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Review Article

Marine Algae – Future Source of Biofuels

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Abstract

The current scenario of world's energy crisis made us to understand the fact that world's fossil fuel resources are in peril of exhaustion and prices are reaching historical heights. Thus, the quest for alternative renewable fuel is gaining attention in global scale. The idea of biofuel is a green alternative liquid fuel technology that would lead to a decrease in dependence on petroleum based fuel in the automobile sector and decreases the atmospheric contamination produced by pollutant gas emissions. Thus biofuel can be used as the basis for a clean substitute for petrol-diesel without any modification and are non-toxic and biodegradable. The sustainable production of the alternative renewable fuel energy is being debated globally and it was increasingly understood that the first generation biofuels are primarily produced from food crops and oil seeds. Because of these concerns the search for new generation biofuel feedstock gained increased interest and so a keen focus was given on non-food and non-terrestrial sources and this leads to the development of second and third generation bio fuels. Among third generation biofuel marine algae has been considered recently as a promising biomass feedstock with great potential for biofuel production because they are existing in large amount and found all over the world. Marine algae reproduces themselves every few days, yield oil exceeding 10x the yield of the best oilseed crops, reduce emissions of a major greenhouse gases with enhanced carbon dioxide fixation. In this current review paper we highlighted the critical overview of using Marine algae as a future source of biofuel.

Keywords: Energy crisis; Biofuel; Biomass feedstock; Marine algae; Carbon dioxide fixation.

Introduction

A fuel is defined as something in which we can obtain energy. If any of the molecule produced during carbon fixation provide energy in a mechanical setting, it is called as fuel. In present situation, the primary energy in which human depends is fossil fuel. But unfortunately the sources of fossil fuels and oil reserves are exhausting very speedy. Moreover these fossil fuels contribute to the negative effects in the environment like emission of harmful gases, climatic changes, rising if sea levels, loss of biodiversity, etc. Rapid industrialization and motorization of the modern world is the main reason for high demand of fossil fuel. In turns, this affects the global economic activities and increases the cost of crude oil. Therefore bio fuel is the only alternative source of energy to meet the global fuel demand. The benefits of using alternative source bio fuel are 1) Obtained from renewable resources 2) Sustainable 3) Cheap 4) Reduce our reliance on foreign energy 5) Reduce greenhouse gas emission. Bio fuel is a fuel derived from biomass, a renewable source for generating bio-energy. This is the fourth largest energy resource available in the world [1].

It is the natural inexpensive form of storage device for energy that can be then used at any time. Biomass is obtained from agricultural or domestic waste and also by anaerobic digestion of sewage that can be converted into solid, liquid and gaseous bio fuel. The term biomass is mostly refers to any organic matter like timber or various crops grown for the purpose of burning to generate heat and power [2]. They are carbon neutral and therefore it is essential to make use of these sustainable fuels and should be replant as harvesting in order to maintain continuous and virtuous carbon cycle. Based on the chemical complex nature of biomass, they are classified as first, second and

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third generation bio fuels. First generation bio fuels are defined in simple terms as fuel obtained from feed stocks that are consumed as human food. This includes corn, sugarcane, wheat, sugar beet sorghum etc. As the uses conventional technologies to extract the bio fuels, they are also known to be "conventional bio fuels". Certain industrial concerns like cost and inefficiency and competition with food crops led to the generation of second generation bio fuels. No second generation feed stock is a food crop i.e., they are no longer used for consumption. This includes agricultural residues, woody crops that are little more difficult to extract and requires advanced conversion technologies for their process. This is why the second generation bio fuels are known to be "advanced bio fuels". This technology depends on biomass resources from agriculture to forestry waste materials. Lignocellulosic processing is a well-known second generation technology. Increased fuel consumption increases the challenge of sustainable supply of feedstock and so the scientists look for an alternative solution regarding these problems.

In the third generation bio fuel, the marine resources, sea weeds and cyanobacteria are attractive source because they can results higher yield with lower resource input. Among these algae is the most promising non-food source of bio fuel and can rapidly grow even in salt water, adverse condition and also in sea water. The algal biofuel contains no sulfur and is nontoxic and highly biodegradable [3]. Depending on the technique and the part of the cell used, algae can be converted into various types of fuels. The increasing interest in the use of algae for production of bio fuel is due to the accumulation of very high level of lipid that can be then easily transesterified into biodiesel. Following lipid extraction, the carbohydrate content of algae can also be fermented into bioethanol or butanol fuel.

Biology of Algae

Algae are uni or multicellular photoautotrophs. Therefore for their growth and production of intracellular storage compounds, they absorb energy from sunlight and fix CO_2 from atmosphere. Thus, they are known as biological solar panels. They are photosynthetically more efficient than other plants and their photosynthetic efficiency is reported as in the range of 3 to 8% compared with 0.5% of terrestrial crops [4]. They are classified into two categories.

Macroalgae

They are multi cellular and consist of different cell structure and function. Generally they are plant like but don't have root, stems, and leaves have simple reproductive structures. They grow faster and reach upto 60 m in length either in salt or fresh water. Mostly they grow on rocky surfaces and some may found to be attached in sandy particles. They are stable multi layered vegetation capturing photons efficiently from sunlight. The macroalgal biomass can be obtained by inshore cultivation established in natural water areas where low tidal activity is found with natural sunlight, heat and nutrients [5]. They are cultivated on lines or ropes, in nets or grown in sea bed. It's productivity depends on favorable temperature regime, optimal nutrient concentration, sufficient sun light radiation and suitable wave action. An alternative approach to avoid occupying of valuable sea shore parts is offshore cultivation. This off shore farm can be designed as algae attached with buoys or the sea bed [6]. To increase the efficiency of off shore cultivation, wind turbine towers are constructed to anchor algal farms and to maintain the wind farm and algal farm simultaneously.

The major advantage in the cultivation of macro algae are shorter life cycles, cost effective and environmental friendly. They do not need fresh water to grow and cause no change in the land they cultivated. They have higher volumetric production rate than microalgae and produce higher biomass densities. The drawbacks of using macro algae are they will not produce significant lipid and requires low temperature, less acidic condition and shorter reaction time [7].

Microalgae

As these are smaller than 0.4 mm in diameter and are very small, they requires microscope and are either belongs to unicellular or multicellular. They are phototropic and usually found as individuals or in groups in marine or fresh water environment and it consume carbon di oxide, nitrogen and phosphorus and it releases oxygen. Their photosynthetic mechanism is analogous to land based plants, but as they possess simple cellular structure and are immersed in an aqueous environment, they could efficiently access water, CO_2 and other nutrients and thus they are highly skilled in converting solar energy into biomass. They are capable of growing in wide range of salinity and chemical compositions. They are used in the synthesis of different value added compounds and cosmetics because they are rich in protein and other compounds of commercial interest. The microalgal lipid content varies according to its growing conditions. The lipid concentration can be increased by optimizing growth determining factors.

The micro algae cultivation can be done by various technologies such as open ponds, closed systems including PBR (Photobioreactor). Compared with other systems, open race ponds are easy to construct and operate [8]. Disproportionate light intensity and control of environment and contaminations are the major drawbacks. Closed systems are found to be highly efficient as they can control the environmental conditions strictly. The other benefits of photo bioreactors are greater temperature control, better control of CO_2 transfer and protection from climate related impacts [9]. The harvesting strategy includes concentration of biomass either by one or two step process and are further processed by drying, extraction and downstream processing steps.

The chief advantage of using microalgae is their dual role in production of biomass which is suitable for rational bio-fuel production and phycoremediation of domestic and industrial waste water. Various types of bio fuel can be produced using algae. It includes (i) Biodiesel by transesterification of algal oil [10] (ii) Bio ethanol produced by fermentation and distillation of sugars [11] (iii) Bio butanol generated from the left over green waste [12] (iv) SVO, algal oil directly used as a fuel [12] (v) Biogas (methane), the main focus of most of the works in microalgae for bio fuel production [13] (vi) Other hydrocarbon fuel variants such as gasoline [9].

Algal oil extraction for biofuel production

The sustainability of algae based bio fuel is determined by the process of algal oil extraction because it is an expensive process. Using appropriate harvesting strategy, the algae is separated from the growth medium and oil is extracted by any of the mechanical or chemical method. The mechanical method includes (i) Expression press (ii) Ultrasonic assisted extraction. In both the methods dry algae can only be used which is energy intensive. The chemical method includes (i) Hexane solvent method (ii) Soxhlet method (iii) Supercritical fluid extraction. The use of chemical solvents may result in safety issues, health problems and environmental pollution. The supercritical extraction is both expensive and energy intensive as it requires high pressure equipment. For economic and efficient oil extraction, many manufacturers use combination of mechanical pressing and chemical solvents. The other method employed is enzymatic extraction in which enzymes are used to degrade the cell walls and this ease the extraction process. But the cost is highly expensive compared to chemical extraction. The osmotic shock treatment can be used to rupture the cells in solution to release cellular components and oil.

Biofuels from marine source

Algae are logical source to make bio fuel. Oil from algae can be potentially processed to produce bio fuels in conventional refineries. Algae can be converted into different bio fuels depending in technique and part of the cell used in the process. The lipid obtained from algal biomass can be extracted and converted into biodiesel and following extraction of lipid, the carbohydrate contents of algae are fermented into bio ethanol and butanol fuel. The list of algae used in the production of biofuel is listed in table 1.

Biodiesel

In the market, transesterification or alcoholysis of triglycerides obtained from vegetables or animal fat yields biodiesel. In this case, lipid and high content of free fatty acid separated from macroalgae are used to produce biodiesel. As macro algae do not contain triglycerides, they are not widely used for bio diesel production. To date, biodiesel from macro algae is sparingly reported and yields very low compared to micro algae [14]. Table 2 gives the list of various macroalgae used in the production of biodiesel and other applications all throughout the world. In order to increase the yield, new techniques like ultrasound irradiation assisted transesterification was used to form emulsion of oil and alcohol and the cavitation formed during this process accelerates the rate of the reaction [14]. Another observation reported that biodiesel from wet biomass is ten times lower from dry biomass and it implies the negative effect of water on transesterification.

Table 1. Marine resources used in biofuel production

Macro algae	Micro algae
Acrosiphonia orientalis	*Dunaliella tertiolecta*
Ulva fasciata	*Isochrysis galbana*
Ulva lactuca	*Botryococcus brauni*
Enteromorpha compressa	*Chalmydomonas reinhardtii*
Caulerpa peltata	*Chaetoceros calcitrans*
Valoniopsis pachynema	*Euglena sp.*
Bryopsis pennata	*Spirogyra sp.*
Caulerpa racemosa	*Phormidium sp.*
Padina tetrastromatica	*Cyanobacteria*
Dictyota adnata	*Tetraselmis suecica*
Lobophora variegate	*Scenedesmus obliquus*
Sargassum wightii	*Nannochloropsis oculata*
Centroceras clavulatum	*Phaeodactylum tricornutum*

Thus dehydration process is necessary to achieve high yield. The conventional biodiesel production consists of various stages including extraction of oil, purification (degumming, deacidification, dehydration) and transesterification. As these steps increases the total production cost, direct transesterification or insitu extraction is carried out in which the oil bearing material directly contacts with alcohol instead of reacting with extracted oil and thus eliminates the two stage process of biodiesel production. Whereas, micro algae can accumulate significant amount of triglycerides amounting 20- 50% of it's cellular weight [15]. It depends on the type of strain and cultivation condition. The micro algae grow for biofuel production is firstly grown under optimal growth condition. Then they are put on a restricted diet nutrient growth media resulting in increased oil production.

Table 2. List of macroalgae used in biodiesel production and their location

Group	Species	Location	Lipid content (%,w/w)	Other uses
Red Algae	*Chondrus ocellatus*	Hawaii, USA	0.9	Used as thickener and stabilizer
	Porphyra perforate	Ireland, Canada, California	5.8	Edible sea weed
	Gloiopeltis fenax	Sea of south China	33.38	Sizing material in silk and other textiles
	Gracilaria crassa	Northern territory, Australia	11	Used as antiviral agent
	Gracilaria corticata	India	10.9	Animal feed
Brown Algae	*Hedophyllum sessile*	California	6.4	Traditional plant food
	Saccharina japonica	Hokkaido, Japan	1.2	Source of glutamic acid
	Nereocystis luetkeana	Cormorant Island	33.6	Edible sea weed
	Sargassam Sp.	Mandapam, Tamil Nadu	1.6	Source of medicinal value
Green Algae	*Caulerpa scalpelliformis*	India	24.4	Animal feed
	Ulva fenestrate	Sea of Japan	5.01	Edible as soups and salads
	Chaetomorpha linum	Tuscany, Italy	60	Used in aquarium
	Enteromorpha fasciata	Tamil Nadu	52.2	Edible sea weed

TAGs synthesis in these species can be enhanced by various conditions subjected to the growing micro algae. It includes causing stress to the microalgae such as temperature, pH, salinity, nutrient (such as nitrogen, sulfur, phosphorous, zinc, iron, etc.) starvation and algal culture age. Increased TAG content enhances the yield and efficiency of biodiesel and the saturated and unsaturated fatty acids present in TAG determines the quality of biodiesel. Table 3 lists the lipid content of different microalgae used in biodiesel production.

In order to enhance the economics of biodiesel production using micro algae, genetic modification and molecular level engineering receives keen focus to increase its photosynthetic efficiency, biomass growth rate, oil content and reduces photo inhibition. To attain a consistent annual yield of oil, photo bioreactors should be used that provides controlled environment to increase the microalgal biomass required for making biodiesel.

Table 3. List of microalgae and lipid content [16, 17]

Microalgae type	Lipid (%, w/w)
Ankistrodesmus sp.	24-31
Botryococcus braunii	25-75
Chaetoceros muelleri	33.6
Chlorella emersonii	25-63
Chlorella protothecoides	15-58
Chlorelle sorokiniana	19-22
Chlorella vulgaris	5-58
Crypthecodinium cohnii	20-51
Dunaliella primolecta	23
Isochrysis sp.	25-33
Monallanthus salina	>20
Nannochloris sp.	20-35
Nannochloropsis sp.	31-68
Neochloris oleoabundans	35-54
Phaeodactylum tricornutum	20-30

Bioethanol

Bioethanol from macro algal feedstock is also a liquid algal transportation fuel. As macro algae are rich in carbohydrate and contains only little lignin, they can be used as suitable substrate for fermentation process for bioethanol production [18]. As these organisms are grown in aquatic environment, the buoyancy allows upright growth in the absence of lignin crosslinking and so they do not have the same lignin crosslinking molecules in their cellulose structures. Due to low lignin content, it contains significant amount of sugars (at least 50%) that could be used in the bio ethanol fermentation. The process is similar to the technological process of common ethanol production. In the production of bio ethanol from macro algae pretreatment plays a major role in the saccharification and fermentation process. This is because as the carbohydrates in the macro algae are not freely available and so mechanical or acid pretreatment could increase the reaction area and make locked sugars in the structural polysaccharides more accessible to hydrolytic enzymes. The acid hydrolysis pretreatment is reported to be highly cost effective but suffers from a drawback of glucose decomposition that occurs during hydrolysis [19]. Thus saccharification is enhanced by combination of acid and enzymatic pretreatment but it is highly necessary to use suitable enzymes to obtain high efficiency in hydrolysis and enzyme recovery [2]. Therefore the high efficient hydrolysis process and efficient fermentation are the two major issues in using macro algae as the feed stock for bio ethanol production. The red algae *Gelidium amansii* composed of cellulose, glucan and galactan and can serve as efficient feedstock for bio ethanol production [19]. The other brown algal species such as *Alarie, Saccorhiza* and *Laminaria* consists of laminarian and mannitol as main energy storing materials and so they are widely used in the bio ethanol production using mannitol and laminarian as substrates [19].

Microalgae also synthesize large amounts of carbohydrates in different combinations in each species that can be fermented to produce bio ethanol. Besides lipids, carbohydrates are the main components that stores energy. The micro algal biomass also needs to be pretreated for the efficient extraction of fermentable sugars. For this, easily handling energy as well as cost effective hydrolysis method can be used. Enzymes or diluted or concentrated acids are commonly used for hydrolysis of algal biomass. Acid concentration, temperature and algal loading are the important parameters to be considered for the efficient release of fermentable sugars from the biomass [20]. High levels of polysaccharides accumulate in complex cell wall in green algae such as *Spirogyra* sp. and *Chlorococum* sp. and this starch accumulation can be used in the production of bioethanol [11]. It is reported that the *Chlorococum* sp. could produce 60% higher ethanol concentrations for samples that are pre-extracted for lipids versus those that remain as dried intact cells. This indicates that microalgae can be used for the production of both lipid based biofuels and for ethanol biofuels from the same biomass as a means to increase their overall economic value [11].

In order to enhance the production of bio ethanol, several attempts have been reported in the development of genetically modified micro algae by introducing ethanol producing genes [21]. Some private company describes the ability of microalgae to produce bio ethanol photosynthetically and launched photosynthetic ethanol production process. However, the technology is under development and investigated for the commercial production of microalgae-based bio ethanol. Another advantage of using microalgae is they are good producers of hydrogen; therefore bio hydrogen can be produced as pollution free renewable green fuel.

Biogas

The organic components in the macro algae like carbohydrate, protein can easily converted into biogas by anaerobic digestion. Thus significant amount of bio gas can be produced from macro algae and the lower content of lignocelluloses aids their biodegradation easier. But this process also associates with several challenges in the bio gas production includes inappropriate C:N ratio and high level of ammonia, pretreatment process and presence of alkaline metals in macro algae that may inhibits the anaerobic process. Therefore to get increased yield of methane, appropriate C:N ratio should be maintained and lower ratio may results in the accumulation of ammonia in the bio reactor that eventually decreases the yield of bio gas [22]. Table 4 lists the various biogas producers. Hydrolysis treatment is the next rate limiting step in the bio gas production and various pretreatment processes like milling, maceration, thermal pretreatment are reported for efficient breakdown of cell wall and bio gas production [23]. Moreover the presence of significant amount of saline, sulfur and halogens also inhibit the growth and productivity of anaerobic microorganisms and cause fouling issues. Therefore pretreatment in both water and weak acid is necessary to remove significant amount of mineral contents.

The micro algal biomass can also be used for the production of biogas along with other carbonaceous feedstock. This results high energy yield and direct use of biomass without drying and so all type of micro algal biomass can be used as feedstock in the anaerobic digester. The common pretreatment methods like acid base hydrolysis or mechanical pretreatments include using autoclave, homogenizers, microwaves, sonication and also enzymatic methods. The important parameter to consider in bio gas production is C/N ratio. The algal biomass have low C/N ratio and it may inhibits the methane yield because it is undesirable for anaerobic digestion. To overcome this problem, co-digestion of algae and LEA biomass with carbon rich wastes had been used successfully to achieve high C/N ratio and enhances the methane yield by reducing ammonia levels below their inhibitory levels [13].

Corn straw in continuous feed digesters is also reported to enhance the biogas production by anaerobic co-digestion [28]. It is also reported that microalgae with low intracellular nitrogen or sulfur content is most suitable for biogas production process. For example, microalgae harvested in stationary phase or microalgae grown in nitrogen/sulfur limiting growth media can also improve the biomass quality for biogas production.

Table 4. Macroalgal biogas producers

Group	Macroalgae	Yield of bio gas (L CH_4/Kg VS)	Reference
Green Algae	*Ulva lactuca*	271	[24]
Red Algae	*G. vermiculophylla*	481	[25]
Brown Algae	*Macrocystis pyrifera*	117.3	[26]
	S. latissima	268	[27]
	Durvillea Antarctica	256	[26]

Advantages of using algae and bio fuel produced from algae

The global production of oil was saturated and people are searching for an alternative option to fossil fuel and therefore the bio fuel is considered as leading energy source for future.

The various other advantages includes,

i. The algal biomass are huge and superior feedstock that act as an alternate to terrestrial biomass for bio energy production [15].
ii. These algae uptake enormous greenhouse gas and release extra oxygen while growing [29].
iii. They are non-edible sources and so there exists no competition.
iv. The algal species are highly biodegradable resource with rapid bioremediation and are non-toxic [15].
v. They shows rapid growth and results in high growth yield and increased productivity [30].
vi. They has high energy conversion efficiency by photosynthesis [31].
vii. They can grow anywhere. Therefore it can possibly grow in oceans, seas, ponds and in polluted non-arable lands [32].
viii. Reduction of algae residues and wastes
ix. Prevent eutrophication and pollution in aquatic ecosystem [33].
x. They can easily adaptable to wide range of climatic conditions [29].
xi. These bio fuel act as sustainable and environmental friendly fuel and are highly effective to meet the present energy demand [34].
xii. Conservation of fossil fuels
xiii. The bio fuel from algae have great reactivity and decrease hazardous emission [30].
xiv. Diversification of fuel supply.

Disadvantages of using algae and algal bio fuel

There are many arguments for and against the use of algae and algal bio fuel. Even though this technique has potential to deliver clean energy, before commercial use science should find solutions to address some of the serious drawbacks associated in this technique. They are listed as follows (i) Increased initial production cost for growing, harvesting, collection, transportation, storage and pretreatment [29] (ii) Lack of monitoring and algal growth control for fuel production [35] (iii) Use of extra water for algae processing 4) Low ash fusion temperature [21] 5) Limited practical experience in bio fuel production [34].

Commercial applications of marine source

The marine algal resources are potentially a prolific source in production of various secondary metabolites [2,15,21,29,30,33,34]. The various other applications includes (i) Used in the production of agar that can be used as food ingredient and in paper and pharmaceutical industry (ii) Used in the synthesis of astaxanthin, a food supplement and food dye additive (iii) Used in making of bio sorbents, an ion exchange material that strongly bind to heavy metal ion (iv) Used for synthesis of various medicinal and industrial chemicals (v) Used in production of different fertilizers (vi) Used in the synthesis of fruit and vegetable preservatives (vii) Finds application in the synthesis of pharmaceutical products in pharmaceutical industries (viii) Used as natural colorant in paper and textile industries. The other uses are listed in Table 5.

Table 5. Other commercial applications

Product	Applications
Alginate	Food additive, textile printing, pharmaceutical, paper, cosmetic and fertilizer industries
Antioxidants	Food preservative, pharmaceutical, cosmetic and chemical industries
Biorefinery products	Various biofuels and chemicals
Carragen	Gels, food additive, pet food, toothpaste
Conditioners	Chemical, cosmetic and farming industries
Extraction of lipids, carbohydrates, starch and cellulose	Gasoline, biodiesel, jet fuel, biogas
Paper pulp supplements	Paper industry
Phytosterol	Food supplements
Pigments	Natural colourants in paper and textile industries
Therapeutic materials	Pharmaceutical industry

Conclusions

It is clear that in order to meet all the energy needs, bio fuel can serve as an alternative fossil fuel and regarded as cleaner way for transport sector. In India there is diverse coastal resource in Indian oceans and these marine sources can efficiently utilized to meet up the future oil demand. For this purpose, seaweeds have to be cultivated in large-scale and processed for extraction and therefore it needs to be studied in detail to attain nations' economical energy needs and production of bio fuel. Globally, there is a much potential for bio fuel market and in order to increase the feasibility and reduce the cost of its production and emission of greenhouse gases, the technique still requires technological development. Promotion of bio fuel requires global acceptance and development of efficient bio fuel driven engines. Thus, for strengthening the global economy and enhancing environmental quality for sustainable bio fuel production the improvement of technological development is required.

Conflicts of Interest

The authors declare no conflict of interest.

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