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Algal bio fuel as an alternative energy source: A review

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Abstract
World population is increasing day by day alarmingly at the same time dependence on fossil fuel increases. As a result of this fossil fuel has become expensive and is near to exhaust. Usage of fossil fuel is creating harmful impact on environment and living biota. The energy crises, especially depletion of fossil fuels has become serious issue. In other way use of fossil and its end products are threatening the life by environmental pollution, global warming, greenhouse effect and rains.
In these conditions algal biofuel is only alternative and renewable source to replace the fossil fuels. It mitigate the harmful effects of fossil fuels on environment and it assist in maintenance of the healthy environment. The main causes for this are high yields, a near-continuous harvest stream, and the potential to site the algal bioreactors on non-arable land. Production of fuel from algae biomass can be done by different approaches as mechanically and non-mechanical way. Extract the biofuel from algae can be done by numerous ways. The most commonly use method is Trans esterification. Conversion of triglycerides into esters and glycerol by using different catalyst is the main strategy of trans esterification.

Keywords: Algal biofuel, trans esterification, renewable energy, enzymatic extraction, algae

1. Introduction
Worldwide population is increasing exponentially and right now requirement of energy also increased. As a result of this consumption of fossil fuel increases. More than 88 % of world population depends up on fossil fuel [5]. Technology development, rise in population, climate change leads to the use of fossil fuel in high rate as a result of this exhaustion in resources and increasing greenhouse gases(GHGs) emission and build-up of GHGs in environment. This impose effect dangerously on biota and environment [36].
Presently world critically facing energy crisis. Over the world many countries are still deeply reliant on fuels as their core source of electricity and transportation fuel. Owing high use and exhaust of fossil fuel leads to increase the price highly in recent days. Hence the only possible solution to overcome energy crisis and their harmful impact on environment, biota is find out a renewable and feasible energy source. There are many renewable energy sources i.e. solar energy, wind and biomass. Among all production of biofuel from algal biomass is the feasible, economically viable and eco-friendly energy source [11, 17, 24].
Biofuel refer to is a liquid or gaseous renewable fuel produced from natural sources. Different types of biological sources can be used to produce biofuel, they are biodegradable, carbon neutral, eco-friendly, sustainable. Bioethanol, bio methanol, biodiesel and bio hydrogen are some varieties of biofuels which are attractive options for transport, industry and other sectors in future those are depend on fossil fuel [44]. At present, numerous countries such Australia, Brazil, Germany, Italy and United States are using biofuels such as bioethanol and biodiesel. Probable this trend will endure to grow and more countries will use biofuels [12, 18].
Among all energy sources oil consumption was more followed by coal, natural gas, renewable source, others, hydro, nuclear energy sources. It is suggesting that usage of liquid energy is more relative to other forms of energy sources (Fig.1).

2. Biofuels as Alternative To Fossil Fuels
The first generation biofuels have reached commercial level and already established in USA, Brazil, and the European Union. These biofuels are mainly derived from food and oil crops including sugarcane, sugar beet, vegetables oil sand animal fats. However impact of these biofuels in transportation sector is still limited due to directly competing with food crops and use in agriculture [1, 5].

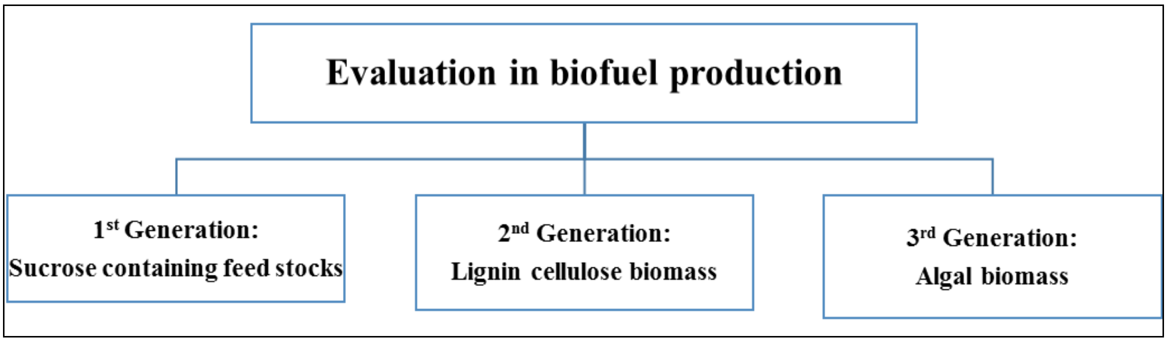
The Second generation biofuels derived from biomass sources are mostly agricultural residue, forest harvesting residue and wood processing residues and nonedible components from food crops along with cultivation of nonfood crops such as jatropha, mahua, tobacco seed and miscanthus [2] Therefore they are not directly competing with arableland and have a lower environment impact than first generation. Howe ver, second generation biofuels have low conversion rates and the conversion processes are not economically feasible at this moment [2, 1].

3. Comparison of Various Biodiesel Sources

Biofuel derived from microalgae are classified as third generation biofuels and have potential for large-scale production. Table1 shows various feed stock for biofuels production, from the table microalgae seems to be the only possible feed stock to completely replace fossil fuel.

3.1 Sources of biofuel production

According to [13], they classified Evaluation in biofuel production in to three categories, i.e. 1st, 2nd and 3rd generations.



3.2 Third Generation Biofuels from Algae

To eradicate and mitigate the vulnerability of energy sector there were variety of biofuel species recommended to substitute fossil fuel. Among all biodiesel and bioethanol fascinated which synthesis from terrestrial plants though owing to requirement of more land area to cultivate has become more hypothesis [15].

In order to overcome this controversies cultivation of algae at sea water or industrial or other wasters gives a conceivable solution [9]. Algae are green unicellular oxygen producing microalgae containing chlorophyll ‘‘a’’ and a potential renewable fuel source [5]. Some variety of algae classes habitation fresh water, others in seawater [8, 36].

Microalgae have the potential to generate significant quantities of biomass and oil suitable for conversion to biodiesel. Microalgae have been estimated to have higher biomass productivity than plant crops in terms of land area required for cultivation, are predicted to have lower cost per yield, and have the potential to reduce GHG emissions through the replacement of fossil fuels [5, 9, 36]. Algae are classified 5 types those are Brown, Green, Red, Blue green and Yellow green algae based on pigmentation [13] (Table 2).

4. Algal Biofuel Production

Production of Biofuel from algae is both economically and environmentally sustainable [9]. Selection of algae species is the vital part in production of biofuel from algae since variety of algae species consist different percentage oil in their cells. Table 3 shown percentage of oil in different algae species. Biofuel production from algae is a multifaceted process. It includes following phases shown in Figure 2 & Table 4. This process includes following phases: 1) Cultivation of algae 2) Harvesting 3) Drying & processing 4) Trans esterification

4.1 Cultivation

There are different ways to cultivate the algae among all, two basic methods uses widely i.e. first one Photo bioreactor method and second one Open pond system.

1. Photo bioreactor (PBR) method

In this system microalgae are culture in enclosed transparent recipient. These recipient available in different size and shape.

Advantages includes: Low capital cost, relative easy maintaining, high surface volume ratio, high productivity per unit area, and the possibility of easily controlling various parameters [39].

2. Open pond system

Open pond cultivation is carried out in shallow basins open to the environment. The most common types are raceway, circular, inclined and unmixed. They are considered relatively inexpensive and easy to construct, as long as the area is relatively flat. Cultivation can be made directly over the soil or some simple surface covering can be used to minimize water loss due to seepage, and other improvements can be made to increase solar energy capture, and decrease contamination issues

4.2 Harvesting And Biomass Concentration

After cultivation of algae next phase is the harvesting it consist different methods among most common harvesting methods as follows sedimentation, filtration, ultrafiltration and flocculation [16].

Selection of harvesting method depend on many factors such type of product, quality of product and density of algal biomass. Among those desired product quality is one of main criteria. Gravity sedimentation is used for low quality desired products and for high quality require products centrifugation is recommended one [33]. Processing is prominent step after harvesting of algal biomass (5-15%) from culture medium to prevent spoilage by hot climate.

4.3 Processing

In this stage the main principle is the algal biomass forward to dehydration to maintain quality and increase its shelf life. There are several methods have been practiced to dry the algal biomass where the most common one consist spray-drying, drum drying, freeze-drying and sun drying [33].

4.4 Extraction of Oil Form Algal Biomass

Extraction of lipids and free fatty acids from processed algal biomass is the next phase. A number novel methods are available for the extraction of algal lipid and it is depends on type of product and algae cell wall. According to Boyd *et al*. (2012)Extraction methods classified into two types includes mechanical action **(**e.g. cell homogenizers, bead mills, ultrasounds, autoclave, and spray drying) or non-mechanical action (e.g. freezing, organic solvents and enzymatic action, ultrasonic extraction)

4.4.1 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.

4.4.2 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, ethanol (96%), or a hexane–ethanol (96%) mixture uses to obtain up to 98% quantitative extraction of purified fatty acids 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 [33]**.**

4.4.3 Ultrasonic extraction

The ultrasonic extraction of algae oil involves intense sonication of liquid which generates sound waves that propagate into the liquid media resulting in alternating high-pressure and low-pressure cycles. During the high pressure cycle ultrasonic waves support the diffusion of solvents, such as hexane into the cell structure.

As ultrasound breaks the cell wall mechanically by the cavitation's shear forces, it facilitates the transfer of lipids from the cell into the solvent. After the oil dissolved in the cyclohexane the pulp/tissue is filtered out. The solution is distilled to separate the oil from the hexane. Ultra-sonication not only improves the extraction of oil from the algae cells but also helps in the conversion into biodiesel. The large scale application of this method is not feasible as it is not cost effective with the amount of oil production [10].

4.4.4 CO_2 Super Critical Extraction

The CO_2 super critical extraction is the most advanced oil extraction method, besides some disadvantages like elevated pressure requirement and high capital investment for equipment. It has got large number of advantages like, the biomass residues that remains after extraction of oil could be used partly as high-protein animal feed and, possibly, as a source of small amounts of other high-value micro algal products.

The algal biomass residue remains after oil extraction can also be used to produce biogas by an aerobic digestion. Which can be further used the primary source of energy for most of the production and processing of the algal biomass. An Additional income could come from the sale of nutrient-rich fertilizer and irrigation water that would be produced during the anaerobic digestion stage. The technology for anaerobic digestion of waste biomass exists and is well developed, and the technology for converting biogas to electrical/mechanical power is well established. The carbon dioxide generated from combustion of biogas can be recycled directly for the production of the micro algae biomass [10].

5. Conversion of algal oil into biodiesel (Tran's esterification)

Biodiesal production is the process of producing the biofuel, biodiesel through the chemical reactions (Transesterification and esterification). Biofuel is a combination of fatty acid alkyl esters. Production of biofuel from microalgae can be done using several well-known industrial processes, among all the most commonly used method is the transesterification. Transesterification, also known as alcoholysis [4].

Transesterification is process in which triglycerides are converts in to diglycerides, and then mono glycerides by reacting with alcohols. Finally monoglycerides converts into esters (biofuel) and glycerol (by-products). These process driven by catalyst. It improves the reaction and yield [41]. The transesterification reaction is represented by the general equation show in the following equation.it consists in three equivalent, consecutive and reversible reactions. The triglyceride is converted stepwise to diglyceride, monoglyceride and finally glycerol and esters. At each reaction step, one molecule of methyl or ethyl ester is produced for each molecule of methanol or ethanol consumed.

Triglycerides →Diglycerides →Mono glycerides → Esters & Glycerol (by –products)

(Triglycerides + 3 CH_3OH)↔Esters +Glycerol)

In this reaction fats or oil (triglyceride) react with an alcohol and form fatty acid alkyl ester and glycerol. Its requires 3:1 molar Catalyst (e.g. alcohol) to oil ratio.

Trans esterification process can be done in numerous ways consist by using different catalysts such as acid catalyst, an alkali catalyst (KOH, NaoH), enzyme catalyst and heterogeneous catalyst however enzyme catalyst are use rarely due to their low affectivity. The alcohols used should be of low molecular weight, ethanol being one of the most used for its low cost. However, greater conversions into biodiesel can be reached using methanol. Although the transesterification reaction can be catalyzed by either acids or bases the most common means of production is base-catalyzed transesterification and the alkali-catalysed trans esterification is about 4000 times faster than the acid catalysed reaction. This path has lower reaction times and catalyst cost than those posed by acid catalysis. The catalyst is prepared by mixing methanol and a strong base such as sodium hydroxide or potassium hydroxide. During the preparation, the NaOH breaks into ions of Na+ and OH-. The

OH- abstracts the hydrogen from methanol to form water and leaves the CH_3O- available for reaction. [43]. Base-catalysed transesterification reacts with alcohol (typically methanol or ethanol) to produce biodiesel and an impure co-products, glycerol.

6. Benefits of using algae for biofuel production

The utilization of microalgae for biofuels production can also serve other purposes. Some possibilities currently being considered are listed below.

Micro algae are becoming important as source of biofuel due to the following momentous advantages over plants and seed.

- Algae grow rapidly at high rate with solar energy conversion efficiency higher than other terrestrial plants due to their simple structure [30, 37].
- Yield oil is approximately 30 times (20-50 % of their biomass) more than the terrestrial oil seed plants [30, 38].
- Algae use waste CO_2 sources, thereby, potentially mitigating the emission of GHGs into the atmosphere while biofuel production [30, 38].
- According to [34, 40] cultivation of algae needs less water than terrestrial crops. Moreover they have ability to effectively grow on non-arable land, in nutrient rich environment and saline water.
- Synthesis oil from algae throughout the year hence can culture algae all over the year and gives high oil yield over other biofuels [37, 38].
- In addition cultivation of microalgae in sewage effluent, industrial waste water can mitigate and reduce the eutrophication in the aquatic environment.
- It does not require application of pesticides and herbicides while culturing [37, 38].
- A number of by products can also be produced from resulting biomass after biofuel extraction such as food, feeder, fertilizer, antioxidant, polysaccharides, pharmaceuticals, biopolymers etc. which can be utilized by human [42].
- In biotechnology algae have a countless impending of producing ethanol due to low content of lignin and hemicellulose as compared to lignocellulosic plants [46].
- According to [26] in biotechnology algae using potentially for production of ethanol owing to consisting of low lignin and hemicellulose as matched to lingo cellulosic plants.

Table 1: (Yusuf Chisti, 2007)

Crop	Seed oil (%oil bywt)	Oil yield (Loil/ha year)	Land area Use (m2 year/kg biodiesel)	Combustion heat (kJ/g)
1st Generation				
Corn	44	172	66	-
Hemp	33	363	33	-
Soybean	18	446-636	18	38.37
Sunflower	20.1	779		-
2nd Generation				
Castor	48	1307-1413	9	
Jatropha	20–60	1892	15	39
Polanga	65-75	20000		
Oil palm	36	5366-5950	2	38.3
3rd Generation				
Microalgae	30-70	58.7-136.9	0.1-0.2	-

Table 2: Classification of algae based on their pigmentation (Dragone *et al*., 2010)

	Colour	Group
1	Brown algae	*Phaeophyceae*
2	Green algae	*Chlorophyceae*
3	Red algae	*Rhodophyceae*
4	Cyanobacteria	*Cyanophyceae*
5	Yellow-green algae	*Xanthophyceae*

Table 3: Oil percentage in different algae species (Chisti, 2007)

S.no.	Species	Oil (%)
1	*Ankistrodimus* TR-87	28-40
2	*Botryococcus braunii*	29-75
3	*Chlorella sp.*	28- 32
4	*Chlorella*	15-55
5	*Cyclotella* DI-35	42
6	*Crypthecodinium cohnii*	20
7	*Cylindrotheca sp.*	16- 37
8	*Dunaliellaprimolecta*	23
9	*Dunaliellatertiolecta*	36-42
10	*Hantzchia* DI-160	66
11	*Isochrysis sp.*	25-33
12	*Monallanthussalina*	20
13	*Nannochloris sp.*	31
14	*Nannochloropsis sp.*	46
15	*Neochlorisoleoabundans*	35-54
16	*Nitzschia* TR -114	28-50
17	*Phaeodactylumtricornutum*	31
18	*Schiochytrium sp.*	50-77
19	*Tetraselmissueica*	15-32

Table 4: Process and steps for production of biofuels from macro algae and microalgae.

Steps for process	Seaweeds or Macro algae	Microalgae
Cultivation	Natural stocks, drift material cultivation (near-shore systems, off-shore systems, open ponds)	Cultivation (photo bioreactors, open ponds)
Harvesting	Manual mechanised	Flocculation flotation sedimentation centrifugation Filtration
Drying & processing or De-watering/Pre-treatment	Cleaning/washing crushing maceration	Dewatering drying
Conversion to biofuels	Biochemical processes: anaerobic digestion (AD) fermentation	Biochemical processes: AD Fermentation thermochemical processes: gasification hydrothermal liquefaction pyrolysis direct combustion trans-esterification and biodiesel production

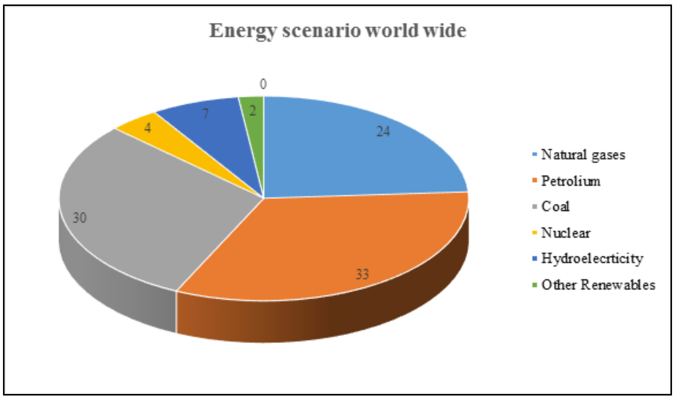


Fig 1: Energy scenario over the world

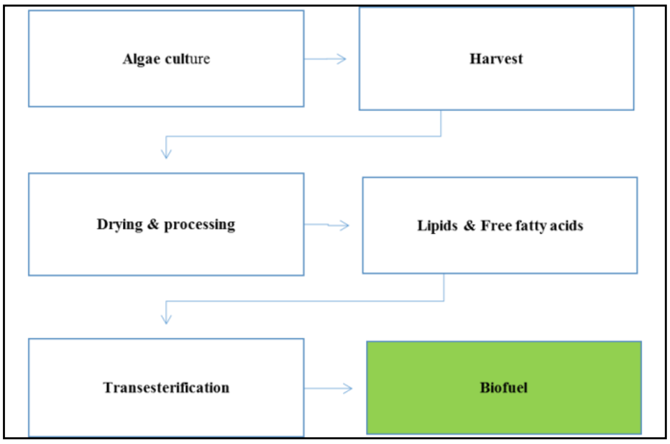


Fig 2: Flow chart of algal biofuel production

7. Conclusion

The present review is addressed to various aspects of biofuel such as enlargements in algal culture and biofuel production technologies and variety benefits of algal biofuel as compared to the other biofuels. Moreover in this review we covered sources of bio fuel, variety of best suitable biofuel algal strains, biofuel production and lastly benefits of using algae for biofuel production. In this article we also discussed the variety of algae cultivation methods and their advantages. This study also reveals the various methods to extract the algal oil and underlines extraction of biofuel from lipids and free fatty acids of algae. This article highlight's the application and utilization of third generation biofuels as the suitable alternatives for fossil fuels exhausting. As reviewed above, algal biofuel is only alternative and technically viable fuel resource. It completely replace the fossil fuels.

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