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Review Article

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Sustainable Biofuels from Algae- Process and Methods Adapted: A Review

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ABSTRACT

Fossil fuels are the most important energy resources and are depleting rapidly. In specific, liquid fossil fuels are projected to diminish in next three decades. Fossil fuels are also directly related to air, water pollution and land degradation. In this scenario, biofuels from renewable sources are the best alternative to reduce the dependency on fossil fuels and also help in maintenance of healthy global environment and economic sustainability. Production of biofuel from food stock, though a good alternative, is generally unacceptable and results in the competition for these resources worldwide. Biofuel production from microalgae provides a sustainable alternative along with many distinctive advantages like faster growth rate, reduction in greenhouse emissions and high lipid production. Algal oil extracted and then converted in to biodiesel through a trans-esterification process. Fatty acid methyl esters in biodiesel are synthesised from the Oil extracted from the algae that is mixed with an alcohol and an acid or a base. Methanol is used as a catalyst in favouring the trans-esterification process. In conclusion, a large scale production of biodiesel from microalgal should be considered with promising prospects compared to the traditional diesel in India and its large scale cultivation should be considered. The production can be made economical by using waste water and marginal land usage of waste land for cultivation of microalgae in India.

Key Words: Microalgae, Biofuel, Nutrients, waste water, Flue-gas, Process integration

INTRODUCTION

Micro algae in particular are single-celled organisms and are found worldwide in aquatic habitats. Microalgae use energy from the sun, carbon dioxide (CO_2) from the air and synthesize carbohydrates, protein, and natural oils by photosynthesis. Micro algae ensure continuous and reliable supply of oil as they can be harvested batch wise throughout the year. This is because of their higher photon conversion efficiency. They can utilize salt and waste water thereby reducing freshwater usage. Non-toxic and highly biodegradable biofuels production by CO_2 sequestration makes micro algae and important candidates for the biofuel production.[1] Algae have number of uses that include feed for animals, act as biological filters in removal of water and air pollutants, as environment and change indicators in space technology, used by people as food to make useful compounds, as indicators of quality of the water, as environmental change indicators for space technology and as systems for laboratory study. Algae cultivation has minimum effects on ecosystem as they can be grown away from the farmlands and forests. Algae can also be grown in sewage water and next to power-plant smokestack.[2] Algae are commercially cultivated for pharmaceutical, nutraceutical, cosmetic, and aquaculture and also to produce considerable volumes of vegetable oil that can be converted into biodiesel, bioethanol, and bio-butanol and biomass that can be burned for generation of both heat and power.[3] Algae are used as a complete protein because it contains essential amino acids that are useful for the synthesis of energy and enzymes. Humans used algae in different fields such as: simple, complex and sulphated carbohydrates give body access to extra fuel, and improve the immune system: it also rich in vitamins, minerals and trace elements, used in dairy products, some alginate products like tooth paste, ice cream and lotions and also utilized as fertilizers, source of cattle feed and soil conditioners. The algae also used in waste water treatment for removal of dangerous chemicals, for removal of excess fertilizers in agricultural forms and fertilizer after being harvested. There are 300,000 different kinds of algae can be found in freshwater, marine, and wastewater all around the world. Algae are straight forward, resembling plants, yet they lack roots, stems, and leaves.[4] Algae (which can be found in unicellular or multicellular forms) are photosynthetic, some are heterotrophic. They can be cultivated in open, closed, hetero and hybrid algae production system, batch and continuous system.

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Cultivation of algae

Site selection and resource evaluation are to be performed for establishment of algal cultivation as discussed by Maxwell.[5] The establishment of an algal cultivation unit include the parameters like water requirement, land surface, study of rocks, salinity of soil and owner ship climatic conditions, evaporation, temperature, and precipitation, carbon supply sources. The following factors are considered in sampling and selection of algae growing rate, (total biomass/ unit time/ volume), Lipid content (amount of free fatty acids and triglycerides), Resistance to environmental changes (temperature, nutrient composition, light), competition with other microalgae species /or bacterial especially for nutrients availability, ease of biomass separation and processing, extraction of other valuable chemicals. Microalgae utilize required amount of a carbon source and light for performing photosynthesis there by generating biomass, Microalgae are able to vary their metabolism in response to environmental changes through biochemical and physiological acclimatization. Microalgae are able to secrete substances that enhance (or) slow nutrient availability to inhibit the growth of competitors.

Algae are grown in open seas or in land based systems. The latter has many advantages including ease of plant management, ease of nutrient application without dilution, close proximity to conversion operations, use of plants with or without holdfast structures and avoidance of open sea problems.[6]

Phototrophic Cultivation in open ponds

Open ponds cultivation is of two types: naturally occurring water systems (lakes, lagoons, and ponds) and man-made ponds (Shallow huge ponds, tanks, circular ponds, and raceway ponds). Open ponds are simpler to build and maintain than most of the closed systems. Disadvantage of open pond include inadequate light usage, substantial amounts of land consumption, evaporative losses, leakage of CO_2 into the atmosphere. The man made ponds were algae are grown are known as "raceway ponds." Algae, water, and nutrients are moved around in these ponds. Flows created by paddle-wheels bring the algae to the surface.[7] The ponds are often kept shallow to allow the sunlight to penetrate till bottom. In continuous is algae-containing water is withdrawn, from one end while CO_2 and nutrients are injected into the pond from the other end. Low output and operational expenses are the main outcomes of simple open pond cultivation.

Phototrophic Cultivation in closed ponds (photo bioreactors)

Photo bioreactors (PBRs) are good alternative for growing algae through open-air raceways.[8] Photo bioreactors are enclosed spaces that are used to grow microalgae in a regulated environment. The returns from PBRs are substantially larger as compared to the open pond systems though they are costlier than the open systems. PBRs are made up of long tubular glass chamber that is simple to sterilise. Microalgae are exposed to carbon dioxide and sunlight in chambers for their optimum growth. PBRs have number of benefits over open ponds that includes easily maintenance of growth parameters (pH, temperature, mixing, CO_2 and O_2) and so better control over the culture conditions, higher volumetric productivity, ability to reach higher microalgae densities, provides safer and protected environment thereby minimizing invasion by competing microorganisms.[9]

Hybrid algae production system (HAPS): HAPS is a combination of the two systems- both open system and a bioreactor. A selected algal strain is usually grown in a bioreactor and is then introduced into open systems. The large inoculum size is necessary for the algae to flourish and overcome the competition in the open environment.[10] Introduced HAPS as a closed pond system to which inoculum is added from the bioreactor for the generation of microalgal biomass designed with coalition with Idaho Sustainable Energy, LLC. The system is designed to overcome the shortcomings of the open systems and also by minimizing the cost of the facility. The problems addressed by the system include control on fluctuations in summer and winter temperature and daily temperature fluctuations, evaporation, pH, salinity, light, algae self-shading, efficient nutrient distribution, efficient gas extraction.[11] Numbers of HAPS units were established in USA after the first 1,00,000L facility in Montana in 2007.

Batch and continuous system: Benvenuti[12] used PBR in a batch or continuous mode of operation continuous bioreactors provide a higher degree of control, Growth rates can be regulated and maintained for extended time periods and biomass concentration can be controlled by varying the dilution rate, the steady-state of continuous bioreactors, results are more reliable and easily reproducible and the desired product quality may be more easily obtained. Controlling the production of some non-growth related products, for instance, presents a hurdle.[13] Batch culturing and constant supplies of nutrients are frequently needed for the continuous process. Wash-out or ideal steady-state growth might be prevented or hindered by wall growth and cell aggregation. If a faster-growing strain eventually overtakes the original product strain, it may go extinct. The viscosity of the mixture and its heterogeneity can make it challenging to maintain filamentous organisms.

Algal cultivation in different environmental conditions

Algae can be grown using specialised light bioreactors or saltwater ponds in the desert eco-system.[14] Maintenance of constant temperature around 70 degrees Fahrenheit is the main challenge in production of algae in desert eco-system.

Desert-based algae cultivation: Algae ideally can be grown closer to the desert, where there is less variation in seasonal sunshine levels and temperatures and hence provide optimum environment to carry out algal production.[15]

Cultivation in waste water: Waste water is a potential source of nutrients for algal cultivation. Among the sources of wastewater i.e., municipal, industrial and agricultural wastewaters, municipal waste water has the highest potential as medium for algal cultivation. Different species of microalgae are known to grow in waste water using variety of organic substrate present in these waters adapting various pH and temperature conditions. These algae grow heterotrophically in the dark and mixotrophically in the presence of light. Further there scope for the removal Nitrate or ammonia phosphorus and heavy metals from this algal biomass offers a very important method of bioremediation. Some fresh water micro algae like *Chlorella saccharophila, B. braunii* and species of marine algae, *Pleurochrysis carterae* can adapt and grow well in untreated waste water.[16]

Marine algae cultivation: Seaweeds especially algae have a significant advantage over land-based algal cultivation as they have all the water minerals required for their cultivation. Macro-algae can grow in many countries were they are tied to floating lines that are anchored. Sea water lakes lagoons are being explored for cultivation of micro-algae in land based salt water system.[17]

Cultivation next to power plants: Coal-burning power plant offers an ideal environment for the cultivation of algae when grown in the premises of these power plants. Hence, continuously operating thermal power plants (coal based) offers an ideal environment for continuous algal biomass production. Hence, this proposes a long term approach as algae are best known to thrive in environments with high concentrations of carbon dioxide, nitrogen dioxide (NO_2) and pollutants released in exhausts of power plants. These airborne contaminants released not only from power plants but also from cars and cement plants, breweries, steel mills and fertilizer companies provide the nutrients required for algal cultivation.[18]

Optimum conditions for cultivation

Sunlight: Algae are autotrophs and they grow well with sun radiation known as insolation. Algae grow well with 2800 hours of annual sunlight, daily temperatures more than 12°C and 200 days in a year without freezing temperatures. That is why algal growth is abundantly present in tropical and subtropical regions where there is ample sunlight.[6]

Water: Algae farming is possible only in presence of water and hence becomes a limiting factor. However, it is overcome by recycling of wastewater which also benefits the nearby municipalities by treatment of water and reduction of water pollution. Microalgae can grow in water resources that are not suitable for growth of other life forms. Microalgae survive by utilizing the chemicals and nutrients in the water to make it fresh through a process known as eutrophication. When wastewater used for algal cultivation has triple- advantages: waste water provides required nutrients for algal growth, cleaned by algae to make it and helps in water recycling in the regions with limited water supply.[19]

Carbon dioxide: Algae require CO_2 as an important raw material required for their growth. CO_2 present naturally in the atmosphere is a greenhouse gas. That helps in trapping of the solar radiation there by keeping the surface warm enough for the life to exist. The increased amount of CO_2 in the Earth's atmosphere due to the burning of fossil fuels has reached dangerous levels leading to global warming. Continuous algae farming for biofuels, thus, bring down the level of CO_2 in the atmosphere, thereby reducing the greenhouse effect. CO_2 released from power plants, oil refineries, and other industrial factories can be given to the algal farms using bubblers from the foot of PBRs that are placed in close proximity to these industries. Hence algal cultivation for biofuel offers method of CO_2 scrubbing for the emissions from this industries.[20]

Temperature: Usually a temperature of 20 and 30°C is required for the growth of algae and the range of temperature used for algal cultivation depends on the strain of algae selected. Algal growth is usually slowed below 16°C, and most species die above 35°C.[21] Abiotic factors like light (quality and quantity), O_2, nutrient concentration, pH, salinity, and toxic chemicals have drastic influence on algal growth. Presence of other biotic factors like bacteria, fungi, and viruses, and operational parameters like rate of mixing, dilution rate and depth of the unit, frequency harvesting and the amount of bicarbonate added would impact the load of biomass produced in algal cultivation.

Harvesting methods

Processing stages include harvesting, dewatering, and extraction of fuel precursors are the necessary steps to convert algae from different sources like ponds, bioreactors and offshore systems into liquid transportation fuels, lipids and carbohydrates.[22,23,24] Whereas processing methods rely on Algal feed stocks.

Flocculation and Sedimentation: Microalgae remain in the suspension even in high growth rates and are well circulated in the medium. Harvesting of microalgae is more challenging due their very small size. Flocculation and Sedimentation is carried out by addition of alum, cellulose, lime, and salts, surfactants, polyacrylamide polymers, chitosan, and various man-made that interact with these chemicals causing flocculation.[25,26,27] Auto flocculation of these algae is influenced by CO_2 depletion.[28] Bio-flocculation occurs with co-culturing of algae with other organisms.[29] Electro flocculation and electrocoagulation as added benefits as they require no additional chemicals.[30,31,32]

Dissolved Air Flotation: Algal clusters increase in size and float to the top by forcing the air through the algal suspension. The bubble size in the dispersion capacity in the solution increases the flocculent efficiency.[33-39]

Filtration: Harvesting and dewatering of algae is done using filtration techniques. Most of the algal cells have the diameter of ten microns and hence pose number of filtration issues. Hence filtration can be more effective when these problems are well understood and addressed. Usually the problems include the blindness, lockage and reduction in the filter effectiveness there by decreasing the filtering rates. Use of good quality filters materials, regulated hydrophobicity or affinity for algae use of dynamic filtering procedure and innovative filtering designs have improved the filtration process.[40-43]

Centrifugation: Centrifuges that are employed industrially are used for harvesting of algae from suspensions[44]. The centrifugation cause includes the cost of equipment running expenses and handling of large amounts of water and algae. The existent rate of centrifugation technology makes it a costly process for handling of large scale algal biomass. Algae can be concentrated using electric fields by using bio harvesting methods.[45]

Drying: Two types of drum driers are used to increase the biomass concentration i.e., methane drum drier and oven style drum driers. The cost of drying process increases sharply with the increase in time of drying and alternate to dryers wind and solar energy can be used. Mechanized facilities with concentrators, cutters are used along with driers. 90% of the 1.6 million dry metric tonnes of seaweed harvested globally using different types of mechanized equipment.[46] To reach high biomass concentrations, drying is necessary. Methane drum dryers and other oven-style dryers have been utilized since drying generally needs heat. However, as temperature and/or time increase incrementally, the expenses rise sharply. Low-humidity environments can be air-dried in, but it will need more room and time. There are also options that use solar or wind energy. For both cultivated and natural systems, manual harvesting is typical. Mechanized harvesting techniques, such as rotating blade mowing, suction, or dredging with cutters, have also been developed. Such automated harvesters are always operated by boats or ships. Pumps can be added to modern seaweed harvesting vessels to transfer harvested seaweeds directly into nets or other containment structures. Seaweeds as a feedstock for biofuels in Ireland described the use of mechanical harvesters in European seaweed businesses.[47,48]

Pre-processing: Pre-processing techniques are very much required for processing of the macro algae. Dewatering, hydrothermal liquefaction, anaerobic digestion and fermentation are the steps that involve handling of water. Dewatering is crucial in transportation of algal from harvesting locations to far-off processing algal biomass to factories and it also improves the shelf life, reduces the weight and cuts down transportation expenses.[47] Macroalgal biomass in shredded or milled form is used in anaerobic digestion and fermentation. Wet biomass at 15–20% solids or 80–85% water content is suited for hydrothermal conversions.[49]

Extraction of algae oil: *Chlorella, Scenedesmus* and *Spirulina* have been dried using a variety of techniques, dehydration of biomass, helps in extension of shelf life and life of the finished product. Algae in commercial scale are spray dried or drum dried or freeze dried or sun dried. Due to the high water content of algal biomass spray drying is not economical for protein or biofuels extraction. Sun drying is not good method to handle successful method for algal powder. Following the drying, the cell disruption helps in the release of the desired metabolites. In accordance with the microalgae type of product to be created, a variety of techniques can be applied, including mechanical action-based as cell homogenizers, bead mills, ultrasounds, autoclaves, and spray drying and non-mechanical action-based as freezing, organic solvents and osmotic shock and acid, base and enzyme reactions.[50]

Mechanical Methods: Mechanical crushing is a direct technique. Expression/Expeller press is used to press oil out of the dried algae. Different strains of algae have distinct physical characteristics and hence different press configurations such as screw, expeller, piston, etc. are used for different types of algae. Ultrasonic-assisted extraction is used in ultrasonic reactor, cavitation bubbles are produced in the reactor. The bubbles collapse close to the cell walls creating shock waves resulting in liquid jets that cause the cell walls to snap and spill contents into the solvent.[47]

Chemical Methods: Chemicals are also used to extract algal oil. Oil is separated using hexane extraction and popular and cheap and is used in food business and relatively cheap. Chemical solvents are extracted by using Soxhlet. Oil from the algae is recovered by repeated washing or percolations with an organic solvent usually hexane or petroleum. Benzene and ether have both been employed are avoided as they cause seriously harm to the skin.[30, 51, 52]

Hexane Solvent Method: Chemicals can be used to extract algal oil. Hexane is used commonly for solvent extraction as it is relatively economical. The inherent risks associated with usage of the solvents make them undesirable. Hexane solvent extraction may also be used along with oil press/expeller method. The residual pulp after pressing is combined with cyclo-hexane to extract the remaining oil content. The pulp is removed from the solution and the oil is extracted into the cyclohexane. Oil in the cyclohexane is extracted by distillation process. More than 95% of the oil present in algae is extracted using the combination of cold press & hexane solvent.[53]

Supercritical fluid Extraction: Supercritical fluid/CO_2 extraction involves using liquefied CO_2 (under pressure) and heated until it possesses both liquid and gaseous qualities. This liquefied fluid is then used as solvent in the extraction of the algal oil.

Algal oil products: Biodiesel, ethanol, and methane, hydrogen are produced from algal oil. These are used as diesel, gasoline, and jet fuel and act as renewable reserves for the production of polymers and chemicals that are derived usually from petroleum at very high environmental cost .[54,55] Transportation fuels from algal oil are able to replace the petroleum-based fuels and could reduce carbon emissions by 30% in the United States itself. Biodiesel gained lot of attention though it is not the only fuel produced from the algal oil. It is predicted that diverse fuels like gasoline, hydrogen, and LPG can be theoretically produced from algae. Biodiesel, ethanol, hydrogen, methane, bio-butanol, gasoline and JP-8 fuel etc. can be produced from algal oil. 75% of biomass of algae produced annually is used in preparation of health supplements, capsules, pills and pastilles in food industries.[56] Nutritional value of a microalgae used as animal feed and aqua feed depends on size and shape, digestibility, biochemical composition, enzymes and toxins.[57] Schlesinger's[58] calculated that 45 to 50% of dry weight of algae is carbon content. Microalgae develop at considerably faster rates in open ponds or photo-bioreactors, algae when high amount of CO_2 is present and hence converted into biomass thus sequestering carbon for generation of biofuel. The advantages of algae are, it is used as biofuels are not harmful, highly biodegradable algae biofuels, depending on where it is grown, it can minimize carbon emissions, high volumes of algae biomass may be produced, and compared to other sources, and biomass can deliver a larger percentage of oil. There is little market rivalry for algae oil. It can be grown in fresh water or seawater and landfills. The disadvantage of algae to produces polyunsaturated, unstable biodiesel. The main drawback, the low levels of free CO_2 needed for peak algal development and the fact that algal grazers are a substantial but mostly unrecognized issue.

DISCUSSION

Generation of algal biomass to be utilized as a raw material for the production of biofuel has been elaborately discussed in the current review. Different methods used for algal cultivation, non-traditional environments where algae can be cultivated, process and different methods of algal oil extraction along with their advantages and disadvantages are comparatively presented. Algal oil not only undergoes trans-esterification to be used as biodiesel but also used in the preparation of many algal oil products as discussed above. The review brings in the importance of algae in biofuel production and different methods of extraction and purification of biodiesel from algal biomass.

CONCLUSION

Carbon-neutral substitute for petroleum fuels is biodiesel made from oil crops. However, the expensive price keeps it from challenging petroleum fuels as a leading alternative. Biodiesel will gain in appeal among consumers and investors when the price of petroleum fuels rises and supplies are reduced. But only a small portion of the current demand for transportation fuels can be satisfied by biodiesel made from oil crops used cooking oil, and animal fat. According to the U.S. Department of Energy, private industry is currently conducting research into effective algal oil production. The predictions from small-scale production experiments prove to be accurate; using algae to produce biodiesel may be the only practical way to produce enough automotive fuel to replace the current global gasoline consumption.

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