Overview of Biorefinery Technology

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Abstract Biorefinery involves integrated systems or routes/pathways for converting biomass into different targeted valuable products such as energy, fuels, and chemicals by various physical, chemical, thermochemical, and biochemical technologies. It has recently gained increasing attention owing to its relevance. International Energy Agency Bioenergy Task 42 defined biorefinery as "the sustainable processing of biomass into a range of biobased products (chemicals, feed, food, or other useful products) and bioenergy (power, biofuels, and/or heat)," with the aim to optimize the full utilization of biomass, maximize its profitability, and concurrently minimize waste generation. An overview of the technologies/possible routes of algal biomass biorefinery for enhanced biomass utilization, most especially for production of several industrially important phycochemicals and bioenergy, has been provided in this chapter. Besides, the chapter also presented the general concept of biorefinery and the summary of the challenges, opportunities, and recent trends in algal biomass biorefinery.

Keywords Algal biomass · Circular economy · Biochemicals · Bioenergy · Enhanced biomass utilization

1 Introduction

Biorefinery has recently gained wider attention owing to its indispensable relevance in sustainable processing of biomass, with the aid of integrated systems or routes/pathways, into a variety of valuable and commercial bioproducts and bioenergy. The later refers to the renewable energy obtained from biomass, while biofuels refer to liquid, gaseous, or solid fuels produced from biomass or organic matter that can be utilized as a replacement for fossil fuels (Reid et al. 2020). Biorefineries thus include facilities that aim to extract multiple high-value products from renewable biomass

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sources such as algae, agricultural residues, urban and wood residues, forest residues and mill residues, as well as herbaceous energy crops and dedicated woody crops (Hingsamer and Jungmeier 2019; Moncada and Aristizábal 2016). These biomass feedstocks can be further grouped into lignocellulosic biomass, starchy biomass, sugar biomass, organic waste biomass, and triglycerides biomass. Biorefineries are thus considered a sustainable solution to replace traditional petrochemical refineries, which are heavily reliant on finite and non-renewable fossil fuels.

Climate change, global warming, and environmental degradation, occasioned by the intensive deployment of fossil resources, are the most severe environmental hitches challenging humanity today (Hassan et al. 2021; Martins et al. 2019; Solarin 2020). These challenges can be ameliorated by employing biofuels of algal origin as an alternative and renewable energy fuel source. Microalgae are ubiquitous organisms that are thought of as traditional substitutes for the viable production of a variety of bioproducts of higher value. However, due to high costs, high-energy requirements, and a lack of readily available biomass and biomolecules, microalgal biorefinery is still very far from being economically feasible (Chew et al. 2017; Chia et al. 2018). Seaweeds (commonly known as the macroalgae) are species of macroscopic multicellular marine photosynthetic organisms. As previously discussed in this book, they are generally categorized into three main groups: brown algae (Phaeophyceae), red algae (Rhodophyta), and green algae (Chlorophyta). The use of seaweeds as feedstock in biorefinery process development is considered as a high potential alternative in the energy, food, pharmaceutical, and medical sectors. However, it is essential to pretreat the feedstocks to make their molecular structure accessible.

With the progressive surge in global population, shortage of fossil fuels, increased energy prices, climate change challenges, and the threat of environmental pollution, mankind are compelled to explore other alternative routes of energy and biochemical sources to meet the increasing energy needs. Currently, huge research efforts are in the areas of identifying new species, maximizing biomass productivity and identifying new and novel strategies to achieving the needs of folder, food, value-added biochemicals, and fuels in the future (Saad et al. 2019). As discussed in previous chapters, energy and fine biochemicals can be produced from the first-, second-, or the third-generation feedstocks (mostly algae) for biorefinery purposes. When compared to other conventional feedstocks, algae have more benefits. For example, the rate of growth of algae has been found to be 5–10 times greater than that of land-based crops in favorable circumstances, indicating a greater rate of production of ideally convertible biomass (Srinivasan and Kulshreshtha 2020; Voloshin et al. 2016; Wang et al. 2023). Besides, some species may contain up to 70–80% by weight of lipids or carbohydrates. Thus, the rising demand for renewable and sustainable resources has led to a growing interest in biorefineries, which convert renewable resources into a variety of bioproducts (fuels, chemicals, and materials) of higher value. One of the most promising resources for biorefineries is algal biomass, which has several advantages over other renewable resources, such as increased lipid yield, greater rate of growth, and the capacity to grow in marginal agricultural land (salty, brackish, and marshy soils) (Sarwer et al. 2022; Ubando et al. 2021). However, biorefineries based on algal biomass development are still in their early stages, and many challenges must be overcome before these systems can be implemented commercially.

This chapter presented the overview of the technologies/possible routes of algal biomass biorefinery for enhanced biomass utilization, most especially, for production of several industrially important phycochemicals and bioenergy. The chapter also gave the general concept of biorefinery and the summary of the challenges, opportunities, and recent trends in algal biomass biorefinery.

2 Concept of Biorefineries

Algal biorefinery is a unified system that integrates the conversion processes of algal biomass and the associated equipment/facility in production of chemicals, power, and fuels in a socially, economically, and environmentally sustainable manner. Every of the refining phase is known as a "cascading phase." For sustainably producing and efficiently utilizing biomass resources, biocascading and biorefining approaches/technologies must be implemented (Balina et al. 2017; Cherubini 2010; Conteratto et al. 2021; de Jong and Jungmeier 2015). The main importance of a biorefinery includes three main aspects: (1) the simultaneous production of both energy (liquid or gaseous biofuels) and value-added materials (feed, food, and chemicals), (2) the use of multiple processes (thermochemical, biological, and/or mechanical processes), and (3) utilization of various raw biomaterials, both from fresh sources and from waste streams (Chew et al. 2017).

Integrating the biorefinery concept into existing industrial parks has the capability to lower the costs of capital and the resulting products. To ensure sustainable growth, strategies for incorporating biorefineries into the future bio-economy must be implemented (Maity 2015). The process of producing bioenergy through biorefinery approach involves numerous steps, including cultivation, harvesting, pretreatment, extraction, and conversion. Pretreatment aims to simplify the complex structure of biomass by, for example, transforming polysaccharides into sugars that can be fermented. There are four methods for pretreatment including physical, chemical, physiochemical, and biological. During the extraction phase, oil is separated from the biomass, resulting in a de-oiled biomass that consists of many components such as carbohydrates, protein, antioxidants, and pigments. The actual composition of these components depends highly on the biomass types and extraction method used (Wiselogel et al. 2018). The extracted lipid is used to produce biodiesel via transesterification, while the remaining components of the biomass are utilized in the synthesis of high-value bioproducts like pharmaceuticals and feed/food ingredients (Gameiro 2016). Figure 1 presents a general overview of biomass biorefinery concept for production of a spectrum of compounds.

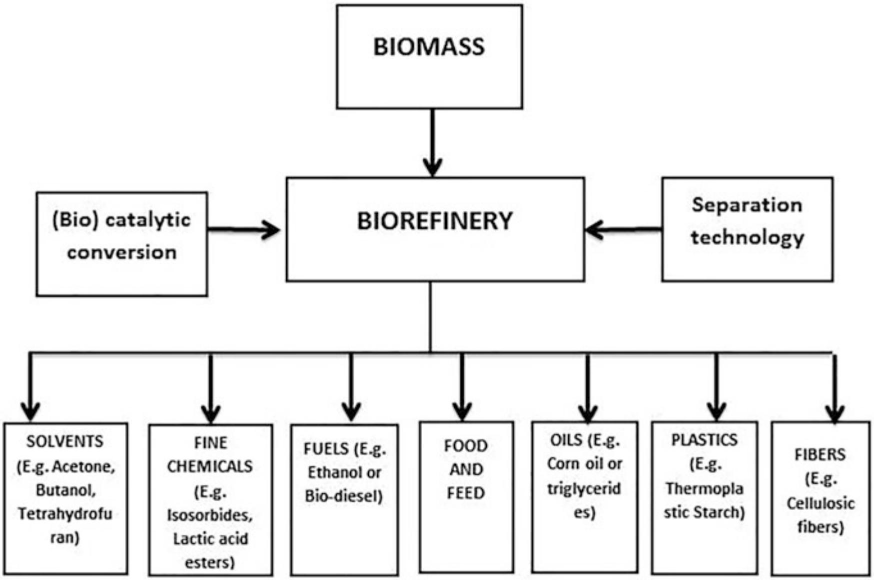

Fig. 1 Typical concept of biorefinery for production of a spectrum of compounds

3 Algal Biorefinery

Algal biorefinery concept is similar to today's oil refineries that produce several fuels and other products from petroleum (Ferreira 2017). Several bioprocessing steps can be employed to extract bioactive compounds, such as carbohydrates, proteins, and lipids from algae. Biorefinery approach has garnered much interest as a process of obtaining fine chemicals, bioactive compounds, and fuels from third-generation feedstocks (Chandra et al. 2019). The idea of using algae as a biomass feedstock for biorefinery looks promising with multiple advantages. It will help in carbon dioxide (CO_2) sequestration, ameliorate the menace of the global warming, and yield components needed for different industrial purposes such as energy, feed, food, pharmaceuticals, cosmetics, fertilizers, nutraceuticals, and other biobased industrial products (Vázquez-Romero et al. 2022). In spite of the huge prospects of algae as biorefinery feedstock, there are, however, some techno-economic challenges. For instance, the present industrial microalgae biomass global productivity and market are still abysmal (15,000–25,000 ton per year) (Fernández et al. 2021; Koyande et al. 2019) and cannot meet up with demand by the industry. The reason for the low rate of production is the inherent high cost of cultivation, harvesting, and extraction (Okoro et al. 2019). As a result of this, algal production is currently directed to the production of high value-added bioproducts. Use of microalgae for energy production can be considered a secondary option due to the fact that it does not command as much price as conventional fossil fuel. Biofuels do not necessarily have to be priced lower than conventional non-renewable fuels. However, biofuel production must be performed with lower energy inputs. Much of the studies only focused on the synthesis of value-added products from algae with relatively few studies on biofuel production, leaving much of the constraints not yet overcome (Halder and Azad 2019). Two main stages have been identified in algae biorefinery processing: (1) upstream and (2) downstream processing. Upstream processing mainly involves algae cultivation. The essential raw materials needed for this stage are space, light, water, nutrients, and CO_2. The algal growth rate and biomass productivity depend largely on many factors, mainly supply of nutrients light intensity, and cultivation system, as discussed in Chapter "Algae Cultivation Systems". Downstream processing of algal biomass includes harvesting, extraction, and purification of phycochemicals. The traditional extraction methods involve physical/mechanical techniques such as manual bead beating, blending, screw press, ultrasound, high-pressure homogenization as well as chemical techniques such as solvent extraction using hexane, acetone, chloroform, and benzene, as well as using supercritical fluid/gas extraction (Aravind et al. 2021). The entire processes are complex, multi-step with huge cost implications. Other methods such as autoclaving and freeze–thawing have also been used which are complex and extremely costly, making the industrial extraction of a single phycochemical from algal biomass an economic challenge. Different products from algal biomass belong to four main cellular components namely carbohydrates, lipids, proteins, and pigments. The resulting by-products or residues can be recycled as nutrients for media during algae cultivation (Abomohra et al. 2018) or used in biorefinery combined heat and power (CHP) plants for electricity generation (Maghzian et al. 2023). Research is presently ongoing to discover and isolate existing or new algal strains with multiple value-added products that can potentially be used as viable inoculum for further biorefinery processing. Many technologies are used to genetically modify and optimize existing algal species to improve strain performance as discussed in Chapter "High Throughput Screening to Accelerate Microalgae-based Phycochemicals". However, the extraction of quality products of higher value from algal biomass on industrial scale is still currently not viable and needs further optimization The need to employ affordable and simple technologies both in the upstream and downstream processing in algal biorefinery was also emphasized (Shahid et al. 2020). Figure 2 presents an overview of integrated algal biorefinery processes, while Fig. 3 provides a typical example of a microalgal biorefinery model.

4 Opportunities and Challenges of Algal Biorefinery

4.1 Opportunities of Algal Biorefinery

Algal biorefineries offer various opportunities for businesses and industries to diversify their products and revenue streams. Algae can serve as a feedstock for production of various high-value-added products including sustainable biofuels, food ingredients, fertilizers, nutraceuticals, and pharmaceuticals. This has the

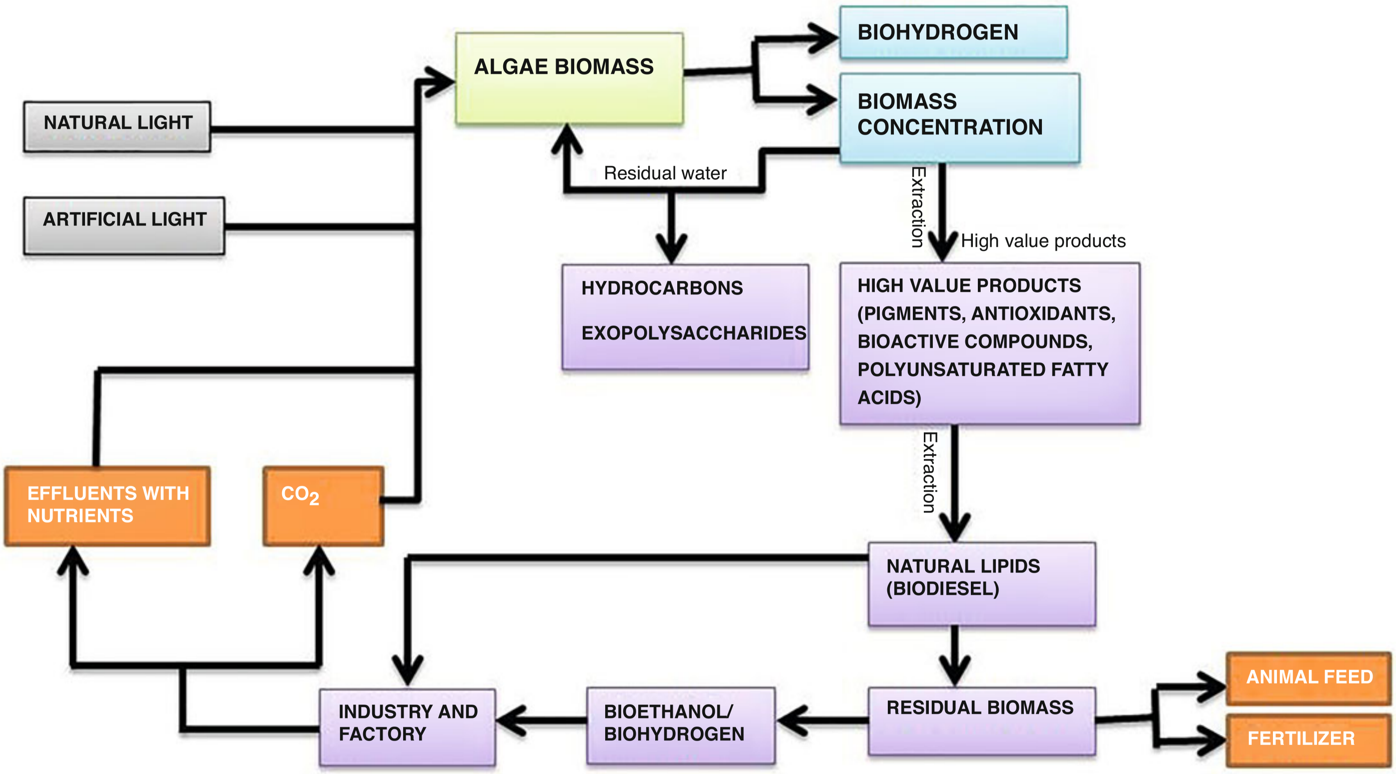

Fig. 2 An overview of integrated algal biorefinery processes showing the closed loop of carbon neutrality

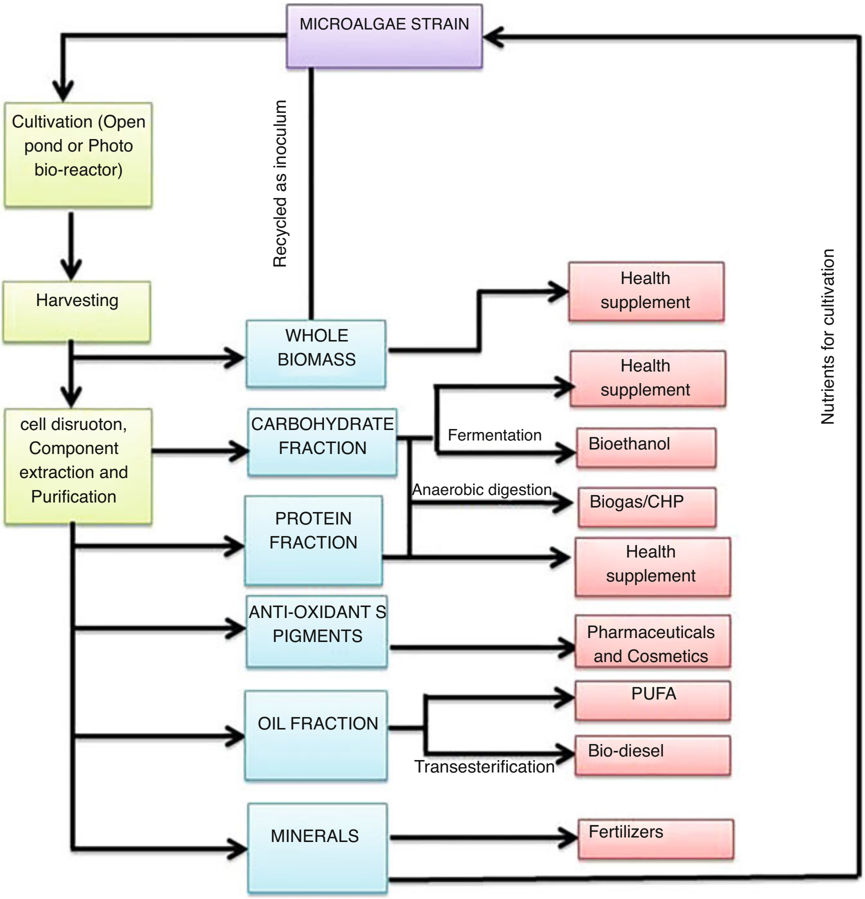

Fig. 3 A typical example of a microalgal biorefinery model

capacity for reduction of dependency on fossil fuels and greenhouse gases emission, increase resource efficiency, and improving the overall economic outcome. In addition, establishment of algal biorefinery could create new jobs and economic opportunities in rural areas. One of the unique characteristics of algae, most especially, the microalgae, is the high lipid content that some strains are capable of producing lipids, especially triacylglycerol (TAG), which is a promising starting material for green gasoline synthesis, green diesel, green jet fuel, and biodiesel (Salman et al. 2023). These biofuels can be produced by either transesterification of the TAG or through combined techniques, such as catalytic cracking and hydroprocessing as discussed in Chapter "Catalyst in Action". Thus, algal biofuels present an opportunity as more sustainable alternatives to bioethanol production from sugarcane and corn or biodiesel from terrestrial oil crops and might even be eco-friendlier than cellulosic ethanol (Bilal and Iqbal 2020). Algae cultivation offers

Table 1 Typical examples of industries where algae are being used as raw materials for commercial biorefinery

Algae-based industry	Location (Headquarter)	Major algal products
Algenol Biofuels	Fort Myers, Florida, USA	Algae-based biofuels (mainly ethanol, gasoline, jet, and biodiesel fuels).
Solix Biosystems	Fort Collins Colorado, USA	Algae-based biofuels and natural ingredients.
Sapphire Energy	Southern New Mexico, USA	Algal biofuels including green crude, biodiesel, and jet fuels.
TerraVia Holdings, Inc. (formerly Solazyme)	South San Francisco, California, USA	Algal oils, ethanol, biodiesel, and jet fuels.
Seambiotic	Israel	Algae-based biofuels.
Aurora Algae (formerly Aurora biofuels)	California, USA	Algae-based biofuels including biodiesel and other algae-based products
Euglena Co., Ltd.	Minato City, Tokyo, Japan	Algae-based biofuels and other algae products.
Biofuels Pty Ltd	Tailem Bend, South Australia	Algae biofuels, Algal oils, BioMax biodiesel.
Algae Farms	Preveza, Greece	Algae bio-oil, biodiesel, algae pellets, briquettes, and other algae products.
Pond Biofuels Inc.	Toronto, Ontario, Canada	Algae biofuels, algal oils, and other algae products

the advantage of utilizing marginal land unsuitable for agriculture and can also be grown in seawater, wastewater, or brackish water that is not in high demand (Debnath and Das 2022). This presents an opportunity for a sustainable source of biofuel that does not compete on the available resources. Microalgae have a significant capability to sequester CO_2 emissions as they require 1.83–2.0 g of CO_2 for every 1 g of biomass produced (Ighalo et al. 2022). Various conversion processes could be employed in the future algae-based biorefinery industries to develop multiple biofuels, such as methane, ethanol, gasoline, aviation fuel, and green biodiesel, as well as valuable by-products such as fatty acids, proteins, and carbohydrates. Table 1 shows typical examples of different global industries where algae are being used as raw materials for commercial biorefinery.

4.2 Challenges of Algal Biorefinery

The main challenges of biorefineries currently include market acceptance in the fossil-based economy, availability and quality of the feedstock, quantities required to meet the market demand, and techno-economic feasibility. For instance, the current production of industrial microalgal biomass is limited to approximately 15,000 tons per year (Ali et al. 2017). The main reason for this relatively low production is the high cost associated with cultivation, harvesting, and extraction of microalgae (Chu et al. 2021). Thus, the challenges peculiar to algal biomass biorefinery can be summarized as follows:

1. *Survival of the organisms*: Algal biorefinery systems currently lack the essential capacity for maintenance of the best laboratory organisms under outdoor conditions. Laboratory cultures get contaminated with surrounding organisms (Fawaz et al. 2018). New technologies such as high-throughput screening (Chapter "High Throughput Screening to Accelerate Microalgae-based Phycochemicals") or integrated artificial intelligence (Chapter "Artificial Intelligence in Phytochemicals Recognition") may enable testing and tracking multiple challenges experienced in outdoor conditions, facilitating search for most suitable algal species and identifying the most harmful conditions which need to be controlled.
2. *Carbon dioxide enhancement*: Generally, many algae grow well when "aerated" with carbon dioxide, despite that its levels above 5% reduces the growth rate of higher plants and animals. Carbon dioxide is a cost driver in microalgae production costs, and industrial-scale solutions are needed for substantially reducing the production costs (Nurdiawati et al. 2019).
3. *Light penetration*: Light is an important parameter for autotrophic cultivation of algae. Generally, the intensity of light penetration often reduces by increased water depth. Moreover, the algal species' efficacy of photosynthesis depends largely on the source of light. In open ponds, results of several studies unveiled that shallow depths provided greater surface area with effective mixing and light penetration (Maltsev et al. 2021). However, no industrial solution is on the market to cultivate phototrophic algae in bulk systems with higher water depth, as used in heterotrophic cultivation systems. Such systems would bring benefits of scaling effects and reduce demand for land, hence reducing the overall production costs.
4. *Environmental dependence*: Generally, the high yields of algal biomass achieved in ponds are often seasonal. This is because the growth rate of algae depends largely on the environmental conditions, especially temperature. Previous studies revealed that some species of algae cannot grow well in cold temperatures, while many face serious challenges at high temperatures. Thus, climate independent systems would highly contribute to whole year production on overall increase of algal biomass (Hua et al. 2021).

5 Possible Routes for Integrated Phycochemical Production

Biorefineries aim to convert renewable biological resources into a range of valuable products, including biochemicals, which are every chemical compound found in living things. Biochemical compounds are essential components of the cells and other structures of the organisms and are greatly involved in the performance of the life processes of the organisms. Carbon is the center of all biochemical compounds, and thus, it is very important to life on Earth. Most biochemical compounds form polymers made up of repeating units of smaller monomers. Carbon, hydrogen, and oxygen represent the main elements in biochemicals, as some only contain these basic elements while others may have some additional elements. The vast number of biochemical compounds in algal cells can be categorized into four major groups: lipids, carbohydrates, proteins, and pigments. Thus, carbohydrate-based biochemicals from algal biomass refer to a group of compounds derived from algal carbohydrates, including sugars such as glucose and fructose, which can be converted into various biochemicals such as bioethanol, biobutanol, and biohydrogen (Ak et al. 2022). Lipid-based biochemicals from algal biomass refer to a group of compounds derived from algae that are rich in lipids. These lipids can be converted into a variety of useful products such as biofuels (mainly biodiesel), fatty acid-derived chemicals, bioplastics, lubricants, and cosmetics (Chozhavendhan et al. 2022).

Protein-based biochemicals from algal biomass are a group of compounds derived from algal proteins including amino acids, peptides, and enzymes. Algae are rich in protein, and some species can contain up to 70% by dry weight protein (Wells et al. 2017). This makes algae a potentially valuable source of high-quality protein for use in food, feed, and industrial applications. Algae contain a wide range of visible light-harvesting complexes termed as pigments. Three major categories of pigments present in algae are chlorophylls, carotenoids (carotenes, astaxanthin, and xanthophylls), and phycobilins (phycocyanin and phycoerythrin). Carotenoids are a very popular type of algal pigments which can serve as antioxidants in, e.g., the food and feed industry. They can also be employed for several activities including, among others antitumor, immunoprophylactic, and anti-inflammatory activities. Examples of common carotenoids are astaxanthin, fucoxanthin, lutein, zeaxanthin, canthaxanthin, and β-cryptoxanthin (Duppeti et al. 2017; Patel et al. 2022). Thus, algae represent promising feedstock for biorefinery for production of various phycochemicals, besides bioenergy and other valuable products. Possible routes or technologies for production of such compounds from algal biomass include among others, biochemical conversion, thermal conversion, and chemical conversion (Fig. 4). Biochemical conversion involves the use of enzymes and microorganisms to produce phycochemicals and bioenergy. Thermal conversion involves the use of heat to convert algal biomass into bio-oil, which can be further processed into various biochemicals. Chemical conversion involves the use of chemical reactions to convert algal biomass into biochemicals. Some potential high-valued chemical compounds found in algal biomass include sulfated oligosaccharides, rare sugars (such as D-glucose, D-galactose, D-mannose, D-fructose, D-xylose, D-ribose, L-rhamnose, glucuronic acid, L-fucose, mannitol, and L-arabinose), proteins and amino acids, pigments, and phenolic compounds. However, development of cost-effective and sustainable biorefineries remains a challenge, and further research is needed to optimize algal biorefinery. Various possible routes/technologies for algal biorefinery are described below based on different targeted products.

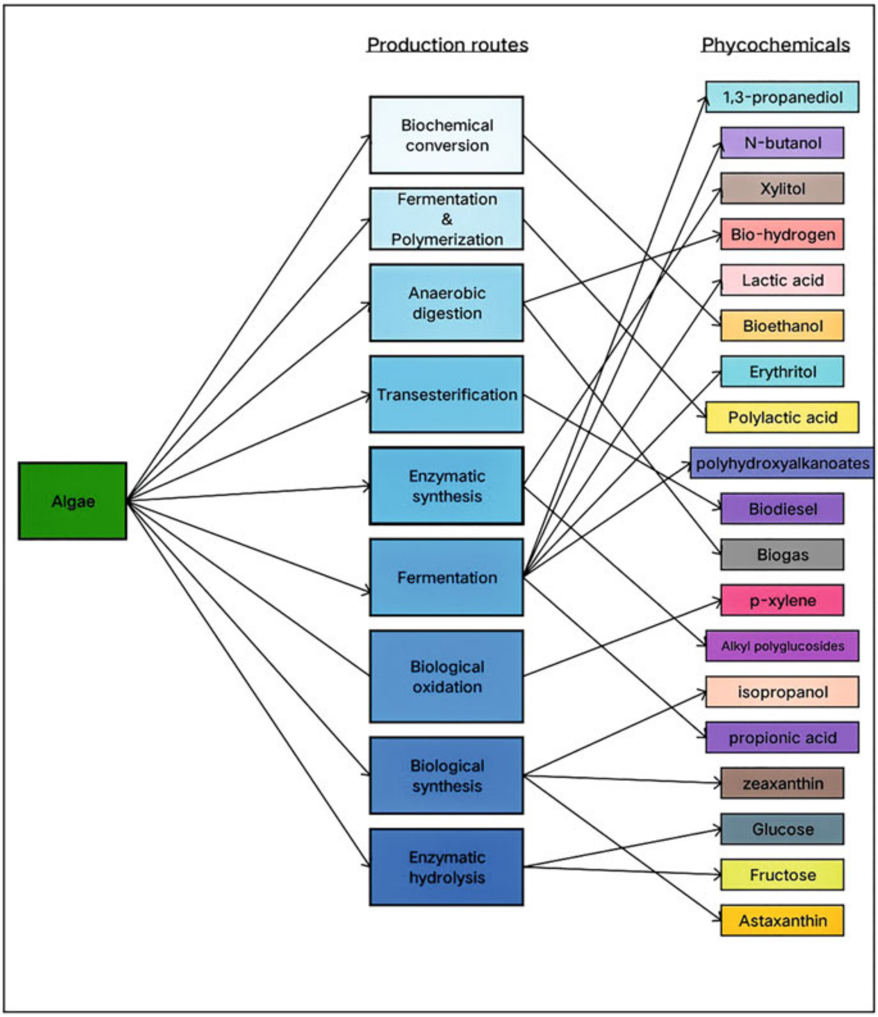

Fig. 4 Algal biomass biorefinery technologies/possible routes for different phycochemicals production

5.1 *Biohydrogen*

Biohydrogen has the potential to be a clean and renewable energy source, as it produces no greenhouse gases or other harmful emissions when burnt (Benemann and Weissman 1977; Nagarajan et al. 2017). It can be produced by algal cells through a process called photo-biological hydrogen production. This process involves using algae to convert solar energy, water, and carbon dioxide into hydrogen through photosynthesis. The algae used in this process are typically microalgae that have been specifically selected for their high hydrogen production potential. Biohydrogen is mainly produced during the algae cultivation.

5.2 Biodiesel

Biodiesel can be produced from algal lipids by transesterification. First, algae are harvested and dried to reduce their moisture content, then lipids are extracted. The extraction can be done through various methods, including mechanical extraction, solvent extraction, or enzymatic extraction. The extracted lipids are then converted into biodiesel via a chemical reaction called transesterification (Bello et al. 2012). This reaction involves the reaction of lipids with alcohol, typically methanol, in the presence of a catalyst. The reaction produces fatty acid methyl esters (FAMEs) (Nisar et al. 2021), which are the main components of biodiesel and glycerol as a by-product. The biodiesel produced in the transesterification reaction is then purified to remove any residual solvent, water, and catalyst. The final product is tested for its quality, including its viscosity, flash point, and fatty acid profile, to ensure it meets the standards for biodiesel (Obiora 2022). Biodiesel production from algae, most especially, the aquatic unicellular green algae (*Chlorophyceae*) is very economical and easy due to their high lipid content (Belousov et al. 2021). For example, Al-Humairi et al. (2022) employed a homogeneous base catalyst as a part of an intensified process in direct and fast production of biodiesel from algae and obtained a 97% yield of biodiesel in 10 min. The by-products of the biodiesel production from algae include the lipid-free biomass and glycerol, which can be further used in many applications. Glycerol is a vital chemical compound with wide applications and can be used for wounds treatment owing to its antimicrobial and antiviral characteristics, preparation of various pharmaceutical and medical products, preparation of several personal care products, scenes filming in the coastal region in film industries, used as substitute to water owing to its higher and more promising acoustic resistance, and as a raw material in the production of nitroglycerin (Pirzadi and Meshkani 2022). Also, it showed high potential for cultivation of oleaginous fungi that can be used also for biodiesel production (Li et al. 2022). The algal biomass which is free from lipids has substantial quantity of nutrients including carbohydrates, P, N, and other micronutrients. Thus, the demand of the nutrients can be lowered by recycling the nutrients in the residual algal biomass (which is free from lipids) during algae cultivation (Abomohra et al. 2018). In addition, algal lipid-free biomass showed high antioxidant and radical scavenging activity (Abomohra et al. 2022). Apart from being a potential nutrient source, it can also serve as an alternative organic carbon source (Kujawska et al. 2021).

5.3 Fatty Acid-Derived Chemicals

Fatty acid-derived chemicals can be produced from algal lipids through fatty acid hydrolysis. This process involves breaking down the triglycerides in the lipids into their free fatty acids (FFAs). The resulting FFAs can then be converted into various chemicals through different chemical processes, such as esterification, oxidation, and polymerization. After lipid extraction, the lipid-free biomass produced can be used in many applications as described in the previous section.

5.4 Bioethanol

Bioethanol can be produced from algal biomass or lipid-free waste by hydrolysis followed by fermentation. This process involves making the sugars in the algae available for fermentation into alcohol by yeast or other microorganisms. The resulting bioethanol can then be purified and used as a biofuel. Bioethanol yield reports range between 5000–15,000 gal acre^{-1} and 46,760–140,290 L ha^{-1} can be obtained from algae (Kumar and Mukund 2018).

5.5 Butanol

Butanol can be produced from algal biomass or lipid-free waste through bioconversion using microorganisms such as bacteria to convert sugars, starches, and other organic compounds in the algal cells into butanol. The resulting butanol can then be purified and used as a biofuel. Compared to bioethanol, butanol has several advantages including a higher energy content, better stability, and lower vapor pressure. Cheng et al. (2015) evaluated the potential of butanol production from the fermentation of *Clostridium acetobutylicum,* and their results revealed that butanol can be produced at a concentration of 0.2 g g^{-1} glucose, when glucose is considered as the only carbon source, but this may be improved by adding butyrate. However, 3.86 g L^{-1} of butanol can be produced from *C. acetobutylicum* when the substrate is microalgae with 1/3 of carbohydrate still remaining in unused form (Efremenko et al. 2012).

5.6 Enzymes, Peptides, and Amino Acids

Peptides and amino acids are two important components of algal biomass, where peptides are short chains of amino acids. Enzymes are proteins that act as catalysts in biological reactions and are employed in different processes in the industry (i.e., production processes of food and biofuels). Algae are a source of various enzymes, including cellulases, amylases, and lipases, which can be extracted and purified for use in these processes. The extraction and purification of these components from algal biomass or lipid-free biomass can be performed using various methods including chemical hydrolysis, enzymatic hydrolysis, and fermentation (Chronakis and Madsen 2011).

5.7 Biopolymers

Biopolymers are polymers made from renewable resources, such as plant-based materials, rather than petroleum. The extraction of biopolymers from algal biomass can be performed through chemical and enzymatic processes, followed by polymerization and shaping into desired forms (Wells et al. 2017). More details about biopolymers and potential of algae for biopolymers production are discussed in Chapter "Algal-based Biopolymers".

5.8 Methanol

Methanol forms one of the largest volumes of biochemicals produced worldwide, where various other fine chemicals such as formaldehyde, olefins, propylene, and gasoline can be synthesized from it. Methanol can also be converted into some aromatic substances. Besides, methanol has been recognized as proven precursors in several industrial processes and as a potential alternative energy for transportation fuels. Conventionally, methanol is synthesized from coal and methane as feedstock materials by combustion but this process results in emission of CO_2, which is one of the major sources of global warming. However, several eco-friendly alternative processes, such as fermentation, have proven to be effective for production of methanol from biomass materials like algal biomass. The total market demand of fermentation products in 2013 was more than 110 million tons at a monetary value of $207 billion USD, where alcohols accounted for the largest share of 94% (Mahato et al. 2021).

5.9 Sucrose/Hexose

Many sugars such as sucrose can be generated from algal biomass and sugar crops after hydrolysis of starch. Most well-established industries and numerous traditional biorefineries use sugar as a feedstock for synthesis of numerous chemicals. Sugars are rich biochemicals generated from biomass which can be converted catalytically to produce value-added fine biochemicals and liquid alkane compounds. Advanced biorefinery use lignocellulosic and hemicellulosic biomass for the production of fine chemicals, where sugars are produced by pretreatment of biomass accompanied by enzymatic hydrolysis. Glucose is normally produced from cellulose, while a mixture of xylose, arabinose, and galactose can be produced by hydrolysis of hemicellulosic materials like the algal biomass. The utilization of lignocellulosic biorefinery process in the synthesis of glucose and other fine chemical products has outstanding results; however, it is still fraught with many biological, technical, and economic challenges before these opportunities can be fully exploited. Some of these challenges are mainly associated with its complex structure and presence of lignin which offers resistance to biological attacks or enzymatic digestion of the biomass (Singh et al. 2022). Therefore, algae can provide a potential alternative due to their simple structure and lacking of lignin. Through catalytic processes, sugars can be converted into useful chemical products such as 5 hydroxymethylfurfural (HMF), furandicarboxylic, and levulinic acid (van der Waal and de Jong 2016). Sugars can also be subjected to selective dehydration, hydrogenation, and oxidation reactions to produce sorbitol, furfural, glucaric acid, hydroxymethylfurfural, 2,5-furan dicarboxylic acid, levulinic acid, methyl vinyl glycolate, and mono-ethylene glycol (van Putten et al. 2016). The production of sugar alcohols like xylitol and sorbitol for industrial applications currently gains traction across the globe due to the direct use of sorbitol as efficient food ingredients, intermediate in the production of isosorbide, and as a monomer for the production of biobased plastics. The global sorbitol demand in 2018 was put at over two million tons, and researches are currently ongoing in developing novel catalytic processes for conversion of sugars into biochemical products like methyl vinyl glycolate and mono-ethylene glycol which are precursors for the production of biopolymers (Barbaro et al. 2019).

5.10 Levulinic Acid and Gamma-Valerolactone

Among the numerous biochemicals that can be obtained from algal biomass, levulinic acid (LA) has profound importance owing to its wide applications in chemical industries (Kim et al. 2020). Apart from LA, γ-valerolactone (GVL) has attracted huge interest in recent years due to its fantastic performance as a biochemical and can be produced by hydrogenation of LA and the esters (Tong et al. 2021). At present, LA is produced through catalyst-acid reactions involving hemicellulose (C5 sugars) and cellulose (C6 sugars). By carefully selected hydrogenation, furfural is converted into FA. The produced FA is hydrolyzed to LA, which will further be converted to GVL through hydrogenation processes. The production of LA follows some series of careful steps. A vital step in the LA synthesis from furfural is the conversion of furfuryl alcohol into LA; necessary precaution is required otherwise a polymer by-product will be obtained. Efficient large-scale production of LA is still a challenging task due to the complex reaction processes involved and the poor thermal stability of intermediates like furfuryl alcohol, furfural, and 5-hydroxymethyl furfural, which may result in the production of undesirable polymetric material, e.g., humins, if not carefully handled (Kim et al. 2020). Attempts have been made recently on the selective conversion of cellulose and hemicellulose to LA and its derivatives with minimal results. Developing highly efficient catalyst and optimizing the catalytic conversion processes are necessary for the efficient yield of LA and GVL from hemicellulose and cellulose. The process of levulinic acid and formic acid consists of two chemical reaction stages: first, hydrothermal decomposition of cellulose at moderate temperatures (190–270 °C), in the absence of catalysts to produce organic water-soluble compounds (glucose and HMF). The second process involves catalytic (solid acid catalyst) treatment of water-soluble compounds at relatively low temperatures (160 °C) to produce formic and levulinic acid. GVL can easily be extracted in high yield from biomass by employing very moderate catalytic hydrogenation reaction of an aqueous solution of levulinic acid, using a commercial ruthenium supported catalyst together with a heterogeneous acid co-catalyst like the ion exchange resins Amberlyst A70 or A15, niobium oxide or phosphate at 70–50 °C, and at low hydrogen pressure of 3–0.5 MPa (Yu et al. 2020).

5.11 Cyclopentanone and Pentanediol

The selective hydrogenation of furfural produced five-heterocyclic ring chemical compounds with an oxygen atom such as 2-methylfuran (MF), tetrahydrofurfuryl alcohol (THFA), and furfuryl alcohol (FA) cyclopentanol (CPL) and cyclopentanone (CPO). These are fine biochemicals and raw materials with outstanding use in the chemical industry. The simplest member of the class of cyclopetanols with a single hydroxyl group are used for making dyes, chemical solvents, perfumes, pharmaceuticals, and other organic products (Zhang et al. 2016). In general, industrial production of cyclopentanol is done by hydrogenation of cyclopentanone, whereas cyclopentanone is traditionally produced by oxidation of cyclopentene using feedstocks of biomass origin or by decarboxylation of adipic acid. However, the oxidation process is inefficient and often polluting. Naturally, cyclopentanols are only found in few plants and in limited quantity thereby making extraction extremely difficult. However, the production of cycloperanol from furfural in biomass products is a vital and efficient green approach. An efficient and high-quality 1,5-pentanediol is produced by reaction of tetrahydrofurfuryl alcohol with hydrogen. This process requires series of steps. The first step involves the hydrogenolysis reaction of tetrahydrofurfuryl alcohol with hydrogen for production of a crude reaction product usually in the presence of a copper catalyst at a high reaction temperature (200 to 350 °C) and pressure (1 to 40 Mpa), until the conversion rate of tetrahydrofurfuryl alcohol is a little less than 80%. The second step requires the separation of tetrahydrofurfuryl alcohol and crude 1,5-pentanediol from the crude reaction product obtained, followed by supplying recovered tetrahydrofurfuryl alcohol as a raw material in the first step. The final step entails obtaining the high-quality 1,5-pentanediol by the distillation of the crude

1,5-pentanediol. Thus, cyclopentanone is one of the valuable biochemicals synthesized by the furfural rearrangement. The process involves hydrogenation of furfural to furfuryl alcohol in aqueous solution, then followed by further hydrogenation of furfuryl alcohol to cyclopentanone through 2-cyclopentenone (Hronec et al. 2013).

5.12 Furfuryl Alcohol, 2-Methylfuran, and Tetrahydrofurfuryl Alcohol

Furfuryl alcohol (FA) (i.e., 2-furanmethanol) is synthesized by decarbonylation of hydroxymethylfurfural at a temperature of or above 135 ° C in the presence of suitable catalyst (palladium or rhodium) by a liquid-phase process. In this process, the furfuryl alcohol is constantly stripped from the reaction medium. FA production consumes about 65% of the total yearly furfural production. Traditionally, furfural hydrogenation could occur on metal catalyst surface for FA production. Numerous bimetallic and monometallic catalysts have been tested as efficient catalysts for hydrogenation of furfural both in the gaseous and liquid-phase reactions, e.g., Co, Cu, Ni, Pt, Ru, Pd, Cu-Co, Cu–Ni, Pd-Cu, Cu–Zn, and Cu–Cr catalysts (Zhu et al. 2020). The Cu-Cr-based catalyst provides higher activity compared to other catalysts. Copper chromite (Cu–Cr) is a well-established catalyst in the furan industry for FA production due to its high performance with about 35–98% in gaseous phase reaction and 98% in liquid phase. However, Cr element is dangerous to health, thereby limiting its wide-scale application. Furfuryl alcohol (FA) or 2-furanmethanol is produced by hydrogenation of furfural in the presence of suitably selected metal or non-metallic catalysts (Cu–Ni, Ni, Co, Ru, Cu, Pt, Pd, Cu–Co, Cu–Cr, Cu–Zn, and Pd–Cu) in either liquid or gaseous state. The 2-MF can be produced directly from furfural in either by liquid or gaseous phase reactions. Liquid-phase hydrogenation using catalyst under alcohols as hydrogen donors has received global research attention due to safety and economic concerns. Likewise, FA, 2-MF, and tetrahydrofurfuryl alcohol (THFA) can also be produced by hydrogenation of furfural under severe temperature and pressure. This process is usually achieved by first hydrogenating furfural to furfuryl alcohol by addition of hydrogen to the C=C bonds of the furfural, and then further hydrogenation of furfuryl alcohol in the presence of nickel-based catalyst resulted in the production of THFA.

THFA is an important water miscible biochemical solvent with a purity of 98.5%. It is a cheap biodegradable biochemical solvent used majorly as a reactive diluent for epoxy resins. It is also an effective solvent for most of the curatives and catalysts employed in epoxy formulations. Besides, it is also employed in the formulation of biocide and pesticide, electronic cleaner, coatings, dyes, printing ink and epoxy curing agent (Mikucka et al. 2023).

2-Methylfuran (sylvane) is a combustible, water-insoluble liquid with a chocolate odor. It occurs naturally in Myrtle and Dutch Lavender used as a FEMAGRAS flavoring substance. It also possesses the capacity for utilization in alternative fuels.

Industrial manufacture of 2-Methylfuran is by catalytic hydrogenolysis of furfural alcohol or from furfural in the vapor phase by hydrogenation–hydrogenolysis sequential reactions. Quite a number of research focused on the direct production of 2-methylfuran from furfural in both liquid and gaseous phase reactions. Catalyst transfer hydrogenation via liquid phase under alcohol as hydrogen donor has gained more attention in recent times due to the fact that it is much safer than the pure hydrogen system and less costly. Many types of catalysts have been used in furfural hydrodeoxygenation to 2-methylfuran. For example, Mo_2C supported on Al_2O_3 or SiO_2 as well as metallic Ru, Pt, Pd, Rh, Ag, Fe, Co, Ni, and Cu (Martín-Pérez et al. 2019).

5.13 Tetrahydrofuran

Tetrahydrofuran (THF) has a wide range of applications. This includes: precursor in anionic polymerization in fiber manufacture and urethane elastomer solvent for many chromatographic techniques, e.g., gel-phase chromatography (Liu et al. 2019). THF is normally synthesized from the hydrogenation of furan from furfural in the presence of same catalyst used for the decarbonylation of furfural. The Pd catalysts enhanced complete conversion of furan to THF while nickel-based catalysts present more attractive option than noble metal catalyst because of cost consideration. Mixing of Ni and Pd/SiO_2 catalyst has been explored and gave comparable hydrogenation activity with high furan conversion (99%) and high THF selectivity (98%) in acetic acid medium at temperature of 40 °C and pressure of 80 bar hydrogen (Liu et al. 2019). One of the major challenges in the efficient THF production process is the need to suppress the rapid coking rate of the catalysts. This process results in the catalyst deactivation, leading to poor THF yield. The coke formation during the process could be reduced by co-feeding of a hydrogen donor. It is found that a hydrogen pressure of 60 bar will achieve the optimum value for THF production.

5.14 Furan

Furan is a heterocyclic organic compound with five-membered aromatic rings, four carbon atoms, and one oxygen atom. Generally, furans referred to all the chemical compounds with such rings. Furan is a volatile, colorless, and flammable liquid with a strong ethereal chloroform-like odor and a boiling point close to room temperature (Kainulainen et al. 2020). It is slightly soluble in water but highly soluble in common organic solvents (e.g., acetone, alcohol, and ether). It is toxic and may be carcinogenic in humans (Gevrek and Sanyal 2021). Furan serves as a starting point for production of other important chemicals. For example, furan can be converted to tetrahydrofuran by hydrogenation. Tetrahydrofuran is used for production of adipic acid and hexamethylenediamine, the raw materials for nylon-6,6 (Kim et al. 2022). Furan can be produced in the laboratory by the oxidation of furfural to 2-furoic acid, accompanied by decarboxylation reaction or by thermal decomposition of pentose-containing materials, and cellulosic biomass materials. The industrial production of furan can be carried out either in two ways: (1) vapor-phase (2) liquid-phase reaction. Due to ease of operation, possibility of catalyst recycling, and simplicity of operation, the vapor phase by the use of hydrogen is technically feasible and more sustainable (Ricciardi et al. 2022). The presence of hydrogen increases the yield of furan due to the increased rate of reactant-product reaction from the catalyst surface (Nakagawa et al. 2013).

5.15 L-Arabinose

Algal cellulose can be converted to L-arabinose by acid hydrolysis accompanied by multiple purification processes (including ion exchange, neutralization reaction, and other chromatographic separations). Algal biomass materials containing hemicelluloses with high amount of xylose or xylan units in their molecules can also be converted to L-arabinose by acid hydrolysis (Arun et al. 2022). Xylose is a pentose sugar used in the production of xylitol and other sweetening additives for foods.

5.16 Pentanediols (PDO) Production Rote

Good yield of pentanediols (PDO) could be produced by conversion of furfural into THFA, followed by further hydrogenolysis over Rh-supported catalysts like SiO_2. The use of Rh (rhodium) catalysts incorporated with silica or carbon and modified with Re, Mo, or W will support the hydrogenolysis of THFA to 1,5-PDO rather than 1,2-PDO (Nakagawa et al. 2013). The production of 1,5-PDO from furfural and THFA has been conducted through well-known metal catalysts such as *rhodium-based catalysts modified with another metals* (Huang et al. 2017). Figure 4 shows a summary of the algal biomass biorefinery technologies/possible routes for phycochemical production.

6 Different Applications of Phycochemicals

Results of many research studies reported in the literature revealed that algae are promising feedstock for biorefinery and production of various phycochemicals, besides bioenergy and other valuable products (Bhatia et al. 2022). Phycochemicals (including biochemicals and bioenergy) have numerous important applications, and some of those applications are presented in the following subsections below.

6.1 Biochemicals

Previous studies revealed that biochemicals produced from algae have several applications (Rizwan et al. 2018; Russell et al. 2022; Zhou et al. 2022). For example, *galacturonic acid* which is a uronic acid derived from galactose is used as an acidifying agent in foods (Norell 2020). It is an oxidized form of galactose and a major component of pectin. Pectin on the other hand has several applications in numerous industries as it is employed in production of frozen foods, jellies, jams, and more recently as a fat and/or sugar replacer in low-calorie foods. It is also used in the pharmaceutical industry for reduction of blood cholesterol levels and gastrointestinal disorders. Likewise, glucuronic and gluconic acids are essential biochemicals that can also be obtained from algal biomass. They are also the fermentation products in Kombucha tea (Bondar et al. 2022). Glucuronic acid (GA) is a common building block of proteoglycans and glycoglycerolipids and is a cyclic organic compound that can also be isolated from urine. It is also present in different gums such as Arabic gum (18%), xanthan, and kombucha tea. GA is also very vital for the metabolism of animals, plants, and microorganisms. Glucuronic acid is also found in other constituents of the body, such as cartilage and synovial fluid (Martínez-Leal et al. 2020). On the other hand, gluconic acid is an aliphatic organic compound with the molecular formula $C_6H_{12}O_7$ and condensed structural formula $HOCH_2(CHOH)_4COOH$ that can be sustainably produced by oxidation of algal biomass-derived glucose. It is one of the 16 stereoisomers of 2,3,4,5,6-pentahydroxyhexanoic acid. Gluconic acid or gluconate is an electrolyte supplement used in total parenteral nutrition. It is also used for maintenance of the cation–anion balance in electrolyte solutions (Bondar et al. 2022). Likewise, hexoses (mainly fructose and glucose) are algal biochemicals and vital metabolic intermediates employed in the formation of storage pools of carbohydrates (majorly starches) or sucrose and other disaccharides for transportation to the rest of the organism (Zhou et al. 2022).

Pentose, a monosaccharide with five atoms of carbon, is another important biochemical that can be obtained from algae. Pentose has the chemical formula of $C_5H_{10}O_5$ and molecular weight of 150.13 g mol^{-1}. Pentoses are very important biochemicals for synthesis of various important compounds such as lactates (Gómez Millán et al. 2019). Pentoses and hexoses are the most common monosaccharides or higher sugars used for easy production of lactate than the trioses. Besides, almost all carbohydrates in nature are pentoses and hexoses, and they are therefore cheaper and more abundant feedstocks for synthesis of lactates and several other vital compounds. However, in order to employ them, it is essential to have a catalyst that is capable of catalyzing a retro-aldol reaction leading to the shorter C3 sugars, which will form lactates readily at higher reaction temperatures. Besides, minute amounts of pentose sugars (xylose, arabinose, and ribose) are present in wine, naturally. Ribose is a constituent of RNA, and the related molecule, deoxyribose, is a constituent of DNA. Likewise, xylitol is a naturally occurring pentose (C5) sugar alcohol and has important applications in food, cosmetic, confectionary, and pharmaceutical industries (Manishimwe et al. 2022; Sundar and Nampoothiri 2022). For example, it is an excellent artificial sweetener that is used widely by the confectionary industry. Also, phosphorylated pentoses (ribose 5-phosphate and erythrose 4-phosphate) are vital products of the pentose phosphate pathway. Ribose 5-phosphate (R5P) is employed in the production of nucleotides and nucleic acids, while erythrose 4-phosphate is used for aromatic amino acid synthesis (Machelart et al. 2020).

Furfuryl alcohol is another essential organic compound having a furan substituted with a hydroxymethyl group. The primary use of furfuryl alcohol is as a monomer for the synthesis of furan resins (Iroegbu and Hlangothi 2019). These polymers can be employed in cements, thermoset polymer matrix composites, coatings, adhesives, and casting/foundry resins. Furfuryl alcohol is also used in the fabrication of foundry resins which is employed in the synthesis of P-series fuels, which are liquid fuels consisting of blend of methyl tetrahydrofuran (MTHF), ethanol, and hydrocarbon (Gómez Millán and Sixta 2020). It is an essential intermediate in the production of fine biochemicals. It serves as a chemical intermediate for production of vitamin C, lysine, and levulinic acid. It can also serve as a lubricant or a dispersing agent (Gómez Millán et al. 2021). Likewise, 2-methylfuran (C_5H_6O) is another member of furans group where the hydrogen at position 2 is replaced by a methyl group. Generally, the algal biorefinery value chain integrates chemistries in the production of numerous important platform biochemicals and biofuels (such as furfural, levulinic acid, and aromatics), which have several applications (Khoo et al. 2019; Knoshaug et al. 2018).

6.2 Bioenergy

Bioenergy is a renewable energy derived from biomass or organic materials, such as algae, energy crops, forest residues, agricultural wastes, and municipal solid wastes. The applications of bioenergy include

1. *Electricity generation*: Bioenergy can be used to generate electricity using technologies such as the combustion of biomass (like the algae, wood, chips, or agricultural waste), pyrolysis, hydrothermal liquefaction, gasification, fermentation, and anaerobic digestion. Algal biomass power plants produce electricity by burning algal biomass to generate steam, which drives a turbine to produce electricity (Chia et al. 2022; Naina Mohamed et al. 2019).
2. *Transportation fuels*: Bioenergy is also used in the production of transportation fuels such as ethanol and biodiesel. Ethanol is produced by fermenting sugars from algae such as microalgae and seaweeds, while biodiesel is produced by chemically reacting algal oils with alcohol (Raheem et al. 2018).
3. *Heating and cooling*: Algal biomass can be used to heat and cool buildings through technologies such as algal biomass boilers and algal biomass-powered air conditioning. In some cases, bioenergy can be used in combined heat and

power (CHP) systems to provide both heat and electricity to buildings (Beal et al. 2018).

4. *Bioproducts*: Bioenergy can also be used to produce a range of bioproducts, including chemicals, plastics, and materials such as biodegradable plastics and bio-composites. These products can be made from renewable sources, reducing the reliance on fossil fuels (Zhou et al. 2022).
5. *Waste management*: Bioenergy can also be used as a waste management solution. For example, biomass/waste from algal processing, algal cultivation, agriculture, and forestry can be converted into bioenergy, reducing the amount of unwanted biomass/waste going to landfills and reducing greenhouse gas emissions (Zhang et al. 2022).
6. *Biogas production*: Biogas produced through the anaerobic digestion of algae and its residues can be used for heating, cooking, and electricity generation (Perendeci et al. 2019; Torres et al. 2021).
7. *Agriculture*: Algal bioenergy can be used to improve agricultural productivity by providing a source of renewable energy for irrigation, drying crops, and powering farm equipment.
8. Industrial processes: Algal bioenergy can be used in industrial processes, such as pulp and paper production, to provide heat and power (Chandra et al. 2019).

7 Recent Trends, Challenges, and Prospects of Algal Biorefinery

7.1 Recent Trends in Biochemicals

At present, multiple research efforts are in the direction of ways to produce advanced value-added biochemicals and biofuels from furfurals, obtained from algae and other biomass materials, in a sustainable manner (Cesário et al. 2018; Zhou et al. 2022). Various types of routes as well as highly active multifunctional metallic and non-metallic catalysts, which constitute future challenges, have been produced for more efficient synthesis of biochemicals from algal biomass products (Choudhary et al. 2020). One step advanced hydrolysis coupled with thermochemical co-processing for algal biomass valorization to biochemicals and biofuels is the kind of technology required. The development of new algal biorefinery processes for co-production in a single-pot synthesis constitutes extreme challenges. Emphasis is placed on batch and continuous processes using acid hydrolysis in the presence of homocatalyst or heterogenous catalyst, which will help maximize the production of furfural and its derivative products from algae (Martín and Grossmann 2016; Sun et al. 2020). In the future, research concerns will be the development of more active catalysts and co-catalysts for biochemical and biofuel production, advancing chemical reaction routes/pathways, improve the knowledge of kinetic and thermodynamic behavior and improve product yield by integrating reactions and product separation.

The massive production of algal biomass conversion in commercial-scale levels is seen to be the main driver of circular and bio-economy (Chisti 2016). The algal biomass hydrolysis with solid catalysts, gasification, and pyrolysis is the conventional processes which can be employed for wide ranging feedstocks. However, variation in products quality and quantity will be noticed due to different nature and composition of feedstocks. The major hindrances to large-scale implementation of algal biochemical refinery industry are due to competitiveness and economy of scale from petroleum and biochemical refinery (Siddiki et al. 2022; Thanigaivel et al. 2022b). Bulk of the present research is on laboratory scale. The scale-up of research outputs is expected to be a major limitation, as well as cost-effectiveness and quality of fractionated products, before green refinery concept and large-scale production of biochemicals will be achieved. In order to maintain the quality of the raw algal biomass products, standard method for collecting, harvesting, storing, and classification needs to be developed. The use of solid catalysts can produce high product quality with minimal wastes and residue content in the chemical conversion process. The research and development of C5 biochemical produced from algal furfural portends huge future opportunities in terms of design and development; and the control of reaction process, which will directly affect the selectivity of tetrahydrofurfuryl furfuryl alcohol, 2-methylfuran, and other high-valued biochemical products (Abomohra and Elshobary 2019). The use of catalytic liquid-phase hydrogenation under alcohol and hydrogen donor is preferred overusing pure hydrogen due to safety and economic considerations. The key issue for 2-methylfuran, levulinic acid, γ-valerolactone, furan, pentanediol, cyclopentanone, and furfuryl alcohol yields from algal biomass is the development of multifunctional novel catalyst with high activity and selectivity which will aid in improvement of overall process performance and minimize waste generated. More so, a thorough understanding of reaction mechanism, engineering design of active catalyst sites will aid in the research and development of C_5 biochemicals produced from algal furfurals. It can also pave the way to produce other potential high-value biochemicals such as feed/food, active compounds, and pharmaceuticals. Research on furfural production from algal sugar platform has gained global traction since it was first reported. (Ahorsu et al. 2018; Hansen et al. 2017). Several researches have focused on process development, technological system of production, and catalyst design. Catalytic upgrading of the furfural/furan-based compounds into biochemicals and biofuels has attracted significant research attention (Gu et al. 2020; Wu and Chang 2019).

7.2 Recent Trends in Bioenergy

Algae represent a promising source of bioenergy because it can be grown quickly and efficiently. Algal biomass contains high levels of lipids and/or carbohydrates that can be converted into biofuels. Many recent advancements including integration of algae cultivation with other renewable energy systems, genetic engineering, wastewater treatment, and carbon capturing have been suggested. Here are some recent trends in advanced integrated bioenergy production from algal biomass;

1. *Hybrid cultivation systems*: Many researchers are developing hybrid systems that combine algae cultivation with other forms of renewable energy, such as solar or wind power. Hybrid systems combine the photoautotrophic and heterotrophic growth of algae. Advances in cultivation systems and methods such as photobioreactors and open ponds have led to increased biomass productivity and reduced production costs (Kumar et al. 2022; Xiong et al. 2021).
2. *Genetic engineering*: Scientists are exploring ways to genetically modify algae to produce higher levels of lipids and other compounds that can be used for biofuels and also improve their efficiency in converting sunlight and CO_2 into biomass with valuable phycochemical production. This can increase the yield and quality of bioenergy from algal biomass at acceptable production cost. For instance, a study reported the possible protoplast fusion of lipid/astaxanthin-rich microalgae (*Haematococcus pluvialis*) with free fatty acid-secreting microalga (*Ochromonas danica*). The study reported a successful genetic recombination where a hybrid organism was obtained with ability to produce both lipids/astaxanthin and free fatty acid secretion (Abomohra et al. 2016a).
3. *Wastewater treatment*: Algae can be employed in wastewater treatment and removal of pollutants, while also producing biomass for bioenergy and other value-added compounds production. For instance, optimization of nitrogen removal from wastewater coupled with biodiesel production using the green microalga *Chlorella* sp. was evaluated by (Abomohra et al. 2022). The results reported 98.0% nitrogen removal under optimized conditions, with simultaneous increase in the lipid content and dry weight of 20.3% and 31.9% respectively, over the control, which led to a rise of 71.5% in lipid productivity. Besides, biochar-derived from seaweeds showed high potential for wastewater treatment. In that context, Jiang et al. (2023) investigated the mechanism of the adsorption of methylene blue (MB) on carbon derived from a seaweed biomass. In the study, an effective endogenous nitrogen-modified seaweed-activated carbon was prepared from *Enteromorpha* seaweed by pyrolysis and employed it in the adsorption of the MB. Results unveiled that the addition of 0.1 g activated carbon to 100 mg L^{-1} MB solution at pH 5 and 30 °C led to the highest removal efficiency of 100% for MB. It was also observed that the adsorbent still displayed 86% adsorption capability even after four cycles of recovery. Molecular dynamic simulation results revealed that the adsorbent displayed a high adsorption capacity for MB.
4. *Algae-based carbon capture*: Algae can also be used for carbon capture and sequestration. By using algae to capture carbon dioxide emissions from power plants, for example, the resulting biomass can then be used for bioenergy production. A recent study investigated the effect of tobacco smoke on the biochemical compositions, cell growth, and biodiesel characteristics of two strains of model *Chlamydomonas* microalgae, CHL-2220 and CHL-2221 (Barati et al. 2022). Results revealed that the specific growth rate of CHL-2220 remained unaffected (i.e., around 0.5 days^{-1}), whereas in CHL-2221, growth reduced

significantly from 0.45 days^{-1} to 0.38 days^{-1} upon exposure to tobacco smoke. Also, a considerable decrease from 15.55% DW to 13.37% DW was noticed in the lipid level of CHL-2221 upon exposure to tobacco smoke. Both strains displayed low-quality biodiesel; however, their fatty acid profiles showed that they are promising nutrient food. Biomass productivity and efficiency of CO_2 sequestration have been observed to increase by improvement in photosynthesis. This improvement in photosynthesis can be achieved by improving the efficiency of enzymes involved in CO_2 fixation, extending the photosynthetically active radiation range to widen the light consumption ability, decreasing the antenna size to prevent energy loss, increasing CO_2 absorption by substituting the existing carbon fixation pathway with more effective pathways and enzymes, and lowering the release of CO_2 captured (Barati et al. 2021).

5. *Extraction methods*: Researchers are developing more efficient methods of extracting lipids and other valuable chemicals from algal biomass. This includes using solvents, supercritical fluid extraction, and ultrasound-assisted extraction. For instance, Abomohra et al. (2016b) investigated an optimized procedure for recovery of esterified fatty acids (EFAs) from the biodiesel promising microalga *Scenedesmus obliquus*. They also examined the effect of diverse solvent blends, pretreatments, time of extraction, and cell-disruption methods on intracellular EFAs and free fatty acids (FFAs) yields. Results revealed that the best solvent blend for the extraction of lipid is the use of chloroform: methanol at the blending ratio of 2:1 for 2 h as it resulted in the highest yield of EFAs. The results also showed that cell disruption is not vital in lipid extraction from *S. obliquus* cells, and besides, it was also noticed that the hot-water pretreatment deactivated the lipases and improved the recovery of EFAs.
6. *Co-production of value-added products*: Biomass from algae can be employed in producing not only biofuels but also other value-added products such as pigments, omega-3 fatty acids, and bioplastics. Co-production of these products can make algal bioenergy more economically viable (Dineshkumar and Sen 2020).

7.3 Challenges in Algal Biorefinery

Algal biorefinery for large-scale production of phycochemicals is faced with numerous obstacles despite its potential benefits. There is therefore a crucial need to address such challenges (as summarized below) to enhance the development and commercialization of the algal biorefinery.

1. *Low conversion efficiency*: The conversion efficiency of algal biomass into biofuels and other algae-based products such as the biochemicals is still relatively low, which limits its commercial viability. Rony et al. (2023) reported that higher yields of microalgae-derived gaseous, solid, and liquid fuels can be obtained by pretreating the microalgal biomass and employment of the appropriate bioconversion processes.

2. *High production costs*: The cost of producing algal biomass is currently high due to the high cost of inputs such as nutrients and energy. (Branco-Vieira et al. 2020) performed the economic analysis of biodiesel production from microalgae in a small-scale facility using a model which assumed 80,000 m^3 of microalgal cultivation, in a set of bubble column photobioreactors installed on 15.247 ha of land, reaching a total of 1811 tons of microalgae biomass and 171,705 L of biodiesel per year. The study results showed that the production cost estimated for microalgae biomass is 2.01 € kg^{-1} and for biodiesel is 0.33 € L^{-1} with biodiesel standing out as the most economic viable option. Thus, the results revealed that despite the project's viability in the medium term, the costs of producing microalgae biomass and biodiesel remain high when compared to fossil fuels. This implies that unless greater technological development is achieved to make the process more economical, it will not be viable in the short term. Therefore, the cost of phycochemicals in general is much higher than the cost of producing conventional synthetic chemicals based on fossil energy.
3. *Nutrient availability*: Algal biomass requires large amounts of nutrients such as nitrogen and phosphorus to grow, which can be expensive and environmentally problematic. To avoid such obstacle, wastewater was suggested to be used for algae cultivation. However, cultivation of algae on wastewater limits the utilization of algal biomass due to possibility of contamination with undesired pollutants or pathogens.
4. *Harvesting and processing challenges*: Harvesting and processing of algal biomass can be energy-intensive and costly. In that regard, Rafa et al. (2021) reported that the conventional harvesting methods for algal biomass such as flocculation, filtration, and centrifugation costs are $*2000, $9884, and $12,500 USD per square hectometer, respectively, which revealed that they are indeed high.*
5. *Scale-up challenges*: Scaling up algal biorefinery from laboratory to commercial scale is difficult due to the complex nature of algal biology, maintaining optimal growth conditions, harvesting and processing of biomass, and managing waste streams. For example, Borowitzka and Vonshak (2017) reported that it is difficult to scale up algal cultures to larger volumes for commercial production since it involves series of complex operations requiring skilled and experienced personnel. First, optimization of the production process and hence the quantity of the inoculum for the large ponds or photobioreactors to reduce the time and cost. Secondly, proper management of the large-scale cultures to prevent substantial contamination or collapse is imperative to minimize the need for re-inoculation. Likewise, further challenges experienced by small-scale laboratory cultures which are not witnessed in the constant environment include among others the maintenance of long-term, stable, high-productivity, large-scale cultures under prevailing outdoor conditions of variable irradiance, temperature, and rainfall.

7.4 Prospects of Algal Biorefinery

Algae biorefinery holds great prospect as *a sustainable alternative for the production of biofuels* and a wide range of other high value-added biochemicals. It has the potential to serve the energy, medical, nutraceutical, food and cosmetics industries by using appropriate species and cultivation conditions to produce the desired products. Algal cells can produce different pigments such as chlorophylls, carotenoids, and phycobilins, which can be used to replace synthetic dyes that are derived from fossil resources. In addition, fossil resources may contain lead impurities that is harmful to humans and usually responsible for allergens and irritants (Okeke et al. 2022; Sharma et al. 2022; Thanigaivel et al. 2022a). Chlorophyll, when used to dye wool and derivatives, are degradable and eco-friendly whereas synthetic colorants are hash, recalcitrant and typically not recyclable. In addition, bioplastic was produced from algae that can produce polyhydroxyalkanoates (PHA). In fact, studies conducted with *Chlorella pyrenoidosa* showed a PHA accumulation of 27% (Cinar et al. 2020). Pigment extraction, followed by PHA separation for bioplastics, could reduce the overall production cost and enhances the economic feasibility of algal biomass.

8 Conclusions

The overview of the technologies/possible routes of algal biorefinery for enhanced biomass utilization, most especially for production of several industrially important phycochemicals coupled with bioenergy, has been provided. Thus, in this chapter, several promising routes or pathways for producing bioenergy and phycochemicals from algal biomass, such as fermentation (bioethanol, butanol, etc.,), anaerobic digestion (biogas), transesterification (biodiesel), enzymatic synthesis (1,3-propanediol and alkylpolyglucoside), biological oxidation (P-xylene), and enzymatic hydrolysis (glucose and fructose), have been identified for enhancement of algal biorefinery. It is therefore recommended based on the findings of this work that shifting focus of algae utilization, processing routes, and investigations from biofuels production to biorefinery co-products production that could guarantee more viable and profitable resources. Due to the importance of biofuel production from algal biomass, integrated biofuel routes are discussed further in the next chapter.

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