marine macroalgae *Ulva ohnoi*, *ACS Sustain. Chem. Eng.* 7 (2019) 17453-17463, <https://doi.org/10.1021/acssuschemeng.9b04669>.
- [105] M.S. Prabhu, A. Israel, R.R. Palatnik, D. Zilberman, A. Golberg, Integrated biorefinery process for sustainable fractionation of *Ulva ohnoi* (Chlorophyta): process optimization and revenue analysis, *J Appl. Phycol.*, 32 (2020) 2271-2282, <https://doi.org/10.1007/s10811-020-02044-0>.
- [106] M. Polikovsky, A. Gillis, E. Steinbruch, A. Robin, M. Epstein, A. Kribus, A. Golberg, Biorefinery for the co-production of protein, hydrochar and additional co-products from a green seaweed *Ulva sp.* with subcritical water hydrolysis, *Energy Convers. Manag.* 225 (2020) 113380, <https://doi.org/10.1016/j.enconman.2020.113380>.
- [107] A. Shrestha, B. Acharya, A.A. Farooque, Study of hydrochar and process water from hydrothermal carbonization of sea lettuce, *Renew. Energy* 163 (2021) 589-598, <https://doi.org/10.1016/j.renene.2020.08.133>.
- [108] E. Steinbruch, D. Drabik, M. Epstein, S. Ghosh, M.S. Prabhu, M. Gozin, A. Kribus, A. Golberg, Hydrothermal processing of a green seaweed *Ulva sp.* for the production of monosaccharides, polyhydroxyalkanoates, and hydrochar, *Bioresour. Technol.* 318 (2020) 124263, <https://doi.org/10.1016/j.biortech.2020.124263>.
- [109] A. Golberg, M. Polikovsky, M. Epstein, P.M. Slegers, D. Drabik, A. Kribus, Hybrid solar-seaweed biorefinery for co-production of biochemicals, biofuels, electricity, and water: Thermodynamics, life cycle assessment, and cost-benefit analysis, *Energy Convers. Manag.* 246 (2021) 114679, <https://doi.org/10.1016/j.enconman.2021.114679>.
- [110] C. Andrade, P.L. Martins, L.C. Duarte, A.C. Oliveira, F. Carneiro, Development of an innovative macroalgae biorefinery: Oligosaccharides as pivotal compounds, *Fuel* 320 (2022) 123780, <https://doi.org/10.1016/j.fuel.2022.123780>.
- [111] C.R.K. Reddy, R.S. Baghel, N. Trivedi, P. Kumari, V. Gupta, K. Prasad, R. Meena, Integrated process to recover a spectrum of bioproducts from fresh seaweeds, Council of Scientific and Industrial Research CSIR, U.S. Patent 10,000,579 (2018).
- [112] J.J. Milledge, P.J. Harvey, Golden tides: problem or golden opportunity? The valorisation of *Sargassum* from beach inundations. *J. Mar. Sci. Eng.* 4 (2016) 60, <https://doi.org/10.3390/jmse4030060>.
- [113] V. Smetacek, A. Zingone, Green and golden seaweed tides on the rise, *Nature* 504 (2013) 84-88, <https://doi.org/10.1038/nature12860>.

- [114] H. Takeda, F. Yoneyama, S. Kawai, W. Hashimoto, K. Murata, Bioethanol production from marine biomass alginate by metabolically engineered bacteria, *Energy Environ. Sci.* 4 (2011) 2575-2581, <https://doi.org/10.1039/C1EE01236C>.
- [115] 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, Efficient ethanol production from brown macroalgae sugars by a synthetic yeast platform, *Nature* 505 (2014) 239-243, <https://doi.org/10.1038/nature12771>.
- [116] 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, An engineered microbial platform for direct biofuel production from brown macroalgae, *Science* 335 (2012) 308-313, <https://doi.org/10.1126/science.121454>.
- [117] R.S. Baghel, C.R.K. Reddy, B. Jha, Characterization of agarophytic seaweeds from the biorefinery context, *Bioresour. Technol.* 159 (2014) 280-285, <https://doi.org/10.1016/j.biortech.2014.02.083>.
- [118] K. Prasad, A.K. Siddhanta, M. Ganesan, B.K. Ramavat, B. Jha, P.K. Ghosh, Agars of *Gelidiella acerosa* of west and southeast coasts of India, *Bioresour. Technol.* 98 (2017) 1907-1915, <https://doi.org/10.1016/j.biortech.2006.07.028>.
- [119] C.T. Matos, L. Gouveia, A.R.C. Morais, A. Reis, R. Bogel-Lukasik, Green metrics evaluation of isoprene production by microalgae and bacteria, *Green Chem.* 15 (2013) 2854-2864, <https://doi.org/10.1039/C3GC40997J>.
- [120] K. Balina, F. Romagnoli, D. Blumberga, Seaweed biorefinery concept for sustainable use of marine resources, *Energy Procedia* 128 (2017) 504-511, <https://doi.org/10.1016/j.egypro.2017.09.067>.
- [121] N. Trivedi, A.S. Mondal, R. Sharma, D. Mone, Marine Macroalgal Biorefinery: Recent Developments and Future Perspectives, *Algal Biorefineries and the Circular Bioeconomy*, (2022) 1-36, <https://doi.org/10.1201/9781003195405-1>.
- [122] M. Alvarado-Morales, A. Boldrin, D.B. Karakashev, S.L. Holdt, I. Angelidaki, T. Astrup, Life cycle assessment of biofuel production from brown seaweed in Nordic conditions, *Bioresour. Technol.* 129 (2013) 92-99, <https://doi.org/10.1016/j.biortech.2012.11.029>.
- [123] 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>.
- [124] J. Langlois, J. Sassi, G. Jard, J. Steyer, J. Delgenes, A. Hélias, Life cycle assessment of biomethane from offshore-cultivated seaweed, *Biofuels, Bioprod. Biorefining.* 6 (2012) 387-404, <https://doi.org/10.1002/bbb.1330>.
- [125] M. Aresta, A. Dibenedetto, G. Barberio, Utilization of macro-algae for enhanced CO₂ fixation and biofuels production: development of a computing software for an LCA study, *Fuel Process. Technol.* 86 (2005) 1679-1693, <https://doi.org/10.1016/j.fuproc.2005.01.016>.

- [126] M. Seghetta, X. Hou, S. Bastianoni, A.B. Bjerre, M. Thomsen, Life cycle assessment of macroalgal biorefinery for the production of ethanol, proteins and fertilizers—a step towards a regenerative bioeconomy, *J. Clean. Prod.* 137 (2016) 1158-1169, <https://doi.org/10.1016/j.jclepro.2016.07.195>.
- [127] P. Fasahati, R. Dickson, C.M. Saffron, H.C. Woo, J.J. Liu, Seaweeds as a sustainable source of bioenergy: Techno-economic and life cycle analyses of its biochemical conversion pathways, *Renew. Sust. Energ. Rev.* 157 (2022) 112011, <https://doi.org/10.1016/j.rser.2021.112011>.
- [128] G. Cooper, J. McCaherty, E. Huschitt, R. Schwarck, C. Wilson, Ethanol industry outlook, *Renew. Fuels Assoc.* (2021)1-40.
- [129] F.M. Gírio, C. Fonseca, F. Carvalheiro, L.C. Duarte, S. Marques, R. Bogel-Lukasik, Hemicelluloses for fuel ethanol: a review, *Bioresour. Technol.* 101 (2010) 4775-4800, <https://doi.org/10.1016/j.biortech.2010.01.088>.
- [130] B.A. Yoza, E.M. Masutani, The analysis of macroalgae biomass found around Hawaii for bioethanol production, *Environ. Technol.* 34 (2013) 1859-1867, <https://doi.org/10.1080/09593330.2013.781232>.
- [131] 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, <https://doi.org/10.1016/j.biortech.2013.09.103>.
- [132] M. Uchida, M. Murata, Isolation of a lactic acid bacterium and yeast consortium from a fermented material of *Ulva spp.* (Chlorophyta), *J. Appl. Microbiol.* 97 (2004) 1297-1310, <https://doi.org/10.1111/j.1365-2672.2004.02425.x>.
- [133] J.H. Park, J.Y. Hong, H.C. Jang, S. 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, <https://doi.org/10.1016/j.biortech.2011.12.065>.
- [134] K.H. Jung, Y. Ji-Hyeon, S.E. Lee, W.Y. Choi, D.H. Kong, H.Y. Lee, Repeated-batch operation of surface-aerated fermentor for bioethanol production from the hydrolysate of seaweed *Sargassum sagamianum*, *J. Microbiol. Biotechnol.* 21 (2011) 323-331, <https://doi.org/10.4014/jmb.1010.10057>.
- [135] J.M. Adams, J.A. Gallagher, I.S. Donnison, Fermentation study on *Saccharina latissima* for bioethanol production considering variable pre-treatments, *J. Appl. Phycol.* 21 (2009) 569-574, <https://doi.org/10.1007/s10811-008-9384-7>.
- [136] G. Roesijadi, A.E. Copping, M.H. Huesemann, J. Forster, J.R. Benemann, Techno-economic feasibility analysis of offshore seaweed farming for bioenergy and biobased products, Battelle Pacific Northwest Division Report Number PNWD-3931 (2008) 1-115.
- [137] M. Soleymani, K.A. Rosentrater, Techno-economic analysis of biofuel production from macroalgae (seaweed), *Bioengineering*, 4(4) (2017) 92, <https://doi.org/10.3390/bioengineering4040092>.

- [138] 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)175–87, <https://doi.org/10.1016/j.apenergy.2014.11.032>
- [139] P. Fasahati, J.J. Liu, Impact of volatile fatty acid recovery on economics of ethanol production from brown algae via mixed alcohol synthesis, *Chem. Eng. Res. Des.* 98 (2015) 107–22, <https://doi.org/10.1016/j.cherd.2015.04.013>.
- [140] R. Dickson, B. Brigljevic, H. Lim, J.J. Liu, Maximizing the sustainability of a macroalgae biorefinery: a superstructure optimization of a volatile fatty acid platform. *Green Chem.* 22(13) (2020) 4174-4186, <https://doi.org/10.1039/D0GC00430H>.
- [141] R. Dickson, J.J. Liu, A strategy for advanced biofuel production and emission utilization from macroalgal biorefinery using superstructure optimization, *Energy*, 221 (2021) 119883, <https://doi.org/10.1016/j.energy.2021.119883>.
- [142] M. Zollmann, A. Robin, M. Prabhu, M. Polikovsky, A. Gillis, S. Greiserman, A. Golberg, Green technology in green macroalgal biorefineries, *Phycologia* 58(5) (1019) 516-534, <https://doi.org/10.1080/00318884.2019.1640516>
- [143] H.W.A. Al-Juthery H. Abbas Drebee, B.M.K. Al-Khafaji, R.F. Hadi, (2020) Plant biostimulants, seaweeds extract as a model (article review), *IOP Conf Ser Earth Environ Sci.* (2020), <https://doi.org/10.1088/1755-1315/553/1/012015>.
- [144] P.S. Shukla, E.G., Mantin, M. Adil, S. Bajpai, A.T. Critchley, B. Prithiviraj, *Ascophyllum nodosum*-based biostimulants: sustainable applications in agriculture for the stimulation of plant growth, stress tolerance, and disease management. *Front Plant Sci.* 10 (2019) 655, <https://doi.org/10.3389/fpls.2019.00655>.
- [145] B. Eef, D. Marlies, K. van Swam, A. Veen, L. Burger, Identification of the Seaweed Biostimulant Market (Phase 1); The North Sea Farm Foundation: AD Den Haag, The Netherlands, 2018.
- [146] J. Aschemann-Witzel, R.F. Gantriis, P. Fraga, F.J. Perez-Cueto, Plant-based food and protein trend from a business perspective: markets, consumers, and the challenges and opportunities in the future, *Crit. Rev. Food Sci. Nutr.* 161(18) (2021) 3119-3128, <https://doi.org/10.1080/10408398.2020.1793730>.
- [147] Y. Liu, X. Ren, C. Fan, W. Wu, W. Zhang, Y. Wang, Health Benefits, Food Applications, and Sustainability of Microalgae-Derived N-3 PUFA, *Foods* 11(13) (2022) 1883, <https://doi.org/10.3390/foods11131883>.
- [148] M. Lahaye, A. Robic, Structure and functional properties of Ulvan, a polysaccharide from green seaweeds, *Biomacromolecules* 8 (2007) 1765–1774, <https://doi.org/10.1021/bm061185q>.
- [149] S. Bleakley, M. Hayes, Algal proteins: extraction, application, and challenges concerning production, *Foods* 6 (2017) 33, <https://doi.org/10.3390/foods6050033>.