Review

Cyanobacteria: A metabolic power house for harvesting solar energy to produce bio-electricity and biofuels

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Abstract

Cyanobacteria are a group of light harvesting prokaryotic microorganisms displaying a vast diversity in terms of their morphology, physiology, and metabolic capabilities, which appear to be important factors for their survival in diverse ecological niches. The metabolism of cyanobacteria does not fit well into a linear understanding of generalized photosynthetic microorganisms. In addition to the water oxidizing photosynthesis accomplished by coupling photosystem I and photosystem II activities, they also possess intersecting photosynthetic and respiratory electron transport chains in thylakoid membranes which help them to adjust electron flow in the membranes and linked energy metabolism as per the need or demand of the situation. The cyanobacteria have an incomplete tricarboxylic acid (TCA) cycle as they lack 2-oxoglutarate dehydrogenase. However, the enzymes, 2-oxoglutarate decarboxylase and succinic semialdehyde dehydrogenase encoded by their genes convert 2-oxoglutarate to succinate, and thereby use this shunt pathway not only to support the cells to maintain production of reducing equivalents (NADPH), but also to provide unique flexibility to its metabolic system that manifested in their various functions some of which are being progressively understood. The existence of unusual TCA cycle shunt in cyanobacteria opens up a new research avenue for engineering cyanobacteria for biotechnological applications including production of various biofuels of high commercial interest. The unique respiratory metabolisms could also be exploited to generate electrogenic cyanobacterial cells for production of bioelectricity in a fuel cell setup.

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1. Introduction

Cyanobacteria are one of the oldest known living phyla with fossil remnants of more than 3.5 billion years [1]. The phylum of the cyanobacteria has been divided into Gloeobacterales, Synechococcales, Spirulinales, Chroococcales, Pleurocapsales, Oscillatoriales,
Chroococcidiopsis and Nostocales [2] (Fig. 1). Gloeobacterales are unicellular and represented by the genus Gloeobacter that lacks thylakoids. The order Synechococcales is one of the largest families numbering eleven and it encompasses unicellular, colonial and filamentous forms of the organism. Order Spirulininales is characterized by coiled trichomes and it consist of a single family. Chroococcales includes the coccoïds containing nearly irregular thylakoids and eight families are assigned to this order. The order Pleurocapsales is fresh-water unicellular having four families and it reproduces by multiple fission [3]. Oscillatoriales includes seven families of those filamentous taxa that have complex cytology. The order Chroococcidiopsidales holds only one genus Chroococcidiopsis thermalis which is an extremophile [4]. While the order Nostocales includes filamentous cyanobacteria and its members have the distinguishable capability of cellular differentiation and consist of twelve families [5]. The diversity of cyanobacteria metabolism is yet to be adequately elucidated [6]. A broad biogeochemical importance and ecological amplitude of cyanobacteria are reflected in their ability to colonize in wide habitats [7]. It can live in symbiotic relationship with fungi, plants and animals and can adapt to variable illumination, harsh environment, and can store food for future consumption [8]. The majority of symbiotic relationship such as cyanolichens has been reported from terrestrial environment. The symbiotic association of cyanobacteria with feather mosses also reported contributing nitrogen fixation [9, 10, 11].

Cyanobacteria are the dominant autotrophes in the marine ecosystem and primary biomass producers responsible for building up coral reefs. Some filamentous orders are widely distributed in brackish, marine and freshwater ecosystems. Few forms are mat forming and some are planktonic in freshwater and warm marine environment [4]. Benthic cyanobacterial forms play a vital role in strengthening the sedimentary area affected by sea waves. These forms are morphologically and genetically more diverse from its planktonic counterparts. Some studies on benthic community suggest that these habitats also have a diverse cyanobacterial communities that can fix nitrogen [12, 13, 14, 15, 16, 17]. Many genera of cyanobacteria are used as biological indicators for the environment and used to sense water quality [18].

Cyanobacteria can adapt efficiently to extreme environmental challenges rendering them competitive to other life forms. They are found in alkaline hot springs [19, 20] and grow at temperatures up to 74 °C [20, 21, 22]. True psychrophilic cyanobacteria are few and most are able to metabolize at near 0 °C but need optimum 15 °C for growth [23, 24]. Filamentous cyanobacteria have been reported from the high acidic environment as low as at pH 2.9. Cyanobacteria are also reported to exist in a harsh alkaline environment in pH as high as 13 [25]. These photosynthetic organisms are also known to thrive under high solar and UV radiation [26, 27, 28, 27, 29]. Halotolerant cyanobacteria, present in the coastal environment colonize euryhaline conditions and can grow in integrated salt environments [30].

Cyanobacteria are pioneer species in new habitats, populate and deliver photo-biomass as a platform for supporting other lives. It can fix an estimated 25 Gt a⁻¹ [31] of carbon in globe from atmospheric CO₂ by capturing the solar energy into energy dense biomass. This route of massive solar energy transformation into microbiological energy medium opens the scope of harvesting various forms of eco-friendly energy sources [32, 33]. Cyanobacteria are becoming excellent candidates with high significance in the field of agriculture, pharmaceuticals, bioremediation and biofuels. Furthermore, the exceptional capability of hydrogen production by these microorganisms has strongly stimulated the interest in the field of bioenergy and bioelectricity [34]. We attempt here to highlight the advancement of knowledge on the utilization of cyanobacteria for production of various biofuels of high industrial interest and the use of these photosynthetic microorganisms as biocatalysts for generating electric power in a fuel cell setup. The progress on understanding of the linked metabolic pathways will also be discussed alongside the aforesaid application aspects of these microorganisms. An initial description on the molecular aspects of photosynthesis has also been included for the reference of the readers to quickly identify some of the relevant metabolic concepts being briefly discussed in the subsequent sections.

2. Harvesting solar energy: photosynthesis

The photosynthetic apparatus in cyanobacteria is present in the thylakoid membranes corresponding to that found in chloroplast of plants. Phycobilisome (PBS), a group of pigmented proteins (phycobiliproteins) present as an ordered array of closely spaced granular structures in the thylakoid membrane, traps light and transfers the captured photon energy into the photosynthetic reaction centers. Hemidiscoidal phycobilisomes are the most commonly found form of light harvesting complex in cyanobacteria. It is composed of two sub domain, the core and the peripheral rods. The core consists of three cylinders composed of allophycocyanin and from it radiates six peripheral rods constituting second sub domain of phycobilisome. The chromophores phycoerythrin and phycocyanin constitute the peripheral rods and traps light. The light energy absorbed by peripheral rod proteins is transferred in a cascading
way to allophycocyanin to PS I or PS II reaction center [35] which collaborate to transfer electrons from water to NADP$^+$. Eventually, the electron is transferred to a P680 pheophytin complex which reduces QA, the bound plastoquinone molecule. QA reduces a secondary quinone QB (semiquinone) leading to the formation of plastoquinol. On the luminal side of PS II, the light-induced chlorophyll cation radical P680$^+$, oxidizes a tyrosine residue, which in turn oxidizes a cluster of four manganese atoms. Splitting of water occurs at this metal center, and the metal cluster is capable of assembling four oxidizing equivalents that act as a hinge to release O$_2$ from two molecules of water. The five successive oxidized forms are termed as S states. The reaction center also contains a non-heme iron atom and a stable tyrosine radical [35]. The intermediary S states may act as a regulatory mechanism and link between S states and the tyrosine radical. PS II is made up of both integral membrane proteins and extrinsic proteins. PSII is also susceptible to damage by sunlight at all light intensities. However, a repair cycle operates within PSII thereby support to sustain PSII activity [36]. The proton gradient generated as a result of this flux is used for ATP synthesis.

The excited electron from PS II travels down to the cytochrome $b_6f$ complex in the z- scheme. The rate limiting step of quinol oxidation in aerobic photosynthesis is catalyzed by plastoquinol-c553/plastocyanin oxidoreductase (Cyt$b_6f$ complex) enzyme. Electrons released from plastoquinol oxidation are accepted by the cytochrome $b_6f$ complex, which provides electrical connection between the PS II and PS I photochemical reaction centers [35], [196]. This complex is coded by pet (photosynthetic electron transport) genes that contains Cyt$b_6$ — a low potential protein, subunit IV, a high energy Rieske iron sulphur protein [2Fe$^2$S] center, Cyt f protein, two $b$ and a c-heme moiety. The proton-pumping cytochrome $b_6f$ complex is a dimer and contains eight firmly bound subunits in the cyanobacterium M. laminosus [37]. The respiratory and photosynthetic pathway in cyanobacteria requires oxidation of the quinone pool by the Cyt $b_6f$ complex and ultimately by molecular oxygen at a terminal cytochrome aa$_3$ type oxidase [38] although obligate role of the later is yet to be clearly elucidated. Thus the cytochrome $b_6f$ complex appears to be part of a common set of elements essential for growth of cyanobacteria by photosynthesis or respiration.

The PS I complex in cyanobacteria uses all of its biochemical machinery to oxidize plastocyanin or other electron carriers and reduce ferredoxin across a vast thermodynamic gradient. The membrane-bound components of the complex comprise of the reaction center P700, a chlorophyll a dimer and the primary donor absorbs light energy releasing electron that is captured by $A_0$, the
primary electron acceptor and a chlorophyll a (Chla) monomer. This electron is then transferred to the secondary electron acceptor molecule A1, a phylloquinone which acts to stabilize the rapid transient charge separation [39]. The psa genes codes for PS I multimeric protein complex and consists of eleven discrete proteins as reported from various cyanobacterial strains. Both monomeric and trimeric cyanobacterial PS I forms has been elucidated. The trimeric form is the prominent oligomeric state at low light intensity, which is the natural habitat environment of cyanobacteria. An enormous antenna complex consists of 90 antenna chlorophyll and 22 carotenoids captures light. The electron transport chain (ETC) in PS I constitute two phylloquinone, six chlorophylls, and three iron sulphur [4Fe–4S] clusters [40]. Cofactors of the ETC in PS I from cyanobacteria and higher taxon like plants are identical. PsAM and PsAX are the proteins found exclusively in cyanobacteria. Rest of the main proteins with all the cofactors are well conserved between plants and cyanobacteria. The electron from secondary electron acceptor A1, i.e. phylloquinone is transferred to three iron-sulphur clusters [4Fe–4S] designated as Fx, Fy, Fz in cascading manner rendering P700 in an oxidized state. From Fy the electron travels to ferredoxin located on the stromal side of PS I. Ferredoxin after reduction leaves its docking site to transfer the electron to ferredoxin-NADP+ reductase that produces the end product NADPH to be used for CO2 assimilation. The soluble electron donors plastocyanin and cytochrome C549 located on the luminal side of PS I receives the electron along the z-scheme and reduces P700 and stabilizes loss of energy due to charge recombination [41]. The changes in copper and iron concentration, however, do not lead to any known alterations in the polypeptide composition of the membrane-bound PS I complex.

The understanding of cyanobacterial F-ATPases is limited. The F1 portion purified from cyanobacterial sources to reconstitute photophosphorylation [42], [43] showed the same five subunits (α, β, γ, δ, and ε) with molecular masses similar to those of other F-ATPases [42]. The integral membrane protein complex i.e. the F0 portion, comprises of single copies of sub units a, b and b’ and about ten copies of subunit c. The extrinsic protein complex attached to the F0 portion has 3α, 3β, 1γ, 1ζ, and 1ε subunits [44]. ATPase enzyme comprises of a total of six sites, of which three are catalytic to which metal and nucleotides bind forming complexes. ATP synthesis occurs in conformity with the transfer of phosphoric acid residue between ADP and water when all the phosphate groups are synchronized to the catalytic sites in active state.

Cyanobacteria have a plant-type ferredoxin — ferredoxin I that transfer electrons from membrane-bound, iron-sulfur centers in PS I to FNRI (Ferredoxin-NADP oxidoreductase). It is a strongly acidic protein with a [2Fe–2S] center that transfers one electron. Ferredoxin-I is evolved from a single gene as evident from the conserved gene clusters. It is replaced in the situation of iron deficiency by the non-iron containing flavoprotein, flavodoxin. Ferredoxin is loosely held in the thylakoid membranes making it easier to serve other electron acceptors e. g nitrite reductase, thioredoxin reductase etc [45]. Flavodoxin is also an acidic protein resembling ferredoxin in net charge and redox properties.

Plastocyanin is a protein of approximately 100 amino acid residues that act as an electron carrier and contains a single atom of copper which is its redox-active component in electron transfer. It is thought that this protein transfers electron from cytochrome f to P700 of PS I in the electron transfer chain of photosynthesis. Experiments indicate that the ‘east–face acid patch’ of plastocyanin is the site for receiving electrons from cytochrome f and the ‘north–face hydrophobic patch’ of plastocyanin is the site for donating electrons to PS I [46].

Cytochrome C549 is another soluble electron carrier protein replaces plastocyanin in some cyanobacteria and algae experiencing copper exhaustion. It permanently replaces plastocyanin in some species. Several isoforms of this protein have been reported along with variations to different growth conditions relating to various physiological roles. There is evidence that this particular protein has functions, both in photosynthesis and respiration. It is distributed uniformly in the cytoplasm. Another low potential cytochrome C549 is found in many cyanobacteria that support the structural stability of PS II.

Cyanobacteria have an efficient CO2 uptake and concentrating mechanism. Central to the mechanism is the carboxysome, a icosaehedral or quasi-icosaehedral protein micro-compartment within the cell whose outer shell holds the Rubisco together with a carboxysomal carbonic anhydrase (CA) [47]. The CA converts the accumulated HCO3- anion to CO2 within the carboxysome. The protein shell of the carboxysome possibly prohibits the efflux of elevated levels of CO2 from itself thereby making it accessible to Rubisco enzyme within the organelle. Active CO2 and HCO3- transporters operate to bring in the substrate. They are present both in the plasma membrane and thylakoid membrane, both in high and low affinity form [48].

In cyanobacteria, the oxygenic photosynthesis and aerobic respiration occur in the same compartment [48]. Some cyanobacteria contain two distinct respiratory chains, one in the thylakoid and the other in the cell membrane. The photosynthetic apparatus is exclusively present in the thylakoids. Components like NADPH, plastoquinone, and a chloroplast type cytochrome b/f complex which are not involved in respiratory system of other organism are also part of the respiratory chain of cyanobacteria [49]. There is significant evidence that the respiratory chain in cyanobacteria is branched and may turn out no chemical reaction is common to all respiratory electron transport pathways. Therefore, no specific sequence of reactions can be said to make up the respiratory electron transport chain as is found in mitochondria of eukaryotic organisms. The lack of complete information on respiration of cyanobacteria is a major roadblock in defining it in a complete manner.

Some cyanobacterial species have developed the ability to extract energy heterotrophically in response to environmentally challenging conditions along with its photosynthetic capability [50]. They catabolize glucose pathway, the glycolytic pathway, and a type IV tricarboxylic acid (TCA) cycle and oxidative pentose phosphate (OPP) to produce ATP, NADPH, and carbon anabolic precursors for further cellular processes as shown in Fig. 2 [51]. All of the above mentioned metabolic pathways, CO2 fixation, gluconegenesis, and glycolysis, are performed in the carboxysome and cytoplasm where different enzymes of both photosynthetic and respiratory pathways exist.

3. Cyanobacteria for bioenergy production

3.1. Electricity from cyanobacteria

The ability of cyanobacteria to grow photoautotrophically has appeared to be one of the major driving forces to explore these bacteria as fuel cell catalysts to generate electric power from sunlight in a self-sustainable manner. The potential application of these light harvesting organisms for integrated waste treatment and power generation through MFC technology is huge due to their usual tolerance to high salt concentration and organic contaminants, survival under adverse environmental conditions (such as, high temperature, low and high pH) and their ability to form stable biofilms and grow symbiotically with a wide range of organisms on earth [52]. However, among the known microbial strains or their consortium reported so far as catalysts in MFCs, the work on cyanobacteria is quite less [53]. Till writing this report, amongst the
total publications on microbial catalysts in MFCs (in open access and SCI journals), only ~ 6.5% on cyanobacteria as compared to ~ 39.7%, ~31.5%, ~12.1% and ~10.2% for Shewanella sp., Geobacter sp., algae and E. coli sp., respectively.

MFC is a device that converts biochemical energy into electrical energy through microbial oxidative catalysis at the anode and parallel reductive catalysis using an electron acceptor, such as oxygen, at the cathode[54]. Like chemical fuel cells, two compartments - the anode and cathode half-cells – are usually separated by a proton exchange membrane in the biofuel cells (BFCs) (Fig. 3). The electrons generated from the oxidation of fuel substrates at the anode are directed to the cathode via an external circuit, and the associated protons are transported across the membrane to the cathodic chamber for sustaining the current generation[55].

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The electrogenic behaviors of cyanobacteria are well documented. However, how the electrons generated in the cellular process are channelized across the electrogenic metabolic pathways (photosynthetic/respiration) to the external environment of these photosynthetic cells are yet to be clearly elucidated. Nevertheless, the presence of intersecting P-ETC and R-ETC in the thylakoid membranes[56] may additionally support the electrogenicity of these microorganisms. In a study, a conserved light-dependent (in the absence of any exogenous organic fuel) electrogenic activity of diverse genera of cyanobacterial strains has been demonstrated [31]. The diversified genera of cyanobacteria including Anabaena, Calothrix, Pseudanabaena, Nostoc, Synechococcus, Synechocystis PCC6803 and Lyngbya shown to have a preserved electrogenic activity originating from the P-ETC[31]. The finding was fundamentally different from those reported on anaerobic MFCs, PMFCs or sediment MFCs, where the electrons for current were ascribed to be generated from R-ETC[57]. Using site-specific inhibitors, the P-ETC was confirmed as the source of electrons. Treatment with PS II inhibitors [3-(3,4-dichloro-phenyl)-1,1-dimethylurea (DCMU) and carbonyl cyanide m-chlorophenylhydrazone (CCCP)] and PS I inhibitor [phenylmercuric acetate (PMA)] led to decrease in electrogenic responses of two cyanobacterial species (Lyngbya and Nostoc) under illumination. Additionally, Duorquinol that competes with DCMU for binding to the QB site on PS II was used to confirm the origin of electrons from PS II. Notably, Duorquinol mimics the activity of PQ by shuttling electrons between PS II to PS I [31](Fig. 4).

As discussed elsewhere, photosynthetic and respiratory chains share several redox active compounds in thylakoid membrane namely the plastoquinone (PQ) pool, plastocyanin (PC) and cytochrome b6f (Cyt b6f). Hence, the study on electrons flux through these shared points may enrich our knowledge on the electrogenic metabolic channels precisely involved in these photosynthetic organisms for discharging the electrons into the environment. From an investigation in Synechocystis sp. PCC 6803 using the metabolic

![Fig. 2. Respiratory electron transport pathway in cyanobacteria.](image-url)
inhibitor DCMU and methyl viologen (a competitor of NADP+ for capturing photosynthetic electrons), it was inferred that the residual photo current produced in presence of DCMU may come from electrons that were initially introduced into the PQ pool from the respiratory chain and afterward used to reduce ferredoxin via PSI. Notably, the photosynthetic and respiratory chains in the thylakoid membrane in this organism share the PQ pool. This suggested that the electrons responsible for generating the current, leave the P-ETC at the reductive side of PS I [58]. Most of the photocurrents is contributed from PS II was also demonstrated for other organism like, Nostoc sp. by using the inhibitors such as, DCMU. Further, chlorophyll-a followed by phycocyanin was reported to be the major contributor to light capture that resulted in increased generation of photocurrent [52]. The mutant strain of Synechocystis sp. PCC6803 lacking chlorophyll binding CP47 protein significantly losses 81–84% photocurrent production capability [59]. In order to transduce the light energy directly and efficiently to electrical power the metabolism of the cyanobacterial cells (Synechocystis sp. PCC 6803) was manipulated rationally by deleting the terminal oxidase complexes and thus, eliminating the possible function of molecular oxygen as an electron sinks. It is likely that the reducing power of cyanobacteria can be dissipated to oxygen through the terminal oxidases during respiration or in times of excess electron production. The result showed higher ferricyanide (a membrane-impermeable soluble electron acceptor) reduction rates as a consequence of creating an excess of reducing power. The gain was higher in dark conditions, especially from the triple deletion (bd-quinol oxidase, cytochrome c oxidase, and alternative respiratory terminal oxidase) strains where the mutant transferred the equivalent of 10% of its aerobic respiratory electron flux to ferricyanide, causing a 23-fold increase in ferricyanide reduction rate compared to the wild-type [60]. To track the source of reductive equivalent that is eventually utilized to generate the transmembrane electron flow and proton motive force responsible for the electrogenicity of the cells and generation of ATP, respectively, the understanding of TCA cycle is also important. The primary function of TCA cycle is to produce NADPH/NADH in addition to provide essential precursor metabolites that are required for the biosynthesis of cellular components, such as fatty acids. Interestingly, the cyanobacteria have a variant of common TCA cycle as they lack 2-oxoglutarate dehydrogenase and succinyl CoA synthetase. The enzymes, 2-oxoglutarate decarboxylase and succinic semialdehyde dehydrogenase encoded by their genes, as studied in Synecococcus sp. PCC7002, convert 2-oxoglutarate to succinate, and thereby this organisms use this shunt pathway to regulate the production of reducing equivalents (NADPH) in addition to other functions most of which are not yet known [61], [62].

The electrons generated from the oxidation of organic substrates are transferred by the bacteria to the anode either or combination of some of the following mechanisms: (i) direct electron transfer (DET) [63], (ii) ‘nanowires’ [64] and (iii) mediating electron transfer (MET) using chemical mediators/shuttling agents [65]. As early as 1985, Tanaka et al. [66] investigated a bioelectrochemical system (BES) employing cyanobacteria, Anabaena variabilis as biocatalyst and 2-hydroxy-1,4-naphthoquinone (HNQ) as artificial redox mediator operated under anaerobic conditions and confirmed current output from the cell. Later on, Synechococcus sp.
when studied as catalyst in photosynthetic microbial fuel cell (PMFC) using HNQ as mediator an increase in cell voltage upon illuminating with light was observed. When glucose was added to the anode solutions after a discharge of 13 h upon illumination, current output of 230 μA was obtained. However, this resulted in low coulombic yield (30%) from glucose due to its incomplete oxidation of all the carbon in the chain [67]. A photosynthetic BES was also developed that utilizes \textit{Synechococcus} sp. PCC7942 and bilirubin oxidase as anodic and cathodic biocatalysts, respectively in H-type cell. The device generated power (maximum 300 mW m$^{-2}$ - 400 mW/m$^{-2}$) without using any special chemical fuel. In another study the photo-anodic current density increased linearly with increasing concentration of cyanobacterial cells in a quinon mediator bound MFC. However, further increase in current was limited by light scattering and large thermodynamic losses in the electron transfer from the photosystem to the mediator [68]. The electron transfer efficiency of \textit{Synechococcus} sp. PCC7942 into exogenous electron acceptors 1, 4-Benzoquinone (BQ) and 2, 6-dimethyl-1, 4-benzoquinone (DMBQ) from the photosynthetic system by entrapping the cells on the surface of the DMBQ- embedded carbon paste electrode was examined and a current density of 10 μA cm$^{-2}$ was achieved [69]. In order to boost up photocurrent generation, two mediators, one soluble (ferriyanide) and one cation based polymeric mediator were used with \textit{lytolyngbia} sp. (CYN82) immobilized on graphite electrodes that resulted a maximum current density of 48.2 μA cm$^{-2}$ [70].

Cyanobacteria also generate current in photo BES via DET mechanism. From power generation point of view, DET from the bacteria to the electrode is more desirable than MET, as the over-potential could be minimized and design as well as operation of the electrochemical cell could be simplified in the former case [71]. A rudimentary design electrochemical cell was reported where the cyanobacteria (\textit{Nostoc} sp.)/carbon nanotubes (CNT) on the anode and \textit{laccase}/CNT on the cathode as catalysts were used. The cell produced a maximum current density of 250 mA m$^{-2}$ and a peak power density of 35 mW m$^{-2}$ without any mediator. The electricity generation capability of the cell was however, significantly improved upon addition of 1,4-benzoquinone as a redox mediator, with a current density of 2300 mA m$^{-2}$ and a power density of 100 mW m$^{-2}$ [52]. A mediator less flexible direct photosynthetic/metalic biofuel cell for mobile use involving purple photosynthetic bacteria (\textit{Rhodopseudomonas palustris}) as a fuel source was also developed that generate a maximum power density of 5.26 μW/cm$^2$ with an open-circuit voltage of 0.089 V [72]. A mediator-free and membrane-less PMFC was constructed where a thin biofilm of \textit{Spirulina platensis} on the gilding gold mesh was used as anode. The PMFC produced a maximum power density of 10 mW m$^{-2}$ [73]. The organism (\textit{Spirulina platensis}) was further investigated in a membrane and mediator less system, to assess the feasibility of using these PMFC as instant-use and portable devices and observed that once the organism was attached to the anode voltage was instantly generated. When two PMFCs were connected, a maximum OCV of 450 mV and 310 mV were obtained for serial and parallel connections, respectively [74]. Native cyanobacteria (\textit{Nostoc} sp.) when illuminated with monochromatic light of different wavelengths, power density of 100 mW m$^{-2}$ and 35 mW m$^{-2}$ were achieved with and without addition of redox mediator [52]. Exceptionally high power density (>100 mW/m$^2$) was achieved by using mediator-less, membrane-free, microfluidics based bio-photovoltaic device using \textit{Synechocystis} sp. PCC 6803 biofilm as catalyst fabricated by using soft lithography techniques with a low melting alloy InBiSn. The approach is suggested to be applicable to any photosynthetic biofilms forming organism [75]. The strain \textit{Synechocystis} sp. PCC 6803 was also reported to produce nanowires in response to electron-acceptor limitation [76].

The performance of PMFC is depend on various environmental factors such as, light intensity, temperature, pH etc. The response of a PMFC with \textit{Arthrosira maxima} as catalyst exhibited sensitive towards temperature and light perturbations. Upon doubling the light intensity from 10 W m$^{-2}$ to 20 W m$^{-2}$, the power densities were increased from 6.7 μW m$^{-2}$ to 9.9 μW m$^{-2}$ at 25°C and 11.2 μW m$^{-2}$to 24.8 μW m$^{-2}$ at 35°C. \textit{Arthrosira maxima} was susceptible to photoinhibition with increase in the light intensity [77]. When the strain itself was used as a carbon substrate for growth of purple non-sulfur bacterium \textit{Rhodospseudomonas pal-ustris} in MFC, a power generation of 10.4 mW m$^{-3}$ was achieved which was higher than the power density obtained by using glycerol and acetate substrates [78].

Photo-electrochemical cells have also been developed by using isolated photosynthetic reaction centers [79], thylakoids [80, 81] or photosystems PSII [82] and PSI in the anode and PSI in the bio- cathode [84]. The constructs however suffers from drawbacks like labor-intensive procedures for isolation, complex immobilization strategies, expensive metals as immobilization supports and stability [52]. The key issues like stability, DET photocurrent production and electrode surface area needs to be addressed to make photo bio electro-catalytic devices practical for real-life applications [85]. Miriam et al. explored seven different configurations of PMFCs stressing on the fact that much scale up might not be necessary to provide enough current to power environmental sensors if excreted organic matter from cyanobacteria or plants are used as feedstock in sediment based MFCs [71].

Synergistic interaction between photosynthetic microorganisms and heterotrophic bacteria (existing in places, such as lagoon, coastal area and microbial mat) was exploited in a sediment-type self-sustained PMFC to generate electricity. Both the sediment and the air-cathode PMFCs showed an increased current in the dark (54 ± 2 μA) and a decreased current in the light. The accumulation of organic compounds leads to increase in current in the dark following the light reactions. The current was decreased following prolong illumination as dissolved oxygen evolved during photosynthesis acted as electron scavenger. There is feasibility to power remote sensors for monitoring environmental conditions by converting solar energy into electricity through the PMFC with apt design strategy [86].

In a study four categories of microbial biocatalysts (\textit{S. cerevisiae}, \textit{Chlamydomonas reinhardii}, \textit{Geobacter sulfurreducens} and \textit{Synecho-cystis} sp. PCC 6803) were studied for in silico modelling of MFCs [87]. Biofilms of green algae (\textit{D. tertiolecta} and \textit{Chlorella vulgaris}) and cyanobacteria (\textit{Synechococcus} sp. WH 5701 and \textit{Synechocystis} sp. PCC 6803) were developed on indium tin oxide-coated poly-ethylene terephthalate (ITO) in a Bio-photovoltaic (BVP) single chamber system that produced a power density of 10.3 mW m$^{-2}$. The four BVPs (each 110 cm$^2$) in series connection generated power sufficient to run a commercial digital clock [88]. A variety of different anodic conductive materials: stainless steel, ITO, carbon paper and glass coated with a conductive polymer polyaniline were used to develop multi-channel BVP device to conduct photosynthetic biofilm studies on filamentous cyanobacterium, \textit{Pseudanabaena limnetica}. ITO offers the largest photo responses with power output 134 pW ± 18 pW nmol$^{-1}$Chl and 472 pW ± 80 pWnmol$^{-1}$Chl during the dark and light cycles respectively, whereas carbon paper showed the lowest power outputs of 22 pW ± 4 pWnmol$^{-1}$Chl and 41 pW ± 4 pWnmol$^{-1}$Chl under corresponding conditions [89]. In another study, phycobiliprotein was extracted from \textit{Spirulina} sp. to composite with squaraine dye to sensitize nanocrystalline TiO$_2$ photoanode for building dye sensitized solar cell, and the photoelectric properties of the cell were also investigated [90].

MFCs can also serve a two-fold purpose of producing electrical power and degrading effluents from agricultural, industrial and
municipal waste water. The use of cyanobacteria as photo-bioelectrocatalysts to generate electrical power represents a simple and sustainable system lacking any significant negative impact on the environment [85]. Production of electricity from Synechocystis PCC 6803 results in no net CO2 production. Under high intensity light, the optimum removal of CO2 was 625 mmol m\(^{-2}\) over 20 h [91]. In another study, a low-cost oxygen-hydrogen bio-fuel cell for generation of electricity using Nostoc as a source of hydrogen was investigated where 1L free cell algal reactor was attached to the anode end of the fuel cell for hydrogen gas input. The cell generated about 300 mV of voltage and 100 mA of current [92]. The studies on the production of hydrogen using Spirulina plantensis and Spirulina maxima were also conducted for supply to a low temperature alkaline fuel cell [93].

3.2. Biofuel production

The photosynthetic organisms are the primary feedstock for deriving various biofuels. Among these renewable biofuel sources, algae and cyanobacteria in general, have some advantages over plants such as, rapid growth rate, possible to produce them in suitable in-house bioreactor, and potential for cultivating them on non-arable land [94]. Many cyanobacteria are also tolerant of marine and industrial waste water. The efficiency of cyanobacteria for converting captured solar energy into biomass in the field is also usually higher than the terrestrial plants [95, 96]. Cyanobacteria have other benefits as well, such as easier genetic manipulation than eukaryotic algae for target fuels production and their ease of excreting directly into the culture medium. Notably, the genome size of cyanobacteria is relatively small and many of the genomes (atleast 41 strains) including Synechocystis sp. PCC 6803 have already been sequenced. Thus it is expected to be less complicated even to perform system biology approaches in these organisms for biofuel production as compared to eukaryotic algae [97].

Production of various biofuels such as, biohydrogen, biodiesel, bio alcohols etc. using different native cyanobacterial strains has been investigated [98]. The biological process of hydrogen production by cyanobacteria can be well exploited in a broad spectrum of applications ranging from food to chemical industries [101], [138]. Almost 14 cyanobacterial genera have been known to produce hydrogen [100]. Hydrogen producing cyanobacterial species may be heterocystous, non-heterocystous and marine [101]. Heterocystous possess unique heterocysts structures that provides a micro-anerobic environment suitable for the nitrogenase activity. These structures are surrounded by a thick envelope that limits the diffusion of oxygen into this site. Conversely, there is a temporal separation between the photosynthetic oxygen evolution and the nitrogen fixation in non-heterocystous cyanobacteria.

Two distinct types of enzymes, namely, nitrogenase and hydrogenase are involved in generating molecular hydrogen. In the process of fixing nitrogen, molecular hydrogen is formed by bioprocess through a largely irreversible process catalyzed by nitrogenase (reaction 1). The maximum rate of hydrogen production is however, within 1/3rd to 1/4th of nitrogen fixation. The whole reaction including the enzyme is sensitive to oxygen, and thus naturally protected and performed within the environment of heterocysts.

\[
16\text{ATP} + 16\text{H}_2\text{O} + \text{N}_2 + 10\text{H}^+ + 8e^- \rightarrow 16\text{ADP} + 16\text{Pi} + 2\text{NH}_4^+ + \text{H}_2
\]

(1)

The nitrogenase enzyme is composed of two enzymes, dinitrogenase and dinitrogenase reductase. Dinitrogenase (a heterotetramer) splits molecular nitrogen into nitrogen atoms while, dinitrogenase reductase (a homodimer) mediates the transfer of electrons from the external electron donor (a ferredoxin or a flavodoxin) in PS I to the dinitrogenase. Three types of dinitrogenase namely, Type I − contains Mo, Type II − contains V and Type III − contains Fe were reported. Hydrogenase is one of the least studied redox catalysts of cyanobacteria. Two distinct types of hydrogenases occur in cyanobacterial species: (1) uptake hydrogenase (encoded by hupSL) present in the thylakoid membrane of heterocysts from filamentous cyanobacteria oxidizes hydrogen in a reaction known as oxyhydrogenation or Knall gas reaction. Some nitrogen fixers increase the accumulation of hydrogenase to recapture the excess hydrogen and oxidize it to produce ATP [102] to fill up the energy deficit. The reaction is thus counterproductive in regards to the industrial production of hydrogen fuel. Therefore, the cyanobacterial species selected for developing hydrogen production process should be devoid of uptake hydrogenase activity which may also be achieved by subjecting specific mutation on the strain. The exact roles of hydrogenases in nitrogen-fixing cyanobacteria are yet to be clearly elucidated. (2) ‘Reversible’ or bidirectional hydrogenase (encoded by hoxFUYH) that either breaks or produces molecular hydrogen [103], [104] is largely a [Ni−Fe]-hydrogenase type consisting of a hydrogenase dimer coded by hoxYH gene [105]. Due to obvious reason of involving the molecular hydrogen in the process, the reversible hydrogenase is very sensitive to oxygen and thus must function under anoxic condition to produce hydrogen. Though this enzyme is not widespread in cyanobacterial species, it is distributed among both nitrogen-fixing and non-nitrogen-fixing cyanobacteria. In addition to the involvement of specialized metabolic pathways mentioned above, many physico-chemical factors that have influence on the photosynthesis-linked production of hydrogen by cyanobacteria are also identified. Light [106], [107], [108], [109], temperature [101], nitrogen source [110], nutrient and carbon source [106], [111], oxygen [112], sulphur [113], hydrocarbon gas, salinity [114], [115], and micronutrients [116] have been studied for the production of hydrogen as reviewed comprehensively by Tiwari and Pandey [101]. Briefly, for hydrogen production by many cyanobacteria the optimum temperature range falls within 30 °C–40 °C. Many nitrogenous compounds including molecular nitrogen inhibit the production of hydrogen by cyanobacteria. The production of hydrogen is stimulated by different sugars with mannose being the one reported as the highest stimulator. The starvation of sulphur and presence of methane enhances hydrogen production in few cyanobacterial species under some selected conditions. Hydrogen production is lowered in some cyanobacteria under increasing salinity due to the consumption of some energy needed for maintaining sodium homeostasis in the cells. The effect is however, not very prominent in case of marine cyanobacteria. Positive effect of trace elements like Cu, Co, Mo, Zn and Ni on the production of hydrogen has been reported due to their nitrogenase activating roles. However in wild cyanobacterial strains, light to hydrogen conversion efficiencies falls below the theoretical maxima of 0.1 % [99]. Under tightly controlled laboratory conditions the maximum efficiencies equivalent to 1 % have been transitorily observed [117]. The low hydrogen production has been attributed to the tendency for [NiFe] hydrogenases to thermodynamically favour the reverse reaction in addition to the general oxygen sensitivity of the enzyme hydrogenases [118]. To improve the cyanobacterial production of hydrogen, various strategies have been reported in addition to the above mentioned studies on various physico-chemical parameters. Among them, combined cultivation of cyanobacteria with other heterotrophic bacteria [119], [120], entrapment of microorganisms within reverse micelles [121], [122], genetic engineering [123], [124], [103], [125], [126], [127], [128], [129], [130], [131], [132],
network [133], [134], [135], [136], [137], [138], [139], and metabolic pathway engineering [140], [141], [142] are documented on improving the cyanobacterial hydrogen production. One attractive genetic engineering approach suggested to improve hydrogen yields is through heterologous expression of an oxygen-tolerant [FeFe] hydrogenase [138]. Additionally, hydrogen generation through photo bioreactor using cyanobacteria may be an attractive option owing to the expected advantages, such as maintaining modest nutrient requirements and efficient capture of solar energy [100]. A biophotocatalytic cell (BPE) system for production of hydrogen gas in oxygenic photosynthesis using cyanobacterium, Synechocystis sp. PCC6803 has been reported [143]. The device was constructed with ITO anode, Pt-coated titanium cathode, and a cation exchange membrane and operated with a bias potential of 1.0 V to 1.4 V. This O2 evolving autotrophs sustained hydrogen production without inducing anaerobic condition in the culture medium or hindrance to photosynthetic O2 evolution for several hours. The improvements made so far on cyanobacterial hydrogen production following various strategies as mentioned above are however, yet to be adequately scrutinized in a large scale photo-bioreactor for developing an economically viable technology.

The basic research on the cyanobacterial production of fatty acids and lipid, which are eventually being used as feedstock for biodiesel production, is limited [144]. Like most of the other organisms, the wild strains of cyanobacteria also produce fatty acids from the precursor, acetyl-CoA. Initially, malonyl-CoA is formed from acetyl-CoA through a rate-limiting reaction catalyzed by acetyl-CoA carboxylase (EC 6.4.1.2). The malonyl-CoA is then entered a reaction pathway leading to the formation of fatty acyl-ACP, which is later directed to synthesis different glycerolipids [144]. The enzyme, phosphoenolpyruvate carboxylase (PEPC) appears to divert the carbon flux away from the fatty acid biosynthesis by acting on phosphoenolpyruvate, the precursor of acetyl-CoA. There is a report that the lipid content in Synechococcus sp. PCC 7002 could be increased by enacting an antisense expression of PEPC-coding gene [145].

There is, however an additional route for converting the formed fatty acids to alkane and alkene where two enzyme families namely, acyl–acyl carrier protein reductase (AAR) and an aldehyde decarbonylase (AAD) are involved in the catalytic process (Fig. 5) [146]. These enzymes can also be heterologously expressed in Escherichia coli for alkane secretion and strains with significant increase (60%) in expression of the selected alkanes over wild-type have also been reported [147]. Wild cyanobacterium strain (Microcoleus vaginatus) also produce branched alkanes [148]. A genetically engineered Synechococcus elongatus PCC 7942 has been studied on the physiological effects for free fatty acid production [149]. Different cyanobacteria namely, Synechococcus sp., Chroococcidiopsis aponinum, and Phormidium sp. have been reported to accumulate elevated lipids [150]. The crude lipids obtained from these cyanobacteria could be promising feedstock for biodiesel production due to their C16 and C18 fatty acid profiles and high level of saturation. Studies conducted during recent past however, showed that although cyanobacteria possess high biomass productivity, it showed a low lipid content reflecting the high metabolic cost of lipid synthesis [151]. It is suggested that a wide range of variables are important to select a species for the large-scale production of biodiesel among which [152], [153] growth rates, lipid content and productivity are the keys issues [144]. Whereas, the type and composition of the fatty acids present in the lipid are also important parameter to assess the species as feedstock for biodiesel production. C10:0, C16:1 and C18:1 fatty acids and their appropriate combination are considered important for production of quality biodiesel. However, the growth temperature also influences the fatty acid composition and their degree of unsaturation. Studies conducted during recent past however, showed that although cyanobacteria possess high biomass productivity, it showed a low lipid content reflecting the high metabolic cost of lipid synthesis [151]. It is suggested that a wide range of variables are important to select a species for the large-scale production of biodiesel among which [152], [153] growth rates, lipid content and productivity are the keys issues [144]. Whereas, the type and composition of the fatty acids present in the lipid are also important parameter to assess the species as feedstock for biodiesel production. C10:0, C16:1 and C18:1 fatty acids and their appropriate combination are considered important for production of quality biodiesel. However, the growth temperature also influences the fatty acid composition and their degree of unsaturation. Studies conducted during recent past however, showed that although cyanobacteria possess high biomass productivity, it showed a low lipid content reflecting the high metabolic cost of lipid synthesis [151].

One of the critical issues in microbial biodiesel production technology that significantly influences the process economy is the efficient extraction and transformation of oil from biomass into biodiesel. The growth rate of cyanobacteria is less as compared to

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**Fig. 5.** Schematic representation of engineered biochemical pathways in cyanobacteria [138]. Core metabolism of photosynthetic processes is shown in black text. Branch points utilized for the production of various compounds are indicated (highlighted pathways) with relevant enzymes catalyzing specific reactions indicated in italics.
other biofuel producing microbes like yeast and *E. coli*. The tiny cell size of the microbe makes them a soup of dilute concentration unfit for biomass processing and harvesting work. Negative charge on the cell surface makes them stable in dilute solutions. Instead of the conventional centrifugation methods, combination of bioflocculation and membrane filtration can be used as concentrating methods for harvesting the cells. A cost effective strategy would be to recycle the water and the nutrient by integrating a continuous system. This can not only increase harvesting efficiency without burdening the subsequent extraction procedures but also augment the growth rate [156], [157]. For fine tuning of efficient conversion of lipid to biodiesel, genetically modified microbes have been used that cut short the down time, increases efficiency and makes the microbes more tolerant towards product toxicity [158]. However multiple genome copies, below par understanding of the metabolic regulation pose hindrance for genetic knockout [159]. To circumvent significant amount of lipid loss during extraction procedure, cell wall less mutant or engineering the species to excrete the fuel directly into the medium was also proposed. With such an attempt *Synechocystis* sp. PCC6803 has been modified to produce and excrete only fatty acids [160]. Membrane lipids can also be degraded into free fatty acids by lipolytic enzymes, an approach termed as Green Recovery System through which diacylglycerols were degraded to produce fatty acid using an engineered *Synechocystis* sp. under CO₂ limiting condition [161]. Enzymatic methods for lipid extraction are preferred over mechanical or chemical methods owing to their mild reaction conditions and higher selectivity [162]. To avoid the cost related issues, immobilized enzymes could be used in combination with microwave/ultra-sonication steps. Cyanobacteria are known to produce cyanotoxins (neurotoxins, hepatotoxins and dermatotoxins) which might pose risk to human health and aquatic water bodies [163]. Hence, screening of the effluent is essential before the recycled water is released into the environment. Direct transesterification process (extraction of lipid and biodiesel conversion simultaneously) was applied to *Synechococcus elongatus* which resulted in 40% yield of FAME (biodiesel). Such processes provide easier product separation in minimal time and reduction in the use of solvents [164].

The cyanobacteria are identified as highly promising feedstock for ethanol production due to their advantages over agricultural crops as they ferment naturally without the need to supplement with yeast cultures as is the case with fermentation of traditional feedstock. However, this fermentation, which takes place in absence of photosynthetic oxygen, is a low energy process working at a minimum level for the mere survival of the organism. To boost the ethanol production, genetic modification appears to be a prudent approach and it was performed on *Synechococcus* sp. PCC 7942. The organism was transformed by including the coding sequences for pyruvate decarboxylase and alcohol dehydrogenase II from an obligately fermentative *Zymomonasmobilis*. The cyanobacterial *rbcLS* operon promoter alone and in combination with the *E. coli lac* promoter was used to express the genes which resulted ethanol yields of 54 nmol L⁻¹ d⁻¹ [165]. Similar transformation was also performed in *Synechocystis*. PCC 6803 under the control of a strong light driven promoter that resulted further increase in ethanol production to 0.2 mmol L⁻¹ d⁻¹ [166]. In another genetic modification work *Synechococcus* sp. PCC 7942 was modified with the cellulose synthase genes from *Glucanobacter xylinus* to produce extracellular non-crystalline cellulose to use as an ideal feedstock for ethanol production [167]. High carbohydrate content (60 % of dry cell weight) accumulated under nitrate limitation condition in *Synechococcus* sp. PCC 7702 has been attributed as a source of ethanol [168]. Substantially high ethanol production (0.75 mmol/g) was however, also reported from native cyanobacterial strain when it was cultivated in a stress condition under high salt concentration medium (1.24 mol L⁻¹) [169]. Further, through a modelling work using the parameters, energy consumed and green-house gas emissions in different ethanol-producing systems employing cyanobacteria revealed that initial ethanol concentrations from 5–50 g L⁻¹ would be sufficient to develop a biofuel production system with reduced energy consumption and air pollution [170].

The alcoholic with longer chain lengths, such as butanol, iso-butanol etc. possess higher energy content and easier to store and transport than conventional alcohol (ethanol) [171]. A genetically engineered *Synechococcus elongatus* PCC7942 was used to produce iso-butyraldehyde and iso-butanol (6230 and 3000 μg L⁻¹ h⁻¹, respectively) directly from CO₂ and the productivity was increased by over expression of ribulose 1,5-bisphosphate carboxylase/oxygenase (Rubisco). The high vapor pressure of iso-butyraldehyde facilitates product recovery and decreases product toxicity. The strain produced iso-butyraldehyde at a higher rate than those reported for ethanol and few other fuel production by cyanobacteria or algae [172]. In a later work, 2-ketobutyrate, which is an intermediate in the biosynthesis of citramalate, was suggested to be utilized in production of propanol and butanol using citramalate synthase which occurs in cyanobacteria [173]. Isoprene, or 2-methyl-1,3-butadiene, a colorless volatile hydrocarbon is suitable as biofuel. In a study, *Synechocystis* PCC6803 was genetically modified with the *Pueraria Montana* IsPS gene to enable the production of isoprene [174]. Further, incorporation of a plant isoprene synthase gene enabled cyanobacteria to produce isoprene [175]. Another important class of hydrocarbon fuel, alkanes has been reported to produce in cyanobacteria by genetic engineering [146]. Genetic modification of *Synechococcus elongatus* PCC 7942 or *Synechocystis* sp. PCC 6803 for the production of ethanol [176], 1-butanol [177], 1,2-propanediol [178], 2,3-butanediol [179], ethylene [180], [181] and 2-methyl-1-butanol [182] have also been investigated. The synthesis of (S) - and (R) -3-hydroxybutyrate was also reported to be feasible by using engineered *Synechocystis* TABd as host [183].

A concept, called “photanol approach” [184] that includes the properties of a chemotrophic organism into a photosynthetic organism (*Synechocystis* sp. PCC 6803) by means of genetic engineering to improve the biofuel production has been introduced. Briefly, in chemotrophic organisms, there are pathways through which C₃ sugars (glyceraldehyde-3-phosphate (G3P)) formed by degradation of different carbohydrates are converted into a variety of alcohols such as ethanol, butanol, propanedio1 etc. Whereas in photosynthetic organisms, C₃ sugars formed are vital intermediates in the biosynthesis of essential complex biomolecules of the organism. In photanol approach G3P represents the central linking compound between photosynthesis and fermentation that reduces many steps to convert CO₂ into biofuel in the transformed organism, which exhibits increased biofuel production efficiency reaching theoretical levels of 100 m³ ha⁻¹ y⁻¹.

The research on cyanobacterial production of methane, which is a highly gaseous hydrocarbon, is limited as the methanogenic activity of cyanobacterial biomass is generally less [185]. Anaerobic digestion (AD) of the remaining cyanobacterial biomass (after lipid extraction say, for biodiesel production) can be utilized to produce CH₄ that raises the energy recovery for the process [183]. There are however, few examples where the metabolism of cyanobacteria is utilized to produce methane. The N₂-fixing *Anabaena* sp. degraded cyanides and thereby producing CH₄ [186] where nitrogenase reduces cyano- nides to CH₄ and NH₃. Other examples describe the production of CH₄ by cyanobacteria in a system either by producing nutrients for methanogenic bacteria [187] or by removing CO₂ from the biogas formed by AD of sludge [188]. The process of CH₄ production alone or coupled to other bioenergy producing processes need further improvement to develop an economically viable technology [97].
For technological consideration, design of cost-effective photosynthetic bioreactors for production of most of the cyanobacteria based products is important which compensates light-based constraints that are not encountered in traditional microbial bioreactors [138], [101], [144]. The bioreactor needs to fulfill certain criteria, such as effective illumination, optimal gas-liquid transfer, easy to operate, low contamination level, low capital and production cost, and minimal land area requirement. The ‘open-pond’ approach is though suggested to be feasible for many such bio-products, the designs are more vulnerable to weather fluctuations and foreign microorganisms. Adequate or luxurious growth of the cyanobacteria is desired for biofuel production. The biomass of cyanobacteria also depends on combined variation of nitrogen (N) and phosphorous (P) content apart from light-dark cycle [189]. The ability to fix atmospheric nitrogen (N2) gives some cyanobacteria an added advantage when N to P ratio is low [190]. A closed loop of the PBR with CO2 producing power plants can eventually deal with the CO2 requirements of the microbe [191]. These benchtop biofuel PBRs can aid in realizing the complete potential of cyanobacteria for commercial biomass productivity. Li and Liao [159] discussed about hybrid systems that amalgamated artificial “light” (wind turbines or photovoltaic solar panels) and biological photosynthetic “dark” reactions. The system enabled efficient uniform light dispersal throughout the culture exploiting the radiation spectrum. Hybrid photo bioreactors involving cyanobacteria encapsulated inside porous silica gel and silica scaffold [192] further indicate their role in reduction of industrially produced CO2 and its conversion to high value products such as, biofuels. A method to encapsulate Synechococcus strains, FCC 6301 and FCC 7002, inside porous silica gels biofuels production in PBR has been proposed through which full biocompatibility and optical transparency of the matrix could be achieved that helped the cells retain their ability to execute photosynthesis for prolong period [193]. Cyanobacterial biofilm culture may be a promising approach for large scale production of biofuels and bio products [194]. Cyanobacteria based PBRs were used for assimilation of CO2 production of hydrogen gas and nitrate and phosphate removal from contaminated waters [32]. Photosynthesis has also been opined as potential way to assimilate carbon dioxide into hydrocarbons, oils and sugars [195]. A schematic on the various metabolic pathways of biofuel production in cyanobacteria is depicted in Fig. 5. It is suggested that with the aid of metabolic pathway engineering and optimization the cyanobacteria may be used as potential source for producing biofuels [144].

4. Conclusion and future directions

Cyanobacteria are wide spread in nature, can colonize almost all environmental niches, and survive in extreme environmental conditions starting from alkaline hot spring to polar locations. These versatile groups of photoautotrophic bacteria can form biofilms and develop symbiotic relationship with other microorganisms and are known primary biomass producer on earth. A significant metabolic versatility, such as, intersecting photosynthetic and respiratory electron transport chains, makes them distinct from other homologues of bacterial and plant photosynthesis counterparts. However, the knowledge on the light supported energy metabolisms, particularly, the TCA shunt and the intersecting electron transport phenomena of this prokaryotic microorganism are yet to be adequately earned to utilize these microorganisms for production of bioenergy through a systematic approach. A concerted effort interlinking genomics, proteomics and metabolic engineering along with the aid of advance molecular and computational biology techniques will not only enrich our knowledge on the different metabolic pathways unique to these photosynthetic microorganisms but also likely to help in elucidating the potential of these resilient organisms for harvesting clean energy including bioelectricity and biofuels. The significant progress in genome sequencing and high-throughput expression has enhanced the insight to engineer microbes for specific metabolic tasks. Notably, the capability of cyanobacteria to transform solar energy into biomass without the requirement of supplementing any carbon sources and possibility of cultivating the cells in small land and in in-house bioreactor have prompted to explore the developing economically viable process for production of bio-energy and many other high value products of industrial importance.

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References


