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ORIGINAL ARTICLE

Macroalgae-derived biohydrogen production: biorefinery and circular bioeconomy

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Abstract

Algae is considered as a promising third-generation biofuel feedstock. Macroalgae is an efficient source of biomass for biohydrogen production. Biohydrogen (H_2) is believed as a sustainable and clean energy carrier with high-energy yield. The pretreatment is essential to enhance the hydrolytic process during dark fermentation. During pretreatment, some inhibitory substances are formed and are controlled by detoxification techniques. This review briefly covers the marine macroalgal species, pretreatment methods for biohydrogen production, and inhibitory components formed during the pretreatment. Lastly, this review suggests the techno economic assessment about life cycle, energy, and economic feasibility in biohydrogen production from macroalgae.

Keywords Macroalgae · Pretreatment · Inhibitors · Detoxification · Biohydrogen

1 Introduction

Algae, a diverse species mainly present in the aquatic region, can perform photosynthesis in the absence of roots, stems, and leaves. According to the size, they are divided into two: microalgae (unicellular) and macroalgae (multicellular) [1]. Algae accumulate carbon dioxide (CO_2) rapidly with high productive capacity and generate carbohydrates, proteins, and lipids [2]. Over 50 years, it is proposed to generate biofuels through algae. It is estimated that globally 30.1 million tons of macroalgae is produced in 2016; among them, artificial cultivations produce 95%, and the remaining 5% are produced naturally. Figure 1 shows the schematic outline of this review. Macroalgae, also known as seaweeds, are found to be significant organisms in the marine ecosystem where they utilize the carbon dioxide and store carbon [3]. Many researchers reported that macroalgae are an effective substrate for biobased fuel production, such as biohydrogen, methane, ethanol, and biodiesel [4–6]. Macroalgae is cultivated onshore and offshore. Factors such as climate, temperature, water salinity condition, etc. are considered for commercial macroalgal cultivation. Offshore macroalgal cultivation is cost-effective while onshore cultivation costs more in terms of processing [7]. But, cost factors in processes such as initial investment, operation, biofuel processing, and maintenance are more than the market cost in offshore farming [8] as macroalgae contain much water. Hence, more is needed for the dehydration method. Algal-based biofuel is considered as a 3rd-generation biofuel. Its development is emphasized to focus on the problem of effects related to the production of food crops and its resource distribution. The importance of algae as potential biofuel feedstock was enhanced significantly in recent years. Mainly, the sugar components of macroalgae are realized as a suitable substance for bioethanol production [4]. Also, oil extracted from

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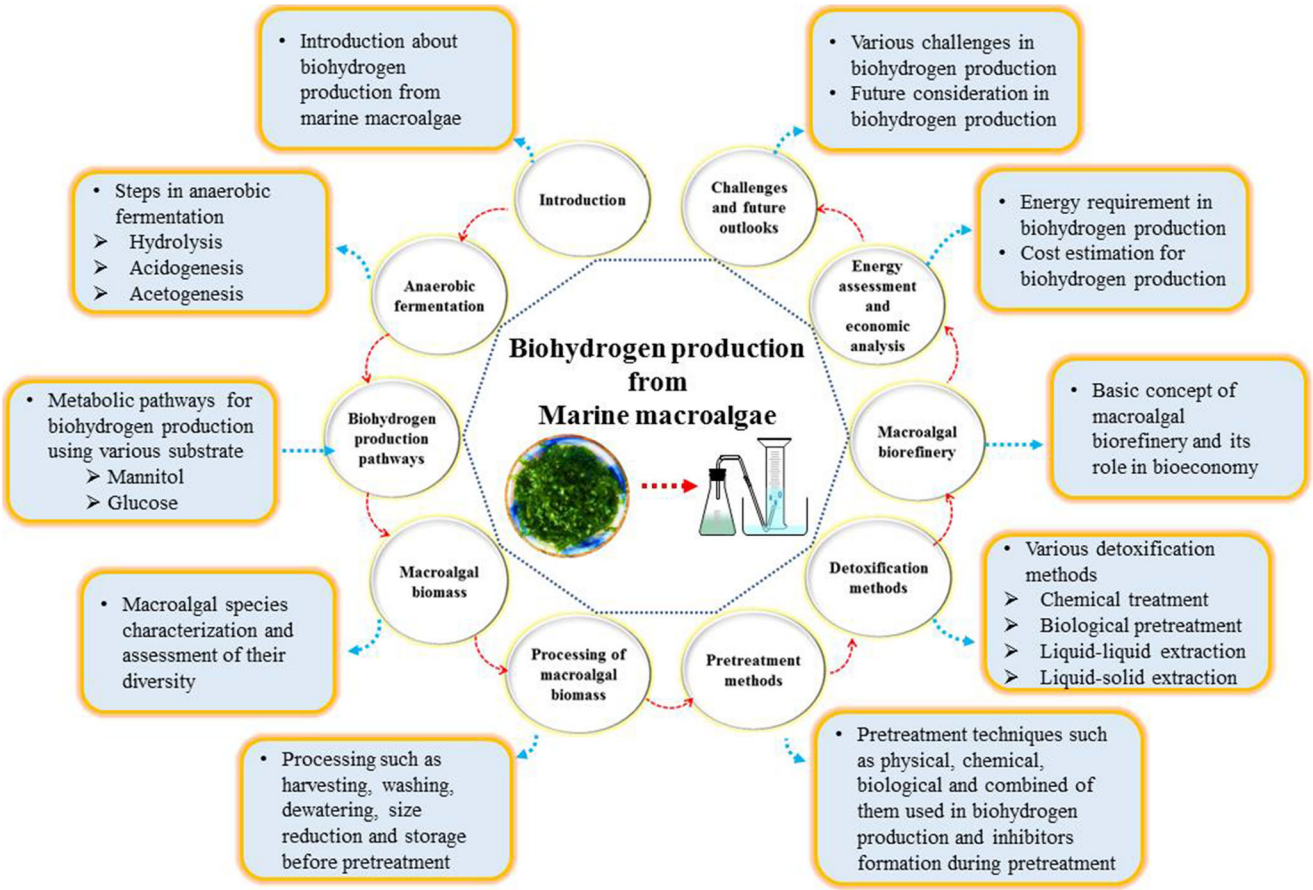


Fig. 1 Schematic outline of the review

algae is feasibly used for biodiesel production. Microalgae receive greater emphasis on biodiesel production as they have a higher growth rate and lipid stock capacity [9]. Higher efficiency of biofuel production from algae is proposed to provide better fuel security for fuel demands.

Biohydrogen is considered a sustainable and clean energy carrier with high-energy yield and is thus a main source of future fuel. Research and development concerning biohydrogen is rapidly increasing in recent years. From the bibliometric analysis, it is possible to assess the scientific activities, research impact, and sources achieved by providing information based on the type of research and its results. Figure 2 shows the number of articles published for biohydrogen production and relevant research development in most productive journals (2010–present). In anaerobic fermentation, hydrolysis is a slow process, which affects the biohydrogen production [10]. Hydrogen-producing microbes generate hydrolytic enzymes that are low in concentration when compared with pure cultures. Thus, pretreatment is required to fasten the hydrolysis and subsequent biohydrogen yield [11]. Generally, an effective pretreatment can improve the breakdown of complex components (carbohydrates) into simpler ones (sugars), preventing the carbohydrate degradation and inhibitor formation with the subsequent fermentation processes. However, pretreatment is one of the most vital but expensive processes in converting biomass to fermentable sugars. The pretreatment cost is assessed as 33% of the total equipment cost in lignocellulosic biomass conversion. Biohydrogen production is affected by recalcitrant/inhibitory compound formation during the pretreatment, which affects the process performance and results in lower hydrogen yields. This inhibitor formation is limited by detoxification techniques such as adding chemical additives, liquid–liquid extraction, liquid–solid extraction, biological treatment, and heating [12]. The algal pretreatment is easier and less expensive compared to lignocellulosic biomass as algae has no recalcitrant component, i.e., lignin. Macroalgae have a potential to be a valuable feedstock for biorefinery. Depending on the type and species of seaweed, it is possible to extract fatty acids, oils, antioxidants, high-value biological components, and other substances. The macroalgal biorefinery context presents a conceptual model for the high-value-added product such as biofuels. The role of the macroalgal biorefinery concept is analyzed in this review. The purpose of the study is to give a clear view about the biohydrogen production from the macroalgae and its circular economy. This review briefly comprehends the marine macroalgal species, pretreatment methods for biohydrogen production, and inhibitory

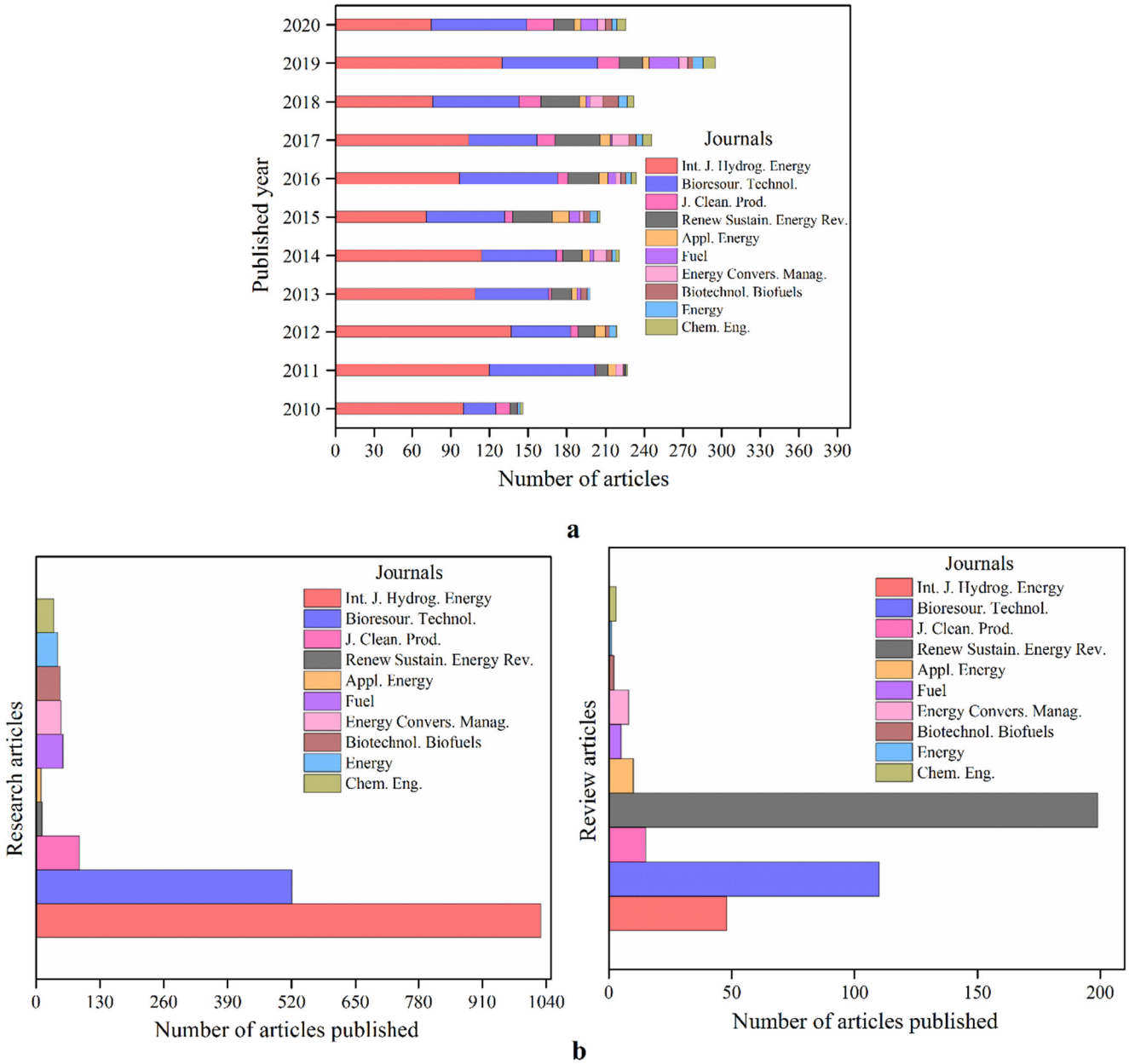
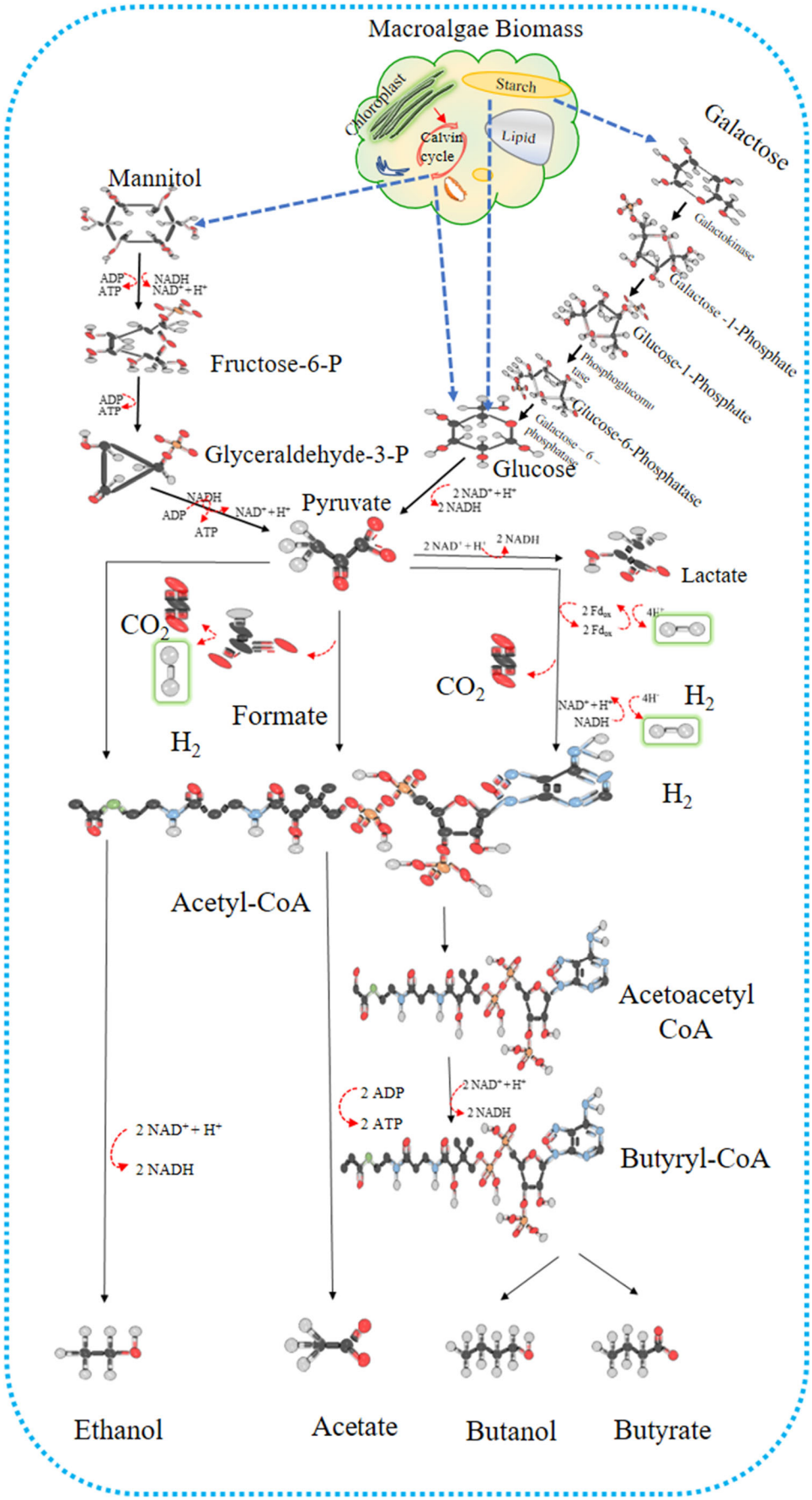


Fig. 2 **a** Number of articles published and **b** comparison of research and review articles published related to biohydrogen in most productive journals during the period (2010–2020)

components formed during the pretreatment. Various detoxification methods, biohydrogen production pathways, and economic and energy analysis during biohydrogen production are also discussed.

2 Anaerobic fermentation—biohydrogen generation

Generally, anaerobic digestion (AD) involves four metabolic steps under the oxygen-free environment: (1) hydrolysis, (2) acidogenesis, (3) acetogenesis, and (4) methanogenesis. In the conventional AD process, hydrogen is not detected as it is directly consumed by methanogens to produce methane (CH_4) and carbon dioxide (CO_2). Hydrolysis, fermentation (acidogenesis), and acetogenesis are the important steps of anaerobic fermentation for hydrogen production. All three steps involved the degradation of biopolymers and conversion to volatile fatty acids (VFAs), followed by hydrogen production (H_2). *Clostridium*, *Enterobacter*, and *Bacillus* are the main microbial species or cultures that produce hydrogen from the carbohydrate-rich substrate [13]. Glucose is hydrolysed into acetic acid with the end product H_2 shown in the following equation [1]:


Macroalgae Biomass
Chloroplast
Starch
Calvin cycle
Lipid
Galactose
Galactokinase
Galactose -1-Phosphate
Glucose-1-Phosphate
Phosphoglucomutase
Glucose-6-Phosphatase
Galactose-6-phosphatase
Mannitol
ADP
ATP
NADH
NAD+ + H+
Fructose-6-P
Glyceraldehyde-3-P
Glucose
Pyruvate
2 NAD+ + H+
2 NADH
Lactate
CO2
Formate
H2
2 Fdox
4H+
Acetyl-CoA
Acetoacetyl CoA
2 ADP
2 ATP
Butyryl-CoA
Ethanol
Acetate
Butanol
Butyrate

◀ **Fig. 3** Different metabolic pathways for biohydrogen production by using **a** mannitol, **b** glucose, and **c** galactose as substrate

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \quad (1)$$

Hydrolysis is a rate-limiting step as it requires a longer duration for the substrate hydrolyzation. In the hydrolysis process, complex substances such as carbohydrates, proteins, and fats are broken down into simpler substances by the fermentative microorganism [14]. Due to the complexity of the structures, biological conversion requires more time, and the process is not effective. Thus, pretreatment is required to disintegrate the cell structures and weaken the structure, which makes the substrate easily available for hydrolysis. Acidogenesis (acid-forming) is the second step in which hydrolyzed organic substances get degraded and produce H_2, CO_2, and VFA by fermentative anaerobic microbes. Acetogenesis is the third step in fermentation in which the biological reaction converts the VFA into H_2, CO_2 with acetic acid as the end product. In this step, acetogens are the main fermentative microbes.

2.1 Biohydrogen production pathways

Hydrogen generation through biological processes garners importance, as it has the least impact on the environment [15]. Production of hydrogen through anaerobic fermentation of biomass is renewable, and sustainable energy production is considered a green energy source. Carbohydrates are significant constituents where monomers are derived and used in biohydrogen production. Mannitol ($C_6H_{14}O_6$), a carbohydrate monomer, is a potential element for biohydrogen production from macroalgae [4]. Mannitol, a simple sugar component of macroalgae, is easily soluble in water, although it is hard to ferment in anaerobic conditions. It creates complications during biofuel production; thus, pretreatment is required to enhance the hydrolysis. Firstly, mannitol is converted into $C_6H_{13}O_9P$ (fructose-6-phosphate) with reduced NADH (nicotinamide adenine dinucleotide) production [4]. Then, $C_6H_{13}O_9P$ is converted into $C_3H_7O_6P$ (glyceraldehyde-3-phosphate), which is further converted into $C_3H_4O_3$ (pyruvate) with acetic acid, ethanol, and butyric acid as end products. In this pathway, hydrogen is produced through ferredoxin and NADH reduced forms, with the hydrogenase as the catalyst. The methanogenesis step could consume hydrogen during fermentation. However, this can be controlled by heating the inoculum and through operating factors such as low pH, high volatile fatty acid concentration, and organic loading. Rafa et al. [16] reported the mechanism of anaerobic fermentation of glucose for hydrogen production. In this process, glucose is converted into $C_3H_4O_3$ with NADH as an intermediate product. Next, $C_3H_4O_3$ is converted into acetyl coenzyme A (acetyl-CoA) and carbon dioxide by pyruvate: ferredoxin oxidoreductase under anaerobic condition. Then it is oxidized by [FeFe]-hydrogenases and yields hydrogen. Alternatively, pyruvate breaks down into formate and acetyl coenzyme A through pyruvate formate lyase. Then formate is converted into H_2 and CO_2 with [NiFe]-hydrogenases or [FeFe]-hydrogenases. In fermentation, acetyl coenzyme A is converted into several organic products such as acetone, butanol, butyric acid, and ethanol with the simultaneous NADH oxidation. Figure 3 shows the metabolic pathway of biohydrogen production using different substrates.

3 Macroalgal biomass as third-generation feedstock

First-generation biofuels depend on food crops such as sugar crops, cereals, and oilseeds, which has led to a series of issues related to food prices, CO_2 emission, and land usage [17] during mass production. Non-food-based biomasses like bagasse, straw, forest residues, and organic waste are the main sources for second-generation biofuel production, affected by technological barriers, collection of feedstock, and cost effects [18]. Biofuels generated from algae are known as third-generation biofuels, which are considered a promising alternate that overcomes the issues related to the production of biofuels in the first and second generations [19]. Algae (micro- and macro-) are considered a third-generation biofuel feedstock. Algae have several advantages like rapid growth rate, being superior in CO_2 fixation, less land requirement, and absence of lignin [18, 20].

3.1 Macroalgal species and types

According to the thallus color, macroalgae are classified into green, red, and brown. In green algal classifications, over 4500 species are present, including 3050 freshwater algal species (*Chlorophyceae* and *Trebouxiophyceae*) and 1500 seawater algae (*Ulvophyceae, Dasycladophyceae*, *Bryopsidophyceae*, and *Siphoncladophyceae*). In red algal classifications, *Rhodophyceae* is the main class that includes two sub-classes: *Bangiophycidae* and *Florideophycidae*. The appearance of red color is due to the presence of pigments such as chlorophyll a, phycoerythrin, and phycocyanin [4]. Among the 6000 red algal species found, most of them exist in tropical regions. The brown algae constitute over 2000 species, among which *Phaeophyceae* is the main class. Its color is due to the presence of chlorophyll a and c, b-carotene, and other xanthophylls [21]. Eight hundred seventy-one macroalgal species are estimated in the Indian marine environment. *Ulva*, *Chaetomorpha*, *Bryopsis*, and *Grateloupia* are mostly found in the southern region of the Tamil Nadu coastal line [22].

3.2 Collection and characterization of macroalgal species

Generally, algae contain various components such as carbohydrates, proteins, ash content, and lipids in various forms. For example, red algae contain carbohydrates in the form of heterosides floridoside [*α-D-galactopyranosyl-(1–2)-glycerol*] [23]. Further, agar, carrageenan, and glucans are the forms of carbohydrates present in red algae. Some algal species contain other forms of carbohydrates such as mannitol, sorbitol, and floridoside. In brown algal species, compounds such as alginate, mannitol, glucose chains, and laminarin are present. Green algae contain polymerized glucose, sucrose, and polysaccharides [24]. Green macroalgae, namely *Ulvacae* and *Cladophoracae* species, are emphasized due to their easy availability and harvesting [25].

3.3 Assessment of diversity

Macroalgae are found 180 m deep in shallow coastal water areas, found on rocks and coral structures. In India, macroalgae are widely spread along with coastal areas; most of the tropical types include 271 and 1153 genus and species, respectively. Over 20,000 ha of marine algae is spread along the coastline of Tamil Nadu. Sahayaraj et al. [26] studied the macroalgal diversity in the southern part of Tamil Nadu. In their study, 57 taxa are identified, among which are 25 taxa in rhodophyta and 18 and 14 taxa belong to chlorophyta and ochrophyta, respectively. Idinthakarai coastal region covers 48 algal species, and is the best site for marine macroalgal collection.

3.4 Analysis of composition

Macroalgae have high water content, minerals, high carbohydrate, protein, and lipids. The absence of lignin [27] and their compositions are summarized in Table 1. Macroalgal species consist of fatty acids, which are saturated (29.92–68.93%), monounsaturated (17.88–39.23%), and polyunsaturated (6.0–17.57%) [28]. Twenty tonnes per hectare of biomass from marine macroalgae is produced yearly. The fucoidan, fucoxanthin, laminarin, mannitol, high-M alginate, and antioxidants are the bioactive components present in marine macroalgae [4].

Table 1 Components present in macroalgal species and their compositions

Components	Macroalgal compositions (% dry weight)
Carbohydrates	Green macroalgae, 25–50% Red macroalgae, 20–60% Brown macroalgae, 30–50%
Proteins	Green macroalgae, 10–30% Red macroalgae, 10–45% Brown macroalgae, 5–15%
Water content	70–90%
Lipids	1–5%

4 Processing of macroalgal biomass

Processing operations of macroalgae are grouped into five main sections: (i) harvesting, (iii) washing and cleaning, (iii) dewatering and drying, (iv) milling, or size reduction, and (v) preservation and storage.

4.1 Harvesting

Harvesting of macroalgae is a significant process in coastal community development for years by providing feed, fuels, and byproducts [29]. Eleven countries in the world are harvesting 1660 tonnes of green macroalgae annually from which *Ulva* spp. are widely harvested in the Korean region [30]. There are generally two techniques in macroalgae harvesting, handheld harvesting and mechanical harvesting. In handheld harvesting, macroalgae are harvested by handpicking. In some cases, a sickle-like tool such as Nejiri or Irish hook is used for harvesting [31]. Mechanical harvesting is performed by using a customized boat, dredge, and mesh conveyor. Mechanical harvesting causes adverse effects on marine ecosystems. Substantially, large-scale harvesting reduces the macroalgal species growth and influences the marine diversity.

4.2 Washing and cleaning

The washing of macroalgae is performed to remove impurities such as epiphytes and extraneous matters by clean water. The cleaning process takes 10 to 30 min at ambient temperatures, preferably 10 to 30 °C. In some cases, macroalgae are exposed to the bleaching process using agents such as Clorox solution, to clean and sterilize macroalgae [32]. Later, macroalgae is hydrated, and the impurities are removed.

4.3 Dewatering and drying

Dewatering is the process of removing water from marine macroalgae through mechanical methods such as pressing and centrifugation. Removing the water content from algal biomass destroys the algae by microbes [32]. In the dewatering process, less energy is used to remove water than evaporation, and it seems better for minimizing the moisture content before drying. The ratio of dry biomass and moisture content is a significant factor for further biofuel processing. Drying is the process of removing the moisture content of

macroalgae and helps the biomass for subsequent treatment steps. The drying process is mostly carried out in sunlight or a hot air oven [6]. Sunlight drying is a widely used method for drying macroalgae. This method is economical as it requires natural weather and no other energy source for drying. Driers using coal fire are used for drying; however, this method is uneconomic for biofuel. The drying process will increase the shelf-life of algae by 20–30% and reduce transportation costs [33]. For sustainable fuel production, air drying is another method to increase the dry biomass content.

4.4 Milling (size reduction)

Milling is the process performed after drying the size reduction of macroalgae. It is then exposed to sieving. Smaller particles tend to have higher reaction efficiency during anaerobic fermentation for biofuel production [6]. Milling is commonly used to increase the surface area to volume ratio to enhance the hydrolysis in the anaerobic digestion. A significant rise in methane yield is exhibited due to the size reduction of macroalgae before anaerobic digestion. Tedesco et al. [34] studied the particle size reduction of macroalgae *Laminaria* spp. through beating pretreatment, and achieved an improvement of 53% in methane production.

4.5 Preservation and storage

Macroalgal storage is essential due to the high water content. If macroalgae is not properly stored, then it is ruined quickly. Once the size of macroalgae is reduced, it is stored at appropriate temperature. Brown algae is stored at ambient temperature. It has more resistance than other algal species to decomposition. But macroalgal periodic growth needs preservation and storage, which is useful in continuous bioenergy recovery. An alternate preservation method is ensiling (wet storage step), which is extensively used to store animal feed. The ensilage method is used to create low-pH conditions, which inhibits the microbial action, and stops the loss of carbohydrate [35]. In the ensiling process, less amount of dry matter is lost than dry storage. In the ensiling method, general methods such as trenches, clamp or heap silage, bunkers, and silos are used to attain the essential oxygen-free condition.

5 Pretreatment methods for biohydrogen production

Bioenergy generation from marine macroalgal biomass involves the biochemical methods for biohydrogen generation from algae, bioethanol production by fermentation of carbohydrates, biodiesel production from algal oil or lipids by extraction and transesterification, and biomethane production from algal biomass by anaerobic digestion. For degrading the algal feedstock for bio-fuel production, pretreatment is required to improve material accessibility. The primary goal of pretreatment is to weaken the biomass refractory structure. The refractory structure of algal biomass obstructs the sugar yield during hydrolysis. Factors such as crystalline structure and matrix polysaccharides are of recalcitrant nature, which acts as an obstacle for the hydrolysis process. The pretreatment method is proposed to increase the surface area and reduce cellulose crystallinity. The pretreatment increases solubilization by depolymerizing the complex structures and breaking down the bond of molecules. Various pretreatment methods such as physical, mechanical, chemical, biological, and their combination are available for biomass disintegration, and enhance the solubilization [36, 37], and subsequent biogas generation [38].

5.1 Physical pretreatment

Physical pretreatment methods typically reduce the particle size and increase the surface area, thus improving the efficiency of other possible downstream pretreatments [39]. Thermal pretreatment is a technique which breaks the cell structure and enhances the biomass solubilization. Temperature increases the internal pressure, which disintegrates the biomass structure and releases the organics. The temperature increases beyond a certain limit and affects treatment efficiency. Jung et al. [40] reported the thermal treatment of *Laminaria japonica*, which resulted in high hydrogen yield (109.6 mL H_2/g COD) at the temperature of 170 °C. Hydrothermal pretreatment is conducted to treat four macroalgal species (*Alaria esculenta*, *Bifurcaria bifurcate*, *Fucus serratus*, and *Laminaria digitata*) at 500 °C, 1 h [41]. The results showed that a high hydrogen yield of 16 ml H_2/g of macroalgae was achieved for *Bifurcaria bifurcate*. The operational conditions, such as extensive pretreatment time and elevated temperature, are the major disadvantages in thermal treatment, which resulted in the formation of inhibitors and consumed more energy [42]. Microwave treatment is a treatment method for enhanced biomass hydrolysis by thermal and non-thermal effects. The thermal effect is caused by the generation of heat by microwave energy. The athermal effect, also known as the non-thermal effect, is caused by microwave dipole alignment, resulting in heat production and rupture of cell walls. Yeneneh et al. [43] reported the advantages of the microwave such as thermal and athermal effects, heat breaching effects, rapid heating, non-contact heating, and less space requirement. Microwave pretreatment for treating macroalgae *Laminaria japonica* is conducted at different temperature conditions, 100–180 °C, 30 min, and obtained 15.8 mL/g TS hydrogen yield from 160 °C [44]. They stated that 1.9-fold high yield of microwave-treated samples is compared with the control. The microwave pretreatment is effective in enhancing hydrogen production from macroalgae. The main drawback is consumption of more

energy, so it can be reduced by using the combined treatment methods.

5.2 Mechanical pretreatment

Mechanical pretreatment effectively disrupts the biomass and improves the organic release, thus increasing the biogas production. Mechanical methods depend upon milling, grinding, and chipping, which are used to diminish the size, improve the surface area, and decrease crystallinity. Disperser homogenization is a commonly used mechanical treatment for biomass solubilization [45, 46]. Kumar et al. [47] achieved a maximum solubilization of 10.7% and H_2 production of 45.5 mL by treating macroalgal biomass through a disperser. Ultrasonication is another effective mechanical pretreatment method. Its mechanism depends on physical and chemical effects [48]. In this treatment, shear forces, pressure, and temperature generate highly active hydroxyl radicals in the medium, which results in the disruption of substrates. Ultrasonication treats waste activated sludge (WAS) that improves COD solubilization and hydrogen production [49]. The ultrasonication pretreatment of algal biomass caused a 25% improvement in hydrogen production [50].

5.3 Chemical pretreatment

Chemical pretreatment is performed by using the alkalis, acids, and surfactants. It is cost-effective and easy to operate. Biomass is treated through dilute or mild acid to recover sugar and improves hydrolysis in hydrogen fermentation [51]. Sivagurunathan et al. [52] compared the dilute acid pretreatments (HCl, HNO_3, H_3PO_4, and H_2SO_4) and found that H_2SO_4 enhances the rate of sugar recovery and hydrogen yield over other acids. Dilute acid pretreatment improves the hydrogen production from red algae *G. amansi*, and the temperature plays a significant role in hydrogen production [53]. The mechanism of alkaline pretreatment are the dissolution and saponification, which leads to degradation of crystallinity of cell membrane. The $Ca(OH)_2$, NaOH, and NH_4OH are commonly used for alkali pretreatment. Liu and Wang [54] achieved 15 mL/g of H_2 yield from *Laminaria japonica* using alkaline treatment (1.0 mol/L NaOH). Hydrogen peroxide (H_2O_2) produces nascent oxygen [O] that ruptures the glycosidic linkage between carbohydrate molecules. Roy et al. [55] studied the H_2O_2 pretreatment of algal biomass, and achieved an H_2 yield of about 63 dm^3/kg VS. Surfactants are the compounds which have both hydrophilic and hydrophobic properties. They reduce the surface tension, which improves the hydrolysis [56]. Researchers used surfactants to improve the substrate solubilization and biogas generation by combining them with other pretreatment methods [57–59]. The chemical surfactants are toxic when they enter the environment. Biosurfactants such as rhamnolipid are eco-friendly, detoxified, and biodegradable [60]. They are used to enhance hydrophobic activity and control the microbial bond with the substances. For example, rhamnolipid is combined with ultrasonication to improve hydrogen production from anaerobic sludge [61].

5.4 Biological pretreatment

Biological treatments are commonly used for treating algal biomass. They achieved effective solubilization with minimum energy requirement. Amylase, cellulase, lysozyme, glucosidase, and bromelain are some of the enzymes used in biological treatment. Moreover, the treatment efficiency is affected by the type of enzymes used, treatment time, dosage, and type of substrate. Cellulase is the most used enzyme. Srivastava et al. [62] used cellulase for treating rice straw and obtained 2.58 L/L hydrolysate hydrogen yield. The disintegration of biomass using fungi also improves hydrogen production. Zhao et al. [63] carried out fungal pretreatment using *Phanerochaete chrysosporium*, and achieved enhanced H_2 generation of 80.3 mL/g from cornstalk.

5.5 Combined pretreatment

For effective disintegration and better hydrogen yield, various combinations of different pretreatments are used. The cost-benefits, less energy requirement, and rapid processing are the key advantages of hybrid pretreatment methods. Surfactant-assisted mechanical pretreatment enhances hydrogen production from macroalgae. Kumar et al. [47] reported that Tween 80, a non-ionic surfactant, improved the biopolymer releases, and hydrogen production. They also stated that combined pretreatment enhanced the biomass solubilization by 15% over mechanical pretreatment only (10.7%). Biosurfactant is used to enhance the ultrasonication treatment for energy-efficient hydrogen production from sewage sludge [61]. Banu et al. [64] performed an experiment on treating seagrass through surfactant-combined mechanical pretreatment. They achieved energy feasible hydrogen production. The combined microwave-acid pretreatment was studied to treat *L. japonica* and obtained maximum H_2 production of 28 mL/g TS at 140 °C with 1% H_2SO_4 for 15 min [65]. After pretreatment, significant variations or alteration in macroalgal structural compositions are identified due to the pretreatment effect. Using Fourier transform infra-red (FTIR) spectroscopy and X-ray diffraction (XRD), Lee et al. [66] studied the structural variations of *Saccharina japonica* after pretreatment. Macroalgal biomass of *L. digitata* is pretreated by hydrothermal, hydrothermal dilute acid, and enzymes [67]. They reported a comparison of composition variations before and after treatment of algal biomass. The presence of mannitol components was 0.129 g/g VS in non-pretreated substrate; however, 0.149, 0.147, and 0.136 g/g VS were observed after

hydrothermal, hydrothermal dilute acid, and enzyme pretreatment, respectively. Table 2 summarized the various pretreatment methods for biohydrogen generation from marine macroalgal species

6 Formation of inhibitors during pretreatment

During hydrogen production, the complex carbohydrates present in macroalgae break into simple sugars enhanced by the pretreatment. Also, the inhibitory substances, namely furfural, levulinic acid, 5 (hydroxymethyl)furfural (5-HMF) [11], and formic acid [74, 75], are formed. Carbohydrates are degraded into co-products such as acetic acid, carboxylic acid, formic acid, and levulinic acid. Aldehydes and 5-HMF display low toxicity, but depending upon the pretreatment and substrate type, their concentrations may vary and inhibit hydrogen production [76]. Formation of furan aldehydes decreases the sugar yields; therefore, their formation is reduced in pretreatment. During the fermentation, organic acids produced due to the substrate character is reduced by neutralizing the pretreated substrate before fermentation. The formation of inhibitory substances mainly depends on the temperature and time of the pretreatment [77]. The inhibitor effects are influenced by the fermentation environment, the toxicity of the compound, and microbe characteristics. Mirsiaghi and Reardon [78] revealed that inhibitory compounds produced during pretreatment decrease the H_2 yield and process efficiency.

6.1 5-(Hydroxymethyl) furfural (5-HMF)

During pretreatment, glucose present in biomass is degraded and forms toxic elements, such as 5-HMF (5-hydroxymethyl furfural). Srikanth et al. [79] stated that the 5-HMF concentration increases with temperature and pretreatment time. The pretreated substrate contains levulinic and formic acids from 5-HMF through polysaccharide degradation by the acid-thermal pretreatment. The produced acid concentration varies on substrate characterization and pretreatment conditions. Furfural is an inhibitory compound, which affects the microbial metabolism. Furfural is obtained while treating xylose and glucose under severe conditions such as above 170 °C; the concentration of furfural increases with a decrease in glucose concentration. Beyond 180 °C, hydrogen yield is reduced because the sugar is converted into furfural.

6.2 Levulinic acid

Cao et al. [80] performed the microwave-acid pretreatment on *Gracilaria lemaneiformis* at three different temperatures. During the treatment, galactose and glucose are dehydrated and form 5-HMF, which is rehydrated to levulinic and formic acid. During hydrolysis, the end product yield decreases while levulinic and formic acid concentrations increase. The 5-HMF formation ends after 10 min of reaction. The findings revealed that 5-HMF is hydrated and increases the formation of formic and levulinic acid on increasing the pretreatment temperature.

6.3 Tannic acid

Red algal species *G. amansii* is used for butanol production through fermentation. The low production is achieved by the production of inhibitor such as tannins. Besides, pretreatment decomposes the reducing sugars into non-utilizable and recalcitrant compounds such as 5-HMF and other phenolic compounds. In this experiment, *G. amansii* produces more inhibitory compounds than the other hydrolyzed macroalgae. Furthermore, other less toxic inhibitory substances such as terpenic and tannic acids are found during the fermentation process [81].

6.4 Terpenic acid

Macroalgae produce antimicrobial elements, such as phenols and terpenes [82]. Jonsson et al. [81] reported terpenic acid production during fermentation of macroalgal biomass. *Laurencia* is a red seaweed genus containing secondary metabolites, especially terpenes that prevent the growth of marine bacteria. Phenols, terpenes, acetogenins, indoles, fatty acids, and volatile halogenated hydrocarbons are some of the compounds extracted from *Sargassum vulgare* [83].

6.5 Aldehyde

Similar to carboxylic acid, aldehydes contribute to microbial inhibition during hydrogen production [84]. Furan aldehydes produced from carbohydrate are less toxic, but high in concentration, which is present in the pretreated substrate, while aromatic aldehydes from lignin have high toxicity, although the concentrations are low.

6.6 Metallic ions from reactor vessels

The vessel's corrosive reaction produces heavy metal ions such as Cu, Ni, and Fe. These generated ions are also toxic and may slow down the microbe's metabolism during fermentation [23]. The inhibitor formed during fermentation and acid dissociation leads to pH reduction, which decreases the biocatalyst activity.

Table 2 Various pretreatment methods for biohydrogen generation from marine macroalgal species

Pretreatment method	Substrate	Operation conditions	Inoculum	Inoculum treatment	Mode of operation	Biohydrogen yield or production	References
Thermal	*Laminaria japonica*	Temperature, 170 °C Time, 20 min	Anerobic sludge	Heat treatment Temperature, 90 °C Time, 20 min	Batch	109.6 mL/g COD	[40]
Acid	*Gelidium amansii*	Temperature, 150 °C H_2SO_4, 2%	Anaerobic sludge	Heat treatment Temperature, 90 °C Time, 10 min	Batch	0.518 L/g_{VSS}/day	[68]
Acid	*Gelidium amansii*	Temperature, 159 °C H_2SO_4, 2% Solid/liquid ratio, 5.2% (w/w)	Anaerobic sludge	Heat treatment Temperature, 90 °C Time, 20 min	Batch	37.0 mL/g dry biomass	[53]
Acid	*Laminaria japonica*	HCl, 1.0 mol/L Time, 30 min	Anaerobic sludge	Heat treatment Temperature, 80 °C Time, 20 min	Batch	43.65 ± 6.87 mL/g biomass	[69]
Alkaline	*Laminaria japonica*	NaOH, 1.0 mol/L Time, 30 min	Anaerobic sludge	Heat treatment Temperature, 80 °C Time, 20 min	Batch	15.00 ± 3.89 mL/g	[69]
Thermal	*Laminaria japonica*	Temperature, 121 °C Time, 30 min	Anaerobic sludge	Heat treatment Temperature, 80 °C Time, 20 min	Batch	66.68 ± 5.68 mL/g biomass	[69]
Ultrasonic	*Laminaria japonica*	Sonic frequency, 20 kHZ	Anaerobic sludge	Heat treatment Temperature, 80 °C Time, 20 min	Batch	23.56 ± 4.56 mL/g	[69]
Disperser	*Ulva reticulata*	Disperser rpm, 10,000 Time, 30 min	Anaerobic digested sludge	Heat treatment Temperature, 100 °C Time, 30 min	Batch	45 mL/g COD	[47]
Microwave–acid	*Laminaria japonica*	Microwave frequency, 2450 MHz Temperature, 140 °C H_2SO_4, 1% (v/v) Time, 15 min	Anaerobic sludge from mesophilic digester	Heat treatment Temperature, 100 °C Time, 15 min	Batch	28 mL/g TS	[65]
Enzyme	*Kappaphyccus alvarezzi*	Celluclast, 60 U/g algae Temperature, 50 °C	*C. beijerinckii Br21*	–	–	23.8 mmol/g	[70]
Enzyme	*Laminaria digitate*	Glucoamylase, 0.05 g	Sludge from an industrial digester treating swine slurry	–	Batch	44.0 ± 1.2 mL/g VS	[67]
Microwave	*Laminaria japonica*	Temperature, 160 °C Time, 30 min	Digested sludge from WWTP	Ionizing irradiation, 5 kGy	Batch	15.8 mL/g TS	[44]
Alkaline	*Saccharina japonica*	NaOH, 2% Time, 30 min	Digested sludge from WWTP	Ionizing irradiation, 5 kGy	Batch	20.1 mL	[71]
Thermal	*Saccharina japonica*	Temperature, 121 °C Time, 30 min	Digested sludge from WWTP	Ionizing irradiation, 5 kGy	Batch	26 mL	[71]
Thermal—acid	*Saccharina japonica*	Temperature, 121 °C H_2SO_4, 2% Time, 30 min	Digested sludge from WWTP	Ionizing irradiation, 5 kGy	Batch	38.1 mL	[71]
Thermal—alkaline	*Saccharina japonica*	Temperature, 121 °C NaOH, 2%	Digested sludge from WWTP	Ionizing irradiation, 5 kGy	Batch	42 mL	[71]

Table 2 (continued)

Pretreatment method	Substrate	Operation conditions	Inoculum	Inoculum treatment	Mode of operation	Biohydrogen yield or production	References
		Time, 30 min					
Thermal acid	*Laminaria japonica*	Temperature, 121 °C H_2SO_4, 1% Time, 30 min	Anaerobic sludge from sewage treatment plant	Heat treatment and $FeSO_4$ addition Temperature, 100 °C Time, 15 min $FeSO_4$, 400 mg/L	Batch	19.47 mL/g VS	[50]
Hydrothermal	*Saccharina latissimi*	Temperature, 140 °C Time, 20 min	Mixed digestate from pig slurry treating biogas plant	Heat treatment Temperature, 100 °C Time, 30 min	Batch	10.7 mL/g VS	[72]
Microwave	*Chaetomorpha antennina*	Microwave power, 0.36 kW Time, 15 min	Anaerobic digested sludge	Heat treatment Temperature, 100 °C Time, 30 min	Batch	63 mL/g COD	[73]
Surfactant-aided microwave	*Chaetomorpha antennina*	Microwave power, 0.36 kW Ammonium dodecyl sulfate, 0.0035 g/g TS	Anaerobic digested sludge	Heat treatment Temperature, 100 °C Time, 30 min	Batch	74.5 mL/g COD	[73]

WWTP wastewater treatment plant, *kGy* kilogray, *TS* total solids, *VS* volatile solids, *COD* chemical oxygen demand

7 Detoxifications of pretreated macroalgal biomass

Detoxification or biomass conditioning is the better way to limit the inhibition during the fermentation. Biological, physical, and chemical pretreatments are used for detoxification. The choice of detoxification methods depends on the hydrolysates, which are to be treated, and microorganisms are used during fermentation. Detoxification techniques are namely chemical additive treatment, biological treatment, liquid–liquid extraction, liquid–solid extraction and heating, and vaporization. Though detoxification techniques achieve efficient removal of toxicity, it is essential to consider the sugar reduction, cost-effectiveness, and scum generation, which makes this step economically unattractive.

7.1 Chemical additives (alkalis and reducing agents)

Various detoxification agents such as solid and liquid calcium hydroxide ($Ca(OH)_2$) and solid calcium oxide (CaO) are effectively used during hydrogen production [85]. Cao et al. [80] reported that liquid $Ca(OH)_2$ removed less than 30 mg/L of sulfate concentration and simultaneously improved over 30% of H_2 yield when compared with solid $Ca(OH)_2$ and CaO. Detoxification with activated carbon (AC) also reduces the inhibition effect during hydrogen production. Less hydrogen is produced from red-algal biomass by treating with sulfuric acid, while H_2 yield is improved by a combined $Ca(OH)_2$ and AC detoxification method [68]. Park et al. [68] reported that less hydrogen is produced from *Gelidium amansii* using 2% dilute H_2SO_4 at 150 °C temperature for 15 min. It is due to the 5-HMF formation, but further maximum H_2 yield of 53.5 mL H_2/g TS is observed after AC detoxification. The reducing agents such as the sulfur oxyanions sulfite and dithionite improve the fermentation and saccharification [76].

7.2 Biological treatment (enzymes and microbes)

Biological detoxification used bacteria, yeast, and fungi, which are used as biosorbents and improve the process performance. Microbes are capable of detoxifying 5-HMF and furfural, and increase the biofuel yield. Yang et al. [86] used bacterial strain *Burkholderia cepacia* H-2 to perform detoxification of 5-HMF into 2,5-furan-dicarboxylic acid (FDCA), which was beneficial in high biofuel yield production. El harchi et al. [87] used yeast *Pachysolen tannophilus* for biological detoxification to treat green algae and *Ulva rigida* for fermentation.

7.3 Liquid–liquid extraction

Liquid–liquid extraction is a promising detoxification technique that removes inhibitory compounds without any

carbohydrate loss. Roque et al. [88] reported that detoxification strategies involve two processes, liquid–liquid extraction and vacuum evaporation, which is followed by liquid–liquid extraction. Evaporation followed by liquid–liquid extraction process exhibited better removal results of inhibitory elements (formic acid, 100%; phenolics, 88.2%; HMF, 100%; and furfural, 100%) than liquid–liquid extraction (formic acid, 100%; phenolics, 64.2%; HMF, 99.8%; and furfural 96.8%).

7.4 Liquid–solid extraction

Liquid–solid extraction techniques include ion exchange and activated carbon treatment. Orozco et al. [89] reported that 70% of improved H_2 production and 86% of 5-HMF is removed by using liquid–solid extraction (AC) compared with the untreated sample. Park et al. [68] detected less H_2 production from *Gelidium amansii* by H_2SO_4 treatment, whereas further AC detoxification exhibited the improvement in H_2 production. The requirement of a separate process is the major disadvantage of the detoxification technique, which affects the cost-effectiveness of the method. Furthermore, research is required to develop detoxification methods in a cost-effective manner. Table 3 represents the detoxification techniques used to control the process inhibition. Metals like ferrous iron (Fe^{2+}) perform a substantial role in H_2 production [98], which acts in hydrogen-producing metabolism (hydrogenase). Zhao et al. [99] stated that electrons produced during metabolism are combined with H_2 ions, promote the reaction, and produce H_2 in the metabolic pathway. Researchers reported the enhancement of H_2 production by ferrous ion addition. Hydrogen yield increased and reported about 217.4 mL H_2/g glucose at 200 mg/L ferrous ion concentration [100]. Dhar et al. [101] obtained a maximum H_2 production potential of 214 mL by adding 50 mg/L ferrous ion. Yang and Wang [102] achieved 64.7 mL/g H_2 yield from the grass substrate with 400 mg/L zero-valent iron.

8 Macroalgal biorefinery and circular bioeconomy

Macroalgal biorefineries are considered as a sustainable substitute for hydrocarbon-based sources. Therefore, the profitability and feasibility of macroalgal biorefinery was evaluated via life cycle analysis methods [103]. As a whole, the cultivation of macroalgae has been subsidized to ecological renovation and climatic mitigation. On the other hand, the design of sustainable macroalgal biorefinery needs optimization of factors such as the input of energy and supplies utilized for cultivation, macroalgal yield and characteristics, energy utilized for drying of macroalgae, and materials used for macroalgal treatments. The cost analysis of the aforementioned steps highpoint the requirement of decrement in cultivation prices. Besides, integration of processes, such as bioenergy with valuable co-products in a biorefinery approach, is essential. Table 4 represents the different macroalgal biorefineries and their product yield. Figure 4 shows the schematic representation of the macroalgal biorefinery.

8.1 Co-product formation in biorefineries

The macroalgal biorefinery is still focusing on mono-product recovery, whereas the residues from the treatment process are considered waste. Most of the research reports are concentrating mainly on mono-product recovery. The biofuel and multiple product recoveries in an integrated biorefinery process do not show considerable adverse impacts on productivity. Besides, the utilization of chemicals in an integrated biorefinery is decreased to approximately 30–40%, and reducing the costs of the overall macroalgal treatment process [113]. Therefore, extraction of salt, glycoprotein, polysaccharide (example, ulvan), and cellulose via sequential integrated process is endorsed for the complete utilization of the biorefinery. Prabhu et al. [114] have reported that the liquid portion separated via the pretreatment process can be further treated to obtain starch without alteration in its structure. The separated solid fraction can be further treated for extracting pigments and lipids. Lipids can be further utilized for ethanol production [111]. Further acidic processing of residues by thermo-acidic treatment (temp 85 °C and 0.05 M dilute hydrochloric acid) resulted in the extraction of sulfated polysaccharides. Then the residual matter can be extracted using alkaline (1 N NaOH) treatment. Even though the extraction of proteins using alkali is a faster and extensively employed method, it showed less productivity, i.e., 15% of total protein [115]. However, the productivity can be increased further using extreme alkaline dosage. Lastly, the residual matter rich in cellulose content can be subjected to anaerobic digestion for biogas production or can be subjected to microbe-mediated fermentation to generate value-added products. On the other hand, the extracted cellulose can be utilized as a feedstock for multiple product recovery [116].

8.2 Utilization of dark fermentation effluents

A significant amount of organic effluents that could not be converted into hydrogen remains within the digester after the dark fermentation process. This effluent can be utilized and valorize further for biofuel production and multiple product recovery to make the entire process economically profitable. The residual organics from the dark fermentation process can be separated into a liquid fraction (rich in acetate, butyrate, propionate, lactic acid, and ethanol) and a solid fraction (rich in solid materials refractory to biological processes). Cooney et al. [117] suggested that only 10–20% of energy can be recovered from dark fermentative biohydrogen of organic

Table 3 Detoxification techniques used to control inhibitors formed during pretreatments

Detoxification method or techniques	Chemical or agents or enzyme used	Detoxification conditions	Substrate used	Pretreatment methods used for biofuel production	Inhibitory compounds and their removal (%)	Improved biofuel yield	References
Chemical	AC	AC, 10% (w/v) Temp, 35 °C Time, 6 h Agitation, 150 rpm	*Gelidium amansii*	Acid	5-HMF, 97	Hydrogen, 53.5 mL/g TS	[72]
Chemical	Activated charcoal	Activated charcoal, 1% (w/v) Temp, 60 °C Time, 1 h Agitation, 180 rpm	Kappaphycus alvarezii	Acid	5-HMF, 70.37 Levulinic acid, 38.8	Ethanol, 0.369 g/g	[90]
Chemical	Calcium hydroxide	Time, 1 h	Conifer pulp	Acid	Sulfate	Hydrogen, 2.26 mol/mol glucose	[85]
Liquid–solid extraction	AC	AC, 5% (w/v) Temp, 60 °C Time, 1 h Agitation, 180 rpm	Starch	Hydrothermal	5-HMF, 85	Hydrogen, 86%	[89]
Chemical	AC	AC, 10% (w/v) Temp, 35 °C Time, 6 h Agitation, 150 rpm	*Gelidium amansii*	Acid	5-HMF	Hydrogen, 37 mL/g TS	[53]
Chemical	Activated charcoal	Activated charcoal, 5%, 10%, 15%, 20%, and 20% (w/w)	Kappaphycus alvarezii	Thermal and acid	5-HMF, 95	Ethanol, 48.1 g	[91]
Immobilization	AC	Sodium alginate, 2% w/v; chitosan, 1% w/v; AC, 2% w/v Calcium chloride solution, 2% w/v	*Gelidium amansii*	Acid	5-HMF, 100	Hydrogen, 4.8 L/L-d	[92]
Chemical	Sodium borohydride	Sodium borohydride, 0, 15, 30, and 45 mM Temp, 60 °C Time, 1 h	Glucose and xylose	–	Furfural, 96.7 5-HMF, 91.7	Hydrogen, 99.3%	[84]
Chemical	AC	AC, 0.5 g Temp, 37 °C Time, 20 min Agitation, 180 rpm	Water hyacinth	Microwave-assisted dilute acid	Vanillin, 84.8 Furfural, 45.4 5-HMF, 39.5	Hydrogen, 134.9 mL/g TVS	[93]
Electrochemical	Electrode–graphite carbon felt	Time, 10 h Agitation, 20 rpm	Rice straw	Acid	p-coumaric acid, 78, ferulic acid, 77, vanillin, 82, syringaldehyde, 94	–	[94]
Immobilization	Alginate and AC	–	Galactose	–	5-HMF, 98	Hydrogen, 26.6 L/L-d	[95]
Enzyme	*Laccase*	*Laccase*, 5–40 U/g Temp, 55 °C Time, 24 h Agitation, 150 rpm	Sugar bagasse	Acid	Furfural and 5-HMF	Hydrogen, 6 mM	[96]
Washing	Water	Time, 30 min	Sugar bagasse	Acid	Furfural and 5-HMF	Hydrogen, 119.7 mM	[96]
Liquid–liquid extraction	1-Butanol, isobutyl acetate, methyl-isobutyl-ketone	Chemicals, 20 g in each Temp, room Time, 4 h Agitation, 120 rpm	Xylose-rich hydrolysate	Acid	Acetic acid, 94.2, Formic acid, 100, Phenolics, 64.2, HMF, 99.8, Furfural, 96.8	Ethanol, 42.2%	[88]

Table 3 (continued)

Detoxification method or techniques	Chemical or agents or enzyme used	Detoxification conditions	Substrate used	Pretreatment methods used for biofuel production	Inhibitory compounds and their removal (%)	Improved biofuel yield	References
Evaporation and liquid–liquid extraction	Liquid–liquid extraction, 1-butanol, isobutyl acetate, methyl-isobutyl-ketone	Evaporation, 80 °C Chemicals, 20 g in each Temp, room Time, 4 h Agitation, 120 rpm	Xylose-rich hydrolysate	Acid	Acetic acid, 96.6 Formic acid, 100 Phenolics, 88.2 HMF, 100 Furfural, 100	Ethanol, 75.6%	[88]
Chemical: Adsorption Over liming Ion exchange	Adsorption, AC Over liming, Ca $(OH)_2$ Ion exchange, PEI	AC, 4% Ca $(OH)_2$: PEI, 1 g	*Gelidium amansii*	Thermal acid	HMF: Adsorption, 89.5 Over liming, 67.4 Ion exchange, 76.2	Ethanol (g/g) Adsorption, 0.47 Over liming, 0.46 Ion exchange, 0.4	[97]

HMF hydroxymethylfurfural, *TVS* total volatile solids, *AC* activated carbon, *PEI* polyethyleneimine, $Ca(OH)_2$ calcium hydroxide, *TS* total solids

biomass without the pretreatment process. Therefore, side streams valorization in a biorefinery concept must be greatly taken into account. The dark fermentation process can be integrated with anaerobic digestion via biorefinery approaches, or the remaining liquid portion rich in volatile fatty acids can be valorized to produce biopolymers.

8.3 Two-stage integrated anaerobic digestion and dark fermentation

The hydrolysis and acidogenesis (dark fermentation) phases are separated from acetogenesis and methanogenesis phases in two-stage fermentation. In the first phase (dark fermentation), biopolymers, including polysaccharides, glycoproteins, and bio-lipids, are transformed into volatile fatty acids and hydrogen. The volatile fatty acids (chiefly acetic and butyric acids) and the residual organic matter are subsequently transformed into methane in the methanogenesis phase. Jung et al. [108] investigated the two-stage integrated dark fermentation with anaerobic digestion treating the macroalgal biomass, *Laminaria japonica*. The authors reported that 7.1% of the total organics was transformed into hydrogen. Next to dark fermentation, the remaining organics obtained via treated effluents from both liquid (35.1% of total chemical oxygen demand) and solid (38.7% of total chemical oxygen demand) are subsequently transformed into methane.

8.4 Dark fermentation integration with biopolymer production or algal growth

Organic-rich effluents having more volatile fatty acid content obtained from dark fermentation can be transformed into feasible and profitable value-added biopolymers such as bioplastic (polyhydroxyalkanoates) or utilized as a medium for growth of algal biomass [118]. Yan et al. [118] integrated biohydrogen and biopolymer generation from algal biomass (*Taihu blue*). Polyhydroxyalkanoates are polyester clusters that are readily biodegraded and gaining consideration as a possible alternative to petrochemical plastics besides other uses such as pharma and fermentative industrial applications [119]. Polyhydroxyalkanoates were produced from effluents of dark fermentative digester treating *Taihu blue* algae using *Bacillus cereus* sp. At flow rates of 30, 60, and 120 L/h, the biopolymer yields of 1.46, 1.83, and 2.26 g/L were achieved.

9 Life cycle assessment

Life cycle assessment (LCA) is used to calculate a feasible way of biofuel production from source to end product. LCA covers the entire processes such as harvesting, treatment methods, end product, and co-product recovery. During artificial algal cultivation, hydrodynamic effect, surface area to

Table 4 Macroalgal biorefinery

S. no.	Macroalgae	Biorefinery approach	Operational conditions	Product yield	References
1	*Chaetomorpha linum* O.F. Müller	Integrated EF-AD	EF: pH 5; Shaking speed, 150 rpm; temp, 28 ± 2 °C; time, 48 h; inoculum, 10% culture of yeast, *Saccharomyces cerevisiae* AD: Batch stirred anaerobic reactor Substrate to inoculum ratio, 50%/50% (v/v); temp, 38 ± 1 °C; digestion time, 30 days	Bioethanol, 0.093 g/g pretreated algae Biomethane, 0.26 ± 0.045 L/g VS	[104]
2	*Sargassum* sp.	Integrated DF-AD	DF: Reactors used, batch fermentors; Inoculum used, yeast, *Caldicellulosiruptor saccharolyticus*; substrate used, 2.5 g/L *Sargassum* sp.; temp, 70 °C; shaking speed 90 rpm AD: batch process; inoculum used, anaerobic granular sludge; temp, 37 °C. pH, 7.0–7.2	Hydrogen, 91.3 ± 3.3 L/kg Biomethane, 541 ± 10 L/kg	[105]
3	*Laminaria japonica*	Integrated DF-AD	DF: ASBR, HRT, 6 days; temp, 35 °C; pH, 5.5; substrate load, 20 g/L AD: UASB HRT, 2 days; OLR, 3.5 g COD/L/day	Hydrogen, 58.5 mL H_2/g COD Methane, 309 mL CH_4/g COD	[106]
4	*Ulva lactuca*	Sequential osmotic shock, enzymatic hydrolysis, pulsed electric field (PEF) or high shear homogenization	Osmotic shock: stirring time, 24 h; temp- or 30 °C. Enzymes: Cellulase Onozuka RS (C0615) (pH, 5; temp, 30 C; dose, 0.5% DW) , pectinase (pH, 4; temp, 25 °C; dose, 0.5% DW), macerozyme R10 (P2401) (pH, 5; temp, 30 °C; dose, 0.25 %DW), and β-glucuronidase (SRE0022) (pH, 4; temp, 30 °C; dose, 0.5% DW) Pulse field: Voltage between 1.2 and 3.0 kV; pulse duration (0.05, 0.5 or 5 ms) High shear homogenization: Specific energy input, 6.6 kWh/kg protein	Protein yield, 39.0 ± 6.2 Carbohydrate yield, 51.3 ± 5.6	[107]
5	*Laminaria japonica*	Integrated DF-AD with recycling of methane effluent	DF: CSTR; pH, 5.5; HRT, 2.7 days; substrate concentration, 31.1 g COD/L AD: ASBRL; temp, 35 °C; HRT, 12 days; OLR, 2.5 g COD/L/day; 309 mL/g COD AD, UASB; temp, 35 °C; HRT, 2 days; OLR, 4.5 gCOD/L/day	113 mL H_2/gTS 227 mL CH_4/g COD 309 mL CH_4/g COD	[108]
6	*Ulva ohnoi* and *Ulva tepida*	Sequential aqueous washing and drying	Washing, 30 min at 40 °C or for 24 h at 25 °C Drying: time, 48 h; temp, 60 °C	Salt yield: 29% for *U. ohnoi* and 36% for *U. tepida* Ulvan yield: 21.5% for *U. ohnoi* and 9.2% for *U. tepida*	[109]
7	*Ulva lactuca*	Sequential mechanical pressing and crushing, heat treatment and organic solvent and alkali extraction	Lipid extraction: chloroform to methanol ratio 1:2, magnetic stirring, 3 h Ulvan extraction: temp, 90 °C; time, 2 h; stirring time, 30 min Protein extraction: temp, 80 °C; filtered using 0.21 μm filter. Cellulose extraction: pH 3; temp, 65–70 °C	Protein yield: 11 ± 2.12 % on dry weight Amino acid yield: iso-leucine; 23.857 ± 11.32 mg/g protein; histidine 22.920 ± 19.68; tyrosine; 12.710 ± 15.42; threonine 13.559 ± 2.65; phenyl alanine; 9.324 ± 13.19; leucine; 6.509 ± 2.37; lysine; 1.450 ± 1.80 mg/gm protein Cellulose yield, 10.35 ± 1.07% on dry weight Ulvan yield, 19.90% by dry weight Lipid yield: Palmitic acid, 69.60 ± 21.36%	[110]
8	*Ulva ohnoi*	Sequential aqueous pretreatment, thermal and chemical extraction	Aqueous extraction: temp, 40 °C; time, 30 min Thermal and chemical extraction, 0.05 M $Na_2C_2O_4$ (1 L) and heated at 85 °C for 1 h	Salt content, 8.2 ± 1.1% w/w Total sugar content, 624–670 μg/mg Ulvan yield, 53.1 mol%	[111]
9	*Ulva lactuca*	Sequential aqueous, thermal, and chemical extraction and AD	Sap extraction: temp, 60 °C; time, 45 min Ulvan extraction: 1 M HCl, pH 2; temp, 95 °C; time, 3 h Protein extraction, % (w/v) of 0.25 M NaOH; temp, 60 °C; time, 1 h	Sap, 14.76 g by dry weight Ulvan, 28.29 g by dry weight Protein, 35.11 g by dry weight Methane, 408 ± 20.02 mL CH_4/g VS	[112]

Table 4 (continued)

S. no.	Macroalgae	Biorefinery approach	Operational conditions	Product yield	References
10	*Ulva fasciata*	Sequential mechanical grinding, thermal and chemical extraction, and water extraction	AD: batch reactors; inoculum to substrate ratio: 1:2; temp, 37 °C; digestion time, 38–42 days MRLE extraction: time, 10 min; centrifugal speed, 8000 rpm; temp, 50 °C Total lipid extraction: 1:2 chloroform to methanol; temp-4 °C; centrifugal speed, 4000 rpm; time, 20 min Ulvan extraction: autoclaved for 2 h at 90 °C; precipitated with chilled isopropyl alcohol for 24 h at − 40 °C. Cellulose extraction: soaked in 50 mL of 0.5 M NaOH solution at 60 °C for 8–10 h and washed with 5% HCl Enzymatic hydrolysis and bioethanol production: hydrolysed and saccharified with commercial cellulase (2% v/v conc) at 45 °C for 36 h; fermented with *Saccharomyces cerevisiae* (MTCC No. 180) culture (109 CFU/mL) for 12 h at 28 ± 2 °C and a shaking speed of 120 rpm	~ 26% of its starting mass as MRLE, ~ 3% as lipid, ~ 25% as ulvan, and ~ 11% as cellulose, ethanol at a conc of 0.45 g/g reducing sugar	[113]

DF dark fermentation, *AD* anaerobic digestion, *ASBR* anaerobic sequential batch reactor, *HRT* hydraulic retention time, *EF* ethanol fermentation, *CSTR* continuous stirred tank reactors, *UASB* upflow anaerobic sludge blanket reactors, *OLR* organic loading rate, *MRLE* mineral-rich liquid extract, *TS* total solids, *VS* volatile solids, *COD* chemical oxygen demand

volume ratio, light penetration, and CO_2 transfer have to be considered [120]. Pilicka et al. [121] stated that 300 kg/year of CO_2 is absorbed during the growing process of *Ulva* sp and also concluded that in comparison with sludge, macroalgal biomass gives 30 times better net environmental performance during biogas production. The LCA of macroalgae begins at the macroalgae harvesting and ends in the final product (biogas) which includes treatment and co-product recovery with cost of initial investment, energy cost, and operation cost. Cost analysis of hydrogen production covers parameters such as capital cost, operating cost, power cost, labor cost, water cost, and general supplies [122]. The total operating cost of 3605.1 million United Arab Emirates Dirhams (AED) was involved during hydrogen production, and cost of hydrogen was about 68.7 AED/kg hydrogen.

10 Energy feasibility and economic analysis

Energy analysis is mainly considered for the implementation of large-scale applications. According to the energy consumed and energy gain, the selection of pretreatment could be cost-effective. Usually, pretreatment needs more energy for biofuel production. For example, mechanical pretreatment consumes more energy than enzymatic treatment. To limit the energy consumption, two or three pretreatments are combined. It increases the treatment efficiency and reduces energy consumption. Many researchers studied the energy feasibility of pretreatment in biohydrogen production [64]. Table 5 represents the energy analysis comparison for different treatment methods during biohydrogen production. Biohydrogen energy production rate (kJ/L/d) and biohydrogen energy yield (kJ/g VS) are calculated using the Eqs. (2) and (3), respectively, which are derived from Kumar et al. [124].

$$\text{Biohydrogen energy production rate (BEPR)} = H_{\text{pr}}/22.4{*}H_{\text{hv}} \quad (2)$$

where

H_{pr} hydrogen production rate (L/L/day) and
H_{hv} hydrogen heating value (286 J/mmol).

$$\text{Biohydrogen energy yield (BEY)} = H_{\text{y}}/2.44{*}H_{\text{hv}} \quad (3)$$

where

H_{y} hydrogen yield (L/kg VS_{added}) and
H_{hv} hydrogen heating value (286 J/mmol).

Economic analysis is another significant aspect considered during bioenergy production from macroalgae. Many

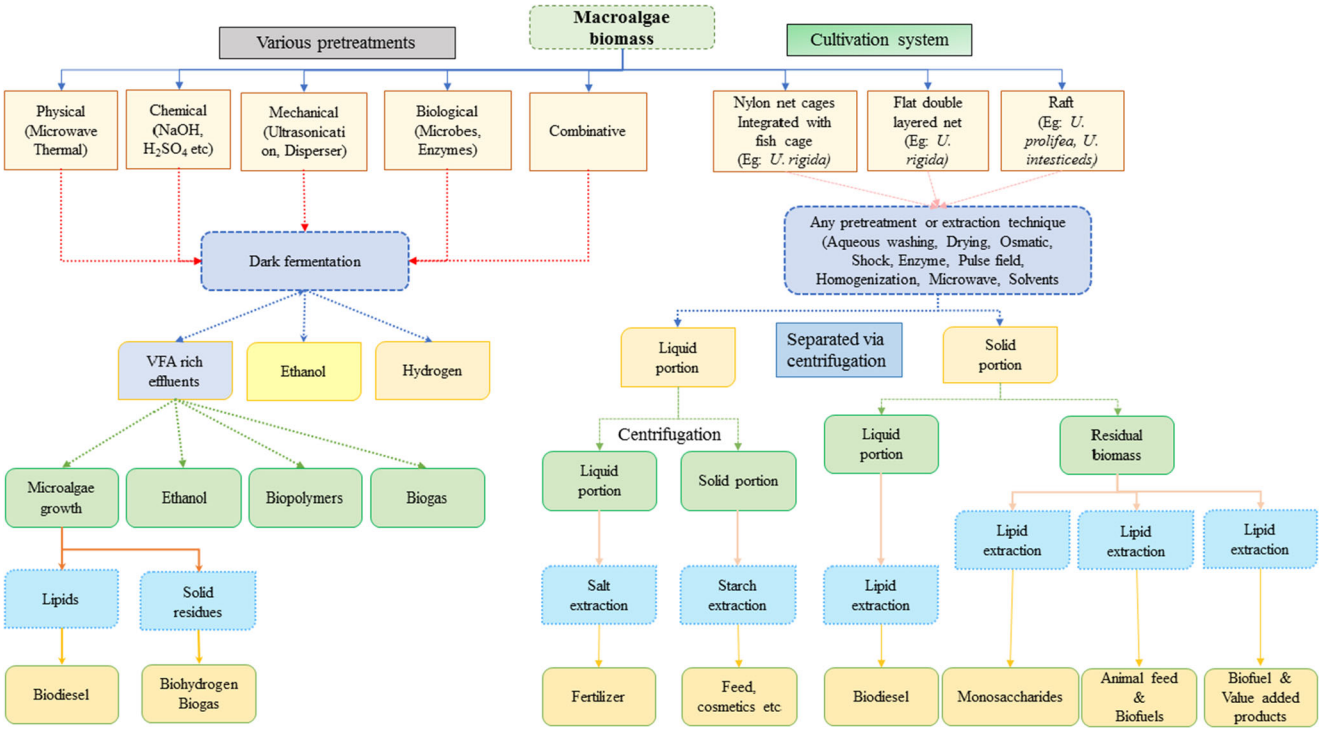


Fig. 4 Schematic representation of macroalgal biorefinery

parameters influenced biofuel generation from marine macroalgae and considered the conversion techniques used in biofuel production. From processing till recovery of end products, economically feasible ways are chosen for macroalgal biofuel production. High-value end products with a cost-effective process enhances the economic viability of macroalgal biofuel generation. Cost-effectiveness is necessary for all processes such as algal cultivation, harvesting algal biomass, and treatment methods for extracting high-value chemicals and upgrading the biofuels for various purposes [125]. Mthethwa et al. [126] detailed the biohydrogen production and its economic analysis. They considered two types of cost estimation, amortization, and operation cost. Amortization cost is estimated based on construction, equipment cost, and other fittings, while operation cost includes treatment cost, chemical cost, and maintenance cost. The following corresponding equations, Eqs. (4), (5), and (6), are used to calculate amortization cost, energy cost, and cost of operation [126],

$$\text{Amortization cost } (A)\ (/\text{m}^3) = (F_c{*}V_c)/(L_t{*}V) \tag{4}$$

where

F_c fermentation unit cost ($/m^3)
V_c unit capacity of treatment (m^3)
L_t lifetime of constructed unit (years)
V total volume of biomass for treatment (m^3/years)

$$\text{Energy cost } (E)\ \left(/\text{m}^3\right) = \left(P_c{*}E_c{*}W_p{*}O_d\right)/V \tag{5}$$

where

P_c power consumption (kW)
E_c electricity cost ($/kW/h)
W_p working period (h)
O_d days of operation (years)
V total volume of biomass for treatment (m^3/year)

$$\text{Cost of operation (CO)}\ (/\text{m}^3) = (C{*}P) + E + (2/100)\,A \tag{6}$$

where

C concentration (kg/m^3)
P unit total cost ($/kg)

Zech et al. [127] stated that the cost of specific biohydrogen production (CSP) is measured as a significant indicator to evaluate the economic analysis of proposed hydrogen production concepts which include production cost and distribution cost. The authors [127] referred to the following equation to calculate the CSP:

$$\text{CSP} = (C_c + A_c + \text{OP}_c + O_c{-}R)/\text{H}_{2\text{prod}} \tag{7}$$

where

CSP cost of specific biohydrogen production,
C_c annual capital costs,

Table 5 Comparison of energy analysis for various pretreatment methods

Pretreatment	Specific energy used (kJ/kg TS)	Input energy (energy loss) (kWh)	Output energy (energy gain) (kWh)	Net energy (kWh)	Net cost	Biohydrogen production	References
Disperser	1469	1.27	0.416	− 0.854	− 0.196	58 mL/g COD	[123]
Disperser thermochemical	742	0.644	1.04	0.396	0.091	129 mL/g COD	[123]
Surfactant-induced microwave	9720	0.054	0.0193	− 0.0347	− 0.0079	74.5 mL/g COD	[73]
Dispersion homogenization	874	12.1	9.2	− 2.9	− 0.667	16 mL/g VS	[64]
Surfactant-induced dispersion homogenization	874	4.84	9.2	4.37	1.005	23.3 mL/g VS	[64]
Rhamnolipid-alkaline pH–induced ultrasonic homogenization	12,607	2.7	5.39	2.6	0.598	55.1 mL/g COD	[61]

VS volatile solids, *COD* chemical oxygen demand

A_c annual consumption cost (includes raw material and energy),
OP_c annual operation cost (includes labor and operation and maintenance)
R annual revenues not related to sale of H_2, and
H_{2prod} annual H_2 production

11 Challenges and future outlooks

Hydrogen production through fermentation has more advantages, such as simple operation and rapid hydrogen production. Moreover, the production of hydrogen through biological routes has gained interest in recent years because it has a significant impact that not only treats organic wastes but also yields clean energy. Inoculum content, type of substrate and reactors used, nutrients, pH, and temperature are the factors which influence the biohydrogen production. Hydrogen-producing microbes are naturally present in excess in sources like wastewater, soil, compost, sludge, and so on. Hence, these sources are used as sources of inoculum for biohydrogen generation [128]. pH is a significant parameter that affects the hydrogenase action of the biohydrogen pathway. A pH of 5.5 is favorable for biohydrogen production, and an increase in pH affects the production of biohydrogen. Temperature is another important factor that also influences the microbe's growth rate. Most studies stated that mesophilic temperature ranges (25–40 °C) are favorable in temperature conditions for biohydrogen production. There is a limitation for galactose-based substrate hydrogen production which enhances the char formations and low biofuel yield [129]. The metabolic pathway and enzyme activity of fermentative microbes are influenced by trace metal concentration which inhibits the hydrogen production [130]. Metals such as iron, zinc, magnesium, and sodium influence the hydrogenase action on the biohydrogen metabolic pathway. *Clostridium* sp. growth is inhibited by lactic acid production when iron concentration goes low (0.56 mg/L) [131]. From this study, it is identified that iron concentration affects the metabolic routes of hydrogen production. Biological hydrogen generation is a clean, innovative method for bioenergy production [132]. A significant improvement, such as a hybrid rector system, advanced metabolic techniques, and gas filtering/separation, makes the hydrogen production easier. Identifying novel hydrogenases, advanced genetic methods, and new environmental technologies makes biohydrogen production more practical and commercially and economically feasible.

12 Conclusion

This review provides an understanding concerning biohydrogen fermentation using marine macroalgae and describes the macroalgal characteristics, pretreatment, inhibitory compound formation, and their detoxification methods. Bioenergy generation through algae provides a sustainable and alternative source of energy. The selection of a suitable pretreatment method could limit the production of the toxic components and achieve cost-effective bioenergy generation. The factors such as efficient energy and economic feasibility depend on the biomass-processing methods and pretreatment conditions. Through the overall review from this article, it was concluded that macroalgae-based biosynthesis provides a better economic and energy feasible circular bioeconomy.

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