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REVIEW PAPER

Algae as a Potential Resource of Biofuel: A Review

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ABSTRACT

In recent time, researchers are very much interested through worldwide to find out some alternative source of energy i.e. renewable energy in form of biofuels from cheaper raw materials by means of bioprocessing as well as biorefining to build up sustainable and green environment.Biorefining is sustainable biomass processing to obtain energy, biofuels and high value products through processes and equipment for biomass transformation. Biofuels are any solid, liquid or gaseous fuels that are derived from living plants or indirectly from agricultural, municipal, commercial or domestic wastes. First generation biofuel are derived from sugars, starch, vegetable oils or animal fats. Second generation biofuels are obtained from lignocellulosic biomass. Third generations biofuels are produced from algae. Algae as well as microalgae are classified as promising candi-dates in biorefinery processes because they are particularly important for obtaining multiple products. Moreover algae have recently gained attention as a potential feed stock for biofuels. Industrial reactors for algal culture are open ponds, photobioreactors and closed systems. Sea weeds are macro algae grown only in the sea and are a good source of phycocolloids. Phycocolloids are polysaccharides and considered as a good source of liquid fuel generation through fermentation. Microalgae appear to be the only source of renewable biofuel that is capable of meeting the global demand for transport fuels. This review paper clearly emphasized on the potential role of algae as well as microalgae to produce biofuels in form of biodiesel, bioethanol, bio-hydrogen and bimethane etc. via thermochemical and biochemical methods.

Key words *Algae, biofuel, photobioreactor, biohydrogen, bioethanol*

Algae as photoautotrophs can trap the solar energy and convert it into usable form. Algae can provide a suitable solution. They have a unique metabolism of sequestering CO_2 that can be redirected into biofuel production through photosynthesis. Algal fuel production reactors can be stationed near waste emission sources that could feed algae its nutrition and in turn provide valuable biofuels. Algae can be grown on deserted wasteland/marginal land. Moreover, algae are better photo synthesizers that can harvest upto 10 % of the incident solar light. Cyanobacteria and red algae contain phycobilisomes which make them more robust in the efficient absorption of polychromatic visible and far red irradiation. Moreover, unlike corn ethanol that can require up to 15 gallons of fresh water to produce a single gallon of fuel (Wu et al., 2008), algal cultivation does not require fresh water. Contrarily, use of algae can help address issues of fresh water scarcity since they can thrive in salt water and under harsh conditions (Um and Kim, 2009). Currently available alternatives that can be processed from algae include: biodiesel, high carbon fuels like isoprene, hydrogen and alcohols. Some of these fuels are already in various stages of development and commercialization. Both cyanobacteria and green algae can hugely impact the biofuel industry. Proof of concept studies have been carried out by several research groups demonstrating their feasibility. However, for a scale-up of these processes and wide scale industrial applicability the present processes face several technical limitations such as low yield and inherent light saturation limitations. To resolve these technical issues, the algae chassis must be optimized for biofuel production Overall, this article attempts to incorporate the recent advances to optimize the algal chassis and the recent advances in the production of various biofuels.

Genetic and Metabolic Engineering of Algae to Obtain Various Biofuels:

While talking about the next generation of fuels, besides energy efficiency, carbon neutrality of the fuel must be taken into consideration. As solutions to handle the waste emissions are discussed, algae can provide a suitable solution. They have a unique metabolism of sequestering CO_2 that can be redirected into biofuel production through photosynthesis. Algal fuel production reactors can be stationed near waste emission sources that could feed algae its nutrition and in turn provide valuable biofuels.

Biofuel from Algae

Figure 1 and 2 schematically represented the bioprocessing and subsequent production of biofuels in various forms respectively.

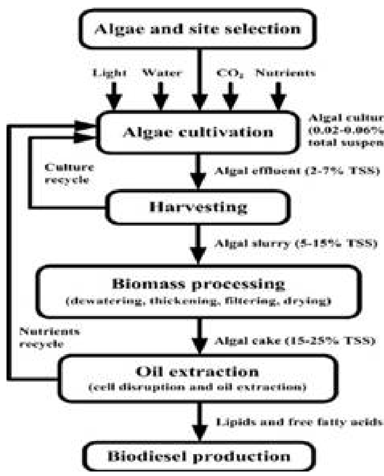

Fig. 1. Algal Bioprocessing

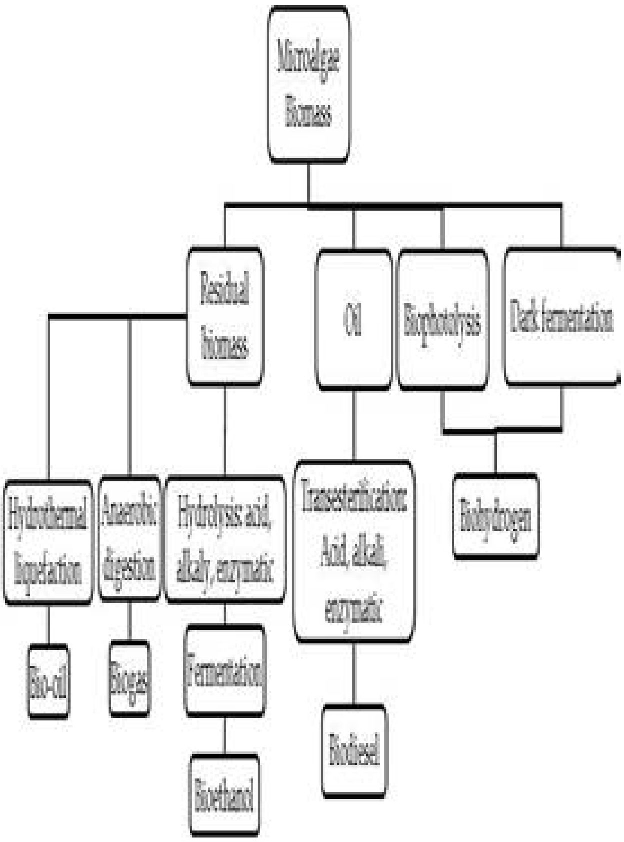

Fig. 2. Production of Biofuels

Algal Biomass Production by Closed Bioreactor

The most common type of closed bioreactor is tubular photobioreactor. Tubular photobioreactor consists of an array of straight transparent tubes that are usually made of plastic or glass. The solar collector tubes are generally 0.1 meter diameter or less in diameter because light does not penetrate too deeply in the dense culture broth that is necessary for ensuring a high biomass productivity of the photobioreactor. Microalgal broth is circulated from a reservoir (i.e. the degassing column in Fig. 3) to the solar collector and back to the reservoir (Chisti, 2007).

Bioalchohol

The first four aliphatic alcohols (namely methanol, ethanol, propanol and butanol) are of interest as fuels because they can be synthesized both chemically and biologically and they have properties that allow them to be used as fuel in internal combustion engines. Blends of ethanol with other fossil fuels have increasingly gained momentum in the transport industry. Deng et al., demonstrated the production of ethanol from *Cyanobacterium Synechococcus* sp. Strain. Recently, butanol has been explored for use as transport fuel. Butanol as fuel has advantage in the existing combustion engines since it has properties close to that of the combustion engines already in use. For a long time butanol production was reported by obligate anaerobes like *Clostridium sp*. Thus, the pathway is oxygen sensitive. Another category of alcohol the 'fatty alcohols' have recently been produced from the photoautotrophic organisms. They are also considered as suitable fuel additives due to favourable fuel properties. Generally fatty alcohols can be produced by two pathways: the fi rst pathway involves the reduction of the fatty acyl- CoA (acyl-ACP) to fatty alcohols. The alternate pathway involves two distinct enzymes, a fatty aldehyde forming acyl-CoA reductase which catalyzes a two electron reduction of fatty acyl-CoA to a fatty aldehyde intermediate, and a fatty aldehyde reductase which catalyzes the reduction of fatty aldehyde to fatty alcohol (Metz et al., 2000).

Bioethanol

In addition to lipids, microalgae biomass contains cellulose and hemicellulose, which can be used as a source of carbon in fermentation processes to produce ethanol (Harun & Danquah, 2011). An advantage of microalgae, in comparison with other crops used for bioethanol production, is their low lignin content, which is almost null in some strains. This allows skipping the biomass pre-treatment stage to perform the hydrolysis of cellulosic material directly. According to (Moen, 2008), brown microalgae give higher bioethanol yields in comparison with other algae species. These natural polymers have been used to obtain the reducing sugar from microalgae in multifunctional processes with a view to the joint production of biodiesel and bioethanol (González & Kafarov, 2010). (Ueda etal, 1996) and (Bush and Hall, 2006), patented processes for the production of ethanol from microalgae. A type of bluish green microalgae called cyanobac-teria

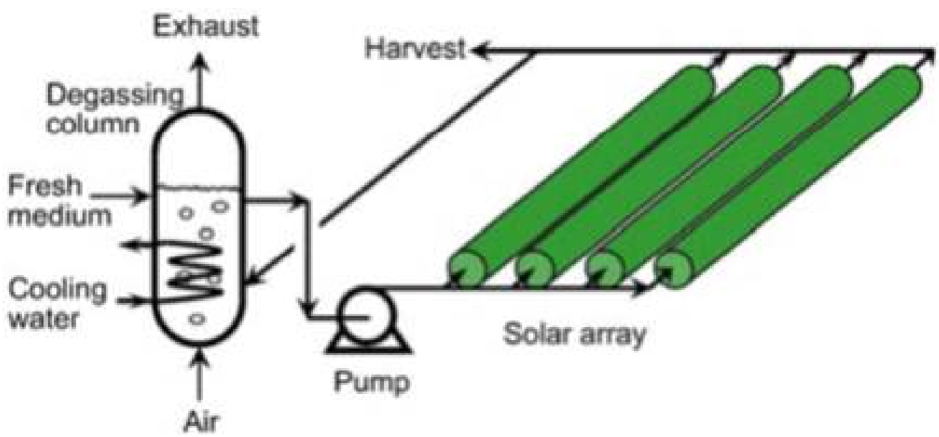

Fig. 3. A Tubular Photobioreactor with Parallel run Horizontal Tubes

produce bioethanol naturally without the need to implement methods to process biomass components (Amin & Wijffels, 2004). Since this bioethanol is the product of the metabolic activities of the strains, it can be extracted in vivo by milking, i.e. the addition of substances to the culture medium to stimulate the excretion of the desired product without the need for genetic manipulation.

Biohydrogen

Hydrogen as a fuel has been shown to be attractive primarily because on combustion it produces water as the only "waste emission". Photoautotrophic organisms are considered as attractive alternatives because they can generate their own feed stock reserves and require only water and sunlight to produce hydrogen. Most known hydrogenases are oxygen labile, and cyanobacteria and green algae are the only known organisms so far that are capable of both oxygenic photosynthesis along with hydrogen production. Efforts are ongoing towards the realization of stable optimal hydrogenproducing algae in an effort to replace a part of our current fossil fuel needs.

Biodiesel

Biodiesel is of significant importance because it has properties similar to that of petrol diesel and can be used with the current available infrastructure. Biodiesel is essentially fatty acids with long alkyl chains used by cells for energy storage and chemical production. It is a clean burning fuel made by the trans-esterification of the triacyl glycerides purified from photosynthetic plants or algae. Microalgae have the ability to accumulate oil in the form of triacylglycerides (TAGs) (Chisti, 2008). However, the lower yields limit their industrial application. Present efforts to obtain high yield biodiesel from photosynthetic microorganisms have been focused on the green algae, *C. reinhardtii* (Msanne et al., 2012). With the availability of the complete genomic information, many genes required for lipid and tri acetyl glycerol biosynthesis have been identified (Riekhof et al., 2005). Researchers have demonstrated that targeted metabolic manipulations can be used to increase lipid accumulation in eukaryotic microalgae without compromising growth.

Biogas

Anaerobic digestion can be applied on microalgae biomass to produce biogas, which is composed mainly by methane and carbon dioxide. This methane is used as fuel itself or can be used to produce other kinds of energy through combustion. This process shows different yields depending on microalgae strain used, reaching values from 0,2 m3/kg to 0,5 m3/kg (Harun *et al.,* 2010). Operating conditions for microalgae biogas production using anaerobic digestion must be optimized, taking into account reaction conditions (mesophilic or thermophilic), temperature, time, organic loading, solid retention time and pH. Main challenge of this techno-logy is related with the reduction of production costs in comparison with other feedstocks, for this reason, among others, commercial production of biogas form microalgae is not implemented yet (González & Kafarov,2011)

High Carbon Compounds

Carbon compounds with C4-C23 length possess higher energy density, hydro-phobicity and compatibility with existing liquid fuel infrastructure and are the predominant constituents of gasoline, diesel and jet fuels (Peralta-Yahya et al., 2012). Heptadecane is the most common alkane found in algae. Short and medium chain alkanes have the potential to be used directly as transportation fuel and have been reported to be secreted by a diverse group of organisms. Algae produce high amount of lipids. It is feasible to convert these lipids into desired alkanes via the formation of aldehydes. Aldehydes to alkanes are catalyzed by a decarboxylase enzyme. Not all alkanes are produced naturally by algae. Optimizing the expression of the alkane biosynthesis genes and enhancing the carbon flux through the fatty acid and alkane biosynthesis pathways can lead to the accumulation and/ or secretion of notable amounts of alkanes. Further, it also becomes important to understand how to control the chain lengths of the produced alkane molecules. Isoprenoids, e.g. the monoterpene pinene and the sesquiterpene farnesene, are considered precursors for future biodiesel or next-generation jet fuel. Cyanobacteria produce carotenoids and extending the carotenoid biosynthetic pathways by introduction of constructs for appropriate terpene synthases should allow the biosynthesis of selected mono and sesquiterpenes. In microalgae, isoprenoids are synthesized via the methylerythritol (MEP) pathway using glyceraldehydes-3-phosphate and pyruvate to generate the basic building blocks of isoprenoid biosynthesis, isopentyl diphosphate (IPP), and dimethylallyl diphosphate (DMAPP). Molecules that could potentially work as gasoline substitutes including isopentenol have been produced by *E.coli* using isoprenoid biosynthesis pathways. Two enzymes from *Bacillus subtilis* that utilize IPP and DMAPP for the biosynthesis of isopentenol were over expressed in E. coli, resulting in production of 112 mg/ litre isopentenol (107, 200). To make these biofuels more promising, the low tolerance of algae to alkanes must be overcome. In-depth studies have shown that the oxidative stress of the organisms increases upon production of these hydrocarbons suggesting that they are possibly the major protection mechanism against the production of these hydrocarbons.

Role of microalgae in microbial fuel cell

Research on renewable methods for producing energy has received utmost attention in last few years. Standing in such a situation, the use of microalgae to convert CO2 into potential biomass coupled with their ability to produce oxygen gas, assumes strategic importance (Popp et al., 2014). Significant research is being carried out in this field to exploit this ability of microalgae and integrate it with microbial fuel cells. This integration becomes especially favourable considering the fact that the phototrophic organisms act as in-situ generators of oxygen which facilitate the reaction in cathode chamber of the MFC. Further, microalgae also effectively removes phosphorous and nitrogen from the wastewater which might not be possible solely by the MFCs (Rozendal et al., 2008). The

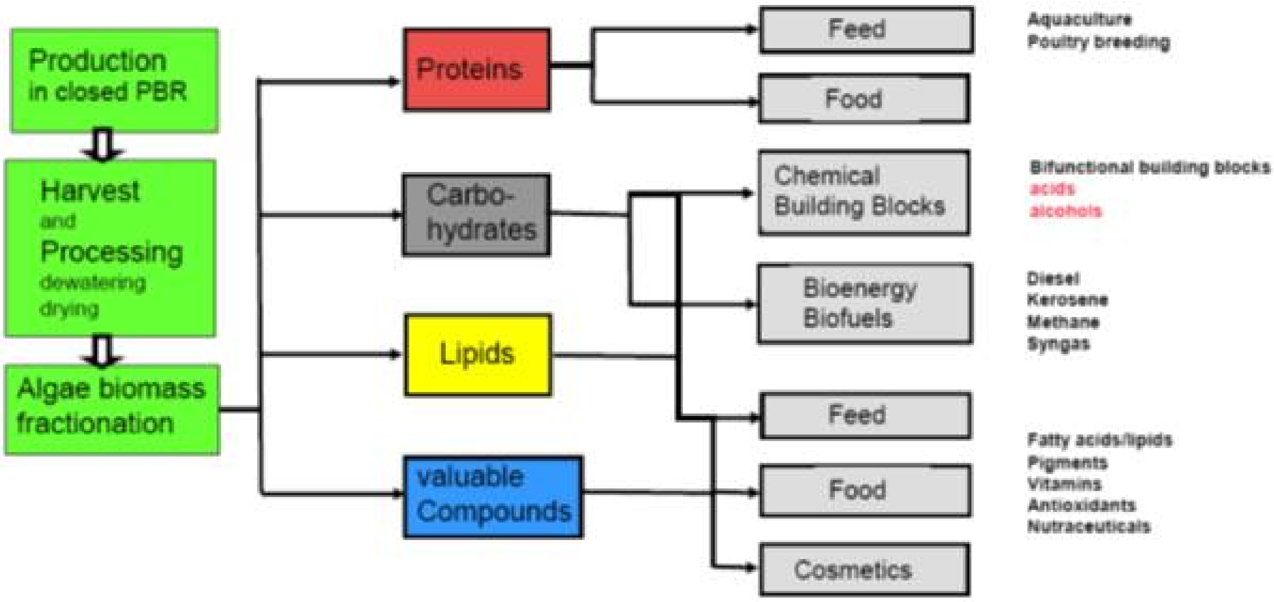

Fig. 4. Utilization of algal biomass in an Algal refinery

use of phototrophic organisms in MFCs leads to the development of photosynthetic microbial fuel cells or PMFCs (Rosenbaum et al., 2010).Algae help in generation of biochemical energy by conversion of solar energy. It accounts for more than half of the photosynthetic output on earth. With their high growth rates and high CO2 fixation rates (can reach up to 6.24 kg/m3 /day), microalgae are being taken into serious consideration for bioenergy production (Skjånes et al., 2007). The photosynthetic process (a biological redox reaction carried out by algae where they use solar energy to produce carbohydrates and oxygen, as well as additional compounds) might be used for energy generation or synthesis of more complex substances. Biological method of CO_2 sequestration using green algae and cyanobacteria is considered as most promising method (Markou et al., 2014).The use of algae for CO_2 sequestration has several advantages e.g. green algae has several applications: mitigating CO_2 to reduce global warming, wastewater treatment, production of biofuels, biofertilizer and other important products like food products, antibiotics and pigments (Kumar et al., 2013). When sunlight falls on algae, they utilize it to carry out photosynthesis, use CO_2 to generate organic matter and biomass, and simultaneously consume oxygen during dark phase and obtain energy by oxidizing the formerly produced organic matter (González del Campo et al., 2013). Conversely, some photosynthetic cyanobacteria could be operated as a bioanode catalyst, in which the formation of biofilm maintains the electrochemical potential.

Algal Biomass Exploitation

The versatile utility of algal biomass including biofuel synthesis is schematically represented by the figure 4(Khan & Rashmi, 2010)

CONCLUSION

Algae can be exploited for the production of sustainable biofuels. Algal biofuels have a tremendous potential for contributing to environmental, social and economic sustainability. Different varieties of biofuels can be manufactured by exploiting algal resources. Bioethanol production by utilizing algae through fermentation route could be a suitable alternative by comparing it with the conventional bioprocess. Moreover it requires less energy consumption. Therefore keeping in view of the above facts nowadays algae as well as microalgae proves themselves as a potential resources not only for the versatile biofuel production but also contributes a significant role to produce so many useful chemicals, food and feed supplement, nutrient suppliers etc.

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