Microalgae as Emerging source of Energy: A Review

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Abstract

Fossil fuel depletion and global warming are key issues to look for renewable and eco friendly sources of energy. Currently, microalgae are gaining increasing interest as a feedstock for production of bio fuels. The reasons for this are their renewability, higher photosynthesis efficiency, high lipid content, biodegradability, and non competition for farmlands and generating acceptable quality exhaust gases. This paper presents an overview of various perspectives of microalgal biofuels as a renewable source of energy.

Keywords: Algae, Transesterification, bio-diesel, raceway, pond, photobioreactor.

Introduction

The worlds anticipated energy requirement for 2030 shall be 50% more than it is today. Global petroleum reserves are finite, and it is analysed that recent rate of petroleum production is much faster than the nature can create. The fast rate decline of fossil fuels along with the environment concerns, increasing the demand to look alternate sources of energy, which can substitute instead of fossil fuels. To overcome these problems biofuels are the promising alternative energy sources for biofuel production. Today much attention has given on the biofuel based on photosynthetic plants such as, soybean, sunflower, coconut, jatropha, karanja, rapeseed, palm but biofuels production from these crops have become a major controversy due to food versus fuel competition. In current scenario microalgae are gaining much more attention as a bio fuel source of energy over traditional crops due to the following reasons:

The rapid growth rates along with high content of lipid makes microalgae as valuable alternative to terrestrial crops for biodiesel production. Algal based biofuels do not compete with matter related to food security concerns, Algal generated biofuels have lower emissions of sulfur oxides and particulate contaminants as compared to fossil fuels, Microalgal cultivation does not require arable land and it can be harvested daily, other benefit of algal biofuels is CO₂ sequestration, because algae use CO₂ more efficiently during photosynthesis than any other biomass source of energy. The prospects of microalgae in development of biodiesel is not very recent and dates to 1978 when the US Department of Energy started a program named “Aquatic Species Program—Biodiesel from Algae” which focused on the surveying of microalgal species for the identification of suitable strains for their culture in outdoor open system.

While numerous studies have extensively reviewed the potential and advantage of using microalgae as biofuel feedstock, there are still many challenges in the development of algal derived biofuels including algal strain selection, biomass cultivation, harvest management and oil extraction. Most of these processes remain in early stages and all efforts to develop algal biofuels need to maximize lipid productivity and reduce production costs as well as energy requirements.

Algae and its Potential

Algae are photosynthetic organisms that can globally distributed and grow in various environment conditions and it is estimated 40,000-60,000 different species of algae are found. They may be autotrophic or heterotrophic. The CO₂, salts and sunlight are required for autotrophic algal species; while the heterotrophic algal species require nutrients and external organic energy source. Microalgae broadly divided into two prokaryotic divisions (Cyanophyta and Prochlorophyta) and nine eukaryotic divisions (Glaucophyta, Rhodophyta, Heterokontophyta, Haptophyta, Cryptophyta, Dinophyta, Euglenophyta, Chlorarachniophyta and Chlorophyta). On the basis on abundance, four most important algal groups are given in table-1.

Algae as a feedstock for biodiesel are in the preliminary stages of research but have shown immense potential to provide alternative and a new generation feedstock. The productivity of microalgal lipid with respect to the dry weight of biomass can be 15 to 300 times greater than that derived from plants. The photo synthetic efficiency of microalgae greater than the the plants there by making it a better prospect for the production of oil or other constituents. Compared to 0.5% for terrestrial plants photosynthetic efficiency of microalgae ranges from 3 to 8%. Many species of algae are able to convert sunlight, nutrients, and CO₂ into proteins, carbohydrates, and lipids with high growth rates that double their biomass up to five times in a 24
hours. Microalgae can be harvested daily and serve as a feedstock for biofuels, food (edible oil, nutraceuticals), fish feeds and chemicals. Microalgae can be used as a source of feedstocks for the production of biodiesel, methane, ethanol, butanol, and hydrogen depending on the constituents of the microalga (starch, sugar, or oil). Table 2 shows the yields of bio-oils produced from a variety of crops.

**Microalgal Collection**

To search and identify fast growing and hyper-lipid producing strains is a main aim of microalgal collection in the case of biofuel production. Method used for algal cell collection is a major factor that must be considered, during algal collection because broken algal cell may lead to failure. Algae mainly require sunlight, CO$_2$, nutrients such as nitrates and phosphates, for their proper growth.

A knife, scooping jar, scalpels, dissolved CO$_2$ and O$_2$ analyser are vials for microalgal samples collection. There is various sampling procedure documented in literature but researchers point of view simple and economical methods of collecting microalgal samples are utilized.

**Algal Cell Isolation**

Conventional and advanced methods are used for algal cell isolation. Single-cell isolation by micropipette, dilution techniques, isolation using agar plates, gravimetric separation, atomized cell spray technique, media enrichment are conventional methods for micro algal cell isolation while micromanipulation, flow cytometry are advanced methods for micro algal cell isolation.

**Algal Culture**

The main growing options for algae on commercial scales are open-air “raceway” ponds or enclosed systems, often called “photo bioreactors.” Both open algal ponds and closed photo bioreactors (PBRs) are generally utilized for algal culture. A closed photobioreactor has better performance than open ponds due to higher algal production and controlling culture environment conditions. However, high culture cost of closed PBRs can be mitigated to make it economical.

**Lipid Extraction**

Extraction of microalgal oil involves various processes. The steps involved in harvesting and expulsion of microalgal oil can include sedimentation, centrifugation, filtration, ultra-filtration, additional flocculation to remove algae from water, drying, and solvent extraction. Among above methods, centrifugation method was found most efficient. The temperature is crucial factor in microalgae drying and extraction of oil from dried algal biomass. Higher temperature reduces lipid yield as well as concentration of triacylglycerides. Various cell disruption techniques such as autoclaving, microwaves, sonication, osmotic shock and bead beating have been evaluated in order to enhance lipid extraction efficiency. In above algal cell disruption techniques for lipid extraction, microwave oven method was most efficient, but solvent extraction was widely used method for researchers point of view due to its easy operation and relatively cheap cost.

**Sample Preparation for Lipid Analysis**

Lipid quantification analysis of microalgae can be done by various techniques such as thin-layer chromatography (TLC), gas chromatography (GC), high pressure liquid chromatography (HPLC). ASTM D6584 and EN 14105 methods are used for lipid profiling of biodiesel feedstock that can be done by GC with a Flame Ionization Detector (FID).

**Algal oil Characteristics for Biodiesel Production**

The lipid constituents of plant and microalgal oils are quite different. Compared to different plant oils, microalgae oils contain a higher percentage of polyunsaturated fatty acids. A high level of unsaturation for biodiesel will result in oxidation of the fuel and will render it off-specification. The fatty acid chains in the lipids present in microalgae can range from C$_{11}$ to C$_{26}$, though the common chain length usually observed is C$_{14}$ to C$_{22}$. The fatty acid constituent may be saturated or unsaturated (with up to six double bonds). After identification of algal strains, lipid content analysis and fuel properties are important parameters to check the potential of biodiesel fuel as a substitute of diesel fuel. For this various fuel properties are considered such as density, cold filter plugging point, cetane number (CN), oxidative stability, ignition quality, lubricity and combustion heat. Chain length, number of double bonds and amount of each fatty ester components are determines both fatty acids and triglycerides. Ignition quality of fuel and presence of unsaturated fatty acids are represented by the saponification values (SV) and iodine value (IV) respectively. Higher iodine values means higher unsaturated fatty acids (UFA) present in the oil and heating of higher unsaturated fatty acids produced the polymerization of glycerides, which have deteriorating effect on lubrication properties. And thus unsuitable for biodiesel. With the help of empirical equations the CN, SV and IV can be determined from FAME of oils. Biodiesel feedstock which have a high degree of saturation is more resistant to oxidation. Suitable culture conditions must be adopted in order to improve the fuel qualities of algae biodiesel that must fulfill the International Biodiesel Fuel Standards.

Microalgae can be used as a source of feedstocks for the production of biodiesel, methane, ethanol, butanol, and hydrogen depending on the constituents of the microalga (starch, sugar, or oil). The lipid portion of microalgae can be diverted for biodiesel production, whereas, the sugar comprises primarily of cellulose can be hydrolyzed and fermented to bioethanol.
Table 1
The four most important algal groups in terms of abundance

<table>
<thead>
<tr>
<th>Algae</th>
<th>Known Species (approx)</th>
<th>Storage materials</th>
<th>Habitat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diatoms (Bacillariophyceae)</td>
<td>100,000</td>
<td>Chrysolaminarin, (polymer of carbohydrates) and TAGs</td>
<td>Oceans, fresh and brackish water</td>
</tr>
<tr>
<td>Greenalgae (Chlorophyceae)</td>
<td>8000</td>
<td>Starch, and TAGs</td>
<td>Fresh water</td>
</tr>
<tr>
<td>Blue–green algae (Cyanophyceae)</td>
<td>2000</td>
<td>Starch, and TAGs</td>
<td>Different habitats</td>
</tr>
<tr>
<td>Golden algae (Chrysophyceae)</td>
<td>1000</td>
<td>TAGs and carbohydrates</td>
<td>Fresh water</td>
</tr>
</tbody>
</table>

Table 2
A variety of crops and their bio-oils yield

<table>
<thead>
<tr>
<th>Substance</th>
<th>Gallons of oil per acre per year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn</td>
<td>15</td>
</tr>
<tr>
<td>Soybeans</td>
<td>48</td>
</tr>
<tr>
<td>Sunflower</td>
<td>102</td>
</tr>
<tr>
<td>Rapseed (canola)</td>
<td>127</td>
</tr>
<tr>
<td>Oil palm</td>
<td>635</td>
</tr>
<tr>
<td>Microalgae</td>
<td></td>
</tr>
<tr>
<td>Based on actual biomass yields</td>
<td>1850</td>
</tr>
</tbody>
</table>

Algal Biodiesel

Transesterification method is used to convert algal oil into biodiesel. Transesterification process of lipids to biodiesel conversion can be performed by using acid and base catalysts, or a combination of both are used. Base catalysis gives rapid reaction than acid catalysis, but it is also depend upon selection of the types of lipids that are transesterified. Nagle and Lemke investigated the effect of acid and base catalysts on the conversion of algal oils and pointed out that acid catalysts resulted in consistently higher yields. So transesterification process of biodiesel production is several steps chemical reaction in which triglycerides first converted to diglycerides, diglycerides to monoglycerides, and monoglycerides to free fatty acids and glycerol (as byproduct); If a lipase is used, hydrolysis and esterification may take place simultaneously, but the thermal liability of that enzyme does not crate industrial scale.

\[
\text{CH}_2\text{-OCOOR}_3 \text{ Alchol} \quad \text{R}_3\text{COOR}^\prime \text{ CH}_2\text{OH} \quad \text{Methyl ester} \\
\text{Triglyceride Catalyst} \quad \text{R}_3\text{COOR}^\prime \text{ CH}_2\text{OH} \\
\text{CH}_2\text{-OCOOR}_2 + 3\text{R}^\prime\text{OH} \rightarrow \text{R}_2\text{COOR}^\prime + \text{CHOH} \\
\text{H}_2\text{OCOOR}_1 \quad \text{R}_2\text{COOR}^\prime \quad \text{CH}_2\text{OH} \\
\]

Biodiesel production by transesterification

Biomethane

Meier was first proposed the concept of algal fuel for bio methane production from the carbohydrate fraction of cells. Oswald and Golueke developed this idea further, and developed economic analysis to produce methane gas from algal biomass in large raceway pond. Algal biomass can also be utilized for biogas production. There are many green plants and straw based large scale and small scale plants of biogas are installed in Poland, however, till date algae have not been used as such a fuel. Some algal species like Macrocystis pyifera, have been explored as potential methane sources. Despite globally distributed seaweed biomass, anaerobic digestion for biogas production is not up to the mark.

Anaerobic bio-hydrogen production

Bio photolysis of water can be used for the production of biological hydrogen through green algae and cyanobacteria. Hydrogen production by autotrophic organisms can be one of the dominant renewable sources of energy in near future. Under specific conditions algal species can also be used in hydrogen production. Three different paths for hydrogen production have been proposed: direct photolysis and indirect photolysis, and ATP-driven hydrogen-production. To enhance algal based hydrogen production technology. Cost of the huge photobioreactor and hydrogen storage devices cost must be reduced.

Fermentation

Commercially ethanol is produced in different countries from and starch crops and sugar crops by the process of fermentation. Corn contains maximum 70% starch, and globally one of most valuable feedstock for ethanol based bio industry. Large variety of carbohydrates is used for ethanol production. Fermentation of sucrose is achieved by utilising commercial yeast such as, Invertase, Saccharomyces cerevisiae and zymase enzymes. The hydrolysis of sucrose can be performed in the presence of invertase enzyme that converts it to glucose and fructose.
Second, enzyme zymase converts the fructose and glucose into ethyl alcohol.
\[ C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \]

**Conclusion**

Producing oil from algae has various advantages over crop based biomass on various aspects. Unfortunately, comparatively high costs of algal biomass based biofuel are the biggest challenge so far. Microalgal biomass cost of production for open pond and a photobioreactor are much higher than crude palm oil and also from petrodisels. Thus the use of residual byproducts through biorefinery can boost the economics of the whole process algal biofuels.

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