A review paper on deriving biofuel from microalgae and producing biodiesel as an alternative to nonrenewable diesel.

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Abstract

Blinded use of fossil fuels has led a drastic change in the facet of the world from last few decades. Rising fuel prices, increases global warming and an increase in the tension amidst the countries have led to a sharp rise in the valuation of crude oil, which hitherto has acted upon as the driving fuel behind the transport sector. This has led to a mass research for alternatives in the course of fuel. This has been narrowed down to biofuels, which are derived biologically. Among the various generations of fuels (which has been described further) has further focused the researchers over the use of microalgae, which due to its chemical composition has attracted the entire scientific community, along with its easy and bulk availability added on. This paper discusses the use and scope of micro algae for deriving biofuel and processing bio diesel from it.

Keywords

Microalgae, biofuels, biodiesel

Introduction

Since the Industrial revolution that took place in around 1760 the world has gone through a major change. The arrival of new technology in the form of steam engines which sooner manifested into powerful, fast petroleum derived vehicles changed the face of human civilization. The rapid growth in the wages, arrival of new inventions and rising standards of living alongside increased purchasing power led to a blind race of advancement. Since then till today the race has continued and will so be in the coming decades considering the fast paced life and increasing population. However, the side effects of such activities are not invisible now and are visible in the form of growing environmental concerns and global warming. On the other hand, the increasing cost of petroleum is putting extra burden on the fiscal estimates of countries, especially the non-oil producing countries which remain a net importer of oil for their industrial and commercial needs. This has led to a new search towards the alternatives of petroleum in the global scientific community. Biodiesel is a sustainable hotspot for long term energy security. Biodiesel is a biodegradable, practically identical heat of ignition, eco-friendly, sustainable, contains sub-atomic oxygen, which helps in easy burning of fuel, clean consumption and can possibly altogether decrease harmful discharges and have low sulfur content. Biodiesel is an alternative fuel similar to conventional or 'fossil' diesel and can be produced from waste cooking oil, animal oil/fats and waste straight vegetable oil. Biodiesel can be classified as 1st generation, 2nd generation, 3rd generation or 4th generation depending upon the source of production. First generation biofuels are produced directly from food crops. However, these biofuels will put a direct burden on food availability and are not suggested for wide scale production.2nd generation biofuels are produced from non-food crops, such as cellulosic biofuels and waste biomass (stalks of wheat and corn, and wood). Examples include advanced biofuels like bio hydrogen, bio methanol but technological

Constraints are putting hurdles in their commercial production. 3rd generation biofuels are produced from micro-organisms like algae. Similarly, to 3rd generation biofuels and 4th generation biofuels are made using modifications in the chemical and molecular structures of algae and is a subject concern of biomedical stream. The natural algae strain is genetically modified to enhance carbon capture and lipid production. Of all the generations of biofuel production, the 3rd generation biofuels have become a subject of choice amongst the

researchers. It holds the capacity to capture 183 GT of carbon dioxide against 100GT of biomass production as compared to 77GT of carbon dioxide against the production of 100GT of biomass production [1]. Thus, it is evident here that the cultivation of microalgae not only shall give a boost in the field of biofuel, but at the same time can help in the lowering of carbon dioxide remnants in the air at a much faster race in comparison to conventional plants due to its high photosynthesis rate and yield till 12000.00 L/ha, that is clearly much more than agriculture produce and thus can generate 10 times biofuel [2]. Alongside biofuel, it can also be used to produce vivid ranges of products such as hydrogen which can be produced by bio-photolysis [3], bio-oil via thermo-chemical transformation [4], bio methanol through fermentation [5-6], and green diesel through hydrothermal liquefaction [7]. However, the commercial cultivation of algae is economically not feasible as of now due to large amount of nutrients required that has to be synthetically delivered, especially the consumption of nitrogen and phosphorous requirements, although the requirements of nitrogen and phosphorous could be supplemented by using municipal sewage waste water which has high contents of such nutrients as said above [8]. It has also been found that the single cell algae strain due to its simple structure as compared to multi cell algal strain which has a quite complex structure gives more oil recovery and shows faster pace of growth rate [9]. Lipid profile and fatty acid profiles can be enhanced by supplying the increased amount of glucose and vitamins [10].

The following review is focused towards bringing out the current advancements in the microalgae production and cultivation methods that would help researchers to broaden their attempts in bringing micro-algae towards an economically feasible and technologically viable state of production. This paper shall further focus on different harvesting techniques and conversion of lipids into biodiesel.

Microalgae

They are primary photosynthetic organism and use light, carbon dioxide and inorganic salts for their extension and development. Due to their fast rate of growth they can be considered as a renewable source of energy. They are found in fresh, brackish as well as marine water- sediments and columns and could be found living in colonies or individually. Due to their recognizable protein content and oil content, they can be used as a source of oil production or animal feed stocks. They can also be used for human consumption due to their dietary supplements. Table 1 shows a comparison of microalgae with plants considering multiple factor such as cultivation technology and the incubation period.

Table 1: Comparison of algae and plants [11]

Factor	Microalgae	Conventional plants
Cultivation method	Cell Bioengineering	Farms
Oil content	50-77	20-30
Incubation period	14-20days	4-6 months

With more than 2.5 lakes of species available of microalgae strain [12] the proper selection of the proper strain also poses another challenge as each strain varies amongst the factors. Table 2 shows the lipid and oil contents of different strains of microalgae as of now analyzed Chlorella pyrenoidosa gives the optimum amount of oil content and lipid production [13].

Microalgae cultivation

The cultivation of microalgae is a little complex as compared to conventional plants and requires a temperature range of 20-30° C and adequate exposure to sunlight and proper amount of Nitrogen, Phosphorus and iron. As already discussed the nutritional requirements could be supplemented by using sewage waste water as it is found to be rich in such nutrient contents. The cultivation of microalgae could be done in an open system (that contains open raceway ponds with paddlewheels agitator and multiple bioreactors) or in closed systems which contains multiple bioreactors of different types such as flat-panel, tubular, floating or bag type bioreactor [14-15].

Open pond cultivation system

Due to its simplicity and ease of doing, this is one of the most commonly employed methods of microalgae culture. During the 2nd world war, Germany used this method for the cultivation of microalgae for food production for its army [16]. Under photographic conditions, algae utilize sunlight and carbon dioxide as an

energy source for its photosynthesis. Open cultivation can come in many forms such as raceway, shallow big and circular and are most often with agitators for proper mixing of algal cells and nutrients. The size of these ponds is limited to a maximum of 10000 m^2 due to mixing constrains of algal cell and nutrients [16], however, recent cultivation is being done on areas up to several acres by using artificial paddle wheels alongside coating the pond walls with synthetic membrane to stop leakage and mitigate contamination problems [17]. As already discussed nutrients can be supplemented by using sewage water [8]. These tanks are easy to maintain and clean and are mostly dependent on sunlight thereby reducing channel costs. However, since the atmosphere is prone to open it becomes quite difficult to control the contamination. It also becomes complicated in terms of controlling the external factors such as climatic changes which many times causes less cellular density due to shadowing of cells [16].

Table 2: lipid and oil contents of different strains of microalgae

Algal strain	Lipids (%)	Oil content (%)	Proteins (%)	Carbohydrate (%)	Nucleic acid (%)
Anabaena cylindrica-	5-8	-	42-55	26-31	-
Botryococcusbraunii	28-74	25-75	-	-	-
Chlorella vulgaris	15-23	63.1	52-59	13-18	3-4.5
Chlorella pyrenoidosa	21-52	26-41	56	26.5	-
Chlorella prototecoides	22-54	56-59	-	-	-
Chalmydomonasrheinhardii	20	1.5	47	17.5	-
Dunaliellabioculata	7	7	48	3.5	-
Dunaliellasalina	6.5	6.5	56	31	-
Euglena gracills	13	15-21	38-60	15-19	-
Prymnesiumparvum	21-37	21-37	29-46	26-34	1.5-2.5
Porphyridiumcruentum	8-13	10-13	27-38	41-58	-
Scendesmus obliquus	11-13	11-13	51-57	11-18	3.5-6.1
Scendesmusdimorphous	15-39	15-13	8.1-18.5	20-51	-
Scendesmusquadricauda	1.8	1.8	46	-	-
Schizochytrium sp.	51-78	51-78	-	-	-
Spirogyra sp.	10-20	10-20	5-19	32-63	-
Spirulina maxima	6.5-7.5	7.1	61-72	14-17	4-4.6
Spirulina platensis	5-8	5-8	45-62	8.5-13	2.5-5.1
Synechoccus sp.	11.2	11.2	62.5	15.1	5.1
Tetraselmismaculata	3.01	3.01	52.3	15.1	-

Thus it is open to reduction in productivity and more losses due to variation in water temperature, vapor losses and carbon dioxide dispersal etc. [18]

Closed cultivation system

Closed cultivation system is also called photo bioreactors and the algae is cultured in a closed equipment where all the factors are artificially introduced and controlled as per the requirements. PBRs facilitate better control of culture environment such as carbon dioxide supply, water supply, optimal temperature, efficient exposure to light, culture density, pH levels, gas supply rate, mixing regime, etc.[19].

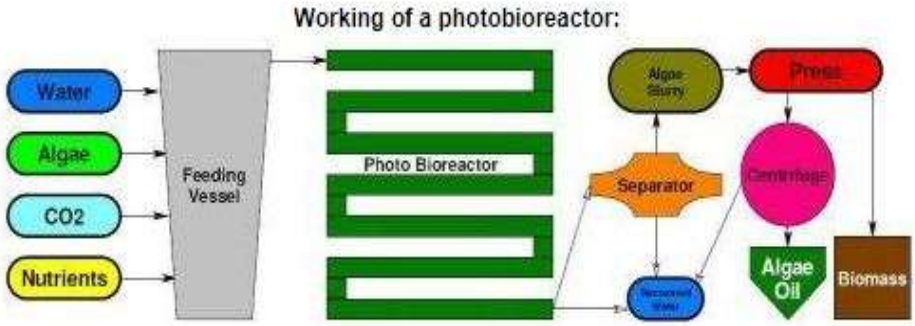

Figure 1: A closed photo bioreactor [19]

Due to proper missing facilities carbon dioxide fixation also becomes very easy. PBRs offer maximum efficiency in using light and therefore greatly improve productivity. Typically, the culture density of algae produced is 10 to 20 times greater than bag culture in which algae culture is done in bags - and can be even greater[19].Despite higher biomass concentration and better control of culture parameters, data accumulated in the last two decades have shown that the productivity and production cost in some enclosed photo bioreactor systems are not much better than those achievable in open-pond cultures from the economical point of view they also prove to be costlier from the conventional open pond systems.

Harvesting

It accounts for almost 25-35% of total production cost and selection of appropriate farming process rely upon the features of chosen algal strain as it may result in varying production efficiencies. High water content and negative charge characteristics also create an additional cost of drying the feed. An optimum harvesting method should be low cost, utilize minimum resources and must cover a variety of algal strains. Algae harvesting is done in two steps in which in the first step biomass is filtered from the bulk and in the next step it is more concentrated. The process of concentrating the biomass is called is called Thickening. Of all the available harvesting techniques such as flocculation, sedimentation, floatation and micro filtration, flocculation is the most commonly used process in which a solution of sodium hydroxide is added to the culture which is further washed with distilled water to remove the salt concentration and then dried for about 24 hours [20].

Lipid extraction

Since most of the investigations done on lipid extraction has been done for the purpose of agricultural applications, much less work has been done in the field of extraction for biodiesel production. Microalgae are aquatic plants and thus they have only 24-27 %w/w of dry biomass over a wet biomass thereby making water removal as a cost incentive process. As of now no reliable search has been done on extraction of oil directly from the wet feedstock. Two of the most commonly used methods for lipid extraction are the “Organic Solvent method” and the supercritical fluid extraction method.

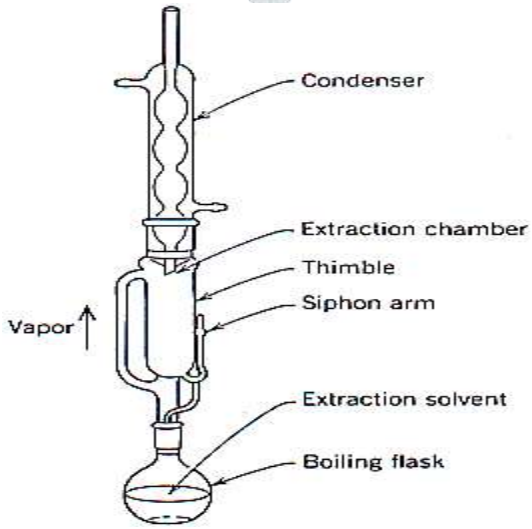

Figure 2: A basic soxhlet apparatus

Organic solvent method

In the organic solvent method, a blend of polar solvents and non-polar solvents such as a mixture of hexane with isopropanol or chloroform with methanol is used [21]. The extraction of lipid from the algal biomass is done on a Soxhlet apparatus which contains of 3 chambers i.e. an organic solvent holder which is continuously heated, an extractor and a condenser that condenses the evaporated organic solvent. Figure2 shows a basic Soxhlet apparatus.

Supercritical Fluid extraction method

It has been widely found that the extracted lipid via the organic solvent method is toxic in nature and has major pollution concerns as well. The supercritical fluid extraction method is more cost effective as the solvent has not to be recovered and has been found to show less toxicity and pollution concerns. It is defined as the process of separating one liquid from another using a supercritical fluid as a separating agent. Carbon dioxide is the most commonly used extracting agent, however may times it uses methanol or ethanol as a solvent. The process is done mostly above the temperature of 31° C and 74 bar of pressure to keep the carbon dioxide in supercritical state. The features of the supercritical fluid can be shifted by varying the pressure and temperature, allowing selective extraction. Lipids can be eliminated using pure CO_2 at higher pressures, and then phospholipids can be removed by adding ethanol to the solvent. The cost of the SFE operation could be further reduced by planting the process near coal fired power plant where carbon dioxide is readily available. Figure 3 shows a diagram of a typical SFE apparatus.

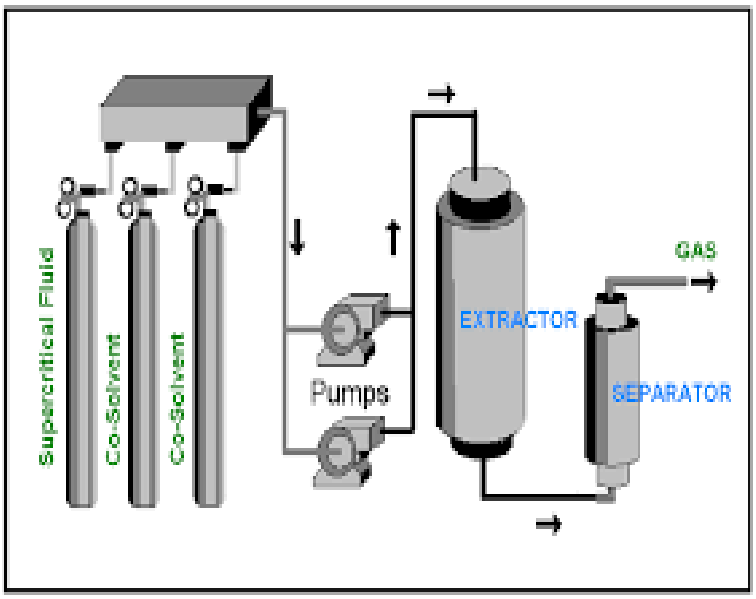

Figure 3: sfe apparatus with coslovent chambers [22]

The carbon dioxide is heated slight above its critical temperature and supplied under supercritical pressure to the extraction area where microalgae is placed where it does the extraction and could be further recycled for reuse. Suganya T et. al. while extracting lipid from Schizo chytrium limacinam obtains around 40% of lipid [23]. Crampton et.al conducted lipid extraction from Pavlova at 50Mpa and 60^{0} C obtained 18% of lipid yield [24]. Seo et.al. extracted lipids from B. Braunii and obtained 28% of yield [21]. Thus, the yield of lipid depends upon the variety of the strain being targeted as well as the operating conditions. The amount of lipid extraction increases with temperature but the rate of extraction diminishes along with the increase in duration of the process [25].

Effect of temperature and time on lipid yield

Total lipid yield increases along with increase in temperature but the rate of extraction decreases along with the duration. Mouahid et.al conducted the extraction process over 20 gm of soaked microalgae at 30 Mpa pressure and at temperatures of 60^{0}C and 80^{0}C and found the results as shown in table3 [25]. It was found that at 60^{0}C yield was higher as compared to 80^{0} C.

Table 3: Effect of temperature on lipid yield

Time(mins)	Yield (60^0C)(%w/w)	Yield(80^0c)(%w/w)
20	0.035	0.025
40	0.056	0.032
60	0.057	0.035
80	0.058	0.035

Effect of pressure on lipid yield

The experiments when conducted on 20g microalgae at 60^0C resulted into increased lipid yield by increasing the pressure. The rate of lipid extracted also increased along with the time for which pressure was applied [25,26]. The experiment was applied using different sets of pressure and different parameters of time. Table 4 shows the variation with pressure.

Table 4: Variation of lipid yield with pressure

Time(mins)	Yield(10Mpa)	Yield(20Mpa	Yield(30Mpa)
20	0.003	-	0.035
40	.000.009	-	0.056
60	-	0.024	0.057
80	-	0.029	0.058

Effect of crushing

Due to the presence of cell wall which poses a challenge in lipid extraction, it was found that the well crushed microalgae gave better yield as compared to non-crushed or partially crushed algae. Thus it was clear that if the cell wall of the lipid is destroyed, lipid yield increases [27].

Effect of coslovent

It was also found that the co solvent plays a major role in the lipid extraction. In Experiments done over Hexane, ethanol and Acetone, Ethanol gave the maximum amount of lipid yield [26, 27].

Table 5: Use of different co solvents and yield

Solvent	Total yield (%)	Lipid/dry biomass (%)
Acetone	60	4.7
Ethanol	73	5.7
Hexane	33	2.6

Conversion of Algal oil to Biodiesel

After the lipid is extracted, next step remains are the conversion to Biodiesel. For this purpose, either thermos-chemical or biochemical process could be used. The conversion is done using Transesterification process in which glycerides are converted to fatty acids which is the biodiesel. In a conventional twin step process of transesterification, firstly the lipids are extracted from the stock and then they are converted to biodiesel. The conversion process summates over the transformation of triglycerides into di-glycerides and later the conversion of di-glycerides into mono-glycerides which is further translated to fatty acids and glycol (which is a byproduct of the process). During the process different researchers Have used different catalysts. Miao et.al. used calcium oxide obtained from recycled chicken eggshells as a catalyst and got a recovery of 95% [28].

However, this two-step process is not only time and cost intensive but at the same time quite complicated. In order to remove this overlapping task, the extraction and the conversion process is carried simultaneously where the same alcohol that acts as a solvent for extraction acts as the agent for biodiesel conversion via esterification [29-30]. Bankovicet al. used ultrasound methanolysis process and achieved almost 80% of biodiesel yield [31].

Engine performance

Makareviciene et al conducted the experiment with a B20 (20% of algal biodiesel blended with 80% of pure diesel) and found that the effective utilization of heat produced during the combustion process was quite lower than the pure diesel. This happened due to less volatility of algal biodiesel. However the physical and chemical properties were quite closer to that of pure diesel [32].The experiment was conducted on a Ricardo E6 indirect injection diesel engine over ME20 and ME10 (algal oil with 20% of methanol and algal oil with 10% of methanol) and found that the combustion properties were quite closer to the pure diesel, however engine torque was found to be less and the noise increased, showing a requirement of engine design modification [87].Table 6 shows the comparison of algal biodiesel oil with diesel[32-37].

Table 6: Comparison of algal biodiesel oil with diesel

Properties	Diesel	Microalgae Diesel	European norms
Density(kg/m^2)	8333	886.02	867-895
Viscosity(cSt)	2.36.7	4.473	3.5-5.1
Flash point(^{0}C)	58.51	165.52	120 Min
Cetane number	56.463	48.312	51 Min
Calorific value(kj/kg)	45,253	40,891	-
Cloud point(^{0}C)	6.1	7.1	-4.1
Pour point(^{0}C)	-10.2	-12.3	-1-041
Sulfur (mg/kg)	-	8.14	10 Max
Water (mg/kg)	59.1	220.1	500 Max
Acid value(mg KOH/g)	-	0.374	0.5 Max
Iodine value(gj$^{2/100g)}$	-	91.123	120 Max

Engine emissions

Jaya Prabhakar et al. conducted the experiment on a kirloskar four stroke single cylinder engine and found that the exhaust emissions of microalgae diesel blend were quite less than pure diesel. The engine running on the blend consumed more fuel due to reduced volumetric efficiency of the engine as compared to that run on pure diesel [37].

Conclusion

From the above discussion it is very clear that micro algae have a great scope in the field of science and technology. Its easy availability will turn out to an advantage in the quest for a renewable low cost fuel alternative. Once the production is commercialized it would also open up pathway for self-employment for a huge amount of people. Moreover, it can also be helpful in reclaiming waste lands. The study of Jaya Prabhakar et al. shows that microalgae has a potential to be used as an alternative to diesel fuel and gives promising results.

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