Algal Biodiesel as an Emerging Source of Energy: A Review

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Abstract

One of the major problems that the world is facing is dependence of fossil fuels for our day to day energy requirement. The increasing use of fossil fuel directly relates the global warming issues due to increased greenhouse gas emissions. Due to high dependence and usage of this fuel, a decline in its availability is being observed; hence it is necessary to look for alternative fuels. Biodiesel from microalgae seem to be most promising renewable biofuel that has the potential to completely displace petroleum derived transport fuel without adversely affecting supply of food and others crops products. Oil productivity of many microalgae greatly exceeds the oil productivity of the best producing oil crops. The present review covers about the potential of microalgae, algal culture techniques, lipid extraction methods for making algal biodiesel and economic challenges [1-4].

Keywords:

Algal Biodiesel, Source of Energy, energy requirement, renewable biofuel

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Introduction

Algal biomass is currently an area of immense interest for scientists and policy makers due to the anticipated increase in global oil demand by the emerging economies of China and India, and the recent increase in global oil prices during the last few years. The basic sources of energy are petroleum, natural gas, coal, the major disadvantage of using petroleum based fuel is atmospheric pollution. Petroleum diesel combustion is a major source of greenhouse gases (GHG). Apart from these emissions, petroleum diesel combustion is also major source of other air contaminants including NOx, SOx, CO, particulate matter and volatile organic compounds [4,5], which are adversely affecting the environment and causing air pollution. Algae are basically large and diverse groups, of simple, typically autotrophic organisms, ranging from unicellular to multicellular forms. They have the potential to produce considerably greater amounts of biomass and lipids per hectare then any kind of terrestrial biomass [6, 7]. Most importantly, due to their photosynthetic nature, autotrophic algae do not compete with starting plant materials for biofuel production, on the contrary, algae fix and thus reduce the amount of CO_2 in the atmosphere, a gas that contributes to the process of global warming. In fact, few startup companies are now experimenting with the idea of harvesting carbon dioxide streams emitted from coal plants for the autotrophic, photosynthetic growth of microalgae [8].

The biodiesel generated from biomass is a mixture of mono-alkyl ester, which is currently obtained from trans-esterification of triglycerides and monohydric alcohols produced from various plant and animal oils, but this trend is changing as several companies are attempting to generate large scale algal biomass for commercial production of algal biodiesel. Recent researches [9,10] are showing that oil production from microalgae is clearly superior to that of terrestrial plants such as palm, rapeseed, soybeans or Jatropha. This review provides a brief overview on the researches currently which are underway in laboratory on industrial scales.

Potential of micro algae

Algae will grow in most water sources with varying pH levels from fresh drinking water, saline or brackish aquifers to wastewater effluent [11]. In many countries, biodiesel is produced mainly from soybeans. Other sources of commercial biodiesel include canola oil, animal fat, palm oil, corn oil, waste cooking oil. But the recent researches have proved that oil production from microalgae is clearly superior to that, unlike other oil crops, they can double their biomass within 24 hours [12, 13, and 14]. Microalgae are potential to be used as a raw material for biodiesel production, as it meets all of these requirements. They possess high growth rate and provide lipids fraction for biodiesel production [15]. Micro algal lipids are mostly neutral lipids with lower degree of unsaturation. This makes micro algal lipids a potential replacement for fossil fuel. Teressa Mata et al. [16] have presented a comprehensive review on the microalgae for biodiesel production. He points out that, in spite of dependence of oil yield on the particular algal strain, the oil contents of microalgae are generally much higher than the other vegetable crops. Table 1 lists the oil contents of some typical oil.

Typical oil yields from the various biomass sources in ascending order.
Table 1

S.N.	Crop	Oil yield (l/ha)
1	Corn	172
2	Soybean	446
3	Peanut	1,059
4	Canola	1,190
5	Rapeseed	1,190
6	Jatropha	1,892
7	Karanj (Pongamia pinnata)	2,590
8	Coconut	2,689
9	Oil palm	5,950
10	Microalgae (70% oil by wt.)	136,900
11	Microalgae (30% oil by wt.)	58,700

Data sources: Chisti [10]; Lele [17]; http://journeytoforever.org/biodiesel_yield.html.

First of all, the microalgae can be produced all year round and therefore, quantity of oil production exceeds the yield of the best oilseed crops, e.g. biodiesel yield of 58,700 l ha^{-1} for microalgae containing only 30% oil by wt., compared with 1190 l ha^{-1} for rapeseed or Canola [18], 1892 l ha^{-1} for Jatropha [10], and 2590 l ha^{-1} for Karanj (Pongamia pinnata) [17].. The production of biodiesel from microalgae has multiple advantages and has been termed the third-generation biofuels [8]. Unlike other oil crops, microalgae grow rapidly. Microalgae commonly double their biomass within 24 h, and biomass doubling times during exponential growth are commonly as short as 3.5 h. Oil content in microalgae can exceed 80% by weight of dry biomass [9,19,20], and oil levels of 20–50% are quite common. An excellent review on this topic has recently been published [11]. Algae require only a few basic resources to grow successfully CO2, water, sunlight and nutrients.

Production of micro algal biomass

Microalgae are photosynthetic, photosynthetic growth of microalgal biomass require a light source, carbon dioxide, water, inorganic salts and temperature of 15 and 30°C (~60-80 °F) for optimal growth . However, in order to minimize costs, algae is often grown using sunlight as a free source of light, even though it lowers productivity due to daily and seasonal variations in the amount of available light. The growth medium for algae must contain essential nutrients such as nitrogen, phosphorus, iron, and sometimes silicon [21] for algal growth. Algae are traditionally cultivated either in open ponds, known as high rate ponds (HRP), or in enclosed systems known as photobioreactors. Each system has its own advantages and disadvantages. The microalgae can be grown in both open-culture systems such as ponds, lakes and raceways, or in highly controlled closed-culture systems like photobioreactors, similar to those used in commercial fermentation processes. Microalgal biomass contains approximately 50% carbon by dry weight [10, 22].All of this carbon is typically derived from carbon dioxide. Producing 100 t of algal biomass fixes roughly183 t of carbon dioxide. Biodiesel production can potentially use some of the carbon dioxide that is released in power plants by burning fossil fuels [10,23]. This carbon dioxide is often available at little or no cost The only practicable methods of large-scale production of microalgae are raceway ponds [24,25]. and tubular photobioreactors [26].

(1) Open Raceways

Open ponds do not allow microalgae to use carbon dioxide as efficiently, and limits biomass production [10]. In this system, the shallow pond is usually with about 1 foot deep; algae are cultured under conditions identical to the natural environment. The pond is usually designed in a “raceway” or “track” configuration, in which a paddlewheel provides circulation in mixing of the algal cells and nutrients. The raceways are typically made from poured concrete, or they are simply dug into the earth and lined with a plastic liner to prevent the ground from soaking up the liquid. Baffles in the channel guide the flow around bends, so as to minimize space and loss. Medium is added in front of the paddlewheel, and algal broth is harvested behind the paddlewheel, after it has circulated through the loop. Although open ponds cost less to build and operate than enclosed photobioreactors, this culture system has its intrinsic disadvantages. Since these are open air systems, they often experience a lot of water loss due to evaporation. Biomass productivity is also limited by contamination with unwanted algal species as well as organisms that feed on algae. In addition, optimal culture conditions are difficult to maintain in open ponds and recovering the biomass from such a dilute cell yield is expensive [25].

(2) Closed photobioreactors

Photobioreactors are another method to cultivate microalgae. Photobioreactors can overcome the problems of contamination and evaporation encountered in open ponds [27,28]. The biomass productivity of photobioreactors can be 13 times more than that of a traditional raceway pond on average [10]. Harvest of biomass from photobioreactors is less expensive than that from a raceway pond, since the typical algal biomass is about 30 times as concentrated as the biomass found in raceways [10]. There are many different shapes of bioreactors, but they usually fall into two broad categories: 1) use of natural light or 2) use of artificial illumination. Enclosed photobioreactors are often tubular to allow for a greater amount of light penetration. Thus tubes, whether helical or straight provides more surface area to volume ratio for easy growth of algae.

However, enclosed photobioreactors also have some disadvantages. Variations in light and temperature are common in all photoautotrophic systems, causing suboptimal growth of the microalgae. The scale-up is very difficult in these systems, and warrants a high cost to do so [25]. The initial capital cost alone is very high, due to their complexity, and differences in design and construction [28]. Another problem shared between open ponds and photobioreactors is the light penetration issue. Light penetration is inversely proportional to cell density (Chen 1996) and decreases exponentially with penetration depth. Another common problem with bioreactors is the oxygen level will build up as the algae undergo respiration, and the toxicity with high oxygen contents will kill the microalgae. To counter act this, modern photobioreactors employ an oxygen scrubber to remove the gas from the system and expel it to the atmosphere.

Methods of Lipid Extraction

Various methods for extraction of lipids from microalgae have been reported in literature but most common methods are expeller/oil press, liquid–liquid extraction (solvent extraction), supercritical fluid extraction (SFE) and ultrasound techniques.

(1) Solvent extraction

In this method, algae paste in water is extracted by adding organic solvents, such as benzene, cyclo-hexane, hexane, acetone, chloroform etc. Solvent destroys algal cell wall, and extract oil from aqueous medium because of their higher solubility inorganic solvents than water. The oil may be separated from the solvent extract by distillation process. And the solvent can be recycled for further use. Hexane is reported to be the most efficient solvent in extraction because of its highest extraction capability and low cost [29,30]. Besides, this an improved lipid extraction method have been reported in which two-steps for extraction process is used [31]. In first step ethanol is used for extraction and then, hexane is used in second step for purifying the extracted lipids and about80% of lipid recovery yield was observed. Butanol has also been shown effective in extracting lysophospholipids. But the major disadvantage of this is the high boiling point of solvent and thus it poses difficulty in evaporation and it extracts more impurities due to its high polarity [32].

(2) Ultrasound

Another competent mechanism to be used in extraction of microalgae is via ultrasound. This method involves the exposure of algae to a high-intensity ultrasonic wave, which creates tiny cavitation bubbles around cells. Collapse of bubbles emits shockwaves, shattering cell wall thus disrupting the later and releasing desired compounds into solution. More than 90% extraction of fatty acids and pigments from Scenedesmus obliquus, have been reported using this method [33] and it was concluded that ultrasonic waves increases the extraction rate. Further research is needed to be done for commercial applications.

(3) Supercritical fluid extraction (SFE)

Another commonly employed method of extraction is supercritical fluid extraction (SFE) [34], which is extremely time efficient. It makes use of high pressures and temperatures to rupture the cells. The effect of temperature and pressure has been studied by Canela et al. [35]. Their study reveals that the temperature and pressure of SFE did not have any effect on yield of extracted compounds. However, it has influenced the extraction rate. Andrich et al. [36] have investigated the kinetics of SFE in extraction of Nanochloropsis sp. to produce bioactive lipid (polyunsaturated fatty acids, PUFA). PUFA profile was about the same when different SFE conditions applied (temperature range between 45 and 55 8C and pressure 400–700 bar). However, SFE system and solvent extraction using hexane were found to give similar results on lipid extraction. Further studies by Andrich et al. [37] with Spirulina platensis for extraction of PUFA found that SFE system gave higher yield and fatty acid composition compared to the solvent extraction.

(4) Enzymatic extraction

In this process water is used as solvent with the cell wall degrading enzymes to facilitate an easy and mild fractionation of oil, proteins and hulls. The oil is found inside plant cells, linked with proteins and a wide range of carbohydrates like starch, cellulose, hemi-cellulose and pectin. The cell content is surrounded by rather thick wall which has to be opened so that the protein and oil can be released. Thus, when opened by enzymatic degradation, down-stream processing makes fractionation of the components possible to a degree which cannot be reached when using the conventional technique like mechanical pressing. This is the biggest advantage of enzymatic extraction process over other extraction methods. But the cost of this extraction process is estimated to be much higher than most popularly used solvent based extraction processes [38]. The high cost of extraction serves as a limitation factor for large scale utilization of this process.

Algal production process: Transesterification of algae oil

Biodiesel production from microalgae can be done using several well-known industrial processes, the most common of which is base catalyzed transesterification with alcohol. Parent oil used in making biodiesel consists of triglycerides (Fig. 1) in which three fatty acid molecules are esterified with a molecule of glycerol. In making biodiesel, triglycerides are reacted with methanol in a reaction known as transesterification or alcoholysis. Transestrification produces methyl esters of fatty acids that are biodiesel, and glycerol (Fig. B1).The reaction occurs stepwise: triglycerides are first converted to diglycerides, then to monoglycerides and finally to glycerol.

Step1:-

CH_2-$COOR_1$ Catalyst CH_2-OH

CH-$COOR_2$ + CH_3OH ⟶ CH-$COOR_2$ + CH_3COOR_1

CH_2-$COOR_3$ CH_2COOR_3

Triglyceride (parental oil) | Methanol (Alcohol) | Diglyceride | Methyl ester (Biodiesel)

Step2:-

CH_2OH Catalyst CH_2OH

$CHCOOR_2$ + CH_3OH ⟶ $CHCOOR_2$ + CH_3COOR_2

CH_2COOR_3 CH_2OH

Diglyceride | Methanol | Monoglyceride | Methyl ester (biodesel)

Step3

CH_2OH Catalyst CH_2OH

$CHCOOR_2$ +CH_3OH ⟶ CHOH +CH_3COOR_3

CH_2OH CH_2OH

Monoglyceride | Metanol | Glycerol | Methyl ester (Biodiesel)

Fig. 1. Transesterification of oil to biodiesel. R1–3 are hydrocarbon groups.

In transesterification process requires 3 moles of alcohol for each mole of triglyceride to produce 1 moles of glycerol and 3 moles of methyl esters (Fig. 1). The reaction occurs stepwise: triglycerides are first converted to diglycerides, then to monoglycerides and finally to glycerol. Industrial processes use 6 mol of methanol for each mole of triglyceride [39]. This large excess of methanol ensures that the reaction is driven in the direction of methyl esters, i.e. towards biodiesel. Yield of methyl esters exceeds 98% on a weight basis. Transesterification is catalyzed by acids, alkalis [39, 40] and lipase enzymes [41]. Alkali-catalyzed transesterification is about 4000 times faster than the acid catalyzed reaction [40].Consequently; alkalis such as sodium and potassium hydroxide are commonly used as commercial catalyst at a concentration of about 1% by weight of oil. Alkoxides such as sodium methoxide are even better catalysts than sodium hydroxide and are being increasingly used. Use of lipases offers important advantages, but is not currently feasible because of the relatively high cost of the catalyst [39]. Alkali catalyzed transesterification is carried out at approximately 60°C under atmospheric pressure, as methanol boils off at 65 °Cat atmospheric pressure. Other alcohols can be used, but methanol is the least expensive. To prevent yield loss due to saponification reactions (i.e. soap formation), the oil and alcohol must be dry and the oil should have a minimum of free fatty acids. Biodiesel is recovered by repeated washing with water to remove glycerol and methanol.

Conclusion

The major limitation for algal biodiesel is the production cost and energy input requirement while producing and harvesting the microalgal biomass. Different researchers claim different theories on this topic. More innovations are still needed for the development of technologies which reduce costs while increasing the yields. Producing low-cost micro algal biodiesel requires primarily improvements to algal biology through genomics, transcriptomics, proteomics, and metabolomics. Further the recent advancement in photobioreactor engineering can also lower the cost of production.

Along with this relative high production cost of biodiesel can be reduced by glycerol which is main by product of biodiesel production, about 10%(w/w) glycerol will be generated by biodiesel production which can be used various commercial chemical applications[42].

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