Chapter 13
A Review on Biofuel and Bioresources for Environmental Applications

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Abstract Microalgae are considered one of the most promising feedstocks for biofuels. Interest in algae-based biofuels and chemicals has increased over the past few years because of their potential to reduce the dependence on crude oil-based fuels and chemicals. Algae is the most suitable and sustainable feedstock for producing green energy. However, numerous challenges associated with declining fossil fuel reserves as energy sources have accounted for a shift to biofuels as alternative product from algae. Algae is a source for renewable energy production since it can fix the greenhouse gas (CO_2) by photosynthesis and does not compete with the production of food. This chapter, therefore, presents a review on the prospects of algae for biofuel production and also highlighted in this article is the macroalgae-based biofuels energy products obtained from algae as the raw biomass. In a nutshell, algae are the most sustainable fuel resource in terms of environmental issues.

Keywords Algae · Biofuels · Bioresources · Macroalgae · Microalgae · Renewable energy

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13.1 Introduction

In the beginning, the first generation of bioenergy strategies involved biofuel production based on sugar, starch, vegetable, or animal oils using conventional technology [1, 2], but these methods have been globally criticized because they competitively consume food resources [3]. To overcome this problem, the second generation of bioenergy uses non-edible or waste vegetable oils and agricultural wastes such as lumber, straw and leaves which availability are less [4]. Terrestrial bioenergy production systems are now facing issues related to indirect emission and carbon debt from land clearance and hence are becoming a sustainability hurdle for further expansion [5–8]. Therefore, Trivedi et al. [9] has reported that a more sustainable feedstock had to be evolved to overcome these limitations. Microalgae standout as the most suitable and sustainable third-generation feedstock for producing biofuels [9–11].

Methods to convert biomass to competitive biofuels are increasingly attractive as fossil hydrocarbons are likely to become scarce and costly [2]. Interest has now been diverted to the third-generation biomass like algae, since the first-generation feedstocks (edible crops, sugars, and starches) are under serious controversy considering the competition between food and fuel feud [12] and the second-generation biomass (lignocellulosic biomass) are limited by the high cost for lignin removal [2]. Algae is a very promising source for renewable energy production since it can fix the greenhouse gas (CO_2) by photosynthesis. The average photosynthetic efficiency is 6–8 % [13] which is much higher than that of terrestrial biomass (1.8–2.2 %) [2].

Energy security is a major issue faced by countries all over the world. The increasing energy consumption has dropped the fuel resource by maximum. The total global petroleum consumption is still increasing due to intensified energy consumption [14]. In 2007, there were 806 million cars and light trucks [15] which is expected to increase up to 1.3 billion by 2030 and 2 billion by 2050 [16]. Currently, one-fifth of the global CO_2 emission is due to transportation and trucking [14]. It is critical to realize the negative impacts imparted on the global environment by fossil fuels that has drifted the exploitation of alternate fuels. The green replacement of fossil-based petrofuel is the trending strategy that has gained much attention from scientists all over the world. Biofuels have the potential to replace existing conventional fuels, reinforce energy security and reduce the emission of both greenhouse gases (GHGs) and other air pollutants [14]. Biofuels are considered sustainable, renewable, and environment-friendly fuels. Biofuels such as bioethanol, biobutanol, and biodiesel are produced from sugar beet, sugar molasses, soybean, or rapeseed. Biodiesel is alkyl esters obtained from transesterification of fatty acids (FAs) obtained from renewable biomass.

The sustainability revolution is the defining challenge of our time to meet increasing needs in the energy–food–water nexus without compromising the ability of next generations [17]. Sustainable agriculture based on annual grains and perennial high-biomass yield plants along with new biorefineries could produce a myriad of products from biofuels (e.g., butanol and hydrogen), biomaterials, to food. Sustainable agriculture and new biorefineries could be cornerstones of the coming sustainability revolution based on the most abundant renewable bioresource biomass [17]. A variety of biofuels have been proposed, such as cellulosic ethanol [18], n-butanol [19, 20], isobutanol [21, 22], long-chain alcohols [23, 24], electricity [25, 26], alkanes [27], FA esters [28], hydrogen [29, 30], hydrocarbons [31, 32], and waxes [33]. In terms of the entire life cycle, the production of any biofuels from biomass sugars is a nearly carbon-neutral process [34, 35].

Numerous challenges associated with declining hydrocarbon deposit, such as petroleum fuel reserves as energy sources, have accounted for a shift to biofuels as alternatives [36]. Since its early commercialization as a substitute for petroleum-diesel for nearly ten years now, biodiesel as biofuel has remained a good global fuel for running automobile engines [36]. Many interesting factors have been ascribed to this success. Among others, biodiesel is chemically non-toxic in nature, biodegradable, and can simply be prepared via transesterification under mild conditions [37]. In addition to insignificant contribution to CO_2 and other particulate matter emissions, it could be employed directly in conventional petroleum-diesel engines given optimal performance, particularly due to very low sulfur and aromatic contents and compatible flash, cloud, and pour points [37–39]. This article focuses on the prospects of algae for biofuel production and the macroalgae-based biofuels energy products that can be obtained using algal biomass as the raw material.

13.1.1 Developing Bio-based Resources Products

There is a growing urgency to develop novel bio-based products and other innovative technologies that can unhook widespread dependence on fossil fuel. Renewable, recyclable, sustainable, triggered biodegradable bio-based products can make a difference in the environment today and tomorrow. A bio-based product derived from renewable resources having recycling capability and triggered biodegradability with commercial viability and environmental acceptability is defined as a "sustainable" bio-based product [40]. Switching to the use of renewable resources whenever the appropriate technology is available is a more sustainable and environmentally responsible approach. Indeed, the conversion to a bio-based economy will take time, but there is now a major effort underway where plant-/crop-based renewables are serving as complementary resources to conventional feedstocks to meet the ever-growing needs for chemicals, materials, and other products [41]. Biotechnology is key to the continued progress in this area.

Plant-/crop-based (i.e., bio-based) resources are defined as source material derived from a range of plant systems, primarily agricultural crops, forestry products, and processing streams (including microbial) in the food, feed, and fiber industries [42]. Plant-based inputs may take several forms including wood, cellulose, lignin, starch, amino acids, proteins and may be sourced from many different places, e.g., from biomass, crop residue, dedicated crops, and crop processing by-products [42]. The current goal is economic and renewable suites of products from new biorefineries, which will include production of primary products and coproducts together [41]. The primary bio-based products can include oils, commodity or specialty chemicals, and materials.

13.1.2 Developing Renewable Energy Sources

There is now widespread acknowledgment that renewable bioresources have considerable potential to increase national energy security and to minimize anthropogenic effects on the environment. However, the transition to renewable resources from fossil fuels must meet certain replacements in the economic arena. It will require significant advances in science and technology development to both meet such criteria and to ensure sustainable enterprises [42]. There are many options on how to most effectively use biomass to generate energy. A major consideration is the source of biomass. In the USA alone, forestry sources and crop residues are a 260 billion-kilogram source of biomass that is not utilized today [41]. The Minnesota Agri-Power Project uses crop parts in an integrated manner. Some 620,000 metric tons of alfalfa are converted into feed with an additional net energy output [42]. Specifically, the leaves are processed into a high-protein animal feed, while the stems are gasified and combusted to produce 75 MW of electricity per day [41]. Although many biomass materials can be used directly, most require conversion to either ethanol or to biodiesel. Biodiesel is produced from any fat or vegetable oil, such as soybean oil, through the chemical process of transesterification. Both the alcohol and biodiesel can be used as a diluent in commercial fuels.

In the USA, the market potential for the production of ethanol from corn stover (the stock, cob, leaf, and husk) is as high as 38 billion liters if cost of production can be reduced [43]. As noted, the stated issue is economics, but it is really an "available technology" issue. A tremendous amount of research is being conducted on finding more efficient ways to convert biomass to fuels. New second-generation biocatalysts are being evaluated for the simultaneous saccharification and fermentation of biomass-derived sugars for generating fuel ethanol [44]. If the plant-derived material is structural biomass, then certain constituents, such as lignin and cellulosics, predominate and new techniques, such as integrated combustion or organometallic chemistry, may provide opportunities to better utilize this type of source [41].

13.2 Algae

Autotrophic microorganisms such as algae seem to be a promising way out for unceasing energy appetite [45]. Algae can be directly converted to energy [14]. The hydrocarbon content of algae distinctively the FAs and acyl glycerides [46] has the potential to counter the diminishing fossil assets [47]. The oil extracted from algae can be used for biodiesel production. The residual biomass rich in sugar fraction can be used for production of biobutanol and bioethanol by fermentation. The algal cells suspended in nutrient rich water acts as a reliable biomechanism that efficiently converts nutrients and CO_2 to hydrocarbons [14].

The interest in algae-based biofuels and chemicals has increased over the past few years because of their ability to reduce the dependence on petroleum-based fuels and chemicals [9]. Algae is touted to be the most suitable and sustainable feedstock for producing green energy as the whole process is carbon neutral in nature and can also be utilized for environment cleaning applications [9]. The present-day option for immediate and sustainable alternate fuels lies with algal biofuels. Algae are the most sustainable fuel resource in terms of food security and environmental issues [14].

Algae are diverse group of photosynthetic organisms ranging from unicellular (microalgae) to multicellular (macroalgae) forms. They have chlorophyll as primary photosynthetic pigment. Commonly, algal population falls under two broad categories (1) microalgae: microscopic algae that grows in freshwater and marine environment and (2) macroalgae: comparatively large, multicellular organisms that grows in marine environment. There are two main populations of algae: filamentous and phytoplankton algae. These two species, in particular phytoplankton, intensifies rapidly to form algal blooms [48]. Though the main storage compound of these algae is starch, oil can also be produced or induced to accumulate within the biomass. The faster growth rate and greater lipid content of microalgae compared to oilseed crops urge researchers to develop technologies for algae utilization in biodiesel production instead of plant oils [6]. Algae-based biofuel production has very less degree of intrusion in the food versus fuel dispute of tomorrow which is an added advantage [49]. Algae can be cultivated on unproductive or abandoned land [50], and it is also very efficient in utilizing the nutrients from wastewater including nitrogen and phosphorus [11] due to its rapid growth rate and the nutrients can be recycled back to the soil by fertilizing the waste by-products [2].

13.2.1 Microalgae

Microalgae are microscopic, unicellular, and phototrophic organisms that falls under the following categories: (1) diatoms (Bacillariophyceae), (2) green algae (Chlorophyceae) and (3) golden algae (Chrysophyceae). Cyanobacteria (Cyanophyceae) such as *Arthrospira platensis* and *Arthrospira maxima* are also referred to as microalgae. Diatoms are the dominant life form in phytoplankton and probably represent the largest group of biomass producers on earth. Green algae are abundantly found in freshwater than in marine waters. The golden algae are similar to diatoms and produce oils and carbohydrates. Microalgae are efficient producers of lipids and other great metabolites that work by utilizing nutrients in the presence of solar energy [14]. The algal species found suitable for biofuel research includes different species of Chlorells sp., Dunaliella sp., Botryococcus braunii, and Nannochloropsis sp. [51].

Autotrophic microalgae are capable of using carbon dioxide and solar energy to synthesize organics such as protein and lipid for their growth. Most of the production of autotrophic microalgae for biodiesel production occurs in indoor photobioreactors that consumes heavy illumination for photosynthesis [14]. In comparison, heterotrophic microalgae are more flexible for the cultivation condition (can grow under light-free condition) and have been found capable of accumulating higher lipid in the cells. The lipid content of heterotrophic Chlorella protothecoides was 3 times higher than that of the autotrophic ones [52–54]. Microalgae commonly double their biomass within 24 h and biomass doubling time during exponential growth can be as short as 3.5 h and under specific cultivation conditions, their oil content can exceed 50 % by weight of dry biomass [45]. Microalgae require less land for cultivation than terrestrial crops, can grow in non-potable water, and do not displace food crops [46, 55].

Microalgae have been recognized as an alternative third-generation feedstock not only because they remove carbon dioxide from the atmosphere, but also because they contain a much higher lipid content per biomass than other plants [10, 11]. Marine microalgae species growing in seawater can also reduce freshwater consumption [56]. In addition, it can be grown with wastewater which indicates a high environmental sustainability of this feedstock [57]. In finding an appropriate application of algal lipid at industrial level, the FA profile analysis is an important task. Recently, there has been an increased interest in the development of alternative methods that improve FAs profile analysis [9]. These methods involve mainly three criteria: (1) direct transmethylation of lipids, (2) elimination of the need for preliminary extraction steps, and (3) using a single-step derivatization procedure for generating fatty acid methyl esters (FAMEs) to denature the protein fraction [58].

Microalgae have the potential for coproduction of valuable products such as carbohydrates, lipids, proteins, starch, cellulose, polyunsaturated fatty acids (PUFAs), pigments, antioxidants, pharmaceuticals, fertilizer, energy crops [59–61], and natural colorants and also as biomass that can be used as animal feed after oil extraction [9]. The most widely used biofuel is bioethanol, which is produced from sugar-based (sugar beets and sugarcane) and starch-based (corn, wheat, barley, etc.) feedstocks [62], while technology leading to conversion of lignocellulosic materials (bagasse, corn stover, rice straw, switch grass, etc.) into ethanol is still under development [56]. Microalgae are photosynthetic microorganisms that convert sunlight, water, and carbon dioxide to algal biomass [63]. Microalgae are being explored at a faster rate as potential oil source for biodiesel production. About 25,000 species are reported out of which only 15 are employed as commercial oil producers [64]. To this end, microalgae represent an exceptionally diverse but highly specialized group of microorganisms adapted to various ecological habitats. Many microalgae have the ability to produce substantial amounts (e.g., 20–50 % dry cell weight) of triacylglycerols (TAGs) as a storage lipid under photooxidative stress or other adverse environmental conditions [46].

13.2.2 Macroalgae

Macroalgae or "seaweeds" are fast-growing multicellular plants growing in salt or freshwater that can reach sizes up to 60 m in length [65]. Seaweeds are lower level plants with undifferentiated roots, leaves, and stems. Seaweeds are classified into three broad groups based on their pigmentation: (1) brown seaweed (Phaeophyceae), (2) red seaweed (Rhodophyceae), and (3) green seaweed (Chlorophyceae) [66]. Macroalgae are photoautotrophic and thus produce and store organic carbons (i.e., carbon sources for biorefinery) by utilizing either atmospheric CO_2 or HCO_3 [67]. Due to the high photosynthetic ability of macroalgae, they have the potential to generate and store sufficient carbon resources needed for biorefinery. Advantages of macroalgae as biofuel feedstock includes atmospheric CO_2 mitigation, entrapment of HCO_3 in the water bodies, thereby reducing the acidic nature of water bodies and acid rain hazards, promoting green fuel for green Earth [14]. Globally, red is the most species-rich group (6000) followed by green (4500) and brown (2000) [68]. Brown algae mainly grow in tempered to cold or very cold waters, and red algae grow especially in intertropical zones. The green algae grow in all types of water environment [69]. Macroalgae is cultivated at present for food production, fertilizers, and hydrocolloid extraction in Asia with China, Korea, Philippines, and Japan accounting for about 72 % of global annual production [70]. Currently, the only industrial product of significance from macroalgae is hydrocolloids extraction [2]. There are several reviews on biofuel production from algae, but they focused on microalgae utilization [69] or only one technique like biogas production from macroalgae [71].

13.3 Energy Products (Biofuels) from Algae as Bioresources

13.3.1 Biodiesel

Algae can be used as a feedstock for obtaining a number of energy products. Algal biodiesel is a carbon-neutral fuel, which means it assimilates about as much CO_2 during algal growth as it releases upon fuel combustion [72]. For this reason, algae-based fuels are said to be the most effective and sustainable response to climate change [57]. Biodiesel production from these requires release of lipids from their intracellular location, which should be done in the most energy-efficient and economical ways. Transesterification is the most usual method to convert oil into biodiesel [73]. Transesterification converts raw and viscous microalgal lipid (triacylglycerols/free FA) to lower molecular weight FA alkyl esters [74]. The current trend of carrying out transesterification reactions is through the enzymatic route. Lipase enzymes can be used for transesterification purpose. These enzymatic biocatalysts are of two types: extracellular and intracellular lipases [75]. Particular attention has been dedicated to the use of lipases as biocatalysts for biodiesel production due to their favorable conversion rate obtained in gentle conditions and relatively simple downstream processing steps for the purification of biodiesel and by-products [9]. Algal biodiesel has also been found to meet the International Biodiesel Standard for Vehicles (EN14214). Selection of species for biodiesel production depends on fuel properties and oil content along with engine performance and emission characteristics [76].

Biodiesel has good combustion characteristics and reduces smoke and carbon dioxide emissions by 78 % compared to petrodiesel [77]. Biodiesel production and utilization can promote us forward for a safer living and lights rural development by generating employment opportunities. Biodiesel obtained by various methods such as pyrolysis, dilution, transesterification, microemulsion, and supercritical processes have different qualities and properties [14]. To date, macroalgae biodiesel has been reported sparingly and yields are much lower than those of microalgae [78, 79]. The first report on biodiesel production from macroalgae focused on the comparison of thermochemical liquefaction and supercritical carbon dioxide extraction techniques [80] and another report compared the biodiesel production from both macroalgae (Cladophora fracta) and microalgae (Chlorella protothecoides) and it demonstrated the weaknesses of the former for biodiesel. Macroalgae is usually converted into biooil (lipids and free FAs), and then, the lipids are separated for biodiesel production. The high content of free fatty acids (FFAs) in the oil can restrain the target transformation although the FFAs are also precursor of biodiesel [2].

13.3.2 Biogas

The macroalgae exhibit higher methane production rates than the land-based biomass. Biogas production is not yet economically feasible due to the high cost of macroalgae feedstocks, which needs to be reduced by 75 % of the present level [81]. Microalgal biomass after lipid extraction comprises of proteins and carbohydrates that can be digested via anaerobic means to generate biogas, a renewable fuel [9]. Biogas contains a mixture of gases; mainly carbon dioxide (CO_2) and methane (CH_4). There are four main stages in the biogas production: hydrolysis, acetogenesis, acidogenesis, and methanogenesis [82]. The direct energy recovery during biogas production via anaerobic digestion (AD) could be more profitable when the algal lipid content in microalgae is lower than 40 % [83]. Biogas production is a long-established technology. Biogas production from macroalgae is more technically viable than for other fuels since all the organic components (carbohydrate, protein, etc.) in macroalgae can be converted into biogas by AD, and also the low lignocellulose content make their biodegradation easier than their relative microalgae to produce significant levels of biogas [84, 85].

13.3.3 Bioethanol and Biobutanol

Bioethanol can be fermented from all kinds of macroalgae by converting their polysaccharides to simple sugars and by employing appropriate microorganisms. Since macroalgae have various carbohydrates such as starch, cellulose, laminarin, mannitol, and agar, carbohydrate conversion to sugars and the choice of appropriate microorganisms are pivotal for successful bioethanol fermentation. Some of the species used for ethanol production are Cholorococcum, Chlamydomonas, and Chlorella. Fermentative ethanol production from microalgae such as Chlorococcum and Chlorella vulgaris results in better conversion rates than that of other species [9]. Brown algae is a principal feedstock for bioethanol production because they have high carbohydrate contents and can be readily mass-cultivated with the current farming technology [86–90]. Biobutanol can also be produced from macroalgae through the acetone–butanol (AB) fermentation using solventogenic anaerobic bacteria such as Clostridium sp. [68].

Biobutanol and bioethanol are clean burning fuels and considered environmentally safe as greenhouse gas emission is comparatively lesser than fossil fuels. On combustion, they emit carbon dioxide and water. Micro- and macroalgae are fast-growing carbon-accumulating biomass venturing alcoholic fuel production [14]. Quantity of alcohols obtained from algae is much dependent on the reaction parameters [91]. Bioethanol from microalgae can be produced by fermentation of biomass or direct cellular reactions [92]. Fermentation by B. Custersii produced 11.8 g/L ethanol from 90 g/L sugar in a batch reactor, and 27.6 g/L ethanol from 72.2 g/L sugar in a continuous reactor [93]. Also, results from Tan et al. [94] concluded that E. Cottonii could be a potential feedstock for bioethanol production. Bioethanol and synthetic biodiesel from algal feedstock are two liquid algal transportation biofuels [2]. Extracted algal biomass can be pretreated to convert starch to glucose after which biological hydrolysis is done to produce ethanol. Biobutanol production is generally done by biochemical reactions facilitated by Clostridium species [14].

13.3.4 Isobutanol

Isobutanol is one of the most perfect biofuels for meeting needs of current internal combustion engines (ICEs). It has an energy density similar to n-butanol (i.e., 29.2 MJ/L), approximately 84 % of the energy content of gasoline, is of limited miscibility with water, and is completely miscible with gasoline [95]. The branched structure of isobutanol yields a better octane number than n-butanol. Isobutanol can be produced by glycolysis followed by the Ehrlich or 2-keto-acid pathway [95, 96]. This pathway decarboxylates keto acid, the intermediate amino acid precursor, into isobutyraldehyde and then reduces it to isobutanol [17].

Heterologous pathways for isobutanol production from sugars have been introduced to a number of microorganisms, such as *Escherichia. coli* [23] and *Bacillus subtilis* [97, 98], important industrial microorganisms; *Corynebacterium glutamicum* [99], a bacterium known for its high levels of amino acid production; *S. cerevisiae* [100]; and *Clostridium acetobutylicum* [101], a cellulolytic bacterium that produces isobutanol directly from cellulose. In addition, the isobutanol-producing pathway has been introduced to several microorganisms for producing the desired product from proteins [102] or CO_2 supplemented by solar energy [103] or electricity [104].

13.3.5 Biooil

Thermochemical conversion techniques, including pyrolysis and liquefaction, can convert biomass to liquid biooil [105] quickly. Pyrolysis of macroalgae for biooil, in recent years, has attracted increasing interest. On the one hand, macroalgae can be easily harvested from water and dehydration; on the other hand, pyrolysis is likely to be the most tolerant method to the high ash content of the algae compared to other biochemical methods. Pyrolysis is accomplished at temperatures between 400 and 600 °C and atmospheric pressure but requires dry feedstock. During the pyrolysis process, organic structures are decomposed into vapor phase, gas compounds, and a carbon-rich solid residue (char). The vapor phase then condensed into liquid product called biooil (or biocrude) [2]. Liquefaction is a process by which biomass undergoes complicated thermochemical reactions in a solvent medium to form mainly liquid products. Hydrothermal liquefaction (HTL) is a process using water as reaction medium, carried out in sub-supercritical water (200–400 °C) under sufficient pressure to liquefy biomass for biooil production [106, 107]. The liquid biooil is usually separated by extraction of the reaction mixture with organic solvents such as dichloromethane, trichloromethane, and acetone.

13.3.6 Biomethane

Biomethane from biogas is a fuel source that can be converted to heat and electrical energy on combustion [108, 109]. Combustion of methane in Internal Combustion (IC) engines happens by oxidation of methane. Combined heat and power gas (CHG) engine burns methane to CO_2 completely [110]. Carbon dioxide from biogas and flue gas from combustion of biomethane can be recycled back to the culture system as nutrients [111]. Recycling flue gas and CO_2 from biogas as feed for carbon mitigating autotrophs can take the process in feasible way. Recycling the culture water can reduce nutrient usage by 55 % [112]. Syngas obtained by gasification method is a typical source of methane. Syngas has low calorific value of 4–6 MJm–3 that still can be used to run engines for heat, power and drive turbine for electricity [14].

13.3.7 Biohydrogen

Biohydrogen is a zero-emission fuel considered to be much safer than all other fuels. Hydrogen carries energy that can be used to replace gasoline in the vehicles. On combustion, it reacts with oxygen to give water. Water produced is radiant and energy obtained is lesser than spent in production. Combustion in internal engines can drive out power and electricity useful for beneficial activities. Hydrogen as fuel is used in space craft propulsion as it has the highest heating value. Efficient utilization of hydrogen fuel for running vehicles is been considered as the hot topic in hydrogen combustion science. Electric power of 5HW is generated by utilizing hydrogen at volumetric flow rate of 119.7 mol/h using proton exchange membrane and fuel cell [113]. Biohydrogen production is coupled with fuel cells to harvest energy proficiently [114, 115]. Possibly, hydrogen can be used in fuel cell vehicles (FCV) and hydrogen internal combustion engines (H-ICE) [14].

13.3.8 In Vitro Hydrogen

Hydrogen is the best biofuel for future FCVs mainly due to its cleaner by-product (water) and higher energy conversion efficiency through a proton membrane exchange fuel cell (PEMFC) than an ICE, whose energy efficiency is restricted by the second law of thermodynamics [116]. Hydrogen can be produced from biomass and sugars through chemical catalysis (e.g., gasification [117], pyrolysis [118], gasification in critical water [119], and aqueous-phase reforming [120], dark anaerobic fermentation [121], light fermentation [122], microbial electrohydrogenesis [123], and their combinations). However, all these approaches suffer from low product yields, possibly dirty products, or low productivity. In vitro synthetic biosystems for biomanufacturing are the production of the desired products by assembling a number of purified enzymes or cell lysate and coenzymes [22, 124, 125, 126, 127, 128]. In vitro non-natural synthetic pathways can be designed to produce hydrogen by splitting water powered by the chemical energy stored in a number of sugars [126].

Alternatively, hydrogen can be produced from the biomass sugars cellulose and hemicellulose. In this process, a partial hydrolysis of cellulose mediated by endoglucanase and cellobiohydrolase can produce long-chain cellodextrins and glucose [2]. Cellodextrin and cellobiose phosphorylases can produce glucose-1-phosphate (G-1-P) [29]. Similar to the remaining pathway, all glucose units and G-1-P can be converted to hydrogen [29].

13.3.9 Biojet Fuel

Upon combustion, the aircraft jet fuel produces carbon dioxide (CO_2), water vapor (H_2O), nitrogen oxides (NOx), carbon monoxide (CO), oxides of sulfur (SOx), unburned or partially combusted hydrocarbons, particulates, and other trace compounds. These factors jointly create a challenge for the aviation industry to ensure the security of fuel supplies and to minimize the unwanted harm to the environment. Aviation alters the composition of the atmosphere globally and can thus drive climate change and ozone depletion [129]. The aviation industry is concerned about reducing its carbon footprint by using an eco-friendly fuel for air transport. Renewable jet fuel for the aviation industry, also termed biojet fuels, could reduce flight-related greenhouse gas emissions by 60–80 % compared to fossil fuel-based jet fuel. Green biojet fuel is made by blending microalgae biofuels with conventional petroleum-derived jet fuel to provide the necessary specification properties [130]. The oil of microalgae can be converted into jet fuel by hydrotreatment (hydrotreated FAs and esters, HEFA). This process is also certified according to ASTM standard D7566. The resulting fuel can therefore be used commercially in blends containing a minimum of 50 % conventional jet fuel. This fuel is also referred as hydrotreated vegetable oil (HVO), hydrotreated renewable jet (HRJ) or bio-derived synthetic paraffinic kerosene (Bio-SPK). Currently, research is under way to produce biofuel from microalgal source. Two flights in the past have been tested successfully on the jet fuel made from algae oil [131].

13.4 Prospects of Algae as Biodiesel (Biofuels) Feedstock

Among all single-cell organisms (SCO), algae are as promising as yeast and bacteria. A number of interesting factors have been ascribed to this fact. They are widely available and can be grown anywhere with practical consistencies, thereby limiting any competition with edible vegetable oils. Unlike many energy crops, algae can have up to 100 times more oil content. Theoretically, depending on the strength, algae species can produce up to a yield of 20,000 gallons of feedstock per acre of land [132]. Biofuels from algae feedstock will potentially replace a higher percentage of fossil fuels used as automobile fuels than the other sources. The estimated market size for algae is $425 billions, which is more than twice the expected market size for other traditional biofuels. Thus, the algae options stand a market worth hundreds of billions of dollars.

While biodiesel is considered the main obtainable fuel produced from algae, other important fuels can similarly be produced, thus enhancing their exploitation potentials. Fuels such as methane, hydrogen, ethanol, and biogasoline can be generated from algae. The biomass residues are applicable as sustainable feedstock for combustion. Other important areas of applications for algae include environmental management and production of other products. Algae derivatives have excellent bioremediation properties and therefore suitable for treating waste and sewage water through the removal of toxins and nutrients. Pigments, nutraceuticals, and even fertilizers can successfully be produced from algae [36].

It could be seen that producing oil from algae and subsequently biodiesel as well as other products is considered highly efficient by many researchers [133–135]. The processes of cultivation, oil extraction, and final conversion into biodiesel are basically comparable to those of other edible crops such as soy, sunflower, and palm. It is particularly important to note that, unlike other crops, algae can be cultivated even in harsh conditions, including salty and sewage-receiving areas. On the one hand, macroalgae has high mineral or ash content, mainly comprised of K, Na, Ca, and Mg [136] which is not beneficial for the use of macroalgae as a fuel. On the other hand, the alkali metal can be potential catalyst of hydrothermal process. It is prudent to get high-quality biofuel in large quantities.

13.5 Significance of Algal Biomass for Biofuels

Aquatic biomass could also be used as raw material for cofiring to produce electricity, for liquid fuel (biooil) production via pyrolysis, or for biomethane generation through fermentation [66]. Cell walls of diatoms have been composed of polymerized silica and accumulate oil and chrysolaminarin. The freshwater green algae *Haematococcus pluvialis* is commercially important as a source for astaxanthin, *Chlorella vulgaris* as a supplementary food product, and the halophilic algae *Dunaliella* species as a source of β-carotene. Extracted biomass proposed to be used as fertilizer or animal feed is significant in adding economic value to the process [14]. Coproducts such as pigments, agar, carrageenan, and other bioactive compounds are value-added products that can be removed before fuel conversion of biomass [137]. Methane, butanol, and ethanol can be effectively produced by fermentative digestion of residual algal biomass by selective microorganisms [138]. Though algae are aquatic, they use less amount of water than terrestrial plants [139]. No herbicide or pesticide is recommended in algal cultivation [55]. Growth of algal population in wastewater promotes them as dual-purpose choice for biofuel production and organic load degradation [140]. Biochemical composition of algal biomass can be changed by varying the growth parameters, thus inducing richness of targeted biomolecular fractions in resultant biomass steering to the purpose of cultivation [141].

13.6 Environmental Applications

13.6.1 Biomitigation of CO_2 Emissions Using Microalgae

Biological CO_2 mitigation has attracted much attention in the last few years. A large volume of CO_2 is emitted from the power plants and industries into the environment. Therefore, the use of flue gas emissions from an industrial process unit, as a source of CO_2 for microalgae growth, provides a very promising alternative to current greenhouse gas (GHG) emissions mitigation strategies [9]. Microalgae can fix carbon dioxide from different sources, which can be categorized as (1) CO_2 from the atmosphere, (2) CO_2 from industrial exhaust gases(e.g., flue gas and flaring gas), and (3) fixed CO_2 in the form of soluble carbonates (e.g., $NaHCO_3$ and Na_2CO_3) [142]. Chlorococcum littorale, a marine alga, showed exceptional tolerance to high CO_2 concentration of up to 40 %. It was also reported that Scenedesmus obliquus and Spirulina sp. showed good capacities to fix carbon dioxide when they were cultivated at 30 °C in a temperature-controlled three-stage serial tubular photobioreactor [143]. Microalgae Selenastrum sp. can efficiently utilize both bicarbonate salt and carbon dioxide gas as carbon source in culture media [144]. Microalgal species have a high extracellular carbonic anhydrase activity which is responsible for the conversion of carbonate to free CO_2, to facilitate CO_2 assimilation [145].

13.6.2 Bioremediation of Wastewater and Polluted Soil Using Microalgae

The use of algae for bioremediation of wastewater was first investigated in the 1950s by Oswald and Gotaas [146]. Algae utilize the nutrients present in the wastewater for its growth. The wastewater discharged into the water bodies is hazardous to the environment and can cause various health problems in human beings. One of the benefits of using algae in wastewater treatment is that algae produce O_2 during photosynthesis, which promotes aerobic bacterial degradation of the organic components. Bacterial degradation, in turn, produces CO_2, which promotes photosynthesis and the algal uptake of inorganic nutrients [147]. Algae can be used in wastewater treatment for a range of purposes, such as removal of coliform bacteria, reduction of both chemical and biochemical oxygen demand, removal of N and/or P, and also for the removal of heavy metals [148]. Microalgae can also act as a potential sink for removal of toxic and harmful substances from the soil. Microalgae can help in bioremediation of heavy metal ions such as iron and chromium. The three algal species, *Hydrodictyon* sp.*,* *Oedogonium* sp. and *Rhizoclonium* sp., were used for the bioremediation of heavy metals (cadmium and zinc) present in the wastewater derived from coal-fired power generation [149]. Algae have the capability to sequester, adsorb, or metabolize these noxious elements into substantial level [150]. Microalgae possess different molecular mechanisms that allow them to discriminate between nonessential heavy metals from those essential ones for their growth [151].

13.7 Conclusion and Perspective

The versatility of algae is a promising parameter for them being prompted to be used as a biofuel resource. Algae possess a huge potential for using as a raw material in biorefinery as it is capable of producing a wide spectrum of products. It is the most beneficial feedstock for the production of biofuels and chemicals in the near future. Biofuels from algae would be a cornerstone of the sustainability revolution because it will increase energy security and decrease greenhouse gas emissions. In addition, microalgae have inherent advantages that make them environmentally sustainable compared to first- and second-generation biofuel feedstock. Macroalgae integration into a biorefinery is promising for its efficient conversion to biofuels. However, research must be intensified to identify novel and the most appropriate algae species with high oil contents and fast growth rates in a specific environment. Attention should therefore be directed toward their improved performance and productivity.

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