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Review

Algal biorefinery: A sustainable approach to valorize algal-based biomass towards multiple product recovery

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ABSTRACT

In recent years, ever-increasing socio-economic awareness, and negative impact of excessive petro consumption have redirected the research interests towards bio-resources such as algal-based biomass. In order to meet current bio-economy challenges to produce high-value multiple products at a time, new integrated processes in research and development are necessary. Though various strategies have been posited for conversion of algal-based biomass to fuel and fine chemicals, none of them has been proved as economically viable and energetically feasible. Therefore, a range of other bio-products needs to be pursued. In this context, the algal bio-refinery concept has appeared with notable solution to recover multiple products from a single operation process. Herein, an algal-based bio-refinery platform for fuel, food, and pharmaceuticals considering Bio-refinery Complexity Index (BCI) has been evaluated, as an indicator of techno-economic risks. This review presents recent developments on algal-biomass utilization for various value-added products as part of an integrated bio-refinery.

1. Introduction

The biorefinery concept has emerged as integratedprocesses for the conversion of microalgal biomass into fuel and other value-added products (Cherubini, 2010; Thomassen et al., 2018). The multiple and complementary outputs provide a more sustainable and economical approach that focuses solely on fuel production (Salama et al., 2018). Biofuel production from microalgae does not have economic viability based on current capital costs per unit of fuel production (Chandra et al., 2019). Hence, high-value co-products must be generated to improve the economics of a microalgae biorefinery.

Micro algae can be microbial factories producing various compounds other than lipids for biodiesel. Being composed of lipids (7–23%), carbohydrates (5–23%), and proteins (6–52%) (Chandra et al., 2014), microalgae can be ideal feedstock to commercially important value-added products used in food, nutraceutical, cosmetic, and a pharmaceutically active compound (Haznedaroglu et al., 2016). Capturing the value of multiple components can be fulfilled with an integrated biorefinery (Oh et al., 2018), which maximize product outputs from the single biological material.

The biorefinery concept stems from petroleum refineries, which produce fuels, oils, and other materials for use in the chemical industry (Roux et al., 2017). A biorefinery involves a cascade of processes that can use all the raw material components while preventing loss or damage to any products. A sustainable extraction of these compounds considering green chemistry principles is significant challenges in algae-based biorefinery (Yellapu et al., 2018). These processes are energy intensive and the maximum exploitation of microalgae biomass while using minimum energy remains the primary focus (Bakonyi et al., 2018). For instance, cost minimization for algal biofuel production is the main objective for the Department of Energy (DOE) outlined in the outlook presented in the U.S. multi-year program plan (US Department of Energy, 2015).

The present review provides state-of-the-art in recent developments on effective algal biomass utilization in a sustainable manner by employing a bio-refinery approach. Further to this, the effective implementation of an algal bio-refinery platform to produce fuel, food, and pharmaceuticals has been discussed with special reference to BCI,

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which is an indicator of the technological and economic risks. This review also presents a comprehensive summary of recent developments on algal-biomass utilization for various value-added products as part of an integrated biorefinery.

2. Algal products

Currently, microalgae and macroalgae represent an important raw material to produce a wide range of products of bioproduct which are categorize under fuel and non-fuel products (Trivedi et al., 2015). Fuel-based products include bioethanol (or biobutanol), biodiesel, biogas, and biohydrogen. Non-fuel products are carbohydrates, pigments (e.g., lutein and astaxanthin), proteins, recombinant proteins, biomaterials, and other bioproducts. Factors like carbon neutrality, wastewater treatment, and biodiesel production support the algal biofuel research and commercial products from microalgae are fundamentally restricted to a few easily cultured species with proven market demand and market value. The mainstream of viable products from algae is derived from marine algae (seaweed) produced for food. They are mostly harvested from wild populations, rather than cultivated (Rebours et al., 2014). Algal non-fuel derived products have readily accessible markets, providing greater margins.

2.1. Algal fuel products

Fig. 1 represents the complete spectrum of algal products. The major biofuels are biodiesel, bioethanol, biogas, and bio-hydrogen. The cellulosic algae structure provides huge amounts of carbohydrates (mannitol, starch) that can be used for bioethanol production. The bioethanol derives from sugars fermentation or conversion of cellulosic biomass through a combination of hydrolysis and fermentation or gasification. Few microalgae species consists of more than 50% of starch, glucose, and cellulose by their dry weight and absolute absence of lignin makes it a potential raw material for bioethanol production. Very recently, Choi et al., (2019) scrutinized the life-cycle potential of microalgal solid fuel comprehensively ranging from cultivation to direct combustion. According to the literature, co-combustion of coal-microalgal solid fuel also display beneficial advantages such as better combustibility and environmental impacts from the CO_2 fixation viewpoint.

Algal biodiesel has a substantial potential to use as a substitute for petrochemical diesel because of its technical competence of no change in engine design and present infrastructure (Yellapu et al., 2018). Algal biodiesel is biodegradable, nontoxic and with a favorable combustion emission profile, producing much less carbon monoxide, sulfur dioxide, and unburned hydrocarbons than petroleum-based diesel fuel. Algal biodiesel contributes towards carbon neutral process, because they do not result in fossil carbon being released into the atmosphere. All of the carbon contained in a biofuel was absorbed from the atmosphere by algae through photosynthesis. This means that when we burn a biodiesel, we simply release the carbon back into the atmosphere, and have no overall effect on atmospheric CO_2 levels. In contrast, fossil fuels contain carbon that has been locked up underground for millions of years. Burning a fossil fuel increases the level of CO_2 in the atmosphere, but it is not balanced out by photosynthesis. Algae are very eco-friendly being non-toxic, do not contain sulfur, and are biodegradable (Liu et al., 2013; Ullah et al., 2014). Lipid saturation index is a significant property that determines biodiesel stability and performance properties to produce high-quality biodiesel. Low saturated fatty acid levels (such as C16:0 and C18:0) are required for better winter operability, highest possible monounsaturated fatty acid levels (such as C18:1) for good stability and lowest possible polyunsaturated fatty acids levels (such as C18:3) for increasing oxidation stability. The principal drawback in biodiesel production is the culture concentration step since the dry biomass represents only 0.1–1% of culture weight, besides this unit operation is costly. These points provoked that many research programs focused on such approaches with the aim to decrease the costs.

Bio-methane, that is produced from anaerobic digestion of organic matter, generally contains a mixture of methane (55 to 75%) and CO_2 (25 to 45%). Algae have been suggested as feedstock to bio-methane in anaerobic digestion, but due to the resistibility of algae cell walls to bacteria degradation, anaerobic digestion of algae yields very low biogas. Low carbon to nitrogen (C/N) ratio of microalga species allows the formation of free ammonia which is an inhibitor to methanogenesis (Gonzalez-Fernandez et al 2018). Algae biomass gives higher biomass yields than those obtained from land based biomass like *Jatropha curcas*, but the high cost of algae feedstock make it uneconomically feasible (Trivedi et al., 2015). The multidisciplinary research approach is vital to establish sustainable technologies. Scaling up of the process to pilot or large scale to generate baseline engineering data will impart relevance in the view of commercialization.

Microalgae and cyanobacteria produce biohydrogen through biophotolysis and catabolism of endogenous substrate (Chandra et al., 2015b; Chandra and Venkata Mohan, 2011, 2014). Biophotolysis of water takes place on the membrane-bound photosynthetic system in the presence of light. The light-dependent biophotolysis metabolic pathways can be differentiated into two distinct categories: direct photolysis and indirect photolysis. Nitrogenases and hydrogenases are two enzymes catalyzing hydrogen production, and they are oxygen sensitive. Nitrogenase activity can be induced by nitrogen starvation. Sulfur deprivation also enhances hydrogen production by inactivating photosynthetic water oxidizing activity, and reaction center of photosystem two (PSII). Unfortunately, manipulation of culture conditions such as adding low levels of sulfate, altering extracellular pH, adjusting light intensity, optimizing medium composition (Laurinavichene et al., 2004; Ma et al., 2011), or changing growth conditions produces only marginal improvements on H_2 yield.

Economic analyses indicated that photobiohydrogens could be produced at a cost between US$10 and US$20 per GJ (Akkerman et al., 2003). This target is difficult to achieve in present state of knowledge, according to Benemann (2000). Before economic barriers can be meaningfully addressed, many technical and engineering challenges have to be tackled. Nevertheless, these economic analyses provide an indicator that the development of low-cost photobioreactors and the optimization of photosynthetic efficiency are the major R&D challenges.

It is also achievable to harness bioelectricity using the photosynthetic machinery of microalgae in a defined photosynthetic microbial fuel cell (PhFC) system (Chandra et al., 2012; Chandra et al., 2015c; Navaneeth et al., 2015; Venkata Mohan et al., 2014). Microalgae initiate charge separation and release electrons and protons, during photophosphorylation chain reactions. PhFC can capture the cellular level electrons directly from the electron transport chain by using external electrode (anode) which are neutralized at the cathode (Ivashin et al., 1998). Reports are available on photosynthesis based electrogenic activities of single strains of green algae (*Chlamydomonas reinhardtii, Phormidium*, etc.) and Cyanobacteria (*Nostoc, Spirulina, Anabaena, Synechocystis* PCC-6803, etc.). These studies reveal the feasibility of bioelectricity generation using microalgae as biocatalyst under oxygenic conditions using CO_2 from atmospheric CO_2 in response to light. However, dissolved O_2 produced during the photolysis of water in oxygenic photosynthesis can be a major limiting factor lowering performance. Algal PhFC is self-sustainable as it can sustain on atmospheric CO_2 and moreover, the resulted biomass can be used for other forms of values additions in a biorefinery format (Chandra et al., 2017a). This study provides a potentially cost-effective, renewable and sustainable electricity option associated with environmental remediation.

Integration of algae-based biodiesel and bioelectricity production with wastewater treatment is a sustainable option for bioenergy production and also towards environmental sustainability (Venkata Subhash et al., 2013). Several studies have been conducted on simultaneous wastewater treatment and energy production. Algal

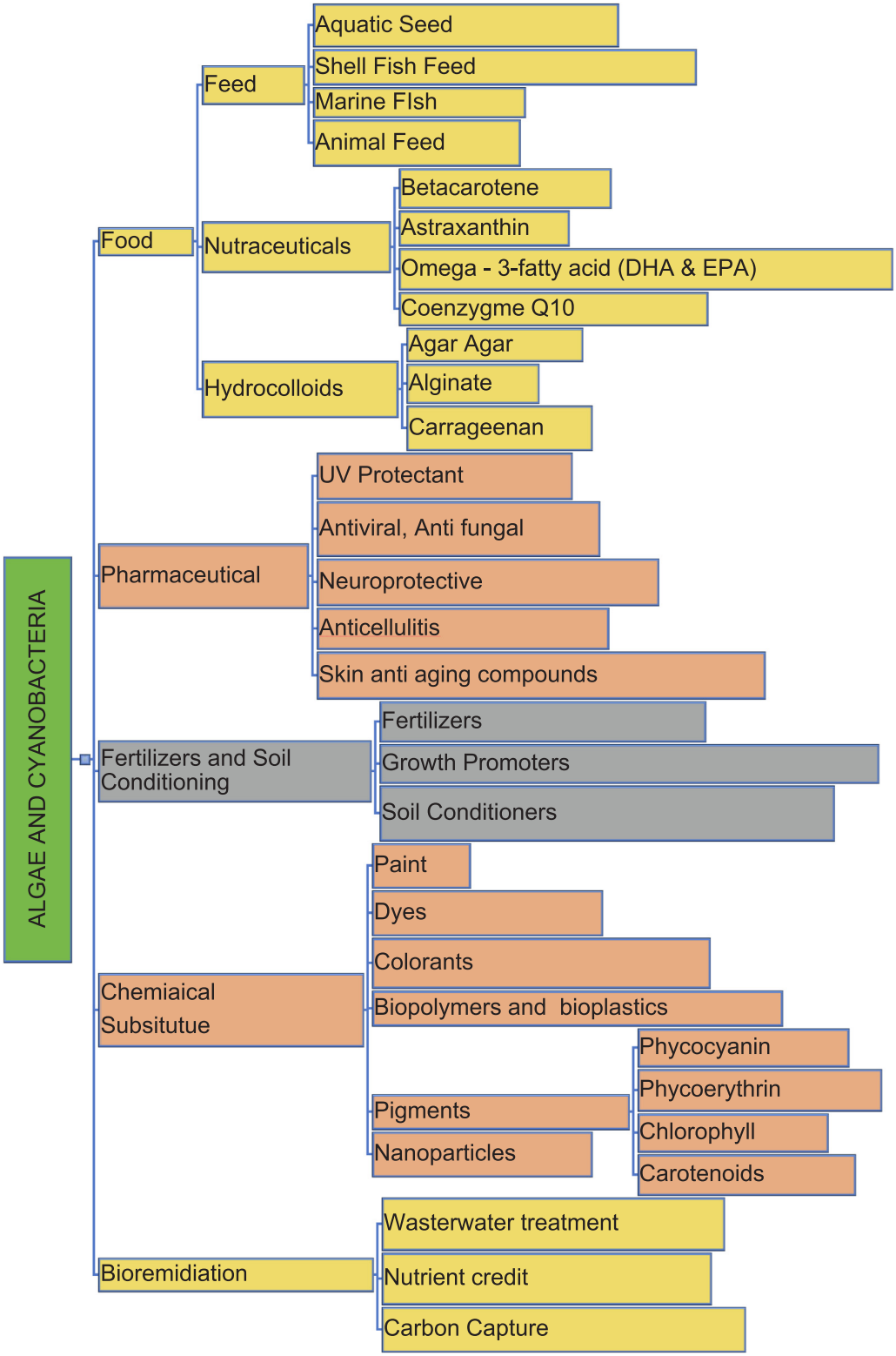

Fig. 1. Spectrum of algal mainstream products and environment benefits from fresh water and marine algae.

biorefinery concept with wastewater treatment will provide efficient utilization of algae biomass for fuel generation and reduces the overall residual waste component of biomass and favors sustainable economics.

2.2. Microalgae food and feed product

Microalgae, especially *Spirulina*, have been already used as food, feed They are useful to derive many value-added products as they are rich sources of proteins, vitamins, minerals, antioxidants, carotenoids, etc. Microalgae are a potential source of superfood for humans from a long time ago, however, its commercials have been utilized only in a few decades since 1950. Microalgae and cyanobacteria were known for its protein source but the increased interest came recently due to the unique natural bioactive biomolecules as vitamins (thiamine,

riboflavin, a-tocopherol), protein (C-phycocyanin, A-phycocyanin), pigments (b-carotene; chlorophyll, etc.) fatty acids (palmitic acid, linoleic acid, oleic acid, stearic acid and c-linolenic acid etc.) source to replace the chemical based compounds (Cuellar-Bermudez et al., 2016). To utilize individual component, it needs to be extracted from the algal biomass and hence, effective employment of the extraction process is a fundamental requirement for algal or cyanobacterial bioactive compounds with applied perspectives.

For isolation of bioactive compounds from algal and cyanobacterial in its bioactive form have technical problems that need to be overcome so that potential active compounds remain active (Cieśla and Moaddel, 2016; Venkata Mohan et al., 2015). These solvents can be toxic when they have food application. Solvent systems, temperatures and reaction times play a crucial role in the extraction and activity of these compounds and largely depend on the specific nature of the targeted bioactive compounds. Integrated biorefinery have an advantage of using non-fuel based products synthesized by algae applied in diverse industries (Fortier et al., 2014).

2.2.1. Lipids and polysaccharides

Algal lipids are sources of materials such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) for the food and pharmaceutical industries (Roux et al., 2017). These components should be valorized as co-products for a microalgae-based biorefinery success. Algae can accumulate 30 to 50% of lipid under certain culture conditions (Chandra et al., 2014; Venkata Mohan et al., 2015). Algal lipids are classified in two groups as per their carbon numbers, i.e., 12–20 carbon fatty acids, and 20 carbon polyunsaturated fatty acids (PUFAs) used in biodiesel production and food production, respectively (Liu et al., 2019). PUFAs, mostly omega-3 fatty acids, have gained distinct attention as they are essential nutrients, protective and curative activities against cardiovascular diseases; however, PUFAs cannot be produced by higher eukaryotes. *Chlorella minutissima* is a good source of EPA while *Crypthecodinium, Thraustochytrium, Ulkenia,* and *Schizochytrium* are rich in DHA.

The production of these PUFAs can be increased by genetic modification, and optimization of growth factors (e.g., light intensity, pH, carbon–nitrogen ratio, temperature, and nitrogen source availability), and novel culture systems (Subramaniam et al., 2010; Trivedi et al., 2015). Biofuel like algal biodiesel are regarded as most important product derived from microalgae. However, algae-based biofuel products could take much longer than originally expected to derive fuels from algae in real application.

Marine algae, that belong to chlorophyte, phaeophyta, and rhodophyta, have been identified as the major source of polysaccharides. Red macroalgae contain large amounts of polysaccharides mostly galactans with alternating repeating units of 1,3-α-gal and 1,4-β-D-gal, and 3,6-anhydrogal. Apart from agarans, found in species of *Porphyra*, *Polysiphonia*, *Acanthophora*, *oiopeltis*, *Bostrychia* or *Cryptopleura*, red seaweeds are also good sources of κ-carrageenan (*E. spinosa*, *K. alvarezii*), λ-carrageenan (*Chondrus* sp, *G. skottsbergii,* and *Phillophora*), carrageenan (*E. spinosa*)], and other heterogalactans building up their carbon backbones.

2.3. Pigments and vitamins

Cyanobacteria contain a membranous structure called thylakoid, where phycobiliproteins are present. Naturally, phycobiliproteins are oligomeric and belong to two major families, i.e., α and β with a common ancestor. The covalently circumscribed prosthetic group often called phycobilins, that are open-chain tetrapyrrole chromophore bearing rings, are mainly responsible for the color characteristics of phycobiliproteins (Sekar and Chandramohan, 2008). Modern research and development in phycobilisomes synthesis and functionality have expanded the potential applications of phycobiliproteins in biotechnology, diagnostic, food, and medicine. Phycobilisomes provide a broad spectrum of products (Chandra et al., 2017b). They are extensively commercialized for fluorescent application in the clinical and immunological analysis. These dyes have also been used as food grade dyes for applications. While these products are of high value, the market is not huge at the moment. and the expectation is that these dyes would not make up a large component of any algal biorefinery.

Microalgae, cryptomonads, red algae, and cyanobacteria produce various pigments with high market value, such as chlorophylls, carotenoids, and phycobiliproteins (found only in, and cyanobacteria). Chlorophylls are responsible for light-harvesting in plants and algae and transfer sunlight energy to the photosynthesis reaction centers. Its recent application includes natural food coloring agents and chlorophyllin having anti mutagenic activity. From the commercial outlook, chlorophyll extracted from biomass or separated from the fraction previous to oil purification could make these pigments attractive high-value products for any biorefinery utilizing photosynthetically produced algal biomass as a feedstock.

Carotenoids have widespread application in food coloring/nutrition and cosmetics. Most studied carotenoids are β-carotene, lycopene, zeaxanthin, lutein, and astaxanthin produced by microalgae. β-carotene has high industrial demand because it is an essential nutrient and natural food coloring agent. Small intestine and liver of humans have enzyme β-carotene-15,15′-dioxygenase, which splits β-carotene into two molecules of retinol (vitamin A), so β-carotene provides a provitamin A carotenoid. Certain microalgae species synthesize excessive amounts of β-carotene for an accessory light-harvesting pigment that protects the photosynthetic apparatus against photooxidative damage. Due to high production rates, the synthesis of β-carotene in *Dunaliella salina* (Zhu, 2015) and *Dunaliella barawil* has been extensively studied (Haznedaroglu et al., 2016). Astaxanthin from *Haematococcus pluvialis* and β-carotene from *Dunaliella salina* are of great interest due to their natural origin and their bioactive properties preventing certain eye diseases for humans, such as age-related macular degeneration and cataract. The productivity of lutein and β-carotene in *S. obliquus* is favored due to its cultivation potential at a high pH along with the concentration of carotenoids related to the observed antioxidant activity (Gilbert-López et al., 2017).

Owing to the phototrophic life, cyanobacteria and algae are habitually exposed to stress conditions especially oxidative stress, which results in the synthesis of numerous efficient protective systems against oxidative and radical stressors. Among these protective systems is the production of pigments, such as carotenes, chlorophylls, and phycobiliproteins, all having high antioxidant and protective properties. By controlling the growth conditions of these organisms, it is easier to exploit their efficiency in biorefinery. Few strains of algae and cyanobacteria have a high potential for industrial utilization because of its rapid growth and different vitamins synthesis. They have numerous metabolic mechanisms for the synthesis of these vitamins, including vitamins A, C, and E. Vitamin E is a mixture of α-, β-, γ-, δ-tocopherols, and tocotrienols, produced solitary by photosynthetic organisms, and it is a lipid-soluble antioxidant (Esquivel-Hernández et al., 2016).

Vitamin C is a water-soluble metabolite with strong antioxidant activity. It is a cofactor for numerous biological enzymes. Vitamin C production is proven in a limited number of microalgae species, including *D. tertiolecta*, under nitrogen deprivation and osmotic stress. According to the Brown, et al. (year), levels of vitamin C across logarithmic and stationary growth phases vary among different microalgae. *Chaetoceros muelleri, Thalassiosira pseudonana, Nannochloropsis oculata, and Zsochrysis* sp. had more vitamin C during the logarithmic phase, whereas *Dunaliella tertiolecta* and *Nannochloris atomus* had more ascorbic acid during the stationary phase. To commercialize algal vitamins, it is necessary to consider algal strain and time of harvesting for vitamin productivity. As vitamins are antioxidants, there might be the possibility of higher vitamin synthesis if they grow under different stress conditions like oxidative, osmotic stress and nutrient stress.

2.4. UV protectant

The group of cyanobacteria and marine algae have a variety of defense strategies that allow them to survive and grow in high UV fluxes. As a metigation strategy these organism synthesis of UV-absorbing compounds, such as mycosporine-like amino acid (MAAs) and scytonemin (Chandra et al., 2019). MAAs exhibit high antioxidant activity by scavenging large amounts of reactive oxygen generated by supersaturated oxygen in deep, light-exposed the water. The primary MAA i.e., mycosporine-glycine is derived precursors 3-dehydroquinate and 4-deoxygadusol of the shikimate pathway. Secondary MAAs are transformed from mycosporine-glycine through the incorporation or removal of amino acids and biochemical conversions. However, an MAA biosynthetic gene cluster in the cyanobacterium *A. variabilis* has been identified that converts sedoheptulose-7-phosphate to shinorine via 4-deoxygadusol and change the 3-dehydroquinite as the precursor (Balskus and Walsh, 2010). It is hypothesized that scytonemin is derived from aromatic amino acids tryptophan and tyrosine, the end products in the shikimate pathway. A scytonemin biosynthesis gene cluster has also been identified, and its UV-A induction has been shown (Rastogi et al., 2015). Due to strong UV absorption and photoprotective properties, MAAs and scytonemin can be used as an active ingredient in the cosmetic and pharmaceutical industries.

UV protectant can be an important product of algal biorefinery because of high market demand and value. For instance, the global demand for this kind of product was more than $7.6 billion in 2012 and is estimated to reach $13.2 billion by 2018 (Oilgae, 2014). In this way, it is possible to maximize the value of the process, to increase value-added products and at the same time to reduce environmental impact. The unique nature of microalgae allows them to contain different pigments including chlorophyll, carotenoids, astaxanthin, lutein, zeaxantin, canthaxantin phycocyanin, phycoerythrin, phycobiliproteins and UV protectants.

2.5. Bioplastic

Polyhydroxyalkanoates (PHAs) acts as a reserve of carbon and energy and are generally known as bioplastic. PHAs are accumulated under conditions of nutrient deprivation or excess reducing power or in the presence of excess organic carbon source. Bioplastic synthesis in algae and cyanobacteria is controlled with the enzyme expression and nutrient ratio especially carbon and nitrogen. Low phosphorous level always promotes bioplastic synthesis in these organisms. The control involves two enzymes, i.e., PHB synthase and phosphotransacetylase. PHB synthase activity was detected in crude extracts from cells grown under nitrogen and phosphorous deficient conditions in the presence of light. The second enzyme was phosphotransacetylase which catalyzes the conversion of acetyl coenzyme A (acetyl-CoA) to acetyl phosphate. The intracellular acetyl phosphate concentration could be controlled, depending on C/N balance and intracellular acetyl-CoA concentration. Acetyl phosphate probably acts as a signal of C/N balance affecting PHB production. Several strains of photoautotrophically grown cyanobacterial strain contained PHB at concentrations few milligrams per gram of dry weight. Under mixotrophic growth conditions in the presence of acetate, PHB reached values greater than 2.5% of dry weight. PHB has chemical and physical properties similar to polypropylene, and show nontoxicity, biocompatibility, and biodegradability (Poirier et al., 1995). However, the cost of PHB produced by algae is currently high due to increased carbon, nutrient, and energy costs.

2.6. Nanoparticles

Biological synthesis of nanoparticles is important due to its biocompatibility, nontoxic effect, economic and environmentally friendly fabrication. Micro algae can survive in presnet of varius viruses, bacteria, and fungi, this property make it suitable for synthesis of silver nano particles. Basniwal and Jain studied the economic and biocompatible synthesis of silver nanoparticles based on *Chlorella* species extract (Basniwal and Jain, 2017). Biogenic synthesis pathway of silver nanoparticles could mitigate emissions of the greenhouse gases (GHG), and its biodegradability and photocatalytic nature make them perfect entity for wastewater treatment. Rajeshkumar et al. (2014) reported that the extract of algae *(Sargassum longifolium)* has the great efficiency to synthesize the silver nanoparticles through a green route, suggesting potential biomedical application. Diatomaceous algae belong to coccolithophore which has distinguished calcium carbonate plate or scale called coccoliths. These coccoliths are at the nanoscale and produced by coccolithogenesis through biomineralization. These coccoliths can have great application in the biomedical field especially in fabricating nanotechnology bases bone implants. They are nature inspired nanoparticles and provide a huge defined surface area for binding proteins and drug molecules which help in tissue and bone regeneration.

Most of the valuable algal substances have potential applications in the food, feed, pharmaceutical, and cosmetics industries. Most of the algal derived products need to compete with conventional markets based on petrochemical feedstock to make a cost effective green technology solution. For the green technology solutions to use the algal biotechnology platform for a wide range of bio-products, there is a need for biorefining approaches. The continued development of biorefineries, along with its contribution to the economy, will lead to a diversification of feedstocks, technologies, and byproducts for the sustainable economic valorization of biomass (Da Silva et al., 2014). As biorefining facilities start to find a world-wide implementation and have an important social impact by reducing the amount of carbon dioxide emissions as it is considered a carbon–neutral process, while simultaneously reducing the contamination of industrial byproducts. Driven by the necessity for sustainable production of energy and high-value-added products from renewable resources, a microalgae-based biorefinery for the production of biofuels, food additives, bioplastics, and fine chemicals has to be well understood.

3. Biorefinery

According to International Energy Agency (IEA), biorefinery is defined as the sustainable processing of biomass into a spectrum of bio-based products (food, feed, chemicals, materials) and bioenergy (biofuels, power and/or heat)". According to US Department of Energy, "A biorefinery is an overall concept of a processing plant where biomass feedstock is converted and extracted into a spectrum of variable products" (Jungmeier et al., 2014) (Chandra et al., 2018). Biorefinery development has two strategic goals first is a substitute for petroleum in favor of renewable domestic raw materials, and second is to establish a strong and stable bio-based industry (Bozell and Petersen, 2010). The first is recognized as the energy goal and the latter as the economic goal (Bozell, 2014). A sustainable biorefinery is focused on various critical aspects, i.e., it should not compromise with a critical need, such as food and animal feed, maintain the regeneration of biomass and diversity, minimum environmental impact, adaptation to changes in the market and various feed and multi-product conversion process (Özdenkçi et al., 2017).

3.1. Classification

3.1.1. First generation

Biorefinery has been categorized as the first generation that consisted in using energy crops based on sugar, starch or vegetable oils with conventional technology, but the use of crops influenced the food markets and generated the polemic of fuel vs. food use of the land. First generation biorefinery has several advantages mainly due to the high sugar or oil content present in their feedstock, as well as the simplicity and low conversion cost into biofuels (Cherubini, 2010; Zabed et al., 2017). However, first-generation biofuels present a serious moral

concern as they compete with the global food supply. In addition, several disadvantages have been reported, including the competition with food production for fertile land, seasonal availability of crops, reduced soil fertility, production yields, and the high fossil fuel consumption employed for crop cultivation and processing (references).

3.1.2. Second generation biorefinery

Second generation biorefinery mainly involves the conversion of organic residues and non-food crops (perennial grasses and short-rotation forestry) different from first generation biorefinery. The feedstock commonly used in the second generation includes lignocellulosic biomass which offers the capacity of the whole plant conversion for biofuel production. The non-food lignocellulosic feedstock is divided into three main groups: homogeneous (wood chips), quasi-homogenous (agricultural and forestry residues) and non-homogenous (municipal solid wastes) (Ho et al., 2014). Lignocellulosic biomass is composed of different amounts of cellulose, hemicellulose, and lignin (Zabed et al., 2017). Lignocellulosic feedstock requires several pre-treatments prior to fermentation processing to release sugars from cellulose and hemicellulose structures. Thermochemical conversion and biochemical conversion are included in these pre-treatment steps. The hydrolysis efficiency of cellulose and hemicellulose is considered the bottleneck in the potential lignocellulosic feedstock for biofuel or biochemical-sproduction (Zabed et al., 2017).

3.1.3. Third generation biorefinery

The complexity and the high processing costs used in the extraction of biomolecules from lignocellulosic materials are the largest barrier to second-generation biofuels production. This technical and economical barrier has led to the search for new feedstock materials, third generation biorefineries that involve biomass without complex, costly pretreatment including algae biomass. Algal biomass represents by far, the most important source in terms of biofuel and value-added product diversity (ref). The biorefinery is a sustainable progression to facilitate the conversion of biomass to the spectrum of marketable products (food, nutraceutical, pharmaceuticals, etc.) and energy without small waste generation (Rathore et al., 2016).

There is a wide-ranging algal spectrum of biorefinery under research. The major drawback of using algae-based biorefineries is their down streaming processing for biomass concentration. Membrane filtration would be widely used for concentrating algae biomass (Özdenkçi et al., 2017; Trivedi et al., 2015), although other separation and concentration processes (e.g., centrifugation flocculation) have been applied. Till today there is no a fully proven method on the sustainability and economic feasibility of biorefinery. Here, we have tried to evaluate the sustainability biorefinery based on BCI considering technology readiness level at the various platform, product, feedstock, and process.

4. Biorefinery evaluation criteria

Biorefinery came to the picture to make the process achievable and economic worthwhile. This concept is parallel to the old petroleum biorefinery model (Jungmeier et al., 2014). For successful execution of biorefineries models which follow the expected result, there is a need to validate the model. Classifying a biorefinery and calculating BCI might provide a real value based on a conceptual biorefinery model. Based on Nelson complexity Index the BCI is developed by IEA bioenergy task 42 (Cherubini et al., 2009). The four features of biorefinery are platforms, products, feedstock, and process.

4.1. Platforms

Platforms are key intermediates which link feedstock with end products, analogous to the platform concept for crude oil fractionation in the petrochemical industry (Cherubini et al., 2009). Key chemical building blocks have been identified for biorefinery and these blocks have been identified as 'pillars' of the classification, since they can be derived from many different conversion processes. They also have the capacity of being converted to marketable products and a staggering number of different fine and specialty biochemicals (Bozell and Petersen, 2010; Cherubini et al., 2009; Jungmeier et al., 2014). In algal biorefinery the green renewable algal biomass act as a platform for the whole biorefinery.

4.2. Feedstock

The feedstock is the raw organic material that is converted into marketable products through the various biochemical process in a biorefinery facility (Cherubini et al., 2009). Feedstock availability is of extreme importance for sustainability and economic efficiency of biorefinery. The feedstock of choice depends on climatic conditions that will affect its availability and desired products. The feedstock selection should consider sustainable year-round supply, low cost of the feedstock, the technology needed for its transformation, and the platform of the feedstock. The algal feedstock is normally subdivided into freshwater, marine and algal processed residues.

Key elements as feedstock price will define the overall biorefinery costs, given that the feedstock usually accounts for about 40–60% of the total operating costs (Cherubini et al., 2009). The feedstock will also directly influence the byproducts in processes and will strongly affect the number of processes incorporated into the processing plant. Table 1 summarizes various feedstock along with technology readiness level (TRL) level values to be used in an algal biorefinery. The transformation processes will vary depending the feedstock. It is predicted that the development of novel biorefineries will lead to a greater variety of feedstocks, technologies, and byproducts for the development of a sustainable supply and transformation of the biomass, with the aim of maximizing the conversion efficiencies, the spectrum of bio-based products and the sustainability.

4.3. Products

The products from the transformation of algal biomass can be categorized into fuel and nonfuel products. The biorefinery can be classified with the nature of the produced outputs, which can be grouped into energy-driven biorefinery and material-driven biorefinery systems (Jungmeier et al., 2014). A list of numerous products from the algal biorefinery is summarized in Table 1. Energy-driven biorefineries are not meant to fully utilize the biomass feedstock into energy products such as biofuels or power, but it represents the most abundant fraction of the biomass. Material-driven biorefineries generate bio-based products (i.e., biomaterials), like food and pharmaceutical products (Cherubini et al., 2009).

4.4. Processes

Biomass is transformed into bio-based products through different conversion processes. These operations englobe fractionation/separation of the biomass into different product streams and are subject of thermochemical and/or biochemical conversion processes (Cherubini et al., 2009). The technological processes include four main subgroups: thermochemical processes, biochemical processes, chemical processes, and mechanical processes. Mechanical processes of biomass concentration and cell disruption are the main processes in biorefining, while thermochemical, chemical, biochemical processes are the major conversion processes (Cherubini et al., 2009). A different process of algal biorefinery has been listed in Table 1.

4.4.1. Biomass cultivation and harvesting

Algal biomass cultivation follows autotrophic, heterotrophic and mixotrophic cultivation (Chandra et al., 2014; Venkata Mohan et al.,

Table 1
The four features of GA biorefinery i.e., platforms, products, feedstock and process for production of food, pharmaceutical and fuel.

Platform		Product		Feedstock	Process	Reference
I	Oil	Single Cell Protein		BGAand GA	Harvesting	(Barros et al., 2015)
		Protein, antioxidants and pigment fraction	Phycocyanin	BGA, MA, GA	1 and 2	(Moraes et al., 2010)
			Phycoerythrin	BGA, MA, GA	1 and 2	(Cai et al., 2012)
			Beta carotene	GA and BGA	1, 3 or 4	(Borowitzka and Borowitzka, 1990)
			Astaxanthin	GA and BGA	1, 3 or 4	(Olaizola, 2000)
			Lutein	GA and BGA	1, 3 or 4	(Grosso et al., 2015)
			Lycopene	GA and BGA	1, 3 or 4	(Poojary et al., 2016)
			Zeaxanthin	GA and BGA	1, 3 or 4	
			Chlorophyll	GA and BGA	1, 3 or 4	
			Fucoxanthin	GA and BGA	1, 3 or 4	(Kanda et al., 2014)
			Canthaxanthin	GA and BGA	1, 3 or 4	(Valderrama et al., 2003)
	C5 and C6 sugars	Carbohydrate fraction	Agar	GA and BGA	1 and 5	
			Carrageenan	GA and BGA	6	
			Alginate	GA and BGA	1 and 5	(Rostami et al., 2017)
			Hydrocolloids	GA and BGA	1 and 5	
	Oil	Lipid Fraction	Fatty acid	GA and BGA	1, 7 or 4	(Karemore and Sen, 2016)
			Eicosanoids	GA and BGA	1, 7 or 4	
			PUFAs (EPA, DHA)	GA and BGA	1, 7 or 4	(Long and Abdelkader, 2011)
			Phospholipid	GA and BGA	1, 7 or 4	(Soares et al., 2016)
	Oil, C5 and C6 sugars		Glycolipid	GA and BGA	1, 7 or 4	
	Oil		ARA	GA and BGA	1, 7 or 4	
			Wax	GA and BGA	1, 7 or 4	(Mathimani et al., 2017)
			GAL	GA and BGA	1, 7 or 4	
			EPA	GA and BGA	1, 7 or 4	
			Fatty acid	GA and BGA	1, 7or 4	
			Eicosanoids	GA and BGA	1, 7 or 4	
			PUFAs (EPA, DHA)	GA and BGA	1, 7 or 4	(Pasquet et al., 2011)
			Phospholipid	GA and BGA	1, 7 or 4	
	Oil, C5 and C6 sugars		Glycolipid	GA and BGA	1, 7 or 4	
	Oil		ARA	GA and BGA	1, 7 or 4	
			Wax	GA and BGA	1, 7 or 4	
			GAL	GA and BGA	1, 7 or 4	(Xu and Mi, 2011)
			EPA	GA and BGA	1, 7or 4	
II	Oil	Protein and pigment fraction	Phycocyanin	GA and BGA	1 and 2	
			Phycoerythrin	GA and BGA	1 and 2	
	C5 and C6 sugars	Antioxidants	Lycopene	GA and BGA	1 and 4	(Gong and Bassi, 2016)
			Zeaxanthin	GA and BGA	1 and 4	
			Chlorophyll	GA and BGA	1 and 4	
			Fucoxanthin	GA and BGA	1 and 4	
			Canthaxanthin	GA and BGA	1 and 4	
			Beta carotene	GA and BGA	1 and 4	
			Astaxanthin	GA and BGA	1 and 4	
			Lutein	GA and BGA	1 and 4	
	Oil	Lipid Fraction	Fatty acid	GA and BGA	7 or 4	(Saifuddin et al., 2016)
			Eicosanoids	GA and BGA	7 or 4	
			PUFAs (EPA, DHA)	GA and BGA	7 or 4	
			Phospholipid	GA and BGA	7 or 4	
			GAL	GA and BGA	7 or 4	
			Wax	GA and BGA	7 or 4	
			ARA	GA and BGA	7 or 4	
			Glycolipid	GA and BGA	7 or 4	
		Lipid Fraction	Fatty acid	GA and BGA	1, 7 or 4	(Viguera et al., 2016)
			Eicosanoids	GA and BGA	1, 7 or 4	
			PUFAs (EPA, DHA)	GA and BGA	1, 7 or 4	
			Phospholipid	GA and BGA	1, 7 or 4	
			GAL	GA and BGA	1, 7 or 4	
			Wax	GA and BGA	1, 7 or 4	
			ARA	GA and BGA	1, 7 or 4	
			Glycolipid	GA and BGA	1, 7 or 4	
	Oil, C5 and C6	Bioactive compound	MAAs	GA and BGA	1, 8	(Orr et al., 2016)
			Scytonemin	GA and BGA	1, 7	
	Oil	Glycerol	Glycerol	GA and BGA	9	(Park et al., 2017)
III	Hydrogen	Bio-H_2		GA and BGA	1, 7	(Gruhn et al., 2016)
	C5 and C6 sugars	Bioethanol		GA and BGA	1, 3	
		Bioelectricity		GA and BGA	MFC operation	(Hou et al., 2016)
	Oil, C5 and C6 sugars	Biodiesel		GA and BGA	1, 3	(Im et al., 2014)
	Oil	Glycerol		GA and BGA	9	(Park et al., 2017)

BGA: Cyanobacterial biomass, GA: Green Algae biomass, MA: Marine, 1: Cell disruption, 2: Protein extraction, 3: Solvent extraction, 4: Super critical CO extraction, 5: Alkali extraction, 6: Freeze-thaw and gel-press 2
processes, 7: Binary Solvent extraction, 8: Methanol extraction, 9: Transesterification.

2015a). Marine algae mostly grow autographically (Golberg & Liberzon, 2015). All these methods are well proven at industrial scale and have a TRL level 9. Algae can be harvested by some methods; sedimentation, flocculation, flotation, centrifugation, and filtration or a combination of any of them. Despite the importance of harvesting to the economic and energy balance viability of micro-algal biofuel, there is

no universal harvesting method for micro-algae.

Centrifugation can handle most algal types with rapid, efficient cell harvesting, but they have high capital and operational costs. For filtration, a wide variety of filter and membrane types are available, but they are highly dependent on algal species. It best suited to large size algal cells but still clogging or fouling are major issues in separation. Whereas ultrafiltration can handle delicate cells, they have high capital and operational costs. Sedimentation of algal biomass is a low cost and potential use for as a first stage to reduce energy input and cost of subsequent stages. This strategy best suited to dense non-motile algal strains. Sedimentation is slow and provides very low final concentration of algal cells. In chemical flocculation, a wide range of flocculants is available, but the removal of flocculants and chemical contamination is a huge disadvantage. Flotation can be more rapid than sedimentation, but they require high capital and operational cost (Milledge & Heaven, 2013).

4.4.2. Cell disruption and extraction

A microalgal biochemical component that is not secreted from cells must be extracted by cell disruption, breakage or its disintegration (Dong et al., 2016). Various cell disruption methods are solid shear, bead milling, cavitation and collapse, pulsed electric field, chemical hydrolysis, enzymatic digestion, subcritical water extraction, and high-pressure homogenization. Bead milling consists of disrupting cells membranes into a chamber filled with beads and agitation (Ghasemi Naghdi et al., 2016). The membrane disruption is due to grinding between beads and collision with beads. The process efficiency depends on many parameters such as the beads diameter and amount, the microorganisms' concentration, the movement and speed of agitators, the solution flow rate and the temperature. Cavitation is the growth and collapse of bubbles due to a transient decrease of pressure, below the saturation vapor pressure. A collapse is a violent event that damages solids surfaces, produces shock waves and disrupts cell membranes.

In chemical hydrolysis, dilute acid pre-treatment can hydrolyze polysaccharides to release monomeric sugars (primarily glucose and mannose) into an aqueous phase that can be separated from solid residue rich in lipids and protein. In enzymatic digestion, enzymes are used to digest specific components of cell membranes. Enzymatic treatment can have large impacts of the permeability of the algal cell walls and may be useful in process optimization, especially certainly lysozyme and certain other enzymes (Passos et al., 2016).

The cell disruption of algae could be performed by using alkali solutions, representing an alternative for lipid extraction. As a normal methodology for the alginate extraction, microalgae species are soaked in a sodium carbonate solution for several hours. The microalgae residues are separated from the solution by filtration. Finally, the alginate is precipitated by adding calcium chloride and dried (Ghasemi Naghdi et al., 2016; Park et al., 2015). The base of the freeze–thaw is the formation of internal and external ice crystals along with the subsequent thawing promotes the cellular rupture. This technology has been used for the extraction of the carbohydrate fraction from algae (Chr. Eilertsen et al., 2014). The main disadvantage of this method is time-consuming.

Traditionally, algae oil is extracted by using solvents such as hexane, methanol, and chloroform (Rombaut et al., 2017). As an alternative for the oil extraction, supercritical CO_2 is a green methodology due to its lower toxicity and lack of reactivity. This technology uses supercritical carbon dioxide as a solvent due to its moderate critical pressure and low critical temperature to perform the extraction of non-polar compounds (lipids) without degradation (Damjanovic-Vratnica et al., 2016). By gel-press, algae are washed, and carbohydrate fraction is extracted with dilute alkaline solutions. Residues are separated with centrifugation followed by filtration through porous silica and concentrated with evaporation. Then, the material is extruded through spinnerets into a cold solution of potassium chloride. Finally, the gelled threads are dewatered by pressure (Amin, 2009).

Lipids are non-polar molecules insoluble in water at ambient conditions. However, the dielectric constant of water is significantly lower at subcritical conditions, allowing greater miscibility with lipids. Hydrothermal liquefaction is a wet biomass conversion process carried out in such conditions at temperatures at 100–374 °C and high pressures at 10–25 MPa (Reddy et al., 2014). Cavitation may be generated by the flow of a liquid from a large area into a small constriction. The liquid velocity increases in the constriction so the pressure drops. If the pressure falls below the saturation vapor pressure, then bubbles are created. When the pressure increases theses bubbles collapse violently producing shockwaves that can damage cell membranes. Shear based devices such as French press and Hughes press use high pressures to force a solution containing microorganisms through a small aperture (Samarasinghe et al., 2012). In the binary solvent extraction, two solvents are soluble and present the behavior of a single homogeneous phase. In these systems, one component is partially miscible under the prevailing conditions, and the other solvent is completely miscible with both under the operational conditions. Different compounds have been extracted by this methodology, such as antioxidants of macro and microalgae.

4.4.3. Thermochemical, biochemical and chemical conversion

Thermochemical conversion utilizes the principle of thermal decomposition of biomass to extract fuel products. Examples of thermochemical conversion processes include gasification, thermal liquefaction, pyrolysis, and direct combustion. Gasification is the chemical process where carbonaceous materials are converted to synthesis gas (syngas). Syngas can be used to make a wide range of fuels and chemical intermediates, or directly burnt as a fuel for gas engines. For thermal liquefaction, the algal biomass will undergo liquefaction to decompose the biomass into smaller molecules with higher energy density. Pyrolysis is the thermal degradation of biomass without the presence of oxygen. This process has the potential for large-scale production and can generate biofuels with medium–low calorific power. Direct combustion involves the chemical reaction between a fuel and oxygen with the presence of air. This process produces carbon dioxide, water, and heat as products. Energy is generated through the combustion of biomass, and higher efficiencies can be achieved with the co-combustion techniques in coal-fired power plants (Chew et al., 2017).

The biochemical conversion illustrates the biological processing of biomass into biofuels. Examples of biochemical conversion processes include anaerobic digestion, alcoholic fermentation, and photobiological hydrogen production. Anaerobic digestion involves the conversion of organic wastes into biogas through cascade microbiological reactions of acidogenesis, acetogenesis and methanogenesis. The biogas produced from algal biomass was found to contain high energy value, and the energy recovery is comparable to that of the extraction from cell lipids. Due to the rising cost of energy, the anaerobic digestion of biomass is becoming attractive as an alternative for fuel production. As for alcoholic fermentation, electrons in an organic substrate are ended up with alcohols during fermentation in which redox reactions occur without exogenous electron acceptors. For instance, the biomass materials which contain sugars, cellulose or starch, are converted into ethanol by yeast.

The photobiological hydrogen production is the conversion of water to hydrogen ions and oxygen by photosynthetic microorganisms, like algae. Firstly, the algae are grown photosynthetically in normal conditions, and subsequently cultured by inducing anaerobic conditions to stimulate hydrogen production. Secondly, the simultaneous production of photosynthetic hydrogen and oxygen gas will take place, and these gases will be spatially separated (Chew et al., 2017). The microbial fuel cell (MFC) devices could be integrated into the biochemical conversion. The main objective of this technology is to recover substrate electrons as electric power or chemicals with simultaneous wastewater treatment. MFC operation includes the oxidation of organic matter at the anode chamber and the generation of electrons and protons that are

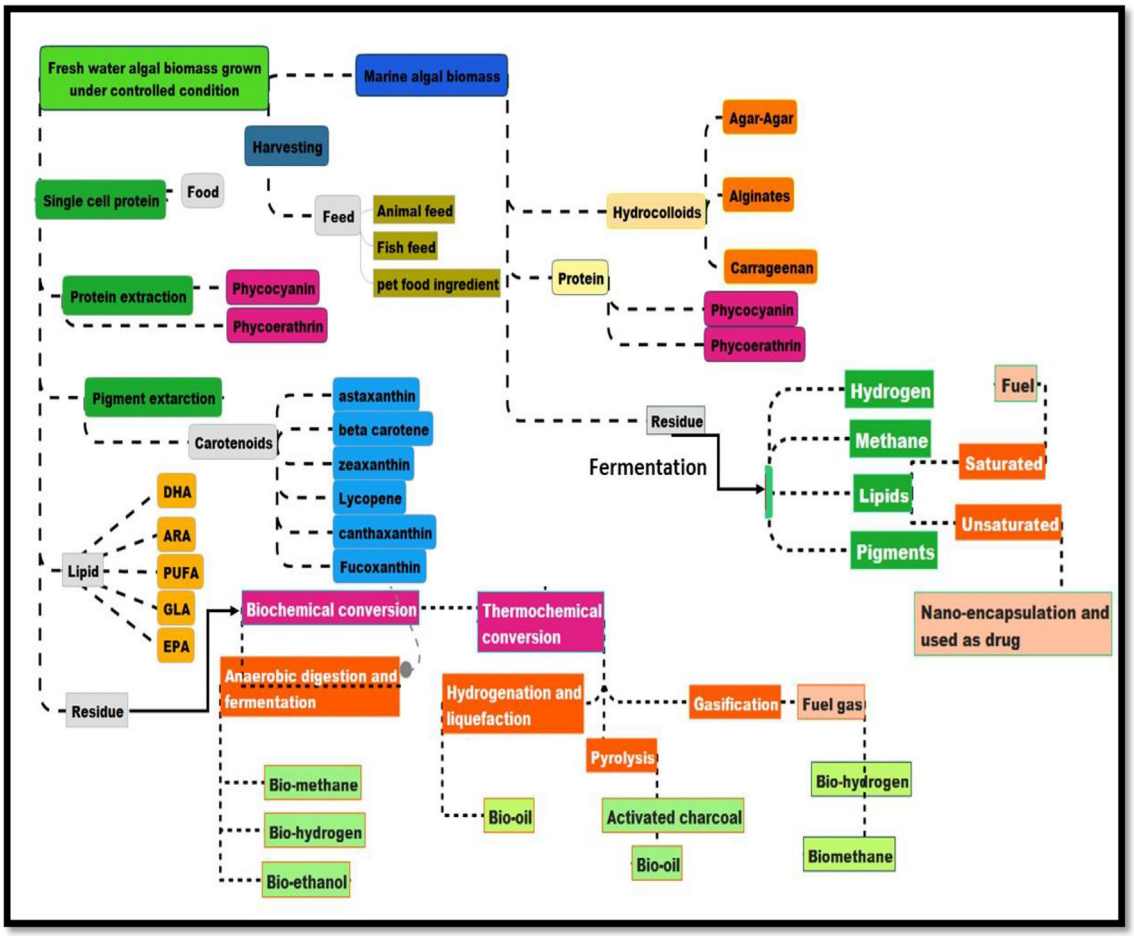

Fig. 2. An integrated Algal biorefinery for fuel and value added products with process. Docosahexaenoic acid (DHA); Arachidonic acid (ARA); Polyunsaturated fatty acids (PUFAs); Eicosapentaenoic acid (EPA).

transported to the cathode chamber where they combine with oxygen to form water. The oxygen in the cathode chamber could be provided exogenously from the air or by a biocatalyst such as algae species like *Chlorella vulgaris* (Kakarla and Min, 2014).

The Transesterification is the reaction of triglycerides with alcohol in the presence of a catalyst to produce fatty acid chains and glycerol. This process can produce fatty acid methyl esters (FAME) by using methanol and ethanol. However, transesterification may be limited by the oil impurities and nature of the catalyst. Determining the reaction conditions such as temperature and time are also a factor that might affect the transesterification process. The reactions of triglycerides to FAME and glycerol are usually catalyzed by an acid or base, using either a homogeneous or heterogeneous catalytic process. Also, conducting transesterification under a supercritical condition can weaken the hydrogen bond of the alcohol. This would enable the complete conversion of triglycerides to esters rapidly as the chemical kinetics is accelerated under supercritical conditions (Chew et al., 2017).

5. Biorefinery complexity index

Based on the four-factors, i.e., (1) Platform, (2) Product, (3) Feedstock and (4) Process, the complexity of biorefinery can be evaluated by calculating BCI (de Jong and Jungmeier, 2015). A complete list of the platform, product, feedstock, and process involved in algal biorefinery is listed in Table1. Initially, each process has been evaluated based on their TRL from 1 to 9 acquired from European Space Agency and United State Department of Energy (Gauthier et al., 2015; Steinberg, 2016). Based on the TRL, the feature complexity (FC) for every single feature at Platform, Product, Feedstock, and Process was calculated as FC = (10-TRA).

Where, FC = Feature complexity; TRA = Technology readiness level; Factors we considered in biorefinery are a platform, product, feedstock, and process. Based on all these parameters BCI can be depicted with Equation (1) and Equation (2) (Chandra et al., 2018).

$$\text{BCI} = (\text{NF Platform} * \text{FC Platform}) + (\text{NF Feedstock} * \text{FC Feedstock}) + (\text{NF Product} * \text{FC Product}) + (\text{NF Process} * \text{FC Process}) \quad (1)$$

$$\text{BCI} = (\text{FCI Platform} + \text{FCI Feedstock} + \text{FCI Product} + \text{FCI Process}) \quad (2)$$

where, BCI = biorefinery complexity index; NF = number of features; FC = feature complexity.

The creation of the biorefinery complexity profile comes to assist the many different biorefinery concepts that are currently in development and implementation, as a general guide for standardizing and comparing the complexity and feasibility of new technologies with existing ones. The number of platforms has a greater impact in the BCI than the other features, given that the platforms are comprised of feedstocks, processes, and products (Jungmeier et al., 2014; de Jong and Jungmeier 2015). International Energy Agency (IEA) Bioenergy Task 42 has defined a biorefinery as “the sustainable processing of biomass into a spectrum of marketable products and energy” (Ghatak, 2011). In a widespread definition, a biorefinery can be defined a sustainable production facility where biomass feedstocks are converted into high-value bio-products as food, feed, chemicals and materials and bioenergy (biofuels, power and/or heat) (de Jong, 2014; IEA, 2009).

The biorefinery concept comprehends a wide range of systems

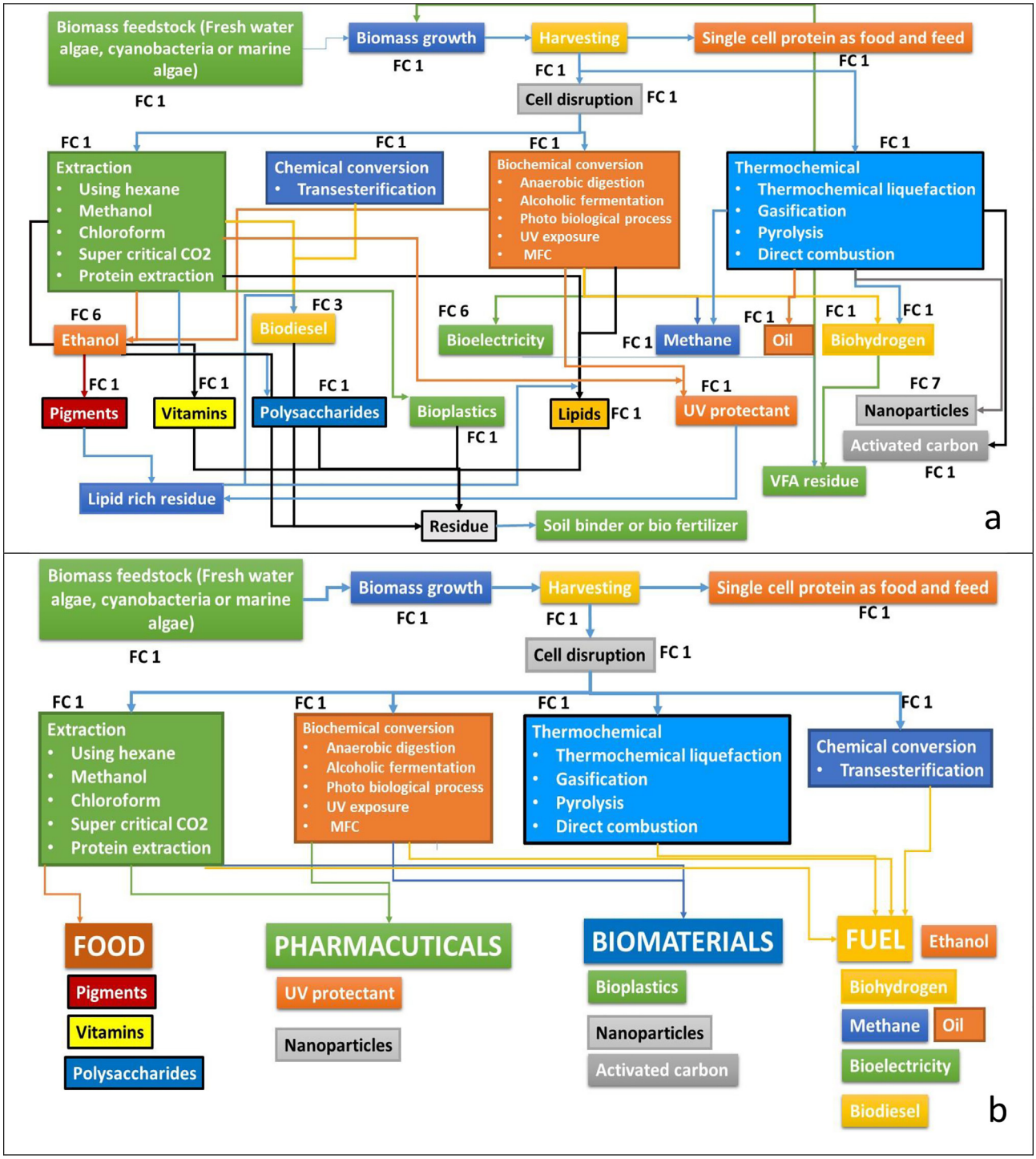

Fig. 3. (a) An integrated process flow of algal biorefinery with featured complexity index at each step depending on technology readiness level (b) Major process involved in product recovery showing complexity of process, representing food require less process them fuel which provide a sustainability to algal food production than algal fuel production.

including a processor, a plant, technologies or even a cluster of facilities that allow the separation of biomass feedstocks into main constituents (lipids, proteins, etc.) (Cherubini, 2010; Trivedi et al., 2015). The essential component of a biorefinery is sustainability which has awakened the interest of many countries for the implementation of biorefineries. In that regard, it has been established that all biorefineries should be evaluated for social, environmental and economic sustainability covering the whole life cycle (IEA, 2009). Thus, the main objective of a biorefinery is the integration of the production of high-value products, biofuels and energy, and raw materials while minimizing wastes and enhancing profitability. Considering all these parameters, we have developed a sustainable algal biorefinery for food, pharmaceutical, and fuel. Based on this an algal biorefinery has been evaluated considering platform, product, feedstock, and process at defined higher TRL level with the established marketable product.

The extraction of numerous products from algal biomass increases the value of the biomass and offers additional balances to the environmental impacts. Fig. 2 shows an integrated algal biorefinery for

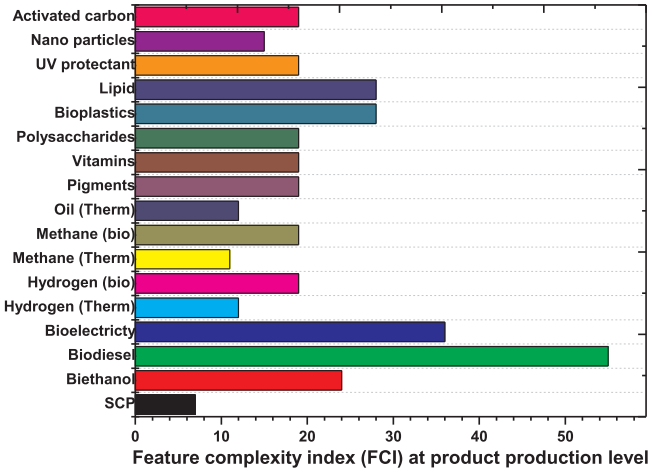

Fig. 4. Biorefinery complexity index of individual product based on technology readiness level and feature complexity index.

recovery of value-added products and fuels. Algae can be easily used as a nutraceutical, food, and feed. *Spirulina* and *Chlorella* are direct sources of single cell proteins. Nutraceutical application also involves utilization of carotenoids, unsaturated fatty acid, and hydrocolloids. Algal biomass can easily subject to protein and pigment extraction, i.e., phycobiliproteins (phycocyanin and phycoerythrin) and carotenoids (astraxanthin, beta-carotene, zeaxanthin, lycopene, canthaxanthin, and fucoxanthin) (Chandra et al., 2015a; Sekar and Chandramohan, 2008). The residual biomass from protein and pigment extraction can be subjected to the second step, where it is processed for algal oil extraction. From the algal oil, high-value omega-3 fatty acids, such as docosahexaenoic acid and eicosapentaenoic acid, can be separately processed and used as value-added products after nano or microencapsulation. The rest of the oil can be used for biofuel production.

The residual biomass (deoiled cake) can be subjected to a range of bio/thermochemical processes like fermentation, anaerobic digestion or pyrolysis, recovery of methane and biohydrogen by using lipid extracted microalgae pulp as shown in Fig. 2. The literature reported the use of deoiled microalgae pulp/cake as fermentative feedstock with biomethanization or acidogenic processes after proper pretreatment (Venkata Mohan et al., 2014). Marine algal biomass is a good source of hydrocolloids (agar-agar, alginates, and carrageenan) and phycobiliproteins (phycocyanin and phycoerythrin). After extraction of these compounds the residual biomass can be subjected to fuel biorefinery for biochemical conversion and thermochemical conversion. Thermo-chemical conversion of algae biomass was also performed for the synthesis of bio-oil and biochar. The high-value co-products can be preferred for economic support of the main process. Integration of algal-fuels in a combined biorefinery concept with simultaneous production of value-added by-products will have a positive impact on the overall process economics.

Algal biorefinery can be used to produce a wide range of value-added products from microalgae in a sustainable way. We proposed an algal biorefinery with FCI in Fig. 3a considering four factors, i.e., Platform feedstock, product, and process. TRL of each factor has been considered without energy input and cost. We tried to explore the feasibility of these processes in an integrated way. We consider the platform as renewable algal biomass at TRL 9 (FCI1). This platform can be divided into three feedstocks, i.e., freshwater algal biomass, marine algal biomass, and cyanobacterial biomass. Cultivation and harvesting are available and proven in an operational environment, so it comes under TRL 9 (FCI1). For the effective extraction and biomass processing, we consider matured technologies to make biorefinery sustainable. The grown biomass gets harvested through various techniques, and most of the techniques are well proved and fall at TRL 9 (FCI1).

A pure culture of cyanobacteria like *Spirulina* or *Chlorella* can be easily used as single cell protein (SCP) or animal feed. However, every algal feedstock cannot be utilized as SCP or animal feed, and hence that kind of biomass is subjected to cell disruption, extraction, chemical conversion, biochemical conversion, and thermochemical process. All these processes are considered at TRL9 (FCI1). There are four main channels to process the algal biomass, i.e., extraction, biochemical conversion, chemical conversion, and thermochemical conversion. All these processes fall under TRL9, while depending on the production process. By analyzing the process and integrating, we found algal food technology require less processing whereas algal fuel biotechnology requires high processing at lower TRL level (Fig. 3b). More number of process at lower TRL makes biorefinery less sustainable.

BCI was calculated for all individual products based on TRL and FCI of platform feedstock, product, and process as illustrated in Fig. 4. Single cell protein (SCP) have minimum FCI of 7, which supports that SCP is the most favorable in biorefinery. In comparison, biodiesel and bioelectricity have BCI 55 and 36, respectively. This BCI results due to the different processes involved in it and there TRL level. The BCI of the proposed biorefinery 361, where 54% of complexities governed by biofuel and only 45% by all product collectively. This indicates that using microalgae primarily as food and pharmaceuticals gives more sustainability rather than fuel alone.

6. Industries involved in algal technologies

There are various institutions, companies, government entities, and scientists actively working around the world to make biofuels and algal

Table 2
Worldwide companies involve in GA research, their products and type of cultivation method.

Company	Product	Cultivation system	References
Algatechnologies (Israel)	Astaxanthin	Closed and semi-closed bioreactors under high light intensity	(Panis and Carreon, 2016)
BioReal Inc (USA)	Astaxanthin	Indoor photobioreactor	(Shah et al., 2016)
Cyanotech (Hawaii)	Astaxanthin, *Spirulina pacifica* as food ingredient	Raceway pond and photobioreactors	(Panis and Carreon, 2016)
Mera Pharmaceuticals Incorporation	Astaxanthin from Haematococcus pluvialis	Raceway pond	(Brennan and Owende, 2010)
Algenol (USA)	Bioethanol, and pigments	Raceway pond, Closed and semi-closed bioreactors	(ElMekawy et al., 2016)
Sapphire Energy Inc. (USA)	Biofuels and	Uses non-potable water, seawater	(Maity, 2015)
Solazyme Inc. (USA)	Biodiesel and biojet fuel	Heterotrophic cultivation and photobioreactor	(Menetrez, 2012)
Sea6 Energy (India)	Food Additives, biofuel, bioplastic, animal feed	Sea water	(Wei et al., 2013)
Muradel Pty Ltd. (Australia)	Biofuels, oleochemicals, biofertilizers, animal feed and building materials	Raceway pond	(Duong et al., 2012)
Cellana (USA)	PUFAs, animal feed, biodiesel and bio jet fuel	Open-pond bioreactor	(Menetrez, 2012)
Solix Algadrients Inc. (USA)	Astaxanthin and DHA	Enclosed photobioreactors	(Radakovits et al., 2012)

products economical and sustainable. Pigments represent a product obtained from algal bio-refineries, currently some companies are established in global market: Algatechmologies from Israel that sells algal astaxanthin; BioReal Inc. that sells the same pigments; Cyanotech (Hawaii) also produce astaxanthin and also Spirulina Pacifica to use as food ingredient; Mera Pharmaceuticals Inc., a marine biotechnology company that produces astaxantin from Haematococcus pluvialis. On the other hand, biofuel companies have been founded that produce a wide range of products such as biofuels, oleochemicals, fertilizers, animal feed, and building materials (co-products with potential use in construction industries). Table 2 summarizes various companies involved in the production of biofuels, protein feedstock, and nutraceuticals. These companies and institutions are working from identifying and optimizing specific strains of algae to develop a sustainable biorefinery.

7. Challenges and future perspective

Microalgae cultivation and biorefinery platform, have gained tremendous attention to synthesize high amounts of a value-added compound such as pigments, vitamins, PUFAs, anti-oxidant, etc. There are still challenges to be addressed, which include biomass cultivation, compound recovery, down streaming processing, energy consumption and methods for scale-up processing. For algal application in food industry, algae cultivation should adhere to the regulations set by the Food and Drugs Administration (FDA) agency to ensure the safety of the use of algae extract for human consumption. Various apprehensions essential need to be addressed for different products, product stability, and long-term stability of algal products. Finally, broad economic and environmental studies should be carried out over the production of high-value compounds from microalgae to evaluate the sustainability of processes.

8. Conclusion

The fundamental step to establish sustainable technologies for commercialization of fuel-based and non-fuel-based products from algae is to develop multidisciplinary research which provides a complete understanding of biorefinery approaches. It contributes to the economy and leads to a diversification of byproducts for the sustainable, economic valorization of biomass. Defining BCI for any biorefinery provides the technological and economic risks towards its sustainability and economic viability. In summary, development of integrated sustainability bio-refinery based on algal-biomass with multiple product recovery will be able to address the control or uncontrol resilience on petro-based resources.

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