

A Review of Marine Algae Biomass: A Sustainable and Renewable Resource for Biofuel Production

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ABSTRACT

The global demand for sustainable energy sources has been driven by energy shortages and the growing concerns over greenhouse gas emissions. Recent studies have highlighted microalgae and macroalgae biofuels as promising renewable energy alternatives that could potentially replace fossil fuels. Unlike biofuels derived from oil crops and lignocellulosic materials, algae-based biofuels do not have the same significant drawbacks. These algae-derived energy sources are not only technically and economically feasible, but also cost-competitive, requiring minimal land, using minimal fresh water, and contributing to the reduction of CO₂ levels in the atmosphere. However, the commercial production of biofuels from microalgae and macroalgae is still hindered by limited biomass availability and high extraction costs. To make algae-based biofuel production more viable, advances in photobioreactor technology, as well as cheaper methods for biomass collection, drying, and oil extraction, are necessary. Currently it is estimated that the cost of marine algae biomass per system ranged from \$6 to \$28 per gallon. Additionally, genetic modifications aimed at enhancing stress tolerance and metabolic processes to boost lipid production are crucial for commercial success. Research is also exploring new technologies, such as algal-bacterial collaborations, to improve algae growth and lipid yields up to 48%. This review discusses the production, sustainability, economic potential, challenges, and potential solutions related to the commercialization of marine algae biofuels.

Keywords: Bioenergy, Biomass conversion methods, Pyrolysis, Fermentation, Biomethane and biohydrogen, Fuel efficient.

INTRODUCTION

The global population is projected to surpass 9 billion by 2050 [1]. Rising global energy costs and increasing demand have placed significant pressure on renewable energy resources, leading to their depletion. The growing use of fossil fuels has resulted in several environmental challenges, particularly the increase in greenhouse gas (GHG) emissions, especially carbon dioxide (CO₂) [2]. Fossil fuels have been the primary energy source worldwide, but their excessive use has caused serious ecological issues, including air pollution [3]. They are the leading contributors to GHG emissions in the environment. Global warming has accelerated at an alarming rate, now surpassing 1.3°C above pre-industrial levels, and is expected to increase by more than 4°C by 2100 [4]. This is mainly due to carbon emissions from petroleum-based energy sources, especially in transportation. This situation calls for a shift towards renewable energy options. Among these alternatives, biofuels are particularly promising because their production process offers significant potential for carbon capture and storage (CCS) [5]. Biofuels can store energy in various forms, such as gases and liquids, which are easy to store in tanks and transport, making them compatible with existing transportation infrastructure [3]. However, there are challenges in terms of the availability of sufficient farmland and clean water to produce the required biomass for biofuel production, while also addressing the environmental impact of carbon emissions from current bioenergy production methods [6].

The oceans cover more than 70% of the Earth's surface and contain over 97% of the planet's water, along with essential minerals that support the growth of algae biomass, which can later be converted into renewable energy [7]. Therefore, producing biofuels from marine algae biomass offers a promising solution for both addressing

long-term climate change and providing sustainable energy sources [8]. Figures 1 and 2 depict the global and Indian coastlines' algae distribution, respectively. Various marine algae biomasses have made significant progress as viable alternatives to traditional energy sources and are considered potential sustainable products [9]. Recently, there has been increasing attention on methods for converting marine algae biomass into a range of valuable products, including fuels [10]. Biofuels are categorized into three generations based on the type of feedstock used. First-generation biofuels are derived from feedstocks such as paddy, sugarcane, wheat, and maize, which are also used as food for humans [3]. These are known as "traditional biofuels" because they are produced using conventional technologies for generating sustainable fuels. Second-generation biofuels are designed to meet commercial and industrial demands, addressing factors like cost, efficiency, and competition with agricultural production [6].

Macroalgae and microalgae are among the most valuable renewable resources in the marine environment, making them promising candidates for third-generation biofuels due to their ability to produce high yields with fewer resources [7]. Macroalgae, in particular, stands out as one of the most promising non-consumable biofuel sources because it can thrive in saline and challenging environments. Marine algae-based biofuels are completely safe, recyclable, and free of sulfur [11]. These algae species contain varying amounts of ash (18% to 55%), sugars (25% to 60%), proteins (5% to 47%), and lipids (5%), with these levels fluctuating based on species and environmental conditions such as sunlight and temperature [12,13]. Depending on the algae type and conversion method, marine algae can be transformed into various energy products [14]. As third-generation fuels, algae-based renewable energy sources offer several advantages, including rapid growth, significant CO₂ sequestration, and the ability to grow on non-arable land, which could help address the global energy shortage [15]. Marine algae biomass contains valuable compounds like acyl glycerides and lipids, which can be used to produce biofuels, thereby reducing reliance on petroleum-based fuels [16]. The oil extracted from marine algae (both macroalgae and microalgae) can be used to produce biodiesel, while the remaining biomass, rich in carbohydrates, can be converted into bioethanol [17]. However, several challenges need to be addressed before the commercial production of biofuels from macro and microalgae can be scaled up to significantly impact global energy needs [15]. This review aims to explore the various strategies for producing biofuels from marine algae (both macroalgae and microalgae), examining the challenges, limitations, and future prospects for sustainable biofuel production.

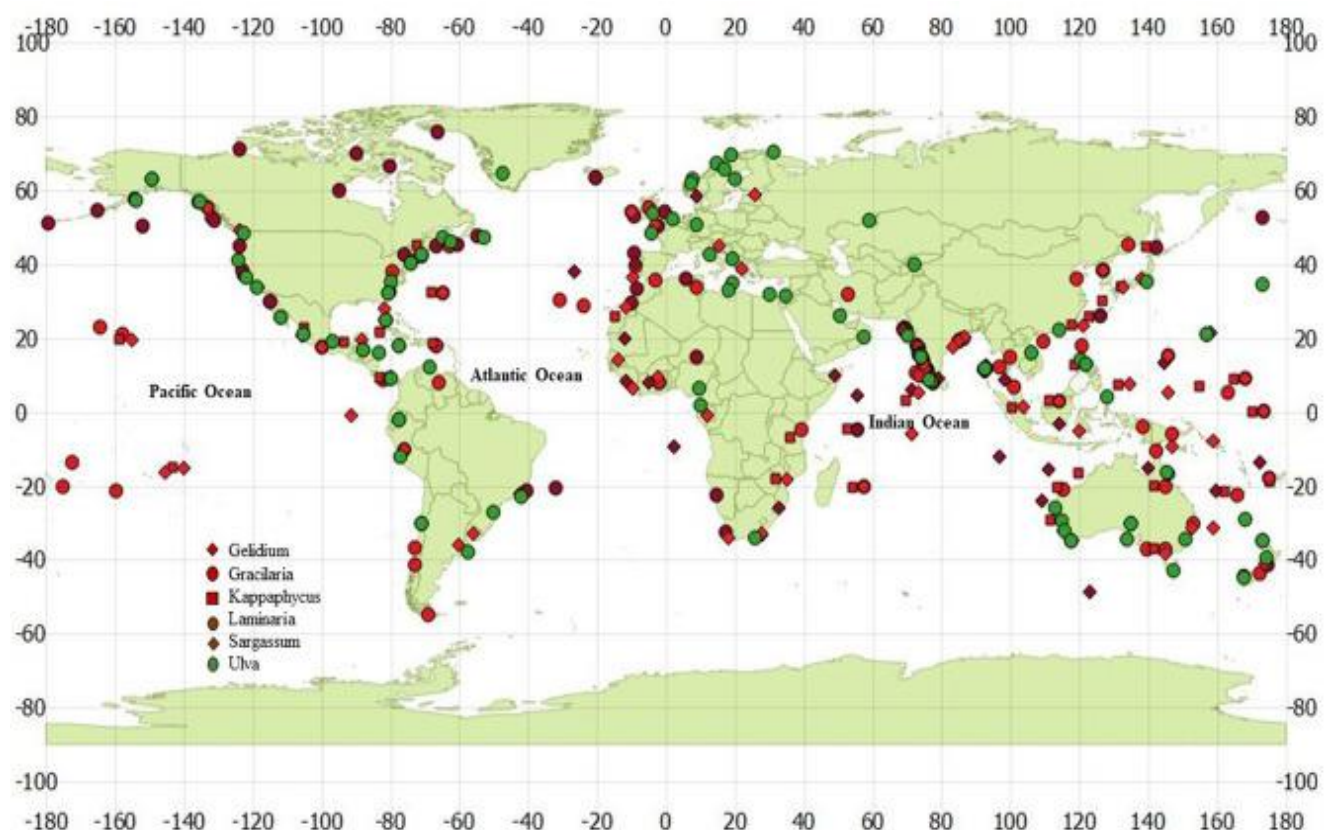


Figure 1. Marine algae enriched coastal regions around the world for biofuel production. [65]

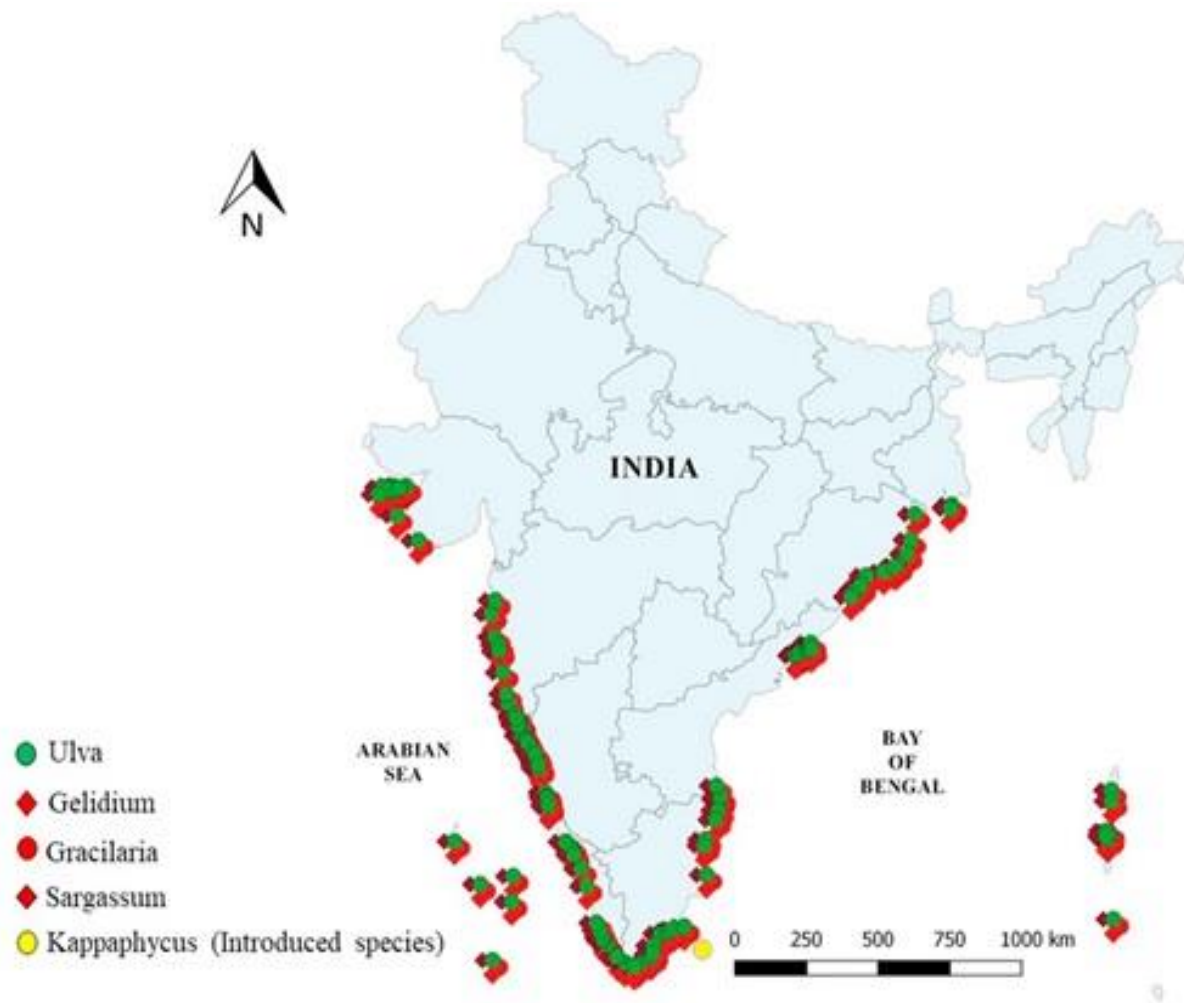


Figure 2. Indian coastal regions enriched with algal biomass suitable for biofuel production. [65]

Macroalgae–Biofuel Production

Macroalgae are large, aquatic eukaryotic organisms that belong to different phylogenetic groups, including Phaeophyceae, Rhodophyta, and Phaeophyta [18]. These algae are capable of growing in a wide range of water environments, including in sewage. Algae grow at rates about twenty to thirty times faster than traditional fodder crops, and the fatty acid content of macroalgae is roughly thirty times higher than that of conventional biofuel feedstocks [18]. Additionally, algae-derived biofuels are highly valuable due to their complete recyclability and sulfur-free composition. The absence of lignin in macroalgae also makes it easier for microbes in biological refineries to break it down and convert it into biomass fuel, compared to terrestrial plants [19]. Figure 3 illustrates the various types of biofuels that can be derived from macro and microalgae from marine sources. After conversion, the leftover biomass can be used for heating, fertilizer, and various other biofuel products [20]. Macroalgae can also be utilized in the production of dietary supplements and animal feed, among other uses. Numerous studies have explored the potential of macroalgae as feedstock for biofuels, including biohydrogen, biodiesel, bio-oil, bioethanol, and biomethane [21]. The majority of these studies have shown positive results for biofuel production from marine macroalgae [22]. The market for marine macroalgae biomass is expanding in value annually, with the Food and Agriculture Organization estimating global marine macroalgal biomass production in recent years to be around 35 million tonnes, worth approximately 12.5 billion USD [23,24]. The Asia-Pacific region, particularly China, has become the largest producer of marine macroalgae, generating 15 billion tonnes valued at 9 billion USD [25]. In this region, various macroalgal species such as *Gracilaria verrucosa*, *Kappaphycus alvarezii*, *Laminaria japonica*, *Pyropia yezoensis*, *Eucheuma* sp., and *Undaria pinnatifida* are being cultivated on a large scale [26]. In contrast, several countries have underdeveloped aquaculture sectors and outdated cultivation techniques. Despite this, efforts to boost the marine-based macroalgae market and aquaculture industry are in the early stages, with industry stakeholders advocating for large-scale marine macroalgae farming [19].

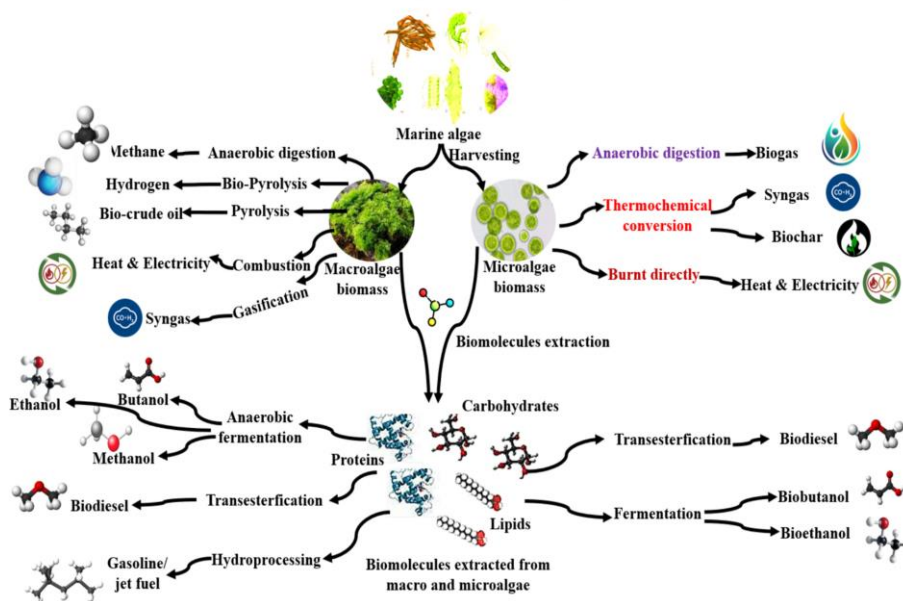


Figure 3. Various forms of biofuels possibly derived from marine macro and microalgae

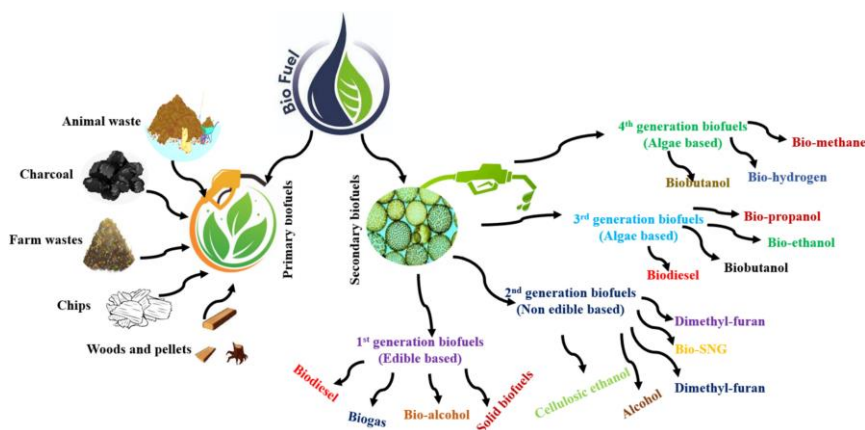


Figure 4. First, second and third generation of biofuels

Macroalgae-Biofuel Conversion Methods

Biofuels are fuels derived from biological materials and can be used in vehicles and various industrial applications. The type of biomass used determines the classification of biofuels into the 1st, 2nd, 3rd, and 4th generations (Fig. 4) [27,28]. There are several biochemical and thermochemical methods available for extracting biofuels from marine macroalgae [29]. Common biofuel production methods include anaerobic digestion, pyrolysis, fermentation, transesterification, and liquefaction [30]. The complex composition of algae biomass can affect the hydrolysis process, leading to a limiting phase that takes longer to complete [31]. This can impact biofuel yields, but the issue can be mitigated by applying appropriate pretreatment methods to break molecular bonds and decompose the complex structure, thereby improving emulsification [32]. The dissolved compounds can then be rapidly utilized during the conversion process, boosting biofuel production [33]. Various pretreatment methods, including physical, mechanical, chemical, biological, and combined approaches, are employed to solubilize the complex substrates in macroalgae [34,35]. Table 1 provides details on biofuel production from different algae species.

Bio-Oil

Bio-oil can be used as fuel for internal combustion engines or as a chemical [35]. Pyrolysis is considered one of the most promising conversion methods for producing bio-oil by heating marine algal biomass in the absence of oxygen. The hydrothermal liquefaction (HL) process applied to *Enteromorpha prolifera* (a green macroalgae) resulted in bio-oil with a dry weight of 23% (v/v) after 30 minutes at 300°C, using sodium carbonate as a catalyst

[35]. Similarly, another study examined the HL process in *Laminaria saccharina* (a brown macroalgae), finding that reaction parameters influenced the production of the highest bio-crude yield (19.3%) at 350°C for 15 minutes [36]. Additionally, researchers utilized microwave methods to produce bio-oil from marine macroalgae, achieving a yield of 18% (v/v) [37]. Another study using a fixed-bed reactor produced bio-oil (47% v/v) from marine macroalgae, also generating a significant amount of biochar as a byproduct [21].

Bioethanol and biodiesel

Bioethanol production from marine macroalgae has gained significant attention from researchers. One study extracted about 0.37% (v/v) of bioethanol from 1 g of *Ulva reticulate* biomass [38]. Another study found that *Ulva intestinalis* yielded 0.081 g of bioethanol per gram of dry weight [39]. A different research group produced bioethanol from *Sargassum* sp., achieving a transformation rate of 89% (v/v) [40]. Using fermentation, *Gracilaria verrucosa* (red seaweed) produced bioethanol with an average yield of 0.43 g of bioethanol per gram of carbohydrates [41]. This results in approximately 90 liters of ethanol per dry tonne of macroalgae [23]. Another study found that scrubbing macroalgae in an acidic medium at 65°C enhanced the hydrolysis of laminarin [42]. By employing saccharification and fermentation techniques, a biomass conversion rate of 91% (v/v) ethanol was achieved from macroalgae waste [43]. Anaerobic digestion with *B. Custersii* produced 11.8 g/L of bioethanol from 90 g/L of carbohydrates in batch reactors, and around 28 g/L of bioethanol from 72 g/L of carbohydrates in continuous reactors [44]. Furthermore, *E. Cottonii* has been identified as a potential biomass source for bioethanol production [44]. In another study, 250 g of *Palmaria palmata* (red algae), primarily composed of carrageenan, underwent acid hydrolysis (0.4 M H₂SO₄) for 25 minutes at 125°C to produce glucose and galactose, which were then converted into bioethanol, yielding 26%. Similarly, *Kappaphycus alvarezii* biomass (16 g) treated with 0.9 M H₂SO₄ at 100°C was saccharified, resulting in a 31% (w/w) yield [45].

Biodiesel is a blend of monoalkyl esters of long-chain fatty acids derived from marine algae biomass [46,47]. Compared to petroleum-based fuels, biodiesel offers superior ignition properties and can reduce fumes and CO₂ emissions by 78% [48]. One study focused on biodiesel production from *Ulva intestinalis*, achieving an efficiency of 32 mg per gram of dry weight [39]. Biodiesel extracted from *Chaetomorpha antennina* and *Gracilaria corticata* yielded 2.4 mL and 2 mL per 10 g of marine algae biomass, respectively [23]. Another research group esterified *Enteromorpha compressa* biomass, which had free fatty acids (FFAs) ranging from 6.3% to 0.34%, and identified two processes for biodiesel production [49]. The FFAs were produced using an acid catalyst in the first step, and the oil was then converted into biodiesel in the second phase [49]. In another experiment, *Cladophora glomerata* was used to generate glucose, which was subsequently converted into FFAs for biodiesel production [49]. Recently, marine macroalgae have been utilized as a carbon source for biodiesel production, with the highest lipid content observed being 48%, which is considered efficient for biodiesel production [17].

Biomethane and Biohydrogen

Marine brown and green macroalgae biomass has been shown to yield biomethane, with yields of 256 mL/g for brown algae and 179 mL/g for green algae [50]. Another study reported that treating *Laminaria hyperborean* through anaerobic digestion produced approximately 70% biomethane [51]. Similarly, a research team found that the biomethane yield from *Chaetomorpha antennina* using the chemo disperser method was about 47.25 mL/g [51]. *Palmaria palmata* (red macroalgae) biomass produced 308 mL/g of biomethane. Other marine algae species such as *Ulva* sp., *Laminaria* sp., *Sargassum* sp., and *Ascophyllum* sp. yielded consistent biomethane production, ranging from about 140 to 280 mL/g [13]. In studies using *Gracilaria* sp., *Laminaria* sp., and *Macrocystis* sp., biomethane yields were reported to range from 260 to 500 mL/g [52].

Biohydrogen is considered a renewable energy source with excellent potential for future energy production and is expected to play a key role as a fuel [53]. Thermal processing of *Laminaria japonica* at 170°C resulted in biohydrogen production of 110 mL/g of COD. Another research team treated *Laminaria japonica* macroalgae biomass with microwave radiation for 30 minutes at 160°C, resulting in a biohydrogen yield of 16 mL/g [54]. In another study, biohydrogen production of 45.5 mL was achieved from *Ulva reticulate* biomass using a disperser method [55]. An alkaline process applied to *Laminaria japonica* yielded 15 mL/g of biohydrogen. Additionally, by treating macroalgae with H₂O₂, a biohydrogen production rate of 63 dm³/kg of volatile

substance was achieved [56]. A study investigating an integrated microwave and acid pretreatment technique for *Laminaria japonica* achieved biohydrogen production of 28 mL/g of biomass in 15 minutes at 140°C using 1% H₂SO₄ [57].

Table 1. Various forms of biofuel production reported from the algae species

Sr no	Algae Species	Brief Production Process	Biofuel Product	References
1	<i>Saccorhiza polyschides</i>	Batch reactor, Biomass Co-digested with bovine slurry in batch reactor at 35°C	Biogas	[3]
2	<i>Chlamydomonas reinhardtii</i>	Biomass pretreated with drying and followed the batch fermentation at 38°C	Biogas	[157]
3	<i>Ulva</i> sp.	Batch reactor, Biomass Co-digested with bovine slurry in batch reactor at 36°C and	Biogas	[158]
4	<i>Scenedesmus obliquus</i>	Algae biomass subjected to hydrolysis at 37°C and 6.8	Biogas	[3]
5	Blue algae	Batch fermentation at 38°C with pH 6.8, with the microcystin biodegradation	Biogas	[159]
6	<i>Saccharina latissima</i>	Batch reactor, Biomass Co-digested with bovine slurry in batch reactor at 36°C and	Biogas	[3]
7	<i>Laminaria digitata</i>	Biomass pretreated with drying and followed the batch fermentation at 38°C	Biogas	[3]
8	<i>Gelidium amansii</i>	Biomass hydrolysed at 150°C with	Biohydrogen	[160]
9	<i>Laminaria japonica</i>	Batch fermentation at 35°C, 7.5 pH under anaerobic condition with 6 days of	Biohydrogen	[161]
10	<i>Chlorococcum infusionum</i>	Alkaline pre-treatment was followed on biomass at 120°C, and used <i>S.cerevisiae</i>	Bioethanol	[162]
11	<i>U.fasciata</i>	0.1 % of H ₂ SO ₄ was used for pretreatment at 100°C for 1 h with cellulose, along with <i>S. cerevisiae</i> (109 CFU mL ⁻¹) 28°C, 120 g for 2 days	Bioethanol	[163]
12	<i>E.intestinalis</i>	Biomass treated by hydrothermal process, 1.5 L of cellulase & isozyme L at 55°C, for 120 rpm for 2 days along with <i>S. cerevisiae</i>	Bioethanol	[164]
13	<i>Gracilaria</i> sp.	Biomass pretreated with 0.1 N of H ₂ SO ₄ , at 121°C for 30 min, along with	Bioethanol	[165]
14	<i>G. amansii</i>	Biomass pretreated with 56-168 mM of H ₂ SO ₄ , at 121°C for 240 min, with viscozyme L and <i>Scheffersomyces stipitis</i> in pH 5.5, 30°C, at 200 rpm	Bioethanol	[166]
15	<i>L. hyperborea</i>	Biomass subjected to extraction with water at 65°C along with <i>Pichia angophorae</i> for 20 min and <i>Zymobacter palmae</i> at 30°C with pH 6.	Bioethanol	[166]
16	<i>Chlorococcum humicola</i>	Biomass subjected to acidic pre-treatment at 160°C with <i>S.cerevisiae</i>	Bioethanol	[3]
17	<i>Spirogyra</i> sp.	Biomass treated with alkaline and subjected to saccharification through <i>Aspergillus niger</i> and <i>S.cerevisiae</i> fermentation	Bioethanol	[3]
18	<i>Scenedesmus</i> sp.	Biomass treated with acidic catalyst at 70°C	Bioethanol	[3]
19	<i>Scenedesmus</i> sp.	Biomass treated with alkaline catalyst at 70°C	Bioethanol	[167]
20	<i>Neochloris oleoabundans</i>	Photobioreactor used and medium supplemented with 0.037 mM of Fe ³⁺ and aerated with 4 % of CO ₂ , 100 µmol m ² S at 2°C	Bioethanol	[168]
21	<i>Nannochloropsis salina</i>	1:1 ration of chloroform-methanol was used to extract the and then alkali transesterification	Bioethanol	[169]
22	<i>Scenedesmus</i> sp.	Batch cultures in BBM & TAP media at 27°C with photoperiod of 14 h:10 h	Bioethanol	[170]
23	<i>Nannochloropsis</i> sp.	Oil from the biomass was extracted by n-hexane and then followed the acidic	Biodiesel	[3]
24	<i>Scenedesmus acuminatu</i>	Optimized culture conditions (25°C, 120 rpm, with 100 µmol photons m ² /s) in	Biodiesel	[171]
25	<i>Spirulina platensis</i>	Biomass extracted with methanol, at 55°C, and 60 % of catalyst, 450 rpm	Biodiesel	[172]
26	<i>Scenedesmus obliquus</i>	Batch culture in along with sterilized municipal effluent at 25°C, 100 µmol photons m ² s ⁻¹ cycle	Biodiesel	[173]
27	<i>Asterarcys quadricellulare</i>	Modified BBM Medium in batch culture at 25°C, 30 µE m ² s ⁻¹ for up to 10 days	Biodiesel	[174]

COST AND ECONOMICS

The economic viability of biofuel production from marine macroalgae biomass is crucial for ensuring the long-term feasibility of cultivation, harvesting, and usage [58]. Due to high labor costs, expensive equipment, and materials needed for various algal farming activities, the revenue generated from biofuel production must be substantial enough to make the process economically viable [59]. While much of the research has focused on the production of biofuels from macroalgae, the overall yields and costs of the biofuels derived from these algae are still relatively small in comparison to their potential [60]. Factors such as the pretreatment of marine macroalgae biomass and environmental conditions, including seasonal changes, can alter the chemical composition of the algae, significantly impacting biofuel production [65].

However, there are cost-effective methods to cultivate macroalgae, including producing valuable byproducts like bio-oil, biogas, biodiesel, and biohydrogen, or integrating macroalgae farms with other aquaculture operations [21,60]. For macroalgae farming to be economically viable, a competitive price of around \$2.5 per kg of algae is necessary [60]. Additionally, combining hatchery operations with algae farming to produce valuable invertebrates, such as scallops, could further enhance economic feasibility. Given the growing importance of biofuels, macroalgae farming has the potential to gain widespread global popularity [7]. Nevertheless, the high costs associated with cultivating macroalgae remain a significant barrier. The current expenses involved in producing biofuel from marine macroalgae are substantial [26]. Although production costs are expected to increase as the industry develops, they could decrease rapidly with improvements in efficiency and flexibility.

Furthermore, the costs associated with converting macroalgae into biofuels should be considered in the economic analysis. Three approaches were evaluated: producing methane using syngas and biomethanol, fermenting marine macroalgae to produce ethanol, and converting algae via hydrothermal liquefaction into liquid fuels [29]. The cost of producing biofuel from *Ulva* sp. was estimated at \$2.21 per kg, with the revenue generated from the ulvan component varying between \$8 and \$10.4 per kg [23]. A comprehensive techno-economic evaluation of macroalgae biomass highlighted costs associated with equipment and operational expenses, including administration, chemical and substrate costs, reagent availability, and scalability. This evaluation suggested an annual production cost of \$3.7 million, with ulvan priced at \$395 per gram, and total production costs amounting to \$1.2 million [23]. The estimated cost for marine algae biomass per system ranged from \$6 to \$28 per gallon [62]. "Both macroalgae and microalgae should be considered together for biodiesel production as they offer distinct yet complementary benefits, addressing various challenges in biofuel development. Macroalgae are capable of producing large quantities of biomass using relatively straightforward cultivation techniques, while microalgae tend to have higher lipid concentrations and faster growth rates, making them well-suited for more efficient biofuel production. Combining the advantages of both types of algae could lead to enhanced biodiesel production that is both scalable and sustainable."

Microalgae as a Viable Source for Bioenergy

The growing demand for sustainable and eco-friendly biomass alternatives has led to an increased focus on microalgae as a promising source for biofuel production [63]. As a result, biofuels have become more attractive as substitutes for petroleum-based fuels worldwide [64]. Many advanced nations have started commercial biofuel production. Biofuels, such as biodiesel and bioethanol, have shown great potential as alternatives to fossil fuels. These biofuels can be derived from various biomass sources, including agricultural residues, fruits and vegetables, hard plant materials, waste, and algae [61,66].

Biofuels derived from biomass are renewable and contribute significantly less to environmental pollution and global warming. Fossil fuels, particularly petroleum, are major contributors to climate change, releasing large amounts of greenhouse gases (GHGs), primarily CO₂. Annually, fossil fuels are responsible for emitting around 29 gigatonnes of CO₂, contributing to a total of 35.3 gigatonnes of CO₂ emissions [67]. In contrast, biofuels, such as algae-derived fuels, have much lower sulfur emissions and contain oxygen levels ranging from 10 to 45%, whereas petroleum fuels have no oxygen content and higher sulfur emissions [68].

Microalgae-based biofuels are considered environmentally friendly, inexpensive, and renewable sources of

energy [69]. These fuels are often referred to as 4th-generation biofuels (Fig. 3), due to their potential to reduce global CO₂ emissions significantly [70]. Studies have shown that one kilogram of algae biomass can capture 1.83 kilograms of CO₂, and certain algae species can also absorb nitrogen oxides and sulfur dioxide as nutrients, alongside CO₂. Approximately 50% of the dry mass of algae biomass consists of CO₂ [71].

The selection and cultivation of microalgae for biofuel production is a critical factor, affecting both the energy content and economic viability of biofuels [19]. The biomass chosen for biofuel production directly impacts greenhouse gas emissions and the sustainability of both environmental and economic systems [72]. Currently, microalgae are receiving considerable attention as a raw material for bioenergy production, offering a promising solution to meet the growing demand for biofuels and the increasing costs of chemical manufacturing [73]. Many countries have started industrializing microalgae biomass for bioenergy production [63]. Microalgae are fast-growing organisms capable of photosynthesizing rapidly, converting up to 10% of sunlight into biomass. Theoretical yield estimates suggest that microalgae can produce about 77 grams of biomass per square meter per day, which is equivalent to roughly 280 tons per hectare annually [74].

Microalgae biomass is increasingly considered a highly beneficial source for biofuel production through various methods. Microalgae do not require arable soil or fresh water for cultivation, making them non-edible and having no impact on the food chain. They can be grown in various conditions, unaffected by seasonal diseases, help reduce greenhouse gas emissions, and even assist in effluent treatment [75]. Many species of microalgae are particularly suitable for biodiesel production due to their high lipid content, which can reach up to 70%–80% in some species, such as *Botryococcus braunii*, which accumulates up to 80% bio-oil in its biomass [76]. Microalgae have the potential to generate 58,700 liters per hectare of algae-derived oil, which can then be converted into 104 liters per hectare of biodiesel [76]. Despite the high functional, maintenance, processing, and conversion costs, algae-derived biodiesel remains a viable option.

Bioethanol, another significant environmentally friendly biofuel, is widely used for transportation [77]. It offers multiple advantages over petroleum-based fuels, including (i) a higher octane number that reduces engine knocking [63]; (ii) a greater oxygen content that produces fewer greenhouse gases during combustion; (iii) a low cost; and (iv) the ability to be used directly in current automobile engines without modifications. Additionally, bioethanol and bio-oil can be blended together. The United States and Brazil are global leaders in bioethanol production, accounting for approximately 75–80% of global production. In the U.S., 187 commercial bioethanol plants mainly produce bioethanol from maize grain [79], while the European Union generates 2.0 billion gallons annually from wheat and sugar beetroot.

Sustainable biofuels, produced from environmentally friendly biomass, are expected to become flexible renewable energy sources, gradually replacing fossil fuels in the future [80]. At present, bioethanol is one of the most commonly used biofuels, typically derived from maize and sugarcane. However, recent technological advancements have led to a shift toward using algae as a source of biofuels [81]. Carbohydrates, in particular, are an attractive feedstock for bioethanol production. Global production of bioethanol has grown dramatically, from 1 billion liters to 39 billion liters in just over two years, and is expected to exceed 100 billion liters soon [82]. Microalgae, which are rich in carbohydrates, can be quickly converted into sugars through fermentation for bioethanol production. Algal species with high carbohydrate content are especially suitable for producing bioethanol [80].

While the production of bioethanol from microalgae is a significant step toward creating environmentally friendly biofuels, there are still challenges related to large-scale production and commercialization of these clean biofuels [31]. The main hurdles in the development of algal bioethanol technologies that need to be optimized for successful marketing include algae biomass selection, pre-treatment processes, and effective fermentation methods [83]. The fermentative production of ethanol is highly dependent on the choice of fermenting microbes. To prevent contamination, fermentation must take place in a sterile environment, which can increase production costs [80]. For microalgae to become a viable substrate for bioethanol production, ongoing efforts are required to address the current challenges, including (i) cultivating algae and generating carbohydrate-rich biomass, (ii) efficient dehydration and harvesting, (iii) biomass pretreatment, and (iv) optimizing fermentation yields [84]. Several carbohydrate-rich microalgae species, such as *Chlorella vulgaris* and *Chlamydomonas reinhardtii*, are considered promising candidates for bioethanol production [85].

BIOMASS CONVERSION METHODS

Regardless of the composition and features of marine algae biomass, various techniques can be employed to convert it into biofuel [86]. The conversion of marine algae biomass into biofuel typically involves three main processes: biological, thermal, and chemical conversion methods.

Fermentation

Marine algal biomass, including both macroalgae and microalgae, along with its by-products, can be used to produce gasoline, octane boosters, bioethanol, and diesel additives, all contributing to reduced greenhouse gas emissions [87]. Due to its similar chemical and physical properties, bioethanol is a viable alternative to gasoline. The production of bioethanol depends on the biochemical profile of marine algae biomass used as feedstock [88]. Algae biomass rich in carbohydrates is commonly used as a substrate for yeast-driven microbial fermentation to produce bioethanol. Since algae are abundant in starch, soluble and insoluble carbohydrates, as well as cellulose, they are considered a promising raw material for bioethanol production [89]. The biomass is finely chopped and then converted into simple sugars with the help of enzymes and acids in the typical fermentation process. These sugars are later fermented into ethanol by yeast, with the final product being distilled for purity. The concentrated ethanol is then utilized as a liquid fuel, substituting gasoline for vehicles. This process significantly lowers feedstock costs, which typically account for more than 80% of the overall cost of alcohol production [7].

The production of ethanol from marine algal biomass requires an additional pretreatment step, which involves both mechanical and enzymatic hydrolysis [91]. Concentrated H₂SO₄ is commonly used to break down the intra- and inter-hydrogen bonds within the algal biomass. After this, the acid is neutralized, and the resulting sugars are separated for fermentation [7]. Various biological catalysts and enzymes have been used to hydrolyze carbohydrates, crystalline cellulose, hemicellulose, and amorphous cellulose [92]. Cellulase and other enzymes are frequently employed to break down cellulose polymers into simple glucose molecules, enhancing the efficiency of the process. One study proposed combining sonication, enzyme treatment, and thermal processes to continuously produce bioethanol from mixed microalgal biomass [93]. Multiple pretreatment stages are necessary in the microbial fermentation process, resulting in varying degrees of cell disruption. Sonication is commonly used to hydrolyze filamentous marine microalgae, while *Cyclotella* cells are lysed using a combination of sonication and enzymatic hydrolysis [94]. The combination of heat, sonication, and enzymatic methods increased the release of carbohydrates, which in turn improved ethanol production [95]. It has also been found that different microbes possess distinct fermentation capabilities, so selecting effective microbial strains is crucial. One study suggested a three-stage approach for the microbial breakdown of marine microalgal biomass to biofuels [96]. In the first stage, carbohydrates undergo fermentation to produce bioethanol. In the second stage, remaining proteins in the algal biomass are fermented to produce additional alcohol. The third stage involves transesterifying the remaining fatty acids to produce biodiesel [97]. This approach allows for highly efficient extraction of energy carriers from marine algal biomass. Research on the hydrolysis of *Scenedesmus obliquus* and *Chlorella vulgaris* biomass using both enzymatic and acidic methods identified the best yeast culture for fermenting the hydrolysate substrate [98]. Acid hydrolysis with 3% H₂SO₄ at 121°C for 30 minutes resulted in 90% sugar extraction and was deemed the optimal pretreatment method for algal biomass [98]. Ultrasonication has emerged as an effective technique for enhancing enzyme accessibility within biomass [99].

Anaerobic Digestion

Anaerobic digestion provides an efficient method for converting algae biomass with high moisture content into valuable gaseous products with high heating values [100]. In this process, microorganisms break down the biomass through a series of biochemical reactions, generating biogas that consists of CO₂, methane, and other gases such as nitrogen and hydrogen sulfides [101]. The chemical composition and the structure of the cell wall play a significant role in determining the biodegradability of marine algae. Factors such as elevated cellular protein content and sodium levels in algae can influence its susceptibility to degradation by ammonia toxicity [102]. Thanks to advancements in anaerobic digestion technology, marine algae are now considered renewable

and sustainable sources for biogas production. The cost-effectiveness of using marine algae biomass in anaerobic digestion has a profound impact on the long-term viability of energy sustainability [103]. Consequently, substantial efforts are being made to improve this technology. As marine algae biomass is renewable, it is an ideal substrate for anaerobic digestion and methane generation [52]. The process involves several stages of metabolic reactions carried out by different microbial groups, such as acetogenesis, hydrolysis, methanogenesis, and acidification. Initially, specific microorganisms use enzymes to break down complex compounds into simpler monomers, which are then converted into volatile fatty acids like propionic and butyric acids. These acids are further transformed into CO₂, hydrogen, and acetic acid by acetogens [104]. The rate of anaerobic decomposition can be influenced by various factors, including the position of the substrate or co-digestion with additional nutrients [105]. Modifying microbial populations responsible for breaking down marine algal biomass can enhance methane production [106].

This method also contributes to effluent bioremediation by generating a range of biological products and energy carriers through the use of marine algal biomass. A study found that *Laminaria digitata*, a brown macroalgal species, significantly impacted biogas and methane production at ambient temperatures [107]. Their results indicated that biogas could be produced at different digestion temperatures (25–55 °C), which influenced methane yields, ranging from 318 to 352 mL per gram of volatile solids [107]. The highest cumulative biogas production occurred at 35 °C, while the optimal methane production was observed at 55 °C, according to their findings [107]. The use of nanoparticle (NP) catalysts like Fe₃C NPs and FeNPs can further enhance biogas production. For example, incorporating FeNPs into an anaerobic digestion system at a constant temperature of 37 °C for two months resulted in a 180% increase in biogas production and a significant boost in methane output. Other nanoparticles such as NiNPs, CoNPs, and metal oxide NPs, including FeONPs and MgONPs, also contributed to increased biogas and hydrogen production yields [108]. Anaerobic digestion offers several advantages over other biofuel methods, such as significantly higher biogas yields compared to biodiesel, no need for drying, and the presence of minerals in both micro and macroalgae that support anaerobic methanogens. Additionally, the potential for co-digestion allows biogas-producing organisms to be recycled or used to improve biogas production by sequestering CO₂, while reducing harmful odors below levels typical of untreated waste [109]. However, there are some challenges with anaerobic digestion, including a low carbon-to-nitrogen ratio due to the high nitrogen content in algal biomass, the presence of cell walls that reduce the bioavailability of intracellular substances, high capital costs, and the fact that anaerobic digestion is typically more feasible for larger-scale operations. Other limitations include long operational and maintenance times, as well as the requirement for large land areas [110,111].

Thermal Conversion

Marine algae are particularly well-suited for large-scale biomass cultivation due to their favorable morphological and physiological characteristics [7]. After harvesting and preparing the biomass, marine algae can be converted into biofuel through various methods, most of which are thermochemical techniques. Thermal conversion processes, including pyrolysis, combustion, and gasification, subject the feedstock to high pressure and temperature, which leads to the production of compounds with low molecular weight and oxygen content [112].

Direct Combustion

Direct combustion of marine algae biomass, with excess air, converts the chemical energy into heat while releasing CO₂, SO₂, NO₂, and water vapor [113]. The temperature at which the combustion occurs, along with the properties of the biomass, determine the levels of emissions and the amount of energy produced during the process. Incomplete combustion can generate CO, CH₄, and particulate matter [114]. Certain catalysts, such as CuCl₂ and MgO, can help reduce emissions to some extent during the combustion of algal biomass [115]. Secondary pollution arises from the greenhouse gases emitted during both complete and incomplete combustion. Marine macro- and microalgae with moisture content under 50% are preferred for direct combustion. However, the energy required for drying and grinding the algae to ensure efficient combustion leads to increased costs [116]. The heat generated by direct combustion of algae biomass can be used effectively, reducing the need for additional drying and grinding. Additionally, co-firing coal with algae presents an opportunity to lower greenhouse gas emissions compared to coal combustion alone [117].

Pyrolysis

Pyrolysis occurs at high temperatures (typically between 500°C and 800°C) in the absence of oxygen, and may or may not involve a catalyst [118]. During this process, biomass is broken down at varying temperatures over extended periods, resulting in fuels with energy content ranging from medium to low. Pyrolysis produces solid biochar, biofuel, and gaseous products. The typical operating temperature for pyrolysis is between 300°C and 600°C, though it can reach 800°C to 900°C under extreme conditions [119]. Since algae cells are relatively small compared to other types of biomass, they require further breakdown. To minimize costs in scientific operations, the algae biomass should have low moisture content to facilitate efficient pyrolysis. Common algae species used in biofuel conversion include *Chlorella vulgaris*, *Chlorella proto-theoides*, *Microcystis aeruginosa*, *Nannochloropsis* sp., and *Scenedesmus* sp. [120,121]. Pyrolysis of marine algae is practical due to its long-term reliability and economic viability for both industrial and domestic uses. The bio-oil produced from heterotrophic algae cells has excellent heating value, low oxygen content, and favorable density and viscosity, which makes it ideal for rapid pyrolysis [122]. The lower oxygen content also improves its storage stability. The pyrolysis process of marine algae, both micro and macroalgae, is influenced by factors like the heating rate, residence time, and use of catalysts. Changes in these variables can alter the composition of the final product [86]. For instance, increasing the temperature above 550°C reduces bio-oil production, while lowering the temperature results in higher biochar production [123]. When converted to biochar, algae biomass, which contains elements such as nitrogen (N), phosphorus (P), magnesium (Mg), and calcium (Ca), is suitable for use as fertilizer. Higher bio-oil yields can be obtained when the algae biomass contains significant amounts of lipids [124]. The presence of a carrier gas enhances the efficiency of the pyrolysis process. The type of catalyst used can also influence the yield, with acidic catalysts increasing biochar production, and basic catalysts promoting bio-oil production [123].

Gasification

Gasification involves the partial oxidation of marine algae biomass, producing a synthetic gas (syngas) composed of CO, CO₂, CH₄, and hydrogen (H). The specific composition and quality of the syngas depend on the type of algae biomass used in the process [125,126]. At high temperatures and pressures (around 10 bar), the dried biomass reacts with water. Through processes like combustion, water loss, devolatilization, and gasification, the algae biomass is transformed into various gaseous substances [127]. The syngas produced can be utilized as fuel in engines or converted into liquid fuels. The use of catalysts enhances the gasification process by increasing hydrogen production, which results in cost-effective solid and gaseous outputs [128]. Several factors influence the gasification of microalgal biomass. As the temperature increases, bio-hydrogen production rises, while the production of methane (CH₄), CO₂, biochar, and tar decreases [129]. The energy produced also increases with temperature. However, as operating pressure increases, gasification becomes less efficient. Using catalysts such as ruthenium-on-titanium (Ru/TiO₂) or nickel (Ni)-based catalysts improves process efficiency, increasing tar removal rates by up to 100%. This also enhances both fuel quality and conversion efficiency [130]. The moisture content and availability of biomass are key factors in thermochemical conversion. Since algae have a water content of 70–80%, large-scale cultivation could pose future challenges [131]. To address this, affordable drying methods will need to be developed for the thermochemical process. Additionally, storage and transportation of algae-based biofuels are complicated due to the gaseous nature of syngas, and thermal conversion of algae biomass has its own drawbacks [132]. Some of these challenges include:

Energy Balance

The energy required to produce algal biofuels may exceed the energy they generate.

Water Use

Algae cultivation requires large amounts of water, and high temperatures can lead to water evaporation, potentially diverting agricultural water resources.

Bio-Oil Issues

Bio-oil produced through thermal treatment tends to have lower energy density, higher viscosity, and greater thermal instability compared to conventional fuels. It may also contain unwanted oxygenated compounds like

aldehydes, acids, ketones, alcohols, phenols, furans, and sugars.

Chemical Conversion

Chemical conversion involves the use of various catalysts, including base, acid, and enzyme catalysts, along with supercritical transesterification. While base catalysts are effective, they are not recyclable, making acidic catalysts more suitable for breaking down materials at a lower cost, especially for oil extraction [133]. However, the enzyme catalyst method is time-consuming and can pose safety risks for large-scale biodiesel production. Supercritical transesterification requires high temperatures above 250°C and steady pressure to extract bio-oil [134]. In transesterification, triglycerides react with alcohol, producing esters and glycerol. This esterification process occurs in the presence of catalysts such as nitrogen (N) or potassium hydroxide (KOH) [135]. To complete the esterification, excess alcohol is used, resulting in the production of mono-alkyl esters, a primary component of biodiesel, and glycerol [136]. Once the reaction is finished, the oil phase is separated from the remaining ester chain and glycerol layer by layer. Before biodiesel can be marketed, it must be tested to ensure it is free from glycerol, catalyst residues, unreacted alcohol, and free fats. Efficient, cost-effective fluid extraction and transesterification processes are necessary for extracting algae-derived biodiesel [137]. After fluid extraction, algae biomass can also be used to generate biogas through anaerobic fermentation, allowing for biogas production without interfering with biodiesel creation [138].

The commercialization of biogas is expected to reduce overall costs and improve biofuel production. Anaerobic digestion is considered the most energy-efficient method for biogas production, especially since it can handle biomass with higher moisture content compared to thermal conversion methods. Esterification has become a widely used process for converting algae biomass into bio-oil [136,139].

The Worldwide Market and Expansion of Marine Algae-Based Biofuel

To meet global energy demands, both developed and emerging nations are increasingly exploring sustainable feedstock sources for bioenergy production [140]. Marine algae are being researched for their potential to provide various substances and extracts, including carotenoids and proteins. By 2024, the global demand for keratin oils and proteins is projected to reach 2.0 billion USD and 35.54 billion USD, respectively [7]. With growing concerns over environmental pollution and chronic diseases, there is a significant shift toward producing algae biomass as an alternative to fossil fuels, with the aim of improving the environment [141]. The industrialization of renewable energy from marine algae has gained momentum due to its independence from fossil fuels [142]. This has resulted in market advantages, supported by innovative technologies that help reduce production costs.

However, challenges remain in both the manufacturing and marketing of marine algae for profit. The concept of a marine algae biological refinery offers a potential solution to these challenges, providing an opportunity for profitable revenue generation [143]. One of the common biorefinery methods involves the extraction of lipids from marine algae for bioenergy production. The extracted fatty acids are converted into biodiesel, while the remaining material is processed through anaerobic digestion to produce biomethane. Globally, biodiesel and biomethane have average market prices of 0.83 and 0.76 USD per liter, respectively [144]. In emerging markets such as India, the current prices for biomethane and biodiesel are approximately 0.59 and 0.89 USD per liter, respectively [145]. In the coming years, increased mass production of carbohydrates, proteins, and lipids from algae will be essential for large-scale operations. With substantial capital and labor costs, economies of scale will play a key role in determining the financial and operational efficiency of the entire process. Although commercial production of algal biofuels is still in its early stages due to cost inefficiencies, the potential for algae cultivation for value-added products and biofuels offers a promising path forward, especially with the potential for scalability and economic viability [146].

Recent Advancements in Biofuel Production

Nanotechnology is emerging as a rapidly advancing technique for enhancing biofuel production across various industries. Due to its vast surface area, nanotechnology is being applied in marine algal biorefineries to synthesize nanoparticles (NPs) that modify the components of algal biomass [147]. One notable approach is the

immobilization of cellulase enzymes using NPs, which can reduce the need for excessive enzyme use, thus improving biofuel production from marine macroalgae. Additionally, the biosynthesis of magnetic NPs for biofuel production is an area of active research [148]. Macroalgae, acting as bio-nano factories, are highly capable of producing metallic NPs in both wet and dry forms [149]. This has led to the development of comprehensive methods aimed at producing cost-effective, renewable biofuels. Previous studies have shown that nanomaterials like graphene could potentially enhance biofuel production by facilitating electron transfer in complex marine environments, which might even improve outcomes in areas like Alzheimer's disease research [150]. However, excessive amounts of graphene can inhibit microbial growth, which is a challenge to its widespread practical application [151].

In terms of biofuel production techniques, combined approaches like pyrolysis, fermentation, and hydrothermal liquefaction are being explored. For example, combining anaerobic digestion with pyrolysis has been shown to increase methane production by 17% and bio-oil yield by 10% [152]. Hydrothermal liquefaction is another promising technology for biofuel production. During this process, 80-85% of the moisture in marine macroalgae is quickly removed for fuel generation [23]. Hydrothermal liquefaction, combined with microwave processing, offers a cost-effective method for transforming algae into biofuels, particularly for applications in aviation [23]. Furthermore, extracting agar from algae before anaerobic digestion has been found to increase biomethane and biodiesel yields [152]. Genetic and metabolic engineering techniques are also gaining traction in macroalgal biorefineries, boosting the development of biotechnology and innovative methods for biofuel production [153].

LIMITATIONS AND CHALLENGES

Marine macroalgae and microalgae are increasingly seen as promising sources for biofuels, offering a viable and beneficial alternative for transitioning to a blue bioeconomy [154]. As illustrated in Figure 5, there are significant challenges and limitations in the production of biofuels from marine algae. While there is considerable expertise in the field, the commercialization of bio-refinery innovations using marine algae as a feedstock faces substantial obstacles. These include a lack of practical knowledge that needs to be addressed before these technologies can be brought to the market. Additionally, cultivating and harvesting algae comes with its own set of difficulties, as does establishing a reliable distribution network for bioenergy production [155].

Other challenges include the selection of suitable algae species, optimizing the hydrolysis and conversion processes using common microbes, and effectively utilizing specific polysaccharides. Scaling up the biological processes involved in algae-based biofuel production remains a major barrier to the industry's growth, and further research is essential to overcome this. Although several laboratory-scale studies are in progress, the real-world application of these innovations remains uncertain in the near term [23]. Biorefineries must integrate all units at a much larger scale, and this scaling-up process needs to carefully consider bio-process efficiency and the quality of the final products. Potential losses during scaling must be managed to ensure that the overall production remains economically viable.

Water usage is another significant concern. As biorefinery processes advance through various biological stages, they require increasing amounts of freshwater. This is especially problematic given the global challenges related to freshwater availability. For bioethanol production, depending on the method, between 1.5 and 10 liters of water are needed for each liter of bioethanol produced [156]. However, researchers are exploring alternatives such as incorporating seawater into the process. Some studies suggest that seawater can be effectively used in algae hydrolysis and breakdown, as well as in bioethanol fermentation. While using seawater has proven to be sustainable in certain contexts, it is still under evaluation in integrated systems for marine algae biofuel production, which involve multiple interconnected processes and challenges.

CONCLUSION

In the near future, developing a holistic approach for biofuel production from marine algae (both macroalgae and microalgae) presents a promising opportunity. Research has identified potential biochemical processes involving various algae species for biofuel production. The growing trend in marine algae trait development, alongside an increasing demand for funded research focusing on comprehensive algae biorefinery techniques, emphasizes the potential to contribute to a growing bio-economy while offering an affordable, renewable energy

source.

Despite these opportunities, several challenges remain, particularly regarding the use of marine algae for biofuels and other valuable chemicals. Issues like the accessibility of algae, large seasonal fluctuations in biochemical processes, and the importance of specific nutrients need to be addressed. There are also limitations in technological advancements and the unpredictable nature of algae biomass yield and quality. Algae biomass can vary significantly based on species, geographical location, and season, which also affects the types and quantities of products produced. While current methods for processing plant biomass are generally effective, further innovation and technology development could offer substantial benefits. Additionally, marine algae biorefineries are still in the early stages of transitioning lab-scale processes to commercial applications. However, biofuels and other algae-based products continue to hold great promise for influencing future energy markets and regulatory frameworks.

Future work will focus on optimizing algae strains, improving biorefinery processes, and developing cost-effective harvesting technologies. Addressing seasonal and geographical variability, enhancing nutrient management, and reducing environmental impact through advanced systems is key. Collaborative research, regulatory frameworks, and market development will drive commercial success for algae-based biofuels.

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