International Journal of Water Resources and Environmental Sciences 1(2): 43-66, 2012
ISSN 2311-2492

DOI: 10.5829/idosi.ijwres.2012.1.2.1110

A Review: ALGAE Used as Biofuel

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Abstract: Increase in the fuel prices, pollution and growing needs making the worlds concern towards biofuel, making the world independent of the fossil fuel. Algae proves to be the best for biofuel production because other plants used in biofuel production are important food sources and require large area for biomass production. This review involves the biofuel production from algae. Algal biofuel play vital role in the sustaining environment by CO_2 absorption and by replacing the fossil fuel. One of the best thing about the biofuel is that biofuel is renewable. Algae are cultured in control conditions and harvested and then its autotrophically synthesized lipid content is extracted from it and fermentation produce ethanol which along with sodium methoxide catalyze the triesterification of triacylglycerol (TAG) this triesterification result in biofuel. Certain byproducts are also produced during this process which includes bioethanol, bio methane, biobutanol, hydrogen with the main product of biodiesel. It is recommended Algal biofuel must be applied on large scale to escape from energy crises and depleting fossil fuels.

Key words: Biofuel · Transesterification · Lipid · Photobioreactor · Microalgae · UOG

INTRODUCTION

Biofuel as a renewable biofuel is a burning issue and seeking popularity day by day in the countrieswhich are dependent for their energy requirements as making them independent.Biofuel technology joining basic and applied sciences and bringing about economic benefits by generating jobs and advocating the emanatingbioenergy industry andmarket [1,2]. Biofuel is solution to two major problems, the energy crises and pollution.Economy truly rely on energy, followingthe present situation the planet requirement will increase by 60% in 2013 [3]. About 70% of the total global energy consumption correspond to fuel,out of which 27% is consumed in transportation and about 30% toelectricity, biofuel aiming to fulfill the approximately 10% biofuel for vehicles by 2020 of European Unionso liquid fuel is in demand [4].

Biofuel is the solution to pollution. Amassmen to fcarbon dioxide in the atmosphere is of great concern, resulting in globalwarming. About 20 billion carbon dioxide because of fossil fuel burning and 2-8 billioncarbon dioxide because of human mediated oxidation [5]. Transport sector have major contribution in amassment of carbon dioxide and consequently GHG emitter increasing global warming [6].

Algal biofuel is also a solution to the problems mentioned above. It belongs to non-vascular plant that may be single celled referred as microalgae or multicellular known as macro algae including cyanobacteria. Algae are most diverse autotrophic organisms having the ability of greater biomass and lipid production [7,8]. Lipid content in microalgae is mainly composed of 50-60% of unsaturated fatty acids and valuable amount of Palmatic acid is also present and talking about unsaturated fatty acid linoleic and polyunsaturated content in 12 and 1 % respectivelyfor biodiesel production[4].Commonly 20-60% of dry biomass weight of total lipid content, its sometime more than 80% in some microalgae depending upon their cultivation conditions [9] e.g. it has been found 28% lipid content in *chlorella* sp.Algae can grow vigorously when provided with appreciable amount of nutrients and a favorable temperature pH and light, chlorella would be the best for dense cultivation [10]. Algae may be cultivated in two types of systems, open pond and enclosed Photobioreactor [11, 12]. The photosynthetic products of algae are important predecessor for biofuel production. Cultivated algae is harvested and subjected for biomass processing which involve dewatering, thickening, filtering and drying. Oil is extracted for the biodiesel production [9]. Leftover is mainly composed of carbohydrate and

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proteins. Carbohydrates can be fermented into ethanol [13]. This ethanol serves as a catalyst for transesterification. Algae are the most preferable for the biofuel production because there is no involvement of agricultural land and its product and it involves the direct conversion of solar energy into biofuel with little carbon evolution and providing the low cost [14]. In previous researches it has been found that microalgae (136,900) can yield 10-20 times more biofuel production than other plants including Jatropha (1,892), Corn (172) and Canola (1,190) etc [4].

Cultivation of Algae: Algae cultivation and processing systems require a high capital input (higher than agriculture) [15]. Four basic requirements for algae cultivation are space,water, light and carbon. Bymaximizing the quality and quantity of these requirements, it is possible to maximize the quantity of oil-rich biomass and the return on investment. Ironically, this can often be done by using underutilized resources or waste products, which can provide additional benefits or even offset the cost of production [16]. Algae may be cultivated through these processes:

Raceway Pond System: This system is not expensive as compare to closed system and open system is more comfortable and have more production than closed system.Ponds are more susceptive to the environmental conditions ponds produce the more quantity of micro algae and occupy more area and more susceptible to contaminators from other bacteria [17]. High water loss in open system is due to evaporation [16]. Mechanical arm stirring in a circular pond motion or more commonly raceway pond ponds, natural sunlight is present in open system; opensystem has also the disadvantages. In open systems is affected by the atmosphere conditions of the open system depends on the environment e.g. sunlight, temperature etc. [18]. Race way ponds are cheap and easy to handle. Bad effect race way pond systems include contamination with waste species such asyeast, algae and bacteria, evaporation, diffusion of CO_2 to theatmosphere and less control over environmental effects, mainly temperature andsolar irradiation [18].

Photo Bioreactor: Most expensive system and modern than the raceway pond system because in open system we cannot control the environmental factors in open system so this condition pushed the scientist to design the closed systems or tubular photo bioreactors [19]. Photo bioreactors, based on containers, tubular or clear

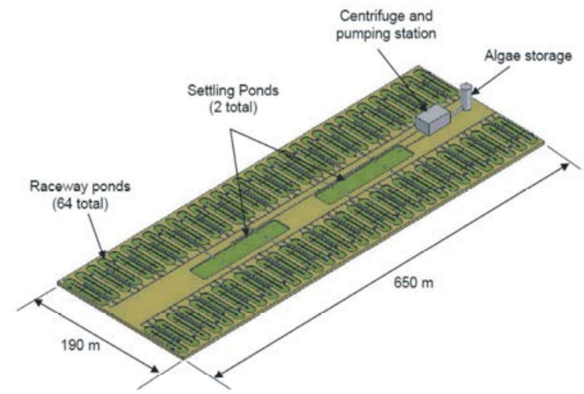

Fig. 1: Raceway system [21]

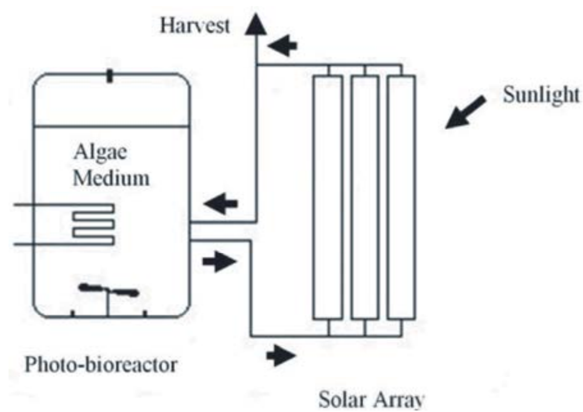

Fig. 2: Basic design of a horizontal tubular photobioreactor [21]

plastic bags, design in which vertical flat plat reactors pumped by air lift,In photo bioreactor system there is much control over the system [20].

Economic of Biofuel Production from Algae: Algae, a favorable substitute for biofuel [5]. Globally, biofuel production from micro-algae is being studied. The biodiesel production from algae, a chief encounter is its economics.it is intensely argued which kind of production methodology is most appropriate [22]. Micro-algae biomass production is usually much costly than crop. Assembly of algal oil demands an aptitude to reasonably make large amount of oil rich microalgae [20]. Biomass production, over-all lipid content and lipid yield are among main constraints that govern the economic viability of using micro-algae as a source of biofuel [10]. Cost effective production of fuel will need that we make use of algal biomass more efficiently [5].

Production charges for microalgae biomass were measured two systems; Photobioreactor and Open raceway p ond [22]. A fabrication system is equipped

Table 1: Comparison of systems[15]

Issue	Raceway systems	Photobioreactor
Cost	Cheap	Expensive
CO2	High	Itself low
Temperature	Usually low because of outgoing gassing	Build up in closed system requires gas exchange device
Cleaning	No issue	Cleaning often required
Biomass quality	Variable	Reproducible
Oxygen	High, depending on pond depth	Low
Biomass concentration	Low 0.1 to 0.5	High 0.5 to 8
Weather dependence	limited	Possible within certain tolerance

Table 2: Comparison of two production system in context of cost [26, 27]

	Raceway pond	Photobioreactor
Initial investment ($.L^{-1})	52	111
Production cost	$ per liter of biofuel produced	
Labour cost	$4.03	$2.96
Other production cost	$3.71	$6.37
Capital cost	$17.35	$15.56
Total cost	$15.09	$24.89
Credit from the sale of algae cake	$0.65	$0.29
Net total cost	$14.44	$24.60
Lipid content	15%	25%
Cost per kg of algae	$2.66	$7.32
Downstream processing	40% of total cost	

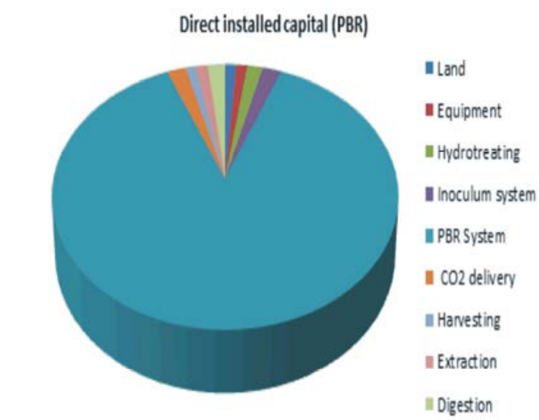

Fig. 3: Cost allocation of PBR [33]

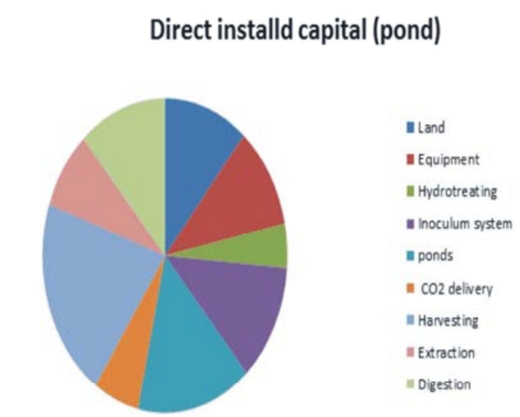

Fig. 4: Cost allocation raceway ponds[33]

towards an extraordinary return per hectare as it minimizes the comparative cost for plots, assembly material and certain maneuver cost [23]. Both method create hundred tons biomass and harvest 183,333kg CO_2 both methods are equate with maximum productivity and development concentration [24,25].

Raceway is thought to be cheap as compare to photobioreactor[28].Even thoughraceways areinexpensive they have small biomass output than photobioreactor(tabel.1) [29-31]. Biofuel production from algae is not reasonable yet, algal biofuel manufacturing can become economically reasonable within 10-15 year[26,32].

Challenges: Growing biofuel industry today is a vital sign by large, reasonable and viable feedstock. Commercialization of biofuel production from algae is still need to minimize the level of uncertainty and insecurity due to techno-economic constraints [34, 35]. The foremost defies now being lectured are following [36].

Harvesting: Microalgae embellish in metropolitan wastewater treatment pools, where they execute a waste refining function, however algal biomass harvesting is usually not adept and there is used a chemical flocculants to confiscate the algal cells that bound additional usage of the algal biomass moreover for biofuel purposes [28].

Production System: Methodological efficiencies related to algal biomass production that display considerable challenges for the advancement of economically feasible large gauge alga biofuel initiatives [37]. Photobioreactor present major operational defies and due to limitations of gas exchange, cannot be greatly commercialized about a 100cm^2. Open pond suffer from contaminations [37].

Genetically Modified Algae: Genetically modified algae is a major challenge because of its detriment effects on economic like sterilization of whole production system and incorporation of new species to the atmosphere [28].

Knowledge Gap: Algae machinery has lot of prospective, not only for algae based biofuel, however also use for food, fodder, Renewable compounds and many other things that are important for a more viable society [38].

Harvesting of Algae: There are different method of harvesting of biomass for each system cultivation but generally harvesting vessel is used for this purpose which cut the algae and drags it inward [39]. Low concentration during growth and few micrometer sizes of algae make its harvesting difficult and costly, contributing 20-30% of the total biomass production cost [40].

Algal Physiology and Biochemistry: Algae are photosynthetic organism use Carbon dioxide and water to oxygen use sun light and add carbohydrates and lipids and these lipids and carbohydrates with hydrogen and alcohols are major biofuel forerunner. So it is necessary to known about metabolic pathways and procedures that operate them in biofuel production. Under unfavorable condition such as high lightintensity some macroalgae start amassment of lipids e.g triglycerols(TAG). Some microalgae species h ave TAG (30-60% of dry weight) in efficient way [42]. Some algae such as cyanobecteria, have lipids contents less than 5% of total dry weight [43], but now this percentage reaches in 20% [41, 43].

Photosynthesis and Light Utilization: When algae are cultured photosynthetically,then photosynthesis is importantly determined in their yield, in contest of biomass production, in contest of growth effecting rate. Theoretical biomass yieldsa value that r anges from100-200 g\m^2\day [45]. Theoretical yield concept is crucial,helpful to carry out the productivity of photosynthetic studies in algae resemble to those that have been present carried in plants [44].

The majority of light that falls on a photosynthetic algal productivity at greater than not cultured in laboratory scale.Cells nearer to the light source have ability to take all the incoming light, reachingclosestcells, in high cell density productivity [45]. Oxidative damage is due to high light intensity. The large amount of heat is dissipated and known to be as wasted. To solve this problem,it was display that small size of chlorophyll antenna can raisedthe effectiveness of light usage [46].

Carbon Partitioning and Metabolism: Lipids and carbohydrates very helpful for biofuel production development and sketching the cultivation approaches. If know about carbon partitioning then will have widespread knowledge of metabolic passageway. Due to a variety of microbes from genomic and transcriptomic information, way analysis and prognostic modeling metabolic networks have been re-built [47]. Plant research also help to known about carbon flux in biosynthetic and degradative pathways [48-53]. In carbohydrates, lipids and proteins present in algae have less capacity to known about that how algal cells manage the fluctuationi.e. flux [55,56].

A connection between starch and lipid metabolism has been recognized. Starch is a general carbon and energy storage complex in algae,and shares the same precursor with the storage lipid TAG. So the starch and TAG may well be inter-convertible and potentially important for biofuel production.Starch is an essential storage compound and its separation lead oil addition.Recent study in higher plants lead that when starch production was reserved, plants seeds stored 40% a lesser amount of oil [52, 54]. These consequences show that starch synthesis related to lipid synthesis,but the nature of the interface is unknown.

Algal Carbohydrates: The cell wall of green microalgae is made up of cellulose and has starch as their main carbohydrate storage compound. Red algae and dinoflagelates used starch as energy sources. Brown algae and diatoms stored laminaria,mannitol (Carbohydrates) as storage food. *Cyanobacteria* storeglycogen [57]. These main food reserve polysaccharides are able for conversion to liquid biofuel. Some of algae totally lack cellulose and some lack cell wall completely. The cell wall of diatoms is made up of silica which is unique among all the algae.

Fermentation: Some microorganisms have ability to perform the process of fermentation; fermenting *laminarian* and mannitolfrom *Laminariahyperborean* to ethanol have been establish [58].

There are two approaches of fermentation to obtaining ethanol from algae[59].

- Standard fermentation

The fermentation is the process in which starches from algae are fermented by yeast and bacteria.

- Self-fermentation

Algae are fermented below dark anaerobic condition.

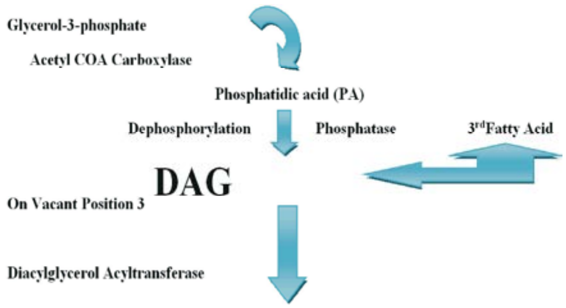

Fig. 5: TAG syntheses by KENEDDY PATHWAY [60]

Lipid or TAG Synthesis: In Algaebiosynthesis of TAG takes place by Kennedy pathway as in plants. Fatty acids produced in the chloroplast are transferred from CoA to glycerol 3-Phosphate at position of 1 and 2 which yields the production of phosphatidic acid [60].DAG is formed from dephosphorylation of DAG in the presence of an enzyme called phosphatase [60]. Third fatty acid attach to the vacant position 3 of DAG catalyzed by specific enzyme diacylglycerol transferase. TAG is important precursor of fuel production [60].

Methods of Oil Extraction: Algal Biomass is most important for production of biofuel and yields about 30 times more oil than other crops [61]. For the production of biodiesel from algae there should be extraction of lipids from cells [62]. There are different methods for oil extraction.

Enzymatic Extraction: This is an easy method but costly in which solvent with cell wall degrading enzymes is used to extract the protein, carbohydrates and cellulose because oil is associated with protein. Cell wall is thickened so enzymatic action takes place [61].

Chemical Extraction: Benzene, Ether and n-hexane can be use to extract the algal oil.In this method oil and fat are extracted from solid material by repeated washing with n-hexane or petroleum ether. This method is known as Sox hlet method which is less costly and can be used at large scale but still there is a limitation due to poor extraction of polar lipids [63].

Ultrasonic Extraction: This method includes the low or high pressure cycle which is generated by noise waves accelerated by intense sonication of liquid. During high pressure cycle ultrasound facilitate the solvent such as hexane by breaking cell wall and oil is released into solvent after this solvent is distilled to separate oil [61].

CO_2 Supercritical Extraction: Beside some disadvantage it is the most advanced method [64]. To obtain the substantial solvent power compression of carbon dioxide takes place beyond supercritical point that is 31°C then this fluid is placed with algal material in extraction vessel. Carbon dioxide penetrates in material due to high diffusion and low viscosity like gas. Carbon dioxide is de-pressurized in separate vessels to collect less solvent residues. The biomass residues remain after oil extraction can be used as animal food with high protein content [65, 66].

Conversion of Algal Oil into Biofuel: After lipid extraction from algae conversion of this oil into biodiesel takes place by chemical processes known as transesterification which can be done by using Alkali catalyst, Acid catalyst and Enzyme catalyst [67]. Due to less affectivity of enzyme catalyst it is rarely used and alkali catalyst can faster the reaction 4000 times more than acid catalyst. Most affective catalyst is Sodium Methoxide [68].

Base Catalytic Transesterification: For the production of biodiesel algal oil must undergo transesterification process. This process requires 3:1 molar alcohol to oil ratio. In this reaction fat or oil combined with alcohol to form fatty acid alkyl esters and glycerol. Excess alcohol can be used as it provides driven the equilibrium towards product side [69]. Reaction completed in three step. In first step triglyceride is converted into diglyceride which is then converted into monoglyceride which lead to the production of biodiesel [70].

Comparison of Algae with Microalgae and Other Plants: Algae are most useful all theworld. They are also goodsource of biofuel production algae can be classified into various types that micro algae red algae. Bluemarble productivity of that indicated to removing alga from fresh wateralgae [71].

Many bioproducts produced during microalgae processing some bioproducts does not use in biofuel production such dyes and pigment but they have high values of bio active compoundsalgae also useful source for skin care many antibiotics have been introduced from

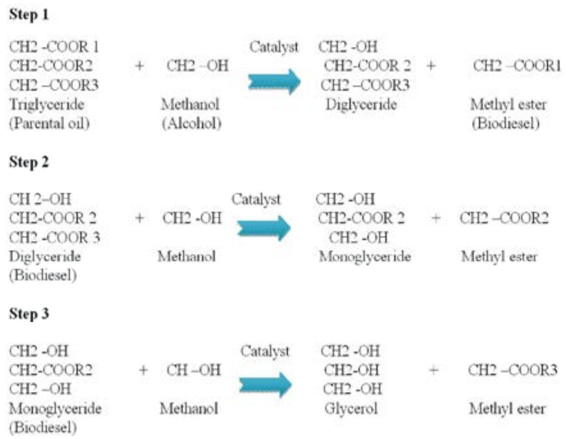

Fig. 6: Transesterification of oil to biodiesel.R1-3 are hydrocarbon groups[70]

Table 3: Production averages for common oil crops [78].

Plant	Oil/acre	Gallons of biodiesel/acre
Algae	6,757	700
Coconut	2,070	285
Jatropha	1,460	201
Rapeseed	915	126
Peanut	815	112
Sunflower	720	99
Soybean	450	62

microalgae the cyanobacteriaalgae spirulina provides many poly saturatedfatty compounds algae not used as primary source of human food means that it good source for biofuel and little impacts on food industry [72].

Microalgae: Second many waste products extracts produced during the processing of algae for biofuel can beused as sufficient animal feed particularly micro algae such as arachidonic, which are often reported in literature to provide manyhealth benefits and is important features that produce cellular biomass and oil [72].

Microalgaealso differentfrom other algae on the basis of color size and habitat [73]. They have higher growth rate than other algae.They also have high rate of biofuel production than other algae [74].

More recently research has been found on the application of metabolic to create microalgaewith optimized productivity of oilproduction and biofuel [75]. The average production of microalgae produces 1and 70 percent lipids and other algae average production of lipids is 90 percent.Biodiesel currentlyobtained fromplants animals not from microalgae [76].

Algae considered plant and classified separately because they lack true roots stems and leaves [76].

Photobioreactor and Microalgae: Microalgae in photobioreactor are used to produce biomass. This comparison is for once year productivity level of 100 of biomass in both cases. Both production methods save same amountofcarbon dioxide. Photobioreactor produce large amount of oil yieldperhectare compared with microalgae. This is due to volumetric biomass productivity of photobioreactoris more than 13 times larger in comparison.

Microalgae are technically feasible.Photobioreactors provide that can betrade to the specific demands of largely production of microalgae to obtain good annual yield of oil [77]. Other plants such as palm tree biodiesel from this plant. For palm oil sourced biodiesel to be competitive with petrodiesel. Microalgae oil can potentially replace petroleum as source of hydrocarbons [77].

Algae Are Used in Making Many Other Products

Fodder for Animals and Fish: They can be obtained from algal residues left after oilextraction and available in market [79].

Food: Presence of nutrients and vitamins in algae, people use it as food which include fats polyunsaturated fatty acid, oils are available in market[80].In Japan 1996 health food are consumed from microalgae of atleast 2400 tons [81].

Pharmaceuticals: A great variety of algal products are being obtained like antibiotics, antiviral or antifungal extracts.

Cosmetics: *Arthrospira* and *Chlorella* are used against skin care treatment e.g. anti-aging cream, collagen synthesis in skin and also in sun protection [82, 79].

Flue Gas CO^2 Emissions as Microalgae Nutrient: Alga need CO_2 as a reactant and bring forth the products of petroleum [82, 83]. Power plants are liable of 7% CO_2 emission from usable energy [81]. 15% CO_2 is excreted from industries [82] is an affluent source for cultivation of microalgae is a competent dispatch for CO_2 fixation [83].

Fuels from Algae: There are following types of algae based fuels

Biodiesel: Production of biodiesel from oil (lipid) by different methods forms (fatty acid methyl ester) FAME and glycerol, used in chemical manufacturing.

Bioethanol: It is used in place of petrol and is obtained by the fermentation of carbohydrate of algae with microbes or yeast. Cars, flexible vehicles can use approximately 10% and 85% ethanol respectively.

Biobutanol: Micro or macro algae are used in the production of biobutanol by fermentation. Higher amount of energy is obtained and is less mordant for internal combustion engine than ethanol.

Biogas: Its production takes place by anaerobic digestion from micro and macro algae by bacteria. Italtersorganic material into biogas having 60%-70% bio methane, while remaining is mainly consists of CO_2. It decreases the need for drying because in this process wet biomass is used. Nutrients carried in digestion biomass can regain from the solid and liquid phase.

Hydrogen: Some species of algae and bacteria are produced in the absence of oxygen. The production of this method is low and energy is excreted b y the cells to produce hydrogen and there is less potential for co-production [79].

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