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Changing Trends in Microalgal Energy Production-Review of Conventional and Emerging Approaches

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The depletion of fossil fuel for energy production is one of the major problems being faced worldwide. As an alternative to fossil fuels, first and second generation biofuel was developed from corn, grains and lignocellulosic agricultural residues. These generations are inefficient in achieving the desired rate of biofuel production, climate change mitigation and economic growth. Therefore, third generation biofuel specifically derived from microalgae have proved to be a promising unconventional energy source. Microalgae are microscopic organisms that grow in salt or fresh water and have been used for producing metabolites, cosmetics and for energy production. The conventional approaches used for biofuel production include pyrolysis, gasification, direct combustion and thermomechanical liquefaction. The search for biological and eco-friendly approaches led to the emergence of Microbial Fuel Cell (MFC), which provide a new solution to energy crisis. Integration of photosynthetic organisms such as microalgae into MFC resulted in a new approach i.e. Microbial Solar Cell, which can convert solar energy into electrical energy via photosynthesis. Microbial solar cells have broad range application in wastewater treatment, biodiesel processing and intermediate metabolite production.

Keywords: Microalgae, biofuel, microbial fuel cell, microbial solar cell, biomass conversion.

Today's world is facing many environmental problems; energy crisis is one of the major issues being faced globally. Population growth and fast industrialization has led to the overexploitation and depletion of non-renewable fossil fuels [1]. Thus, the scarcity of fossil fuels can be compensated by utilizing renewable energy sources such as solar, wind, hydro, tidal, and biomass [2,3]. International Energy Agency (IEA) compared the potential of renewable sources for energy production and reported wastes and combustible sources to be the most promising alternative. Biomass derived from terrestrial and aquatic sources have been exploited for biofuel production [4]. Biofuel production is associated with three generations, namely 1st, 2nd and 3rd generation. First and second generation biofuel were derived from the agricultural sources. These generations utilize food sources, slow processes and have low production capacity which limits its pilot scale use. Therefore, third generation biofuel derived from algal biomass are the best alternative owing to their rapid and higher production as compared to first and second generation biofuels. Unsustainable consumption resulted in scarcity of biomass, reduction of green cover and biodiversity [5,6].

So, nowadays bioenergy research paradigm has shifted towards algal biomass for production of biofuels. Microalgae are photosynthetic microbes which require sunlight, carbon dioxide and inorganic nutrients for growth. It produces huge amount of biomolecules like fatty acids and sugars, which can be converted into biofuels (bio-oil, bioethanol, biodiesel etc.) [7,8]. Microalgal biomass increases the process

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efficiency due to its low hemicellulosic and neglible lignin content [5]. Microalgae have wide range of application in the field of nutrition, environmental pollution, fertilizers and animal feed [9,10]. Biofuel production has been possible with the various conventional (chemical, physical and biological) and emerging (MFC, MSC) methods. The conventional methods have been used to produce biofuel but their requirement for energy, low efficiency and complex process limited their use. With the development in technology, new approaches for biofuel production were designed and used.

Microalgae

Algae are the oil-rich organisms which can efficiently use sunlight, remove contaminants from environment without competing for food or agricultural resources [11,12,13]. Their short generation time enables the rapid biomass recovery. The oil present in algae can be processed into biofuel [14]. Algae consist of macro and micro-algae. Macro-algae also known as "seaweeds" are multicellular rapidly proliferating plants inhabiting in saline or fresh water [15]. On the basis of pigmentation they have been classified into three subgroups: i) brown seaweed (*Phaeophyceae*); ii) red seaweed (*Rhodophyceae*) and iii) green seaweed (*Chlorophyceae*). They consist of a thallus and lack roots, stems and leaves. The algae cultivation for food production and the hydrocolloid extraction on commercial scale in Asia has been practiced since many years. The most cultivated macroalgae include brown algae *Laminaria japonica* and *Undaria pinnatifida*, the red algae *Porphyra*, *Eucheum* and *Gracilaria*, and the green algae *Monostroma* and *Enteromorpha* [16].

Micro-algae are very small in size and inhabit in both marine and freshwater. Their photosynthetic ability allows them to efficiently convert solar energy into biomass. On the basis of pigmentation, chemical nature, the organisation of photosynthetic membranes microalgae have been classified into two prokaryotic divisions and nine eukaryotic divisions. *Cyanophyceae* (blue-green algae), *Chlorophyceae* (green algae), *Bacillariophyceae* and *Chrysophyceae* are the most cultivated microalgae. These organisms can live phototrophically, heterotrophically and even mixotrophically [17]. Microalgae existed on Earth since its environment was formed. These organisms possess chlorophyll, perform photosynthesis for producing oxygen (O_2) and remove carbon dioxide (CO_2) from the atmosphere [18].

Microalgae consist of protein, lipids, pigments (carotene) and vitamins [19]. Microalgae are associated with three elemental attributes which provides commercial applications. They include genetically diverse group of organisms possessing physiological and biochemical characteristics and can produce carbohydrates, lipids and bioactive compounds, etc. They can also cost-effectively integrate the stable isotopes (13C, 2H and 15N) into their biomass. They contain many unexplored organisms which may provide novel unused product source [20].

Applications of Microalgae

Food and dietary supplements

World's population is increasing exponentially but the food resources are not increasing at the same pace. So, there is an urgent need to provide safe food and food materials to meet the everincreasing demands for food. Microalgae can remove carbon dioxide using sunlight and produce organic matter. These form the primary level i.e. phytoplankton and are consumed by zooplanktons, which are further eaten by bigger fish and animals on earth. Therefore, microalgae are supporting life on this earth [18].

Microalgae have also been exploited as food owing to its significant nutritional content. For instance, *Spirulina* has been used as food in Mexico and Chad. *Spirulina* also plays an important role in Chad's economy [21]. Countries like Thailand, China, US and India are also using *Spirulina* as a supplement to the regular diet. The global net production of *Spirulina* is nearly 4000 metric tons [22]. *Spriulina* contains proteins, g-linolenic acid, vitamins and minerals. It is also reported for its therapeutic applications in curing diabetes, arthritis, cardiovascular diseases and even cancer [23]. Antioxidant properties of *Spirulina* are due to phycocyanin and vitamin E present in it [24,25].

A different microalgae *Nostoc* is consumed in China [26]. It is rich in proteins, pigment and provides less fat content, thus making it a healthy choice. *Nostoc flagelliforme* is popularly known as "fa cai". Pigments such as echinenone and myxoxanthophyll, allophycocyanin, phycocyanin and chlorophyll are present in it [27]. It also contains essential amino acids for human nutrition. It has been used in traditional Chinese medicine for the treating diarrhea, hypertension and hepatitis. *N. sphaeroides* (Ge-Xian-Mi) is specie being used as food and herbal ingredients [28].

Chlorella is also cultivated as health food and commercially available in the form of tablets and powder. The first large scale *Chlorella* production unit was setup in Boston, USA. The other countries (Israel, Japan, Czechoslavakia, Taiwan, Malaysia and Indonesia) also followed afterwards [29]. *Chlorella* consists of proteins (51-58% dry weight), carotenoids and vitamins which makes it a suitable health food [30]. It also contains an immunostimulator i.e. â-glucan and helps in reducing blood lipids [29].

Cosmetics

The evaluation of quantity of pigment in microalgae is an important feature to determine cell growth and to check the trophic level. In cosmetics, components of algae are used as thickening agents, water-binding agents and antioxidants. *Arthrospira* and *Chlorella* are the microalgal species utilized in skin care products [31]. Microalgae extracts are present in face, sun protection, hair care and skin care products. Mostly used microalgal species include *Chondrus crispus*, *Mastocarpus stellatus*, *Alaria esculenta*, *S. platensis*, *C. vulgaris* and *D. salina* [20].

Food Colorant

The pigment in microalgae can be used as natural food coloring agent. Some microalgae contain Carotene (â carotene), which is used as a coloring agent in margarine, food additive in enhancing the color of fish flesh and overcome sterility in cattle consuming grains [32]. â-carotene is used as a dye and also provides vitamin C. According to National Cancer Institute, â Carotene is anticarcinogenic and also maintains cholesterol level. It can also minimize the chances of heart disease. Thus, â Carotene production has become more important. *D. salina* is cultivated for â-carotene. However, its efficiency as a food colorant is limited to the instability in light and also the color is prone to bleaching on cooking [20].

High-Value Molecules

Microalgae can be a used for producing new compounds which can act as functional ingredients. Some microalgae live in unfavorable environments of high salinity, high and low temperature, etc. and adapt by producing some secondary metabolites explicitly. Marine microalgae have been exploited for producing polyunsaturated fatty acids (PUFA), which can effectively prevent several diseases. PUFA such as a-linolenic acid (ALA, C18:3n-3), docosapentaenoic acid (DPA, C22:5n-3), and docosahexaenoic acid (DHA, C22:6n-3), effectively provided protection against various diseases like cardiovascular disorders, cancer, type 2 diabetes, arthritis, kidney and skin disorders, depression and schizophrenia. *Dunaliella* species, *Chlorella* species and *Spirulina* species are most cultivated species for producing high value molecules including lipids, proteins, etc. [33,34].

Biofertilizer

Microalgae have also been used in agriculture as biofertilizers and soil conditioners. *Cyanobacteria* can fix atmospheric nitrogen and used as biofertilizers. *Cyanobacteria* as a natural biofertilizer maintain and increase soil fertility along with high rice growth and yield [35]. Application of Blue green algae (BGA) as a biofertilizer, yield increases and the soil physico-chemical properties also improve. On application of biofertilizer, the pH, electrical conductivity and nutritive (nitrogen and carbon) value of residual soil improved. The protein content was also increased in grain. *Nostoc*, *Anabaena*, *Tolypothrix* and *Aulosira* are mostly used for paddy fields. *Anabaena* when associated with water fern *Azolla* fixes about 60 kg/ha/season nitrogen and supplements the required organic matter in soil. *Cyanobacteria* also produce growth-promoting substances which can improve soil.

Pharmaceuticals

Algal organisms can produce biologically active primary and secondary metabolites which can be employed in the pharmaceutical industry [36]. These explicit bioactive compounds are produced by algae for their survival during the competition with neighboring competitor organisms. These algae derived bioactive molecules cannot be produced by chemical synthesis. The culture extracts of *Chlorella vulgaris* and *Chlamydomonas pyrenoidosa* have been reported for their antibacterial potency against both Gram-positive and Gram-negative bacteria. Extracts of green algae, diatoms and dinoflagellates can serve as antifungal agents. Toxins produced by microalgae such as *Ochromonas* sp., *Prymnesium parvum* can be of use in pharmaceutical industries [37,38]. C*yanobacterial* strains produce various intracellular and extracellular metabolites which possess antimicrobial activity.

Environmental biotechnology

Bioremediation, bioassay and biomonitoring are the three basics of microalgal environmental biotechnology. The release of contaminated wastewater into the clean water bodies creates a risk to health of existing flora and fauna. The high rate algae pond (HRAP) system proved to be an efficient in treating contaminated water [39,40]. The HRAP system is most suitable for tropical climate where the sun light is available and the temperature is also warmer. HRAP reduces pollutants and produces algal biomass which can be further used as food for animals and feedstock for producing biodiesel. HRAP algal systems have been successful in treating rubber effluent, palm oil mill effluent (POME) and municipal wastewater. Anaerobic digestion of starch factory wastewater by *Spirulina platensis* reduced phosphate of more than 99% [41]. The HRAP system is also used as end treatment of the pretreated water before channelizing it for human use [39]. *Chlorella vulgaris* grown in HRAP has been used for color removal of the wastewater [42]. A group of five microalgal species grown in HRAP treated landfill leachate [43]. *C. vulgaris* immobilised in alginate effectively removed color from textile dyes [44]. Immobilised *C.vulgaris* and *Scenedesmus obliquus* effectively remove nitrogen and phosphorus from wastewater [45]. Toxic tolerant microalgae are used for first B i.e. bioremediation while sensitive species are employed for rest two B's i.e. bioassay and biomonitoring of environmental pollutants [46].

Microalgae have also been used to detect the toxicity of contaminants such as heavy metals, pesticides and pharmaceuticals. The level of heavy metals in the aquatic ecosystems and even in aquatic organisms such as fish and mussel has been determined using microalgae [47]. The commonly used microalgal species for toxicity analysis include *Pseudokirchneriella subcapitata*, *Dunaiella tertiolecta*, *Isochrysis galbana*, *Chlorela* spp. [48]. Microalgae have also been used for evaluating nutrient enrichment due to nitrogen and phosphorus. For instance, *C. vulgaris*, *Scenedesmus quadricauda* and *Ankistrodemsus convolutus* efficiently helped in assessing nitrogen and phosphorus enrichment in freshwater ecosystems [49].

Biodiesel

Microalgae have been reported for biodiesel production. The microalgal biofuel production is advantageous over other agricultural feedstocks as it doesn't affect food production, fodder and other feedstocks. In Malaysia, palm oil has been used for biodiesel production but the continuous use may lead to scarcity. Therefore, microalgae present an alternative of biodiesel and replace fossil diesel [50]. Amongst all the microalgal species known *Chlorella* has been mostly cultivated for biodiesel production. *C. protothecoides* efficiently produces highly viscous biodiesel with high heating value making it of superior quality. In comparison to the terrestrial plants, microalgae can perform photosynthesis more efficiently and can flourish normally even at high temperature environment with high CO_2 level [51]. It has been reported that microalgae can use produce 280 tons of dry biomass per ha^{-1} yr^{-1} utilizing 9% of the sunlight and eliminating nearly 513 tons of CO_2 [52]. Species which can survive at high levels of CO_2 include *Spirulina* sp., *Scenedesmus obliquus* and *Chlorella vulgaris* [53]. Such microalgae can be used for bioremediation of flue gas which contains nearly 12% CO_2 [54]. Thus, an integrated microlagal system for biofixation of CO_2 along with biodiesel production can be the most fascinating and environmentally beneficial approach. Fawzy [55] reported *Asteromonas gracilis* (new microalgae from Egypt) as a potent feedstock for biodiesel production.

Cultivation of Microalgae

The cultivation of microalgae can be done by four different methods based on the type of metabolism and effect of environmental factors on the growth (figure 1). Four methods are: phototrophic (light as the only source of energy), heterotrophic (organic matter as the energy source), mixotrophic (organic and CO_2 required for photosynthesis), and photoheterotrophic (use light to extract energy from organic matter) [56]. For the commercial biomass production of microalgae phototrophic approach is most viable, as scale up is easy and economical [57,1]. Several abiotic (light intensity, pH, temperature, salinity, nutrients and gaseous content) and biotic (fungus, other algae, bacteria etc.) factors affects the microalgal cultivation in all four methods. Among these temperature and light play vital role in growth of microalgae [58].

Phototrophic Cultivation

For microalgae cultivation, phototrophic mode is most efficient and economical approach as microalgae has higher growth and photosynthetic rates as compare to plants [12]. The ability of microalgae to act as potential sink of carbon by capturing free CO_2 from atmosphere provides additional benefit. It can be done either in open ponds or enclosed photobioreactors (PBRs):

Open ponds

Being practiced from 1950's, this is the oldest and simplest approach of phototrophic cultivation of microalgae for commercial purpose [57]. Now more than 95 % of the large scale algal cultivation is done by this approach [59]. Change in type of material, size, shape, agitation type and inclination, lead to the discovery of different types of ponds systems [60]. Among the various famous designs, raceways stirred by a paddle wheel is frequently used and others systems such as extensive shallow unmixed ponds, circular ponds mixed with a rotating arm, and sloping thin-layer cascade are also used for larger scale cultivation [61]. It is the economical and durable approach, with high productivity in large scale cultivation in comparison to enclosed PBRs. The maintenance and operational expenditure is also low, but energy input required for processing is high [62,2]. Mass transfer for the nutrient distribution and receiving light for metabolic processes, limit the depth of open pond upto 15cm. Design of open pond system is less technical, which make it more prone to factors like light, temperature, pH, gaseous content and biotic contaimants [63]. Due to above mentioned factors, the algal species must be grown in the selective conditions in open ponds [64,65,66].

Enclosed Photobioreactors (PBRs)

PBRs are available in various shapes (tube, bag and plate) and made up of different (glass, plastic etc.) materials. Mass distribution (supply of nutrients and CO_2) and energy supply is efficient in PBRs, which is the major drawback of open pond system [67,68]. Annular, tubular and flat panel reactors are the familiar designs, but all of them are not commercially used for cultivation of microalgae [69,70]. Technical specificity of PBRs makes them suitable for cultivating species with specific requirements of nutrients, pH, temperature and photosynthetic gaseous [71]. The operational choice of continuous and batch mode in PBRs, provides additional benefit to algal producer. Continuous mode give higher control, better growth and biomass yield as compare to batch [72]. But biofouling in PBRs can adversely affect the productivity of biomass and biofuel. Biofouling decreases the penetration of light in PBRs as algal biomass adheres to the surface, which results in the reduction of photosynthetic efficiency. To overcome biofouling, material for PBRs surfaces should be appropriate or coated with functional groups to decrease adhesion [73].

Harvesting of microalgal biomass

After cultivation, separation of algal biomass is done for downstreaming processing to recover product. Near about 30% of production cost is invested in the recovery process of the biomass [74,58,1]. More than one approach is used for the solid-liquid separation to recover desired biomass, as there is no single efficient approach for harvesting [75]. Weissman and Goebel, [76] suggested the use of microstainer for better harvesting as it is a simple and effective approach. For larger quality of biomass, filter presses is method of choice. But slow and inadequate process of filter presses, limits their frequent use in biomass recovery [74]. For shear sensitive algal cells and small scale harvesting microfiltration and ultrafiltration can be applied. Use of these approaches for higher quantity is not feasible and economical, as maintenance cost of micro and ultrafiltration is high [58].Sedimentation, filtration and ultra-centrifugation are most frequently methods used for harvesting, but prior flocculation increase the efficiency of these methods. Microalgal biomass harvesting using fungi is successful in many cases but separation of fungi from algal cell is complicated and difficult [77]. Amalgamation of self-flocculating microalgal species with the desired non-flocculating cells is an alternative and efficient approach for increasing aggregation size, which results inefficient harvesting [78,79].

Microalgal biomass conversions

Conventional approaches

These are differentiated into four types

(Table 1) as follow:

1) Biochemical approach (Anaerobic digestion and fermentation) for methanol and ethanol production.
2) Thermochemical approach (Pyrolysis, gasification, and liquefaction) for bio-oil, fuel gas and charcoal production.
3) Chemical approach (Transesterification) for biodiesel production.
4) Direct combustion for electricity production.

Biochemical approach

Fermentation

The microalgae have potential to supply sufficient nutrients (carbohydrates and proteins) to carry out fermentation by microbes such as bacteria, yeast etc. [80]. It can be carried out under anaerobic condotions, using pre-processed and saccharified biomass for bioethanol production [81]. *Saccharomyces cerevisiae* and *Zymomonas mobilis* are most frequently used microbes for bioethanol production. But, presence of mannitol in some algal species limits the use of anaerobic fermentation. It required oxygen supply and specific microbe (*Zymobacter palmae)* to carry out fermentation [4]. Hirano et al. [82] reported that *Chlorella vulgaris* is a suitable raw material for fermentation due to its high starch content, which is required for bioethanol production. 3.83 g l^{-1} of bioethanol was obtained using *Chlorococum* sp. as fermentation substrate [63]. Bioethanol can be produced via self-fermentation by microalgae. Ueno et al. [83] produced 450ìmolg^{-1} of ethanol by dark fermentation using *Chlorococcum littorale* (Green algae). Other algal species like *Chlamydomonas perigranulata* and agar weed (red seaweed) can also be used for production of bioethanol by fermentation [84,85].

Anaerobic digestion

The use of algae for biogas production gain interest due to low cellulose, negligible lignin content and high level of carbohydrate. Among the various species of algae sea weeds (*Scenedesmus*, *Spirulina*, *Euglena*, and *Ulva*) have higher potential to produce bio gas via anaerobic digestion [86,87,5,88]. The organic matter of the algal biomass is anaerobically converted in to gases (methane, carbon dioxide and hydrogen sulfide). This is carried out in four steps:

1) Insoluble organic compounds having high molecular weight converted to soluble form and this process is catalyzed by enzymes (from anaerobes present in digestor).
2) Acidogensis: - Carried out by acidogenic microbes, which convert soluble matter to fatty acids and alcohols.
3) Acetogensis: - Acetic acid and hydrogen is formed from fatty acids and alcohols by acetogenic microbes.
4) In last step methane and carbon dioxide is produced by methanogens using acetic acid and hydrogen.

Algal species like *Chaetomorpha litorea* [89], *Macrocystis pyrifera* [90], *Chlamydomonas reinhardtii*, *Scenedesmus obliquus* [91] are reported for bio gas production. The factors like heat, protein content of algae and salt level affect the growth of microbes, consequently affecting the bio gas yield. Sodium ions play vital role in inhibition of microbial growth, so salt tolerant microbes are preferred for anaerobic digestion [92,93]. Pretreatment with bacteria enhances the biogas production [94].

Thermochemical approaches

Pyrolysis

It is a process in which algal biomass is thermally degraded in absence of oxygen for biogas, bio-oil and charcoal production. Further classified into following

1) Conventional: - slow process occurs at the rate of 0.1–1 K/s with maximum temperature of 950K.
2) Fast: - rate (10–200 K/s) of process is fast with temperature maxima of 1250K.
3) Flash: - occurs at rate more than 1000 K/s at temperature range of 1050-1300K.

The abiotic factors which affect the efficiency of pyrolysis includes content of ash and water, temperature and time of vapor residence [95]. But algae pyrolysis is less frequently used in comparison to lignocellulosic matter [96]. Algal species like *Nannochloropsis sp.* [97], *Saccharina japonica* [98] found to produce bio-oil of superior quality.

Gasification

The process involves the conversion of algal biomass into a mixture of gases which are flammable. The conversion is carried by incomplete oxidation and the resulting gas mixture (Carbon monoxide, carbon dioxide, methane, hydrogen and nitrogen) is termed as syngas [68,99,100]. The process is being used from more than thirty years for biofuel production. The gasification occurs in presence of oxygen and at temperature more than 1000ºC. It can be carried by two methods: catalytic and non catalytic. The catalytic mode requires less temperature and further research can be done to decreases the temperature requirement and make it more economical [101]. The syngas has wide range of application in fuel and chemical industry. Syngas can be further converted to fuels like hydrogen (water gas shift reaction), hydrocarbons (Fisher-tropsch synthesis) and liquid fuels [102,103,104].

Liquefaction

It produces bio-oil having high viscosity in presence of organic solvents (propanol, butanol, glycerin etc.), gases (carbon dioxide or hydrogen) and catalyst for conversion of biomass [105,104]. The direct conversion of algal biomass to fuel oil can be achieved by using synthetic gas mixture with specific catalyst [106]. It is further categorized into different types. The disintegration of primary structure and then decomposition of constituents of biomass occurs in aqueous liquefaction. Whereas in alkali liquefaction, decarboxylation of ester bonds formed in between hydroxyl group and formate ion occurs. Salts like sodium carbonate and potassium carbonate are suitable catalyst for depolymeration of lager biomolecules (polysaccharides). The use of solvents like acetone, butanol, propanol etc. ease the handling to tarry oil formed in the reaction. High pressure liquefaction can be used to produce bio-oil, but yield is low as compare to pyrolysis and handling is complicated [105]. The use of biodiesel as an extractant has proved to be an efficient method for lipid extraction [107].

Transesterification

This is chemical process of production of biodiesel from oil extracted from algal biomass. It is a multistep process, in which triglycerides (fatty acids) reacts with alcohols in presence of catalyst to produce esters (biodiesel). Among the various alcohols, which can be used for transesterification ethanol and methanol are preferred for larger scale purposes [4]. The catalyst needed for conversion of algal oil to biodiesel can be inorganic (acid and bases) or biological (enzymes). For the production of 3 moles of biodiesel, one mol trigyceride reacts with three moles of alcohol [108]. The removal of organic solvents from product is very critical, as traces of byproduct and solvents results in failure of machines [109]. Mazuber et al. [110] compared acid catalysis to basic for biodiesel production and reported that the basic catalysis is four thousand times faster than acid catalysis. Lipase enzymes are found to be more efficient than other catalyst due specificity, adaptability and high catalytic activity [111]. The genetical modification of *Escherichia coli* BL21 by integrating *LipB68* in bacteria for production of lipase was done by Luo et al. [112]. More than 90% of biodiesel was produced using lipase as catalyst at temperature of 293.15K, which decrease the energy input of process [4]. The factors like triglycerides content, water level, presence and type of catalyst, temperature and molar ratios of substrates affect the yield [113]. With the advancement in technology nanocatalysts are available for conversion, which have potential to improve condition of process and product quality [114]. It has been reported that cell rupture prior to transesterification enhances the rate of conversion [115].

Direct combustion

The electricity can be produced by direct combustion of the algal biomass [116]. It is generally termed as burning; it is a chemical reaction occurring between biomass and oxygen. Heat is produced primarily, whereas byproducts such as carbon dioxide and water are also there. Direct combustion can be a good alternative of burning of nonrenewable fuel in boilers and stoves for domestic use [101].

Novel approaches

Microbial fuel cell (MFC)

Fossil fuels negatively influence the nature owing to the emission of carbon dioxide leading to global warming and atmospheric pollution [117]. However, many countries are finding a piece of cogent way-out for overcoming energy crisis by utilizing renewable sources. As an upshot of all the efforts, one of the latterly proposed alternative energy sources was fuel cell (FC) which generated energy using high value metal catalysts conventionally. FC is better than other energy generators as it doesn't produce polluting gases (such as SOx, NOx, CO_2, etc.) and do not require movable parts [118]. One type of FCs is microbial fuel cell (MFC) which involves microorganism as a biocatalyst compartment for production of bioelectricity in anaerobic condition [119,120]. Although, Potter, [121] described the electrical current generation by bacteria, but its limited applicability was observed even after five decades [122]. However, in the early 1990s, FCs became far more appealing devices; consequently, MFCs were considered as promising technology [123].

MFC is a novel technology for generating electricity using biomass which is otherwise of no use. MFC is a bio electrochemical system which produces electricity by mimicking natural bacterial interactions. MFC can convert chemical energy to electrical energy using the catalytic reaction of microorganisms during catabolism of contaminants from wastewater [124,125,126]. A typical MFC is composed of anode and cathode compartments. Microbes present in the anode compartment oxidize fuel to generate electrons and protons. An external electric circuit provides the medium for transfer of electrons to the cathode while the protons are

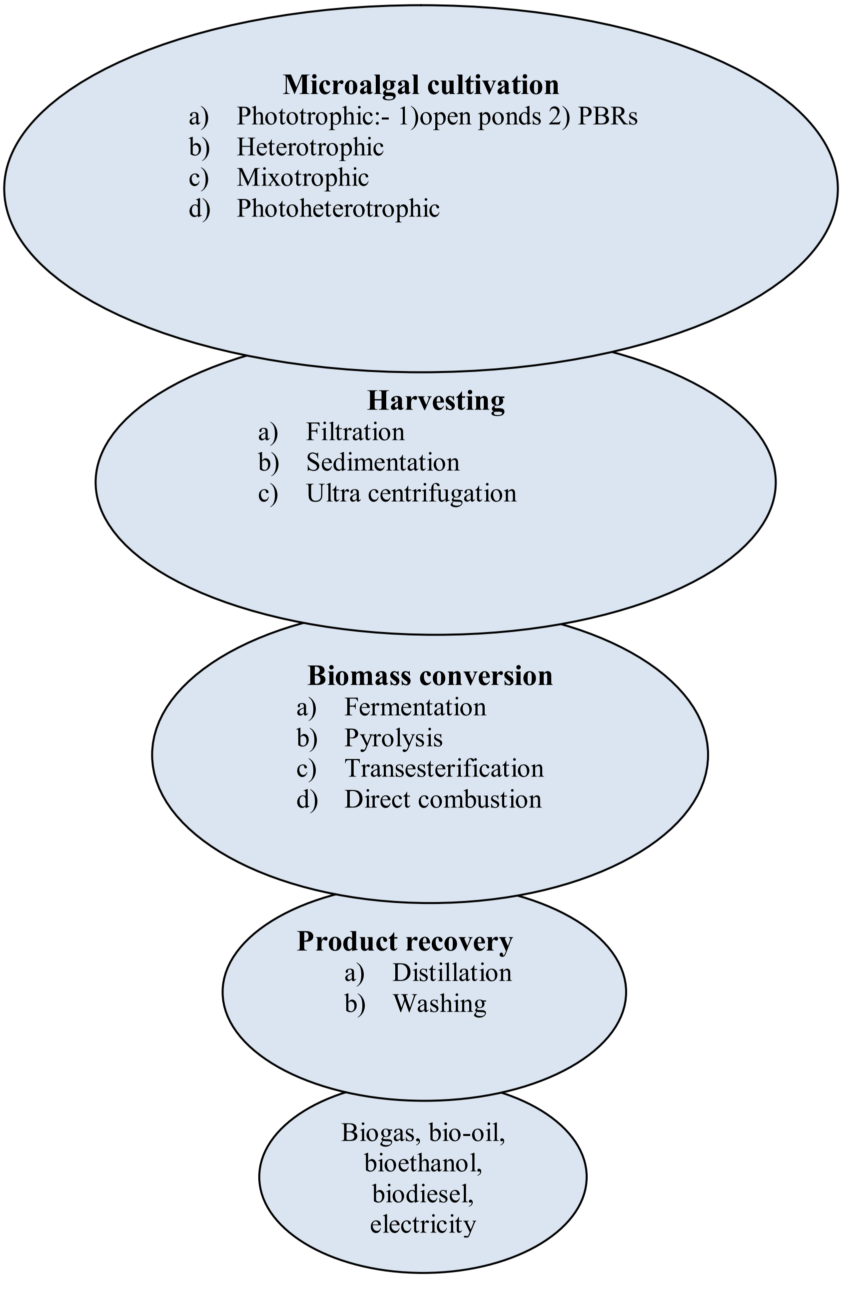

Fig. 1. Flow chart showing process of biofuel production from microalgae

transported via separator. Electrons and protons combine with oxygen to form water in the cathode compartment. MFC's can be used simultaneously to generate clean energy and treat wastewater.

There are two types of MFC: with mediator and without mediator (mediator-less). In case of mediator MFC, the bacteria lacks the ability to use the electrode, therefore, chemical mediators such as neutral red or anthraquinone-2,6-disulfonate (AQDS) are added. For mediator-less MFC, no mediators are added exogenously. The microorganisms can produce metabolic intermediates or end products of anaerobic respiration [127]. In presence of oxygen, microorganisms feed on sugar and produce carbon dioxide along with water. However, in anaerobic environment carbon dioxide, protons and electrons are produced [128].

$C_{12}H_{22}O_{11} + 13H_2O \text{–>} 12CO_2 + 48H+ + 48e-$

Then the cells further utilize inorganic mediators for accepting the electrons produced after crossing the lipid membrane and plasma wall. The mediator starts releasing electrons from the electron transport chain of cell. These electrons will be assimilated by oxygen and other intermediates. The mediator after being reduced transfers the electrons to a depositing electrode and leaves the cell. Therefore, the mediator returns to its original oxidized state after losing electrons and can repeat the process only in anaerobic conditions. On deposition of electrons, the depositing electrode becomes negatively charged. In presence of oxygen, it will collect all the electrons due to its higher electronegativity than the mediator. This forms the basis for generation of electron flow via micro-organisms [129].

Construction

A complete circuit should be designed for generating current using MFC. The mixture solution of mediator and the micro-organism is added to an appropriate substrate such as glucose. This mixture will be kept in an airtight chamber (anaerobic) to allow anaerobic respiration by microbes. An electrode kept in the solution would serve as anode. The second chamber contains another solution and an electrode (cathode). The cathode being positively charged is equivalent to the oxygen sink as it accepts electron. The solution can act as an oxidizing agent but would need large volumes of circulating gas. Therefore, a solid

Table 1. Approaches involved in biomass conversion of microalgae to biofuel.

	Approaches		Process	Product
Conventional approaches	Biochemical	Anaerobic digestion	Anaerbically converted into biofuel	Methanol
		Fermentation	Aerobically converted in	Ethanol
	Thermochemical	Pyrolysis	Thermal degradation in absence of oxygen	Bio-oil, Syngas
		Gasification	Incomplete oxidation of biomass	Syngas
		liquefaction	Direct conversion of biomass to fuel oil	Bio-oil
	Chemical	Transesterification	Chemical conversion of algal oil to biodiesel in presence of alcohols	Bio-diesel
	Direct combustion	Combustion	Burning of algal biomass	Electricity
Novel approaches	Microbial fuel cell (MFC)	Chemical energy is converted into electric energy	Electricity	
	Microbial solar cell (MSC)	Solar energy is converted into electric energy	Electricity	

oxidizing agent can be employed to overcome this problem. The two electrodes should be connected through a wire or any other electrically conductive path. A salt bridge should be attached for completing the circuit and connecting the two chambers. This connection would allow the transfer of protons from the anode to the cathode. Then the reduced mediator carrying electrons would reoxidize after depositing the electrons on the electrode. These electrons then flow through the wire to the second electrode and then to an oxidising material completing the process [129].

Performance of MFCs depends on various factors such as supply and consumption of oxygen in cathode chamber, oxidation of substrates in anode chamber, electron shuttle from anode compartment to anode surface and permeability of PEM [130]. Recently, MFC technology has improved significantly but it is still facing challenges in scale-up and practical application. It encounters various problems such as compartmental turbulence and membrane resistance in proton transportation [131]. MFCs have two major issues in power generation. Firstly, the power production and substrate concentrations are directly related, i.e. concentration of substrate beyond threshold will restrict the power generation [132]. Secondly, high internal resistance due to PEM uses a significant proportion of power generated [130]. To overcome these problems biocathodes have been developed which will improve oxygen oxidation in MFCs [131]. Novel designs of MFCs (single-chamber MFC, stacked MFC and up flow MFC) have been proposed and implemented for amplifying the power generation [123].

Microbial solar cells (MSCs)

This is a novel technology for production of electricity from the solar energy. It exploits the potential of photosynthetic microbes (microalgae) and plants for harvesting solar energy [133]. The electrochemically active microbes are then employed to generate electricity. These cells provide a fixed electric current and can be used in vast areas such as wastewater treatment plant, biodiesel and metabolite production [134]. Yoon, [135] reported a micro-sized MSC, in which anode is made of cyanobacteria (*Synechocystis*). The power (7.09 nW/cm^2) obtained by micro-sized MSC was much higher than previously reported. As solar energy is renewable source of energy, enhancement in MSCs which depend on sunlight for energy production is offering an important and interesting area for future research.

CONCLUSIONS

Employment of alternative sustainable energy resources to replace conventional non renewable fuels is the thirst area of research. Due to high productivity and low land requirement make microalgae the suitable candidate for the purpose. It offers wide range of biofuels including ethanol, diesel and biogas. One of the limiting factors of its large scale production is high input cost of harvesting. So, there is a need for efficient and economical method of harvesting to reduce the input cost. With the advancement in the technology the new approaches for biomass conversion are being discovered and employed in biofuel production. MFC is one such invention, which allows the clean energy production along with the waste water treatment. MSCs are extended form of MFC, where electricity is produced by using biological pathways such as photosynthesis. The future research can be focused on the enhancement of MSCs for energy production.

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