

Review Article

Macroalgae: Source for Sustainable Production of Biodiesel

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Abstract

Globally in order to meet our future demand for transport fuels, there is a huge requirement for new sources of energy. Population growth and associated needs for increased food production drives a scenario of land space and water scarcity, which limits the potential contribution that terrestrial biofuel crops can make to future energy needs in a carbon-di-oxide rich world. In addition, intensive production of terrestrial bioenergy crops requires large amounts of energy intensive chemical fertilizer that contributes to environment pollution. Macroalgae are considered as one of the most promising feedstock for biodiesel production for the environmental and social benefits. Macroalgae have a faster growth rate compared to terrestrial plants. The technology to cultivate macroalgae in waste water without the need for additional fertilizer and with low dependence of freshwater is well developed in countries like Europe. Macroalgae has huge potential to provide a biomass substrate for energy production. Challenges exist in converting macroalgae lipids into algal biodiesel due to the unique characteristics of macroalgae and processing technologies. Recent technological advances in biorefinery present opportunities to develop sustainable and integrated productions of various liquid fuels from macroalgae biomass in economical way within the next decades. This review examines the recent progress of macroalgae based liquid biodiesel production with regard to characteristics and applicability of macroalgae as feedstock.

Keywords: Wastewater; Macroalgae; Biorefinery; Bioenergy; Biodiesel.

Introduction

Algae are a diverse range of aquatic plants possessing chlorophyll, comprising both unicellular and multicellular forms. They are without true stem and roots. Algae can be divided into two groups based on size macroalgae are commonly known as “seaweed” and microalgae are single cell organisms ranging from few micrometers to few micrometers [1]. Algae do not require agricultural land for cultivation and its growth in brackish or salt water avoids competition for land and fresh water [2-4]. The biomass yield of algae per unit area is found to be higher than that of terrestrial plants [5-7].

The Brown seaweeds grown “under cultured conditions” are having yields of 13.1 kg dry weight compared to that of sugarcane which is having yield of 10 kg dry weight [8,9]. Thus algae are considered as the most significant and reliable sources of sustainable biofuels [10] and have the potential for the conversion of carbon dioxide to biofuels and chemical feedstocks [3].

Despite their obvious potential, the economic viability for commercial-scale production of fuel from either micro or macroalgae is found to be low.

The part of the problem lies in the microalgae is the low value calculated for energy return on investment (EROI) compared to that for petroleum products and diesel [11]. This is now being address by a raft of research associates who are aimed at considering the full spectrum of products that might be obtained from microalgae in addition to biofuel, in so called biorefineries [2]. In the case of macroalgae there has been a paucity of research for the production of fuels or developing feedstocks for fuels [11,12-14]. However, the uses of macroalgal feedstocks for non-fuel uses are currently 100 times bigger than that for microalgae [15]. At present, the global utilization of (non-fuel) products obtained from macroalgae is a multi-billion dollar industry [16], with Asia being the main producers [17,18].

The uses of seaweeds include human foods, fertilizers, cosmetics, ingredients and phycocolloids [19]. Alginates, agars, and carrageenans are the major phycocolloids which are widely used in the food industry and have an annual production of 86,000 tones [13,20,21]. Totally 221 species of macroalgae are known to be exploited by humankind worldwide with 66% of the species used as food [22].

The majority of algal biomass comes from specie with five genera, *Laminaria*, *Undaria*, *Porphyra*, *Euchema*, and *Gracilaria*, accounting 76% of the total tonnage for cultured macroalgae [18]. Due to the high cost of vegetable oils, which could be up to 75% of the total manufacturing cost [3], has led to the production cost of biodiesel becoming approximately 1.5 times higher than that obtained from diesel [4,5]. Thus there requires a necessity to find out the alternative economical feedstocks for the production of biodiesel which does not rely on the food supply. Macroalgae is a biomass source and represents a significant source of renewable energy.

Algal oil is efficient for esterification and transesterification reaction of biodiesel production that could meet the global demands for fuels in transportation sector. The growth and annual primary production rates are found to be higher for the macroalgae when compared to terrestrial biomass [18]. This review draws on available literature resources to unravel the opportunities and limitations for exploiting macroalgae as a source of biodiesel and highlights areas where further research work and investment needs to be directed in order to realize their potential as sustainable biodiesel resources.

Features of macroalgae

Macroalgae belongs to the group of plants know as algae. The algae are photosynthetic plants that include the 'phytoplankton' which are single celled and the multi celled macroalgae or seaweeds, size ranging from microscopic to the massive bull kelps (*Durvillaea*) and giant kelps (*Macrocystis*). Macroalgae derive all their nutrients directly from the surrounding water through their tissue. The seaweeds reproduce sexually and their reproductive structures are mostly microscopic. The macroalgae fall into four basic groups: the bluegreen algae (Cyanophyta/Cyanobacteria) are

often associated with blooms in rivers, the green algae (Chlorophyta), the brown algae (Heterokontophyta) and the red algae (Rhodophyta). Red algae are the most diverse group of all. These different colours of algae represent the different photosynthetic pigments or chlorophylls that each algae uses and these reflect different wavelengths of light [23].

Macroalgae are found to be attached to the seabed or a solid substratum such as natural reef, rocks, shells, mangrove roots, boat hulls, jetty pilings, mooring lines etc. They have a limited life span when dislodged; it may only live for hours to several months. Few macroalgae, such as *Caulerpa* species, are grown in soft sediments and anchor themselves either with long root-like rhizoids or by entangling. Both intertidally and subtidally they can be grown. In clear waters, over 200 metres of depth the macroalgae can grow and survive whereas in murky waters this is reduced to only a few metres. The maximum depth for most macroalgae is about 35-45 metres along the coast [24].

Importance of macroalgae

Macroalgae are an important resource for fish and invertebrate species in terms of shelter and food. Rotting will lead to the return of vital nutrients back into the ecosystem. They are often can be used as indicators of water quality. During spring when water temperatures and day lengths increases, coupled with heavy rainfall supplying nutrients from runoff to the coast the macroalgae can bloom in massive quantities. These blooms are found to be harmless and non-toxic. They have several applications in food, chemical industry due to the chemical compounds present in the macroalgae [25].

The growth of macroalgae in off -shore for biofuel production rose in 1970s in USA [26]. The development of macroalgae in the biofuel industry is based on their operations on laboratory or meso-scale [27-30]. Around 100 species of macroalgae are explored for the production of biodiesel. Biodiesel is a renewable source of energy which are derived from the esterification and transesterification of free fatty acids and triglycerides. Sargassum is the abundant specie of algae in India. They are potential reserves for the biodiesel production. Brown seaweed *S. myriocystum* was transesterified to biodiesel after extracting its oil content. Macroalgae can be used as a fertilizer

after the conversion process of fuel, or to produce another biofuel by using them as substrate [31].

Production of macroalgae

The fuel production from algae can be grouped into four main areas:

- i. Cultivation
- ii. Harvesting
- iii. Post harvest treatment includes cleaning, size reduction, preservation and storage
- iv. Energy extraction

By achieving an optimized, energy efficient process in each of these four areas will lead to the success of the macroalgal derived fuel. Improved methods for both seaweed cultivation and harvesting techniques will play a vital role for economic and energetic viability of biofuel from macroalgae [32,33]. For commercial-scale biofuel production the area of concern is the seasonal nature of macroalgae growth. It is essential to develop methods for storage or preservation for fuel manufacturing processes. However, there has been limited research on ways to preserve macroalgae in order to satisfy the continuous process demand [34-36].

Cultivation

The growth of algae is rapid, they float to the surface after it is been released from the bottom. It is decomposed after it is washed to the shore.

Harvesting

The sand content will be lower and washing step prior to oil extraction would not be required if algae is collected from the water's edge and about 100 meters out.

Energy extraction from macroalgae

More research work has been focused in the area of production of biodiesel from microalgae via transesterification. This is due to the higher lipid content in microalgae when compared with macroalgae. The lipid content of macroalgae is around 0.3-0.6%. *Chaetomorpha linum*, *Ulva lactuca*, *Enteromorpha (Ulva) compressa* produces biodiesel which yield 11 % of the total dry macroalgal biomass [37].

Biodiesel

The most critical problem the humanity face is the depletion of fossil resources and environmental pollution. Use of biomass or

biomass derived materials as replacement to petroleum fuel has gained much attention. Biodiesel is derived from vegetable oils or animal fat. It is a mixture of alkyl esters with long -chain fatty acids. Biodiesel has many advantages over diesel. They are biodegradable, contain no sulfur has lubricating properties, biodegradable, energy efficient, less of contaminants like carbon monoxide [38]. To produce biodiesel from bioresources four methods are available: Direct use or blending, Micro emulsion, Thermal cracking, Transesterification. The early approaches used are direct use or blending of raw oils. Micro emulsions of two immiscible liquids results in the dispersion of fluid. The conversion of triglycerides to biofuel is achieved by thermal cracking. It can be performed with or without catalyst. Transesterification is the most popular method to convert vegetable oils or animal fats into fatty acid methyl esters has been investigated in the recent years [39].

International practice adopted the single nomenclature to identify the biodiesel concentration known as BXX where XX is the volume of biodiesel in the diesel. Biodiesel has a high flash point, can be stored transported and handled safer than with conventional diesel fuel. The overall cost of biodiesel production is based on the availability and types of feedstock, production techniques, catalyst and operation cost. The finished biodiesel must meet international standards for using commercially as a fuel [40]. The high cost of feedstocks such as vegetable oils is the main concern of biodiesel production. Hence lower price non edible oils such as *Jatropha* or waste cooking oils are preferred for biodiesel production [41-43]. New generation biodiesel are based on deriving raw materials from algae and other renewable feedstocks which are intended to provide sustainability to the whole biodiesel production process [44].

Algae as a source for biodiesel

The recent research suggests that algae can be used as a substrate for biodiesel production. However there are still many limitations which are needed to overcome to increase the efficiency of the process. Algae can yield 250 times the amount of oil compared to sunflower and about 7 to 31 times that of palm oil. The more studies are from microalgae due to the fact

that increased oil yields as well as faster growth rates [44-45].

Bio-oil extraction from algae

Processing of algae is required after it has been harvested, prior to the production of biodiesel. Firstly the algae should be devoid of sand otherwise can lead to contamination. The method of harvesting is dependent on the amount of sand present in the algae. If more sand is present, the algae need to be washed before further operations. The sand can hinder the extraction step. Extraction is a vital step only if oil from the algae is required to produce biodiesel. Oil can be extracted from algae by several means. Two main simplest methods are using a mechanical press or to use an organic solvent which aids as chemical extraction agent. The mechanical press can be divided into batch or continuous press. For small scale production batch presses are preferred. It can be used as a piston. The screws are used for continuous press, which carry the material forward while pushing the oil outside. Pressing is not energy demanding and takes place at approximately 60°C. In order to extract oil from algae using organic solvent it is necessary that algae should be completely dried. N-hexane is a suitable solvent that can be used to wash as well as extract the oil repeatedly. After the organic solvent has been evaporated, the oil from algae is ready to be used for biodiesel production. Method of pressing and solvent extractions are used in sequence in case of large scale production [30,36,37,44,45].

Transesterification process

Transesterification is a catalytic reaction involving vegetable oil and an alcohol (mainly methanol or ethanol) to yield fatty acid alkyl ethers and glycerol [46]. The catalysts mostly used in the transesterification are alkali based. Examples of alkali based catalysts are KOH and NaOH. Acid and enzyme based catalysts are also been used [47]. The alkali catalysts are faster about 4000 times [48] than the acid catalyst whereas an acid catalyst yields a very low reaction rate. Enzyme based catalysts are expensive to be used for large scale production [49]. Some of its advantages are lower reaction temperature, no negative influence from water and free fatty acid, higher yield of methyl esters and easier purification of glycerol by-product. Due to lower costs of the catalysts alkali based

reactions are preferred. Reaction takes place close to boiling point of methanol (60-70°C). The stoichiometric coefficient suitable for methanol to oil is 3:1 [50]. Based on the scale of production transesterification can be carried out in batch or continuous mode. It can take place in two serial reactors for a higher completion of the reaction [51]. It is very essential that the oil should be free from water and free fatty acids because they will slow the reaction drastically. This is due to free fatty acids will react with alkali catalysts and create soap formation [52]. In order to yield high amount of fatty acid methyl esters free fatty acid concentration need to be lower than 0% and water 0.05% (w/w). If the concentration exceeds than oil it is necessary to go through a purifying process before the transesterification. By the means of sedimentation or centrifugation the glycerol is separated from methyl esters after the process of transesterification. Excess methanol is separated via vacuum flash process. It is then underwent the process of neutralization and washing. An acid is added to neutralize the remains of catalyst and splitting of soaps occurs in neutralization step. Splitting leads into free fatty acids and water soluble salts. Washing step is performed to remove salts, catalyst, methanol, soap and free glycerol from the methyl esters. Methyl esters are then subjected to drying which mark the completion of biodiesel production process [50-53].

Biodiesel production from macroalgae

Traditionally biodiesel is produced by extracting and purifying oil from raw material, by the process of transesterification the treatment of oil is performed [44,45]. The two oil extraction methods are thermochemical liquefaction and solvent method. In solvent method supercritical CO₂ is used as solvent. Liquefaction was found to be efficient method as it yields more amount of oil whereas supercritical method produces long-chain fatty acids [49]. Before evaluating the properties of biodiesel the oils were transesterified. According to the life cycle comparison, Supercritical CO₂ is the cheaper and efficient method to extract oil [50].

In pure algal oil the viscosity is too high and volatility is too low to burn the engine completely hence transesterification is performed for oil [51]. Simultaneous oil

extraction and transesterification can help to lower the production costs; in addition it can also skip the step of purification of extracted oil [52]. In Spain the above stated method has been tested by washing and sun drying macroalgae. The oil content of algal biomass obtained was greater than 3.5%. The usage of raw materials which are available in large amounts and are considered as waste is where the potential of biodiesel lies.

The biodiesel production using sunflower and two macroalgal species namely *Gracilariopsis longissima* and *Chaetomorpha linum* showed the natural resources consumed to be around 30 times higher in processing of macroalgae. This was due to the need of chemicals for extracting oil and high energy needs for the solvent recovery. The oil proportion, heating value and the amount of polyunsaturated fatty acid of microalgae *Chlorella protothecoides* were found to be higher than that of macroalgae *Cladophora fracta* [12,48].

The biodiesel production from macroalgae depends on lipid content, amount of TAGs, degree of unsaturated fatty acids [22]. *Sargassum myriocystum* is a brown algae and has been considered as a good feedstock for the production of biodiesel in spite of its lower lipid content. Some of the new developments in biodiesel production is the use of microspheres of metal oxide as catalysts. In this process free fatty acids and triglycerides are transformed to biodiesel by esterification and transesterification [13]. Hence the macroalgal based biodiesel production is on an experimental level and it requires optimization in order to validate its potential in commercial use.

Biorefinery approach for production of biofuel from macroalgae

Biorefinery is the process of utilizing each component of biomass in an integrated way in order to enhance the economics of the process. In biorefinery process macroalgae components are used to produce biofuels, chemicals and feeds [22,54-56]. Some biologically active fertilizers are produced from macroalgae. The amount of these biomaterials to meet market demand is however don't require large scale production using biorefinery approach for biofuels and chemicals. There might be problems in safety and approval in case of feed production when animal feed productions are integrated

with the production of biofuels and chemicals. Thus it is essential to develop biorefinery concept from the industrial point of view in order to produce liquid biofuels in large scale. All macroalgae cellular components should be utilized properly to produce essential liquid fuels in order to reduce overall production costs. Advantage of different liquid fuels is based on the cellular components present in the macroalgae. In the case of biodiesel production lipid is the suitable one [55,57-59].

Conclusions

Biodiesel is a fast expanding industry and is facing a growing dilemma about a feedstock source capable of keeping up with the demand. This review suggests that macroalgae has the potential for the production of biodiesel. There are significant technological hurdles that are needed to tackle before macroalgal biodiesel is energetically and commercially viable. Integrated biorefinery is an appealing way to lower production costs for microalgae based biodiesel. Destruction of macroalgae, extraction and separation of cell components and conversion of the components to biofuels need to be integrated in biorefinery. Less energy-intensive pretreatment processes like cost-effective harvesting and dewatering prior to extraction and conversion need to be developed. Fully integrated production of biodiesel can be a key solution for zero waste biorefinery of macroalgae. In the near future, biodiesel production from macroalgae is expected to play an important role in the bio based economy.

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