Biodiesel From Algae

Abstract: *Many people from research firms are searching for alternative fuel sources that is renewable, economical and environmentally friendly as fossil fuels are fast depleting. "Biodiesel refers to any diesel equivalent biofuel made from renewable biological material such as vegetable oils/ animal fats consisting of long chain hydrocarbons. It can be used in pure form or may be blended with petro diesel at any concentration".*

However, there are problems with biodiesel made from crops namely the displacement of food and amount of crops it takes to produce a gallon of oil. Algae to biodiesel has been widely discussed among experts in the petroleum industry and considerable who are looking for a more reliable and safer source of energy that is both renewable and easy to maintain.

Thus, algae can prove to be an economic and productive source to manufacture biofuel which is highly productive. As, a result , large quantities of algae can be grown quickly and the process o f testing differential strains of algae for their fuel making potential can process faster than with other crops with longer life cycles.

Niharika Kapoor
M.Sc (Biotechnology)
Manav Rachna International University
Faridabad

1. INTRODUCTION

One of the greatest challenges faced by India and even the Western countries is the "Security of the non – renewable resources" as there are no means to replenish them again once consumed.

The most fundamental importance of using algal fuel is "Less dependence on the fossil fuels".

"The use of algal fuel in our times migh seem of no importance in our times However such products can gain importance in the course of time and might gain equal importance with the petroleum and coal tar products", said Dr. Rudolf Diesel in 1912 .

Worldwide concerns about the increasing global climatic changes, national energy security, rising fuel cost and the diminishing supply of the inexpensive fuels has surged a wave to research for renewable resources which can be made easily available and have environmental benefits.

Biofuels such as bioethanols and biodiesels are coming as competitive alternatives to the petrofuels because they are renewable, are environment friendly and are available in abundance.

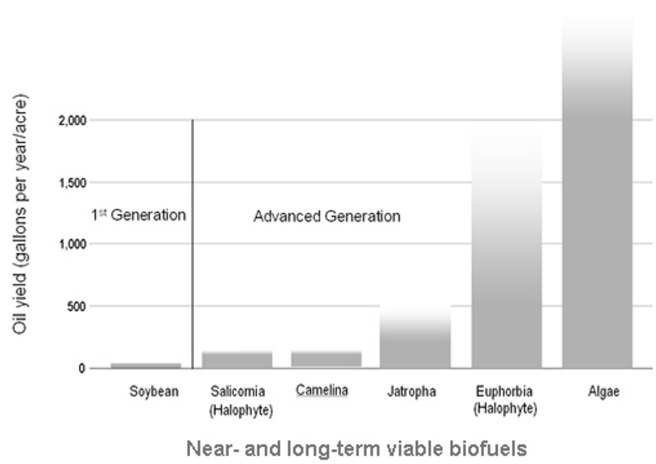

Fig. 1.

These are the most commonly investigated feedstocks. Rapeseed, oil palm, soybean and sunflower are the primary feedstocks utilized for the production of biodiesel .Over worlds 90% biodiesel is derived from rapeseed and sunflower alone.

Microalgae, unicellular photosynthetic organisms, are attractive as a feedstock as they will not displace agricultural crops, can be grown year-round, and can be harvested continually. Algae are also advantageous because they have a high growth rate, ability to thrive in saline water, capability of sequestering carbon dioxide (CO_2), and capability to use nutrients (such as nitrogen and phosphorous) from waste products (such as sewage).Algae typically have a high oil content of 20–50 per cent (dry weight), some strains having an oil content as high as 80 per cent dry weight. Algae are capable of doubling their biomass in a 24-hour period. Algae can produce 8–24 times the triglycerides per area as other biomass resources, enabling the production of 58 700–136 900 litre per hectare of oil per year.

The has led to an accelerated development of technologies to harness algae as a future major fuel source. These technologies include selection of algal strains, genetic enhancement of algal strains through lipid metabolism and other biotechnological modifications, algaculturing techniques, lipid extraction, and biodiesel processing and production.

2. ALGAL STRAINS

Selecting an economical yet highly productive algal strain is highly essential. The DOE's Aquatic Species Program investigated over 3000 viable strains of algae for production of biodiesel based on the strain's robustness, oil content, growth rate and metabolic efficiency between 1978 and 1996. "Maximum biodiesel output per resource input" is the basic criteria used for the selection of algal strains from which high yields of biodiesel can be efficiently obtained.

Cost-effective commercially viable biodiesel production from algae requires utilization of algae species with desirable biomass growth rate, oil production, metabolic production (lipids and hydrocarbons), nutrient input, environmental tolerance and photosynthetic efficiency.· Out of the 3000 strains investigated, 300 strains were identified as having desirable characteristics for biofuel production. Some commercially used algal strains are:

Botryococcus braunii

One of the most extensively used alga species for biodiesel production is *Botryococcus braunii* (*B. braunii*). Varieties of *B. braunii* can have oil contents up to 90 per cent (of dry weight). Different types of *B. braunii* produce different hydrocarbons. *B. braunii* 'race A' produces alkadiene and alkatriene hydrocarbons. *B. braunii* 'race B' produces botryococcene (hydrocarbons of the chemical formula $C_nH_{2n\text{"}10}$ with n=30–37) and methylated squalenes hydrocarbons. *B. braunii* 'race L' produces hydrocarbons that are inconsistent with race A and B. Hydrocracking of crude oil from *B. braunii* produced a final mixture of 15 wt per cent diesel fuel, 15 wt per cent aviation turbine fuel, 67 wt per cent petrol fuel, and 3 wt per cent residual. *B. braunii* is particularly advantageous because its high lipid production causes the cell to float. There are various advantages of using B. *braunii* as rapid growth rate, capable of doubling biomass in less than 40 hrs.

Dunaliella tertiolecta

Chinese patent applications for *Dunaliella tertiolecta* strains with increased growth rate and chlorophyll content were filed by Xin'ao Science and Technology Development Co. *Dunaliella tertiolecta* is an interesting alga species for biodiesel production because it has a high oil content (36–42 per cent dry weight). The claimed *Dunaliella tertiolecta* strains displayed a 5.9 to 17.6 per cent increase in biomass and a 1.0 to 8.9 per cent increase in chlorophyll content. These enhanced characteristics make these strains a much more viable option for algal biodiesel production. The patent applications claiming the enhanced strains also claim methods for developing mutated *Dunaliella tertiolecta* strains by ultraviolet irradiation, high temperature exposure and exposure to ethylmethane sulphonate.

Pseudochoricystis ellipsoidea

The Marine Biotechnology Institute of Japan discovered the alga species *Pseudochoricystis ellipsoidea* in hot springs, which offers promise for the commercial production of biodiesel. The algae produce small chain saturated hydrocarbons (10–25 carbons), which have superior burning qualities over the heavier oils made by other algae strains, such as *B. braunii*.

Chlorella and others

Chlorella is one of the most highly researched genera of algae for the production of biodiesel. *Chlorella* species are a viable algal biofuel biomass because they have a high oil content (15–55 per cent dry weight) and biodiesel production has shown to be highly successful. *Chlorella YJ1* was isolated from secondary discharged water from an urban sewage treatment facility. This species is advantageous because secondary urban sewage can be used as a culturing medium without the need for additional nutrients. *Chlorella YJ1* enables concurrent sewage treatment and biodiesel production.

Genetic engineered species of Botrycoccus braunii

Strain or Species	% Lipid (by mass on drybasis)
Scenedesmus	12-40
Chalmydomonas	21
Clorella	14-22
Spirogyra	11-21
Dunaliella	6-8
Euglena	14-20
Prymnesium	22-38
Porphyredium	9-14
Synechoccus	11

Fig. 2. Species of B.*braunii*

3. HISTORY ABOUT ALGAL GENETICS

During the DOE's Aquatic Species Program, a method for producing stable genetically transformed algae was developed. This method was used to genetically manipulate chlorophyll to over-express ACCase and test the effect on lipid biosynthesis and accumulation. No significant change was however observed in the lipid accumulation. Despite the failure, this was a major step toward the use of transgenic algae for biodiesel production. Genetic engineering will most likely be critical for developing algae strains that embody the enhanced suite of desirable characteristics necessary for cost-effective commercial production of biodiesel.

Increase in production of triglycerides for biodiesel from algae can also be achieved by improving solar energy conversion. One method of improving conversion is to minimize the chlorophyll antenna size by suppression of the *tla1* gene. The patent by Dr Melis Anastasios and Dr Mautusi Mitra described a method of decreasing chlorophyll antenna size involving inhibiting the expression of the *tla1* by inserting a *tla1* mutation into the algal genome.

The genetic modification of algae for easier cultivation and extraction is another method for developing economical algal biodiesel. Cultivation of biomass and extraction of oil from biomass can make up approximately 70–90 per cent of the total production cost. A patent application assigned to Synthetic Genomics, Inc. (recently having entered into a approximately $600 million algal biodiesel research collaboration with Exxon Mobil) describes a method for developing and using genetically engineered algae which secrete fatty acids. Several genetically modified algae species can be used in this process. This method is advantageous because the fatty acids can be harvested without destroying the algal cells.

4. CULTURING OF ALGAE

Production of algae biomass on a large scale is more expensive than growing food crops. Growth of algae requires available light, CO_2, water, nutrients (such as nitrogen, phosphorus, iron and silicon) and temperatures between 20°C and 30°C. Currently, the only practical methods for large-scale algae production are raceway ponds and photobioreactors.

4.1. Raceway ponds

They have been in use since 1950's and are the most extensively employed ponds for this purpose. They consist of a system of closed-loop recirculation channel that is typically about 0.3 m deep. Mixing and circulation required for the stabilized algal growth and productivity is obtained by using a paddlewheel. Raceway ponds are relatively inexpensive to build and operate, but typically have lower biomass productivity because of poor mixing, light and CO_2 availability, and/or contamination.

Waterwheel Factory, Inc., the world's largest water-wheel manufacturer, has applied for one of the few patents for raceway ponds, a curve blade paddlewheel specifically made for algae raceway ponds and methods for creating raceway ponds. The paddlewheel is light in weight with an outer paddle portion to be positioned at angle with respect to the center paddle portion, which reduces drag and increases the amount of water moved.

Fig. 3. World's largest publicly funded project to make fuels from algae.

4.1. Photo bioreactors

Photo bioreactor, is generally a closed apparatus for algae growth, and is essentially designed to overcome some of the problems associated with the raceway pond systems. A single species of algae can be cultivated in photo bioreactors. Algae growth is usually higher than raceway ponds because growth problems associated with contamination, CO_2 and nutrient availability, and poor mixing can be prevented. Despite being much more spatially efficient, photo bioreactors are usually more expensive to develop and maintain than raceway ponds. Disadvantages include algal wall growth, small illumination areas, difficult scale up, limited mass growth and temperature control.

OriginOil, Inc. has applied for a patent for a method and vessel that enhances algae growth. The method and vessel are known by their trademarked names Quantum Fracturing™ and Helix BioReactor™, respectively.

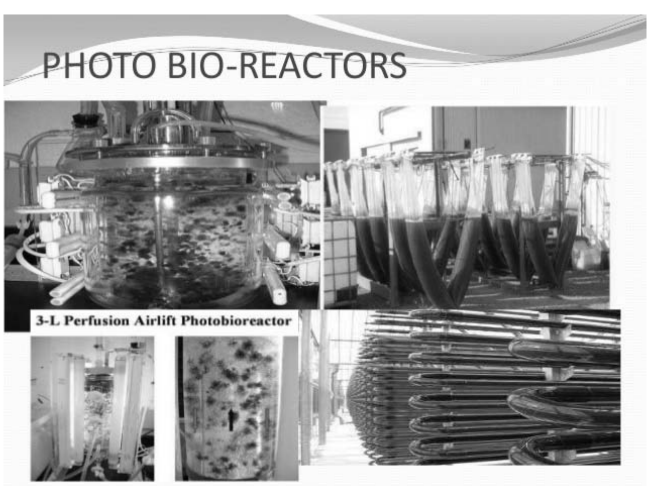

Fig. 4. Photobioreactors

5. EXTRACTION OF ALGAL OIL

Many different techniques for extracting oil from algae have been attempted, most of which are neither cost effective nor efficient. Highly dependent on the quality of the algal oil, extraction involves concentrating and separating algae from the culturing medium, then mechanical (such as pressing or ultrasonic cell lysing extraction) and/or chemical (such as solvent or supercritical fluid extraction) oil removal. Aurora Biofuels has applied for a patent that concentrates and isolates algae from culture at the industrial scale. General Atomics has recently been assigned a patent application proposing a cost effective method for algal oil extraction utilizing steam to rupture cells to release oil. Many methods appear to attempt to remove the extraction process, such as Synthetic Genomics's patent application mentioned above. For algal biodiesel to become commercially viable, research and development must focus on efficient and economical extraction of oil or methods that remove the oil extraction step.

6. BIODIESEL FROM ALGAE

Algal biodiesel is produced by the transesterification of the naturally occurring triglycerides in algal oil with a short chain primary alcohol (typically methanol or ethanol). The transesterification process is typically enhanced by the presence of acid catalysts, base catalysts, enzyme catalysts or supercritical conditions.

Biodiesel is predominantly produced via base catalysis, which is fast and relatively inexpensive. However, base catalysis is very sensitive to water and free fatty acid contamination, which can lead to unwanted ester saponification (soap accumulation). Therefore, base catalyzed production requires pre-processing of raw input oils to remove water and free fatty acids. As algal oil typically contains free fatty acids between 20 and 50 per cent, the cost of biodiesel production can be significantly reduced by making it less sensitive to such impurities.

The oil thus, obtained is called "Green Crude".

The process of producing biodiesesl involves water, inorganic nutrients, light, and CO2 are provided to the algal cultures in the algal 20 biomass production stage. Biomass is then separated from the water and nutrients in the biomass recovery stage, as the latter are recycled back into the algal cultures. The biomass then undergoes extraction to remove its lipid content.

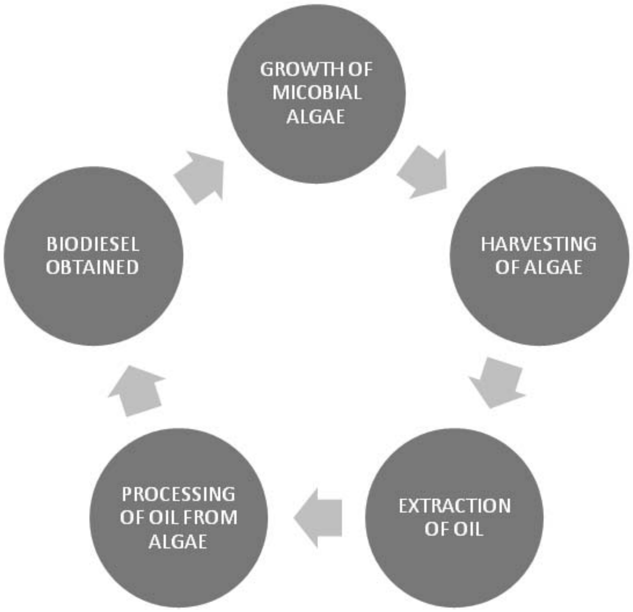

Fig. 5. Detailed Process of Production of Biodiesel from Algae

This lipid content is converted into biodiesel. Spent biomass can be used as animal feed or digested anaerobically to generate gas for electricity while recycling CO_2 emissions back into the biomass production stage.

Carbon is also highly required for the growth of the microalgae thus, should not be overlooked. A 1985 study by Chirac, et al. found that air that was enriched 1% CO_2 lead to a 3.5x increase in the mean doubling time of growth of B. braunii as well as a 5-fold increase in its hydrocarbon production. This effect was not observed when bicarbonate was merely added to the growth medium. One possible solution is to cover the pond holding a high concentration of CO_2 at the surface, thereby allowing the gas to passively diffuse into solution. Even so, the desorption of oxygen and nitrogen gases under the cover prevents us from having a high percent of coverage. Alternatively, it is also possible to inject CO_2 from shallow stumps below the surface of the growth medium. This helps in providing the required amount of carbon.

Constant agitation is also necessary in order to keep the cells in suspension, to disperse nutrients and prevent thermal stratification. Great focus is on the two major means of mixing: the use of either paddle wheels or airlift mixing system.

Other factors important to algal growth, but not considered extensively in the report, include light intensity, temperature control, and the costs resulting from contamination, which open systems are relatively more vulnerable to, as opposed to closed systems.

Algal growth is sensitive to levels of dissolved gases such as oxygen and carbon dioxide. Concentrations of oxygen much higher than air saturation values will inhibit photosynthesis, and at very high levels in combination with sunlight, could potentially damage the cells. Furthermore, algal growth is pH sensitive, an important consideration since the process of photosynthesis will naturally cause the tube pH to rise as greater amounts of dissolved CO_2 are removed from solution as oxygen is introduced.

Once the biomass has been dried two processes must occur in order to create biodiesel: the lipids must be extracted from the biomass and they must undergo a transesterification reaction (Figure 2).

Successful protocols have been established for these processes in the laboratory, still it remains that these laboratory techniques are not particularly successful on an industrial scale with regard to algal biodiesel, although several reaction techniques have been used commercially for the transesterification of tallow and soybean.

The Transesterification Reaction.

During transesterification triglycerides obtained from biological products are processed with a three times excess of alcohol to generate glycerol and alkyl esters. Biodiesel consists largely of these alkyl esters; these must be monoalkyl esters.

The current technique for algal biodiesel production obtains lipids from biomass by means of standard grinding or sonication of the algal cells in order to lyse them, followed by extraction using organic solvents. Although such methods are common for harvesting biochemical products in the laboratory, the industrial scale equivalent usually requires the use to batch reactors, in which sonication and extraction take place in large vats. The harvested lipids are then reacted in a similar batch method using a dissolved or liquid catalyst and alcohol for the transesterification reaction. Generally, a standard react (UEE), who is working on an improved continuous flow tubular reactor. This is filled with a solid catalyst that does not leave the reactor. Oils are flowed through the reactor, undergoing transesterification as they pass the solid catalyst. Biodiesel can be generated at a greater rate using such a design since the tube does not need to be emptied and refilled. Furthermore, since the design of the tubular reactor is not vat-like, it can be smaller and, therefore, easier to transport. The great cost reduction within this system, however, is the elimination of the need to separate product and catalyst following the reaction. Although this design is currently in Phase I and being operated only on a small scale, with algal oil samples provided by outside producers, UEE reports that the design demonstrates greater scalability compared with traditional reaction processes and has partnered with other firms to design a complete algae biodiesel production process from algal growth to extraction and transesterification. It is highly likely that similar systems are utilized in existing plants.

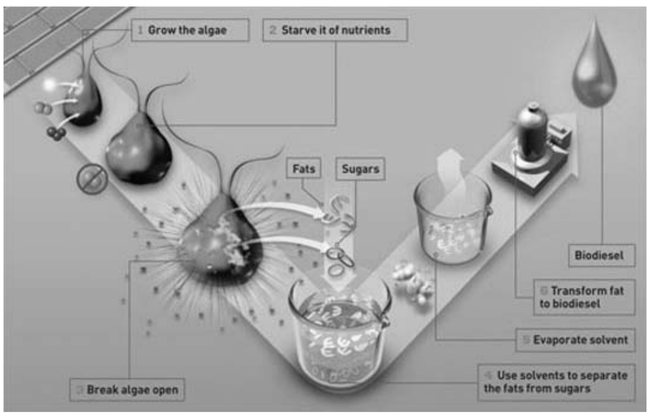

Fig. 6. Extraction of Biodiesel

7. BENEFITS OF USING BIODIESEL

Potential benefits of using algae for biodiesel are:

I. Algae yields could reach a height of 50T of biodiesel per hectare against 2T for competing feedstock such as jatropha.

II. On lipid content (in terms of % lipid content by dry weight) algae scores over all other crops in biomass yield.

III. Bio-oil from algae has molecular structure similar to the resultant fuels obtained from all other natural resources.

IV. Growing algae consumes CO_2 which provides green house gas mitigation benefits.

V. If successful, biofuels from photosynthetic algae could be used to manufacture a full range of fuels including gasoline, diesel, and jet fuel that meet the same specifications as today's products.

8. CONCLUSION

- Microalgal route to biodiesel is a potential alternative to petrofuels.
- Overall economics of the process needs to improvement to be competitive substitute for petrodiesel.
- Routes of improvement in economy lie in both science and technology of microalgae.
- The policies for incentivizing biofuel production that are currently in place, most notably the monetary assistance of the Biodiesel Tax Credit, could potentially allow algae biodiesel to be produced profitably using an open pond system given certain assumptions about the costs of algae biodiesel production.
- Algal fuel is the most promising fuel but more research and development is required to make it a more commercial fuel.

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10. REFERENCES

1. Hill, J., Nelson, E., Tilman, D., Polasky, S. and Tiffany, D. (2006) Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels. Proceedings of the National Academy of Sciences of the United States of America 103 (30): 11206–11210. | Article | PubMed.
2. Demirbas, A. (2008) *Biodiesel: A Realistic Fuel Alternative for Diesel Engines*. London: Springer-Verlag London.
3. Journal "Chemistry Central Journal", article "Algal Biodiesel – a feasibility report", Author "Yihe Gao1, Chapin Gregor1, Yuanjie Liang1*, Dawei Tang1 and Caitlin Tweed 2 .
4. Journal of Commercial Biotechnology , Article "Algae and Biodiesel", Author "Matthew R Preiss and Stanley P. Kowalski.
5. Book of Microbiology "Pelczar".

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