

# An Overview on Developments in Biodiesel Production from Algae

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**Abstract:** Biofuels and bioproducts produced from plant biomass would mitigate global warming. The sourcing of feedstocks, including the impact it may have on biodiversity and land use and competition with food crops. Algae have recently received a lot of attention as a new biomass source for the production of renewable energy. Biodiesel feed stocks derived from microalgae and macroalgae have emerged as one of the most promising alternative sources of lipid for use in biodiesel production. Among these microalgae seem to be promising source of biofuel because they are readily available in nature, the raw materials required are the sunlight, water, carbon dioxide and nutrients (P and N), [1,2]. They are the most fast-growing plant on earth and has short life cycle. Oil content in microalgae can exceed 80% by weight of dry biomass. Algae biodiesel manufacturers are building biodiesel plants close to energy manufacturing plants that produce lots of carbon dioxide. Recycling carbon dioxide reduces pollution. Many countries are now doing extensive research on algae. Considering these facts, this paper provides an overview on developments in biodiesel production from algae.

**Keywords:** Algaeoil, Biodiesel, Transesterification, Pyrolysis, Nanofarming.

## 1. Introduction

The energy demand is growing worldwide. The total energy consumption has increased from 196 EJ ( $10^8$  joule) in 1973 to more than 350 EJ in 2009 and the tendency is rising, [3]. About 80% of this energy is fulfilled from fossil fuels with the green house gas emissions. The reduction of CO<sub>2</sub> emissions in the range of 10-20% by 2020 is internationally specified target (e.g. European union). Currently the fossil resources are not regarded as sustainable and questionable from the economic, ecology and environmental point of views. Because of the many advantages over the conventional energy resources, the production of biodiesel has attracted much attention in recent years.

India is the sixth largest and one of the fastest growing energy consumers in the world due to raising population and consumption power of India. BP Statistical Review of World Energy, [2013] indicates gap between oil consumption and supply is about 2833 thousand barrels daily in India. Bio-fuels to be an appropriate option to be fixed as a solution to these problems

Micro algae are more suitable as biofuel because

- 1) Micro-algae can grow in all environment-ts, even if the temperature of water makes - 2°C. Their lipid content could be adjusted through changing growth medium composition. Salty or wastewater could be used.
- 2) Atmospheric carbon dioxide is the carbon source for growth of microalgae and producing 100 tons of algal biomass fixes roughly 183 tons of carbon dioxide.
- 3) Algae can be fertilized with sewage and waste water.
- 4) Algae Sugars can be fermented to make Ethanol for E85.
- 5) Algae is producing feed for fish and livestock from waste biomass.

**Table 1:** Some algae species for algae oil and their typical oil content, [4,5]

Strain	Oil content (% dry biomass weight)
Ankistrodesmus TR-87	28–40
Botryococcus braunii	25–80
Chlorella sp.	29
Chlorella protothecoides	23–30
Chlorella vulgaris	14–40
Cryptocodinium cohnii	20
Cylindrotheca sp.	16–37
Dunaliella salina	14–20
Dunaliella Tertiolecta	36–42
Nannochloropsis sp.	46 (31–68)
Neochloris oleoabundans	35–65
Nitzschia sp.	45–47
Porphyra Red alga	33 (9–59)
Phaeodactylum tricornutum	20–30
Schizochytrium sp.	50–77
Spirulina maxima	4–9
Tetraselmis suecia	15–23

**Table 2:** Amount of oil produced by various Feedstocks, [6].

Feedstock	Liters/hectare
Soy Sunflower a bean	446
Sunflower	952
Castor	1413
Coconut	2689
Palm	5950
Algae	100000

Main challenges in algal biofuels are algal biology and cultivation, harvesting and dewatering, extraction and conversion and development of co-products.

## 2. Algae Harvesting

### a) Flocculation

Flocculants, or flocculating agents, are chemicals that promote flocculation by causing colloids and other suspended particles in liquids to aggregate, forming a flock.

Alum and ferric chloride are chemical flocculants used to harvest algae. A commercial product called "Chitosan", which is commonly used for water purification, can also be used as a flocculant but is far more expensive. To aggregate microalgae cells the net negative charge of the cells must be neutralized or reduced by adding a so called flocculants such as multivalent cations or cationic polymers. Some of these flocculants may not be acceptable when the biomass is to be used in certain ways, such as feedstock for animals. Higher cell concentrations and gentle mixing helps flocculation since this makes the cell encounters more frequent. Excessive shear force as can be found in centrifugation can disrupt the flocks changing the pH of the solution by adding acids or bases can also act as a flocculent since the ionization of functional groups on the algal cell surface are highly pH dependent. A combination of cat ions and pH can also be used. The main disadvantage of this separation method is the additional chemicals are difficult to remove from the separated algae, probably making it inefficient uneconomic for commercial use.

#### b) Gravity Sedimentation

Gravity sedimentation is a process that separates particles from liquids on the base of their density difference and the particle diameter. If the solids that are to be separated consists of individual particles of sizes of only a few micrometer in diameter the settling rates will be low.

#### c) Centrifugation

Centrifugation is a method of separating algae from the medium by using a centrifuge to cause the algae to settle to the bottom of a flask or tank. Centrifugal separation uses the same principles as gravity sedimentation but enhances the settling rate by centrifuging the particles. This method often replaces the gravity separators, since their higher efficiency and smaller apparatus size for a given capacity.

#### d) Ultrasound

This method uses more energy than centrifugation, has less efficiency and lower concentration factors. Some benefits by using ultrasound compared to centrifugation can be found at lab or pilot scale when other parameters are important than for industrial scale. The ultrasound process is used to harvest microalgae, which is based on acoustically induced aggregation and enhanced sedimentation. Concentration factors of 20 can be reached with low biomass concentrations and low flow rates.

#### e) Filtration

Filtration is carried out commonly on membranes of modified cellulose, with the aid of a suction pump. The greatest advantage of this method as a concentrating device is that it is able to collect microalgae or cells of very low density. However, concentration by filtration is limited to small volumes and leads to the eventual clogging of the filter by the packed cells when vacuum is applied. To avoid these problems we can use another alternative method which involves the use of a reverse-flow vacuum in which the pressure operates from above, making the process more gentle and avoiding the packing of cells. The power requirement around 0.3-0.5 kWh per m<sup>3</sup> broth giving about 3 % solids, the power consumption is thereby much lower than their experiments with a centrifuge. Cross flow filtration

may be applied to concentrate suspensions of fine particles. Cross flow filtration can be useful for suspensions of very small particles Cross flow filtration is not an economical method for larger production

**f) Flotation** Usually flotation is used in combination with flocculation for algae Harvesting in waste water. It is a simple method by which algae can be made to float on the surface of the medium and removed as scum. It is of two types 1) Dissolved Air Flotation. It uses alum to flocculate an algae/air mixture, with fine bubbles supplied by an air compressor. Dissolved air flotation is an economical method, but that filtration is a better method when the size of the algae is not a problem 2) Froth Flotation. Froth Flotation is a method of separating algae from the medium by adjusting pH and bubbling air through a column to create a froth of algae that accumulates above liquid level. The algae collects in a froth above the liquid level, and may be removed by suction. The pH required depends on algal species. Froth flotation and drying are currently considered too expensive for commercial use. The cost of froth flotation was estimated to be too high for commercial use. Although, the cost may be reduced with further research.

#### i) Drying

Following harvesting of the algal biomass, algal slurry moisture content has to be reduced to at least 10% by drying and dehydration. Numerous methods have been employed for drying. Most common methods are sun drying, spray drying, drum drying, and freeze drying. Again,<sup>14</sup> Enzyme Research best drying method selection depends on required operation scale and desired product value. In biodiesel production, lipid-rich feedstock with low water content is required; therefore, microalgae drying has to be carried out. However, drying is energy intensive, which adds to the cost complexity of the overall production process. Various drying systems differ in both energy and cost requirements.

### 3. Algae Oil Extraction

To disrupt microorganisms, such as algae to extract oil, may at first seem as an easy task to be done, but this is not true because the internal pressure inside the organisms can be as high as 20 atmospheres. The structures, cellular walls and membranes, which resist this high pressure, are in fact about as strong, weight for weight, as reinforced concrete. Most of the cell disruption methods developed for use with non-photosynthetic microorganisms can also be applied to microalgae [3]. The ease with which the cells disrupt, the cost of method, the speed of the extraction method applied etc. are to be considered for choosing the recovery of algal oil from the cells.

#### a) Freezing

Ice is 8% greater in volume than liquid water. The desired effect is that the expansion of the water inside the cell as well as the water around the cell will cause the cell walls to rupture from the inside out or be disrupted by the compressive forces.

#### b) Homogenization

Homogenization is the process of reducing the size of particles in a mixture so that the media is uniform

throughout. The process is usually done by expelling mixtures through small valves at high pressure.

#### c) Osmotic Shock

Cell membranes are permeable to many solutes. If a cell is placed in solution, the solute will diffuse across the cell membrane, provided the solute is small enough. If the solutes were suddenly removed from the water surrounding the cell, there would be a net transfer for water into the cell. At the same time the solutes will also diffuse across the cell membrane into the water in order to equalize the concentration inside and outside the cell. If the concentration of solutes in the water is dropped quickly enough, water can engorge the cell causing cell lysis. This process is called osmotic shock.

#### d) Bead Mills

Bead Mills is regarded as one of the most efficient physical cell disruption techniques. These mills consist of either a vertical or a horizontal cylindrical chamber with a motor-driven central shaft supporting a collection of off-centered discs or other agitating element. The chamber is filled to the desired level of beads which provide the grinding action.

#### e) Presses

Suitable press configuration for the extraction is largely dependent on which algae strain that is being used, since there is a vast variation among different strains in their physical attributes such as cell dimensions, rigidity in the cell structures etc. There are many different presses available on the market, i.e. screw, expeller, piston. The amount of oil recovered from the cells depends on many factors. Among those is the rate at which pressure is applied, the maximum pressure attained, the time allowed for oil drainage at full pressure, and the temperature or the viscosity of the oil.

#### f) Cavitation

Cavitation extraction process uses pressure differences and the resulting cavities collapses as a result of the shifting pressures, and these collapses cause high shock waves in the micro environment and this causes the algae's cell membranes to break.

Cavitation is of two types 1) Ultrasonic cavitation utilizes sound to create the oscillating pressure, causing the formation and collapse of cavities. and the other hydrodynamic cavitation. 2) Hydrodynamic cavitation, where the pressure drop over simple geometrics like venturi pipes or orifice are used.

#### g) Conventional Solvent Extraction

These types of solvent-based processes are most effective with dried feedstocks or those with minimal free water. When the hexane, an organic solvent, is introduced to the dry algae sample, the cell wall is penetrated by the hexane and the oil within the cell is dissolved. When the hexane is removed from the algae sample, the oil dissolved in the hexane is transported through the cell wall and effectively removed from the algae cell. The collection of the oil is done by evaporating the hexane off, which will leave the algae oil behind.. The cost of drying the feedstock significantly adds

to the overall production cost and requires significant energy.

Advantages of chemical solvent extraction methods are extracts most of the oil (up to 95% of oil recovery with hexane as solvent) and suitable for small scale. The disadvantages are chemicals are dangerous (hexane is a toxic and explosive chemical), may cause unwanted reaction, waste chemical leads to pollution and after extraction the process needs further separation. Oil that is present inside of the single cell algae is trapped by the cell wall and plasma membrane, which inhibits its ability to easily be exported from the cell. When the algae cells dried, the plasma membrane is degenerated and weakens the cells ability to retain the oil.

#### h) Supercritical Fluid Extraction (SFE)

Supercritical fluids (SCFs) are fluids at pressures and temperatures above their critical values. Critical values represent the highest temperature and pressure at which the substance exists as a vapor and liquid in equilibrium. Supercritical CO<sub>2</sub> has been used in manufacturing to remove caffeine from coffee, to separate high-value oils from plants, and in the laboratory to transesterify lipids into biodiesel from domestic sewage sludge. Supercritical CO<sub>2</sub> has both liquid and gas properties, allowing the fluid to penetrate the biomass and act as an organic solvent, without the challenges and expense of separating the organic solvent from the final product. Transesterification can be conducted by a supercritical methanol process; this process is conducted at high temperature in the range of 200-350 °C and at pressures around 35 MPa. This process leads to the following: 1) absence of catalyst, 2) no saponification, 3) less after-process separation, 4) less sensibility to water content, 5) no problems with corrosive environment and 6) fewer waste products. The reaction time for the supercritical process is extremely short, compared to other transesterification processes. The ability of SFE to operate at low temperatures preserves the algal lipid quality during the extraction process and minimizes the need for additional solvent processing [7,8]. The advantages of this extraction method are efficient method and no waste chemicals. However, the capital and operating costs for a high pressure SFE operations currently limits its potential for biofuel production. Over time SFE applications have targeted lower value products, but not yet commodity chemicals. Technology development and further reductions in costs may lead to processes applicable to biofuel production.

#### i) Heated Oil Extraction

Benemann and Oswald (1996) proposed contacting algae wet paste from a gravitational thickener with heated oil and then combining centrifugal dewatering with oil extraction in a three phase centrifuge which could separate oil, water, and solids (i.e., residual biomass). While this extraction method has never been demonstrated, preliminary analysis suggests it may be viable. However, extraction efficiencies are uncertain and will be species dependent and biomass pretreatments to make oil more available for extraction will need to be investigated.

**j) Biological Extraction**

Biological methods used to capture and extract lipids offer low-tech and low-cost methods of harvesting and lipid extraction. Using crustaceans to capture and concentrate microalgae would appear to be a promising solution for algae oil recovery. The use of enzymes to degrade algal cell walls and reduce the energy needed for mechanical disruption has also been investigated. Demonstrations in large open ponds of brine shrimp feeding on microalgae to concentrate the algae, followed by harvesting, crushing and homogenizing the larger brine shrimp to recover oil have been successful (Brune and Beecher, 2007). Advantage of this method is that it is an efficient method. The limitations are 1) the process needs control condition, enzymes grow and 2) further separation and processing cost is high.

**4. Transesterification**

The principal method of converting biomass derived lipids into biodiesel is transesterification. In this process, the relatively viscous TAGs are reacted with methanol in the presence of a catalyst to produce FAME, which more closely resemble petroleum-based diesel fuel and glycerol as a co-product. High conversions are achieved in this reversible reaction by either adding an excess of methanol or removing glycerol as it is formed; both strategies have been used in commercial processes.

There are a number of variations of the transesterification process and biodiesel manufacturers will optimize the process for the each feedstock by balancing yields against equipment, catalyst, methanol and energy costs. In the case of algal biofuels, the feedstock composition is uncertain and will likely vary over time since changes in production temperature, light intensity and nutrient levels all affect algal lipid composition. Consequently, process optimization will need continuous attention in a production environment with the flexibility to deal with varying feedstock composition.

**5. Hydroprocessing**

The alternative path from biomass derived lipids to liquid fuels is hydrotreating or hydroprocessing, where the oil is reacted with hydrogen over a catalyst and then isomerised to produce a targeted mixture of alkanes, water, CO<sub>2</sub> and CO. The alkane mixture can be fractionated to produce a synthetic kerosene jet fuel and hydrogenation-derived renewable diesel (HDRD) or green diesel. HDRD is compatible with petroleum processes and existing fuel infrastructure, and can be blended with petroleum products in any proportion. The glycerol moiety of the TAG is converted to propane, which can be combusted to provide process heat or liquefied and sold as LPG.

**6. Single-Step Extraction**

The Single Step Process. does not requires initial dewatering & also does not requires chemicals or heavy machinery for extraction. The process harvests, concentrates and extracts oil from algae, and separates oil, water and biomass in one step in less than an hour. The Quantum Fracturing technology combines with electromagnetic pulses and pH

modification to break down cell walls and release oil from the algae cells. In base-catalyzed microwave transesterification involves the attack of the alkoxide ion to the carbonyl carbon of the triglyceride molecule which results in the formation of a tetrahedral intermediate. The reaction of this intermediate with an alcohol produces the alkoxide ion. The rearrangement of the tetrahedral intermediate gives rise to an ester and a diglyceride. In a similar way, diglyceride is transesterified to form methyl ester and monoglyceride, which is converted further to methyl ester and glycerol [9]. Microwave effect on the transesterification reaction is twofold: 1) enhancement of reaction by a thermal effect, 2) evaporation of methanol due to the strong microwave interaction of the material [10,11]

The single-step extractive transesterification process has the potential to provide energy efficient and economical route for algal biodiesel production. Microwave-assisted extraction and transesterification in situ transesterification process of dry algal biomass was proved to be fast and easy method with improved purity to produce biodiesel from dry algal biomass [12].

**7. Pyrolysis Technologies**

Pyrolysis is a phenomenon related to decomposition of biomass under the condition of oxygen deficiency and high temperature. Pyrolysis previously was first used for the production of bio-oils or bio-gases from lignocellulose. However, such a technology may be more suitable for microalgae because of the lower temperature required for pyrolysis and the higher-quality oils obtained [13]. Fast pyrolysis has proved to be a promising way to produce bio-oils compared to slow pyrolysis [14,15] for the following reasons:

- (1) the fast pyrolysis process is time saving and requires less energy compared to the slow pyrolysis process.
- (2) less bio-oils were produced from slow pyrolysis.
- (3) the viscous bio-oils from slow pyrolysis is not suitable for liquid fuels.

**8. Extraction Using Nanotechnology**

United States Department of Energy's Ames Laboratory and Iowa State University have developed groundbreaking "nanofarming" technology that safely harvests oil from the algae so the pond-based "crop" can keep on producing. Their approach to overcome the challenges of algae biodiesel production are to develop non-invasive oil extraction methods with high recyclability and regrowthability of algae, design new sequestration method for selective isolation of the suitable fuel feedstocks from hydrocarbons of algae. Catilin and Iowa State University Center for Catalysis (ISU-CCAT), members of the National Alliance for Advanced Biofuels and Bioproducts (NAABB), are working on their pioneering algal oil extraction technology using mesoporous nanoparticles to selectively extract and sequester targeted fuel-relevant and high value compounds within the algal lipid mixture. The balance of the algal oil, which contains free fatty acids and triglycerides, will be converted to biodiesel using Catilin's commercially available T300 catalyst. This technology is efficient and solid catalyst provides a cost effective conversion route [16].

## 9. Conclusion

Since oil crisis in the mid 1970s, finding new energy resources to replace petroleum has been a hot topic worldwide. Because of the many advantages over the conventional energy resources, the production of biodiesel has attracted much attention in recent years. There have been numerous publications on the production of biodiesel made from vegetable oils and other oil-plants. The production of liquid transportation fuels from algal biomass is technically feasible. At present, the high cost of oleaginous materials and algae oil extraction methods are the main problems hindering commercial production of biodiesel. Lipid fraction and productivity are two of the strongest drivers of economic viability [17]. Therefore, finding cheaper oleaginous materials and improving transesterification technologies are the key to producing biodiesel successfully. Cost of producing microalgae biodiesel can be reduced substantially by further researches and findings, which will help to justify the investment in technology development and infrastructure to make algal biofuel a viable fuel for the future.

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