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Review Article

SYNTHESIS OF BIODIESEL FROM MICROBIAL ALGAE

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ABSTRACT
Continued use of petroleum sourced fuels is now widely recognized as unsustainable because of depleting supplies and the contribution of these fuels to the accumulation of carbon dioxide in the environment. Renewable, carbon neutral, transport fuels are necessary for environmental and economic sustainability. Biodiesel derived from oil crops is a potential renewable and carbon neutral alternative to petroleum fuels. Unfortunately, biodiesel from oil crops, waste cooking oil and animal fat cannot realistically satisfy even a small fraction of the existing demand for transport fuels. As demonstrated here, microalgae appear to be the only source of renewable biodiesel that is capable of meeting the global demand for transport fuels. Like plants, microalgae use sunlight to produce oils but they do so more efficiently than crop plants. Oil productivity of many microalgae greatly exceeds the oil productivity of the best producing oil crops. Approaches for making microalgal biodiesel economically competitive with petrodiesel are discussed.

Keywords: Biodiesel, Renewable Energy,Soxhlet's procedure, Transeterification.

INTRODUCTION

Microalgae comprise a vast group of photosynthetic, auto/heterotrophic organism which has an extraordinary potential for cultivation as energy crops. These microscopic algae use photosynthetic process similar to that of higher-developed plants. They are veritable miniature biochemical factories, capable of regulating carbon dioxide (CO), just like terrestrial plants[1]. In addition, these micro-organisms are useful in bioremediation applications[2-4] and as nitrogen fixing biofertilizers[5]. This review article discusses the potential of microalgae for sustainably providing biodiesel for the displacement of petroleum derived transport fuels in India. The need of energy is increasing continuously, because of increase in industrialization as well as human population. The basic sources of this energy are petroleum, natural gas, coal, hydro and nuclear[6]. 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[7], which are adversely affecting the environment and causing air pollution. These environmental problems can be eliminated by replacing the petroleum diesel fuel with an efficient renewable and sustainable biofuel.

Algal biomass is one of the emerging sources of sustainable energy. The large-scale introduction of biomass could contribute to sustainable development on several fronts, environmentally, socially and economically[8]. The biodiesel generated from biomass is a mixture of mono-alkyl ester, which currently obtained from transesterification 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. Biodiesel is non-toxic and biodegradable alternative fuel that is obtained from non-renewable sources. 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[6, 9, 10]. But the recent research has proved that oil production from microalgae is clearly superior to that of terrestrial plants such as palm, rapeseed, soybeans or jatropha[11, 12]. Important advantage of microalgae is that, unlike other oil crops, they can double their biomass within 24 hr. In fact the biomass doubling time for microalgae during exponential growth can be as short as 3 to 4 hr, which is significantly quicker than the doubling time for oil crops[13]. It is for this reason microalgae are capable of synthesizing more oil per acre than the terrestrial plants which are currently used for the fabrication of biofuels[1] and using microalgae to produce biodiesel will not compromise production of food, fodder and other products derived from crops .In theproduction of energy from micro algal biomass, two basic approaches are employed depending on the particularorganism and the hydro-carbon which they produce. The first is simply the biological conversion of nutrients intolipids or hydrocarbons. The second procedure entails the thermo-chemical liquefaction of algal biomass into lipidor hydrocarbons. Lipids and hydrocarbons can normally be found throughout the micro algal biomass[17]. Theyoccur as membrane components, storage products, metabolites and sources of energy for microalgae. Algal strains,diatoms, and cyanobacteria (categorized collectively as microalgae) have been found to contain proportionally highlevel of lipid (over 30%). These microalgal strains with high lipid content are of great interest in search for sustainablefeedstock for production of biodiesel.

Potential of microalgal Biodiesel

The enormous amount of burning of fossil fuel has increased theCO level in the atmosphere, causing global warming. Biomass is focused as an alternative energy source, as it's a renewable resource and it can fix atmosphericCO through photosynthesis. Among biomass, algae (macro and microalgae) usually have a higher photosynthetic efficiency thanother biomass producing plants. Biodiesel from microalgae appears to be a feasible solution to India, for replacing petro-diesel. The estimated annual consumption of petroleum product in India is nearly about 120 million tonnes per year, and no other feedstock except microalgae has the capacity to replace this large volume of oil. To elaborate, it hasbeen calculated that, in order for a crop such as soybean or palm to yield enough oil capable of replacing petro-diesel completely, a very large percentage of current land available need to be utilized only for biodiesel crop production, which is quite infeasible[13]. For small countries, in fact it implies that all land available in the country be dedicated to biodiesel crop production. However, if the feedstock were to be algae, owing to its very high yield of oil per acre of cultivation, it has been estimated that less than 2-3 percent of total Indian cropping land is sufficient to produce enough biodiesel to replace all petrodiesel currently used in country. Clearly microalgae are superior alternative as a feedstock for large scale biodiesel production. Microalgal strains with high oil content are of great interest in search for sustainable feedstock for the production of biodiesel . Algae can have anywhere between 20-80% of oil by weight of dry mass.

Production of microalgal biomass

The microalgae can be grown in both open-culture systems such as ponds, lakes and raceways, or in highly controlledclosed-culture systems like photobioreactors, similar to those used in commercial fermentation processes. Thephotosynthetic growth of microalgal biomass require light, carbon dioxide, water, organic salts and temperature of 20-30 °C. As the production of microalgal biodiesel require large quantities of algal biomass, so to minimize the expense the biomass must be produced using freely available sunlight[13].

Microalgae can be grown on large scale in photobioreactors or raceway ponds[19-22]. Aphotobioreactor is basically a bioreactor which incorporates some type of light sources. While almost anything that it would be possible to grow algae in could technically be called a photobioreactor, the term is more commonly used to define a closed system. Many different designs of photobioreactors have been developed, but a tubular photobioreactor seems to be most satisfactory for producing algal biomass on the scale needed for biofuel production.A tubular photobioreactor consists of an array of clear transparent tubes that are usually made of plastic or glass. These solar collectors capture the sunlight for photosynthesis. Microalgal broth is circulated from a reservoir such as the feedingvessel/recirculating shown in to the solar collector and back to the reservoir. Aphotobioreactor is typically operated as a continuous culture during daylight[13]. In accontinuous culture, fresh culture medium is fed at a constant rate and the same quantity of microalgal broth is withdrawn continuously. Feeding ceases during the night; however, the mixing of broth must continue to prevent settling of the biomass[19]. As much as 25% of the biomass produced during daylight might be consumed during the night to sustain the cells until sunrise[23, 24]. To maximize sunlight capture, the tubes in the solar collector are generally placed horizontally flat on the surface. The ground beneath the solar collector is either painted white or covered with white sheets of plastic[19,25, 13] to increase reflectance, which will increase the total light received by the tubes. Biomass sedimentation in thetubes is prevented by maintaining a highly turbulent flow. This flow is produced either using a mechanical pump or a more gentle airlift pump[26-30].

Different Type Technique for Improving Algal Biomass Yield

Algae cultivation has four basic and equally important requirements: carbon, water, light, and space. By manipulating requirements, it is possible to increase the quantity of oil-rich biomass[13, 31]. Carbon dioxide is the first requirement. In order to maximize algal growth, CO needs to be provided at very high levels, much higher than the naturally available. Rather than becoming an expense, this need forCO creates a unique opportunity to control air pollution and simultaneously reduce the cost of algae culture. The flue gases from industrial processes, and in particular from power plants, are rich in CO that would normally be released directly into the atmosphere and there by contribute to global warming. By diverting the CO fraction of the flue gas to algae cultivation facility, the CO can be diverted back into the energy stream and the rate of algal production can be increased[31, 32].

Water, containing the essential salts and minerals is the second requirement for growth. Fresh water is a valuable resource as for the salts and minerals needed; however, algae cultivation can be coupled to another type ofenvironmental remediation that will enhance productivity while mitigating pollution. High nutrient wastewater fromdomestic or industrial sources, which may already contain nitrogen and phosphate salts, can be added to the algal growth media directly[33]. This allows for algae production to be improved cheaply, while simultaneously treatingwastewater[31].

Extraction of oil form algal biomass for biodiesel Production

There are various methods to extract the oil from algae among them there are four method are well known for extraction mechanical press, Solvent extraction, Supercritical fluid extraction and Ultrasonic assisted

Mechanical Press

In this method microalgal biomass is subjected to high pressure resulted ruptures cells wells and release the oil. This method is easy to use and more importantly no solvent is required. In this methods, extract a large percentage (70-75%) of the oils out of algae biomass.

Solvent Extraction

Algal oil can be extracted using chemicals. Organic solvents (such as benzene, cyclohexane, hexane, acetone and chloroform) mixed with microalgae biomass, they degrade microalgal cell walls and extract the oil because oil has a high solubility in organic solvents. Solvents used in this methods are relatively inexpensive, result are reproducible and Solvent is recycled. The oil extracts by this method is 60-70%.

Supercritical Fluid Extraction

This method is more efficient than traditional solvent separation methods. Supercritical fluids have increased solvating power when they are raised above their critical temperature and pressure points. it produces highly purified extracts that are free of potentially harmful solvent residues, extraction and separation are quick, as well as safe for thermally sensitive products. This can extract almost 100% of the oils all by itself. In the supercritical fluid carbon dioxide (CO_2) extraction, CO_2 is liquefied under pressure and heated to the point that it has the properties of both a liquid and gas. This liquefied fluid then acts as the solvent in extracting the oil.

Ultrasonic-Assisted Extraction

This method based on Cavitation. Cavitation occurs when vapour bubbles of a liquid form in an area where pressure of the liquid is lower than its vapour pressure. These bubbles grow when pressure is negative and compress under positive pressure, which causes a violent collapse of the bubbles. If bubbles collapse near cell walls, damage can occur and the cell contents are released. This have advantage over other extraction method such as extraction time is reduced, reduced solvent consumption, greater penetration of solvent into cellular materials, improved release of cell contents into bulk medium. This can extract almost 76-77% of the oils all by itself.

Enzymatic extraction

In the process of enzymatic extraction 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 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 muchhigher 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.

Chemical extraction

The Soxhlet method is the most commonly used solvent extraction method, used for the extraction of oil from various plants and algal strains. According to the Soxhlet's procedure, oil and fat from solid material are extracted by repeated washings (percolation) with an organic solvent, usually n-hexane or petroleum ether, under reflux in a special glassware called Soxhlet extractor. The method has got several advantages like large amount of extraction using limited solvent, it is cost effective and become more economical if used at large scale. Despite of these advantages there are certain limitations like, poor extraction of polar lipids, long time required for extraction, hazards of boiling solvents etc. But still this method is the most popular and generally used in all oil extraction laboratories[39]

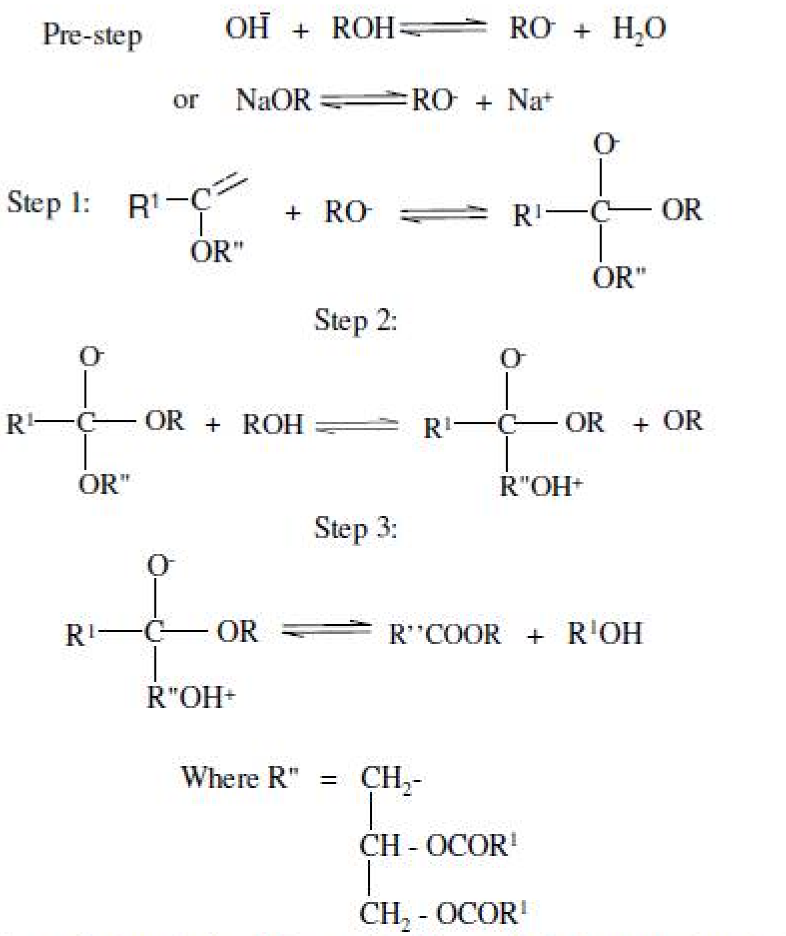
Conversion of algal oil into biodiesel

The typically used process for commercial production of biodiesel is explained. Any future production of biodiesel from microalgae is expected to use the same process[13].

Transesterification of Algal Oil

Biodiesel production from microalgae can be done using several well known industrial processes, the most common of which is base catalyzedtransesterification with alcohol. The transesterification is the reversible reaction of fat or oil (which is composed of triglyceride) with an alcohol to form fatty acid alkyl ester and glycerol. Stoichio-metrically, the reaction requires a 3:1 molar alcohol to oil ratio, but excess alcohol is (usually methyl alcohol is used) added to drive the equilibrium toward the product side[45]. This large excess of methylalcohol 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[46]. The reaction occurs stepwise: triglycerides are first converted to diglycerides, then to monoglycerides and finally to glycerol[13]. Transesterification can be done in number of ways such as using an alkali catalyst, acid catalyst, enzyme catalyst, heterogeneous catalyst or using alcohol in theirsupercritical state; however enzyme catalyst are rarely used as they are less effective[47].

The alkali-catalyzedtransesterification is about 4000 times faster than the acid catalyzed reaction[46]. Consequently, alkalis such as sodium and potassium hydroxide are commonly used as commercial catalysts 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[13, 46].



R^1 = Carbon chain of fatty acid, R = Alkyl group of alcohol

Basic Catalyst Transesterification Mechanism

CONCLUSION

As discussed above, the algal biodiesel production is gaining importance for its ability to replace fossil fuels, its environmental benefits and the fact that it is a renewable source of energy.It is only biodiesel that can potentially completely displace liquid fuel derived from petroleum. Economics of producing microalgal biodiesel need to improve sustaniblity to make it competetive with petrodiesel but the level of improvement nesseccery appears to be attainable.Producing low cost microbial biodiesel require primaly improvements to algal biology through genetic and metabolic engineering.

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