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Review

Algal biomass valorisation to high-value chemicals and bioproducts: recent advances, opportunities and challenges

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Algal biomass valorisation to high-value chemicals and bioproducts: recent advances, opportunities and challenges

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Abstract: Algae are considered promising biomass resources for biofuel production. However, some arguments doubt the economical and energetical feasibility of algal cultivation, harvesting, and conversion processes. Beyond biofuel, value-added bioproducts can be generated via algae conversion, which would enhance the economic feasibility of algal biorefineries. This review primarily focuses on valuable chemical and bioproduct production from algae. The methods for effective recovery of valuable algae components, and their applications are summarized. The potential routes for the conversion of lipids, carbohydrates, and proteins to valuable chemicals and bioproducts are assessed from recent studies. In addition, this review proposes the following challenges for future algal biorefineries: (1) utilization of naturally grown algae instead of cultivated algae; (2) fractionation of algae to individual components towards high-selectivity products; (3) avoidance of humin formation from algal carbohydrate conversion; (4) development of strategies for algal protein utilisation; and (5) development of efficient processes for commercialization and industrialization.

Keywords: biomass valorisation; algal biorefinery; bioproducts; valuable chemicals; algae fractionation.

1. Introduction

The depletion of limited fossil resources and growing environmental problems, for example, global warming and environmental contamination, are two major concerns (Sambusiti et al. 2015). Currently, a large proportion of chemicals and fuels are derived from fossil resources such as petroleum oil, natural gas, and coal (Yamaguchi et al. 2017). The heavy reliance on fossil resources causes excess emissions of CO_2, which leads to global warming (Khoo et al. 2019a). Thus, developing technologies for sustainable energy and chemical production attracts concerns worldwide, which can relieve traditional fossil resources burdens. Much of the attention has been drawn to biomass technology. Developing biomass technology aims to mitigate the reliance on fossil resources and greenhouse gas emissions and establish a sustainable strategy (Jones et al. 2014). Among the biomass feedstocks, algae are also recognized as a viable feedstock for renewable energy production due to advantages such as short growth cycle, low demand for growth conditions, and the ability to grow in aquatic environments (Obeid et al. 2019; Zhou et al. 2020a). In addition, algae, which convert sunlight, CO_2 and water to organic nutrients, are photosynthetic organisms with a high photosynthetic rate (see supplementary material) (Bharathiraja et al. 2015). Hence, the utilization of algae as a source of energy can somehow mitigate greenhouse gas emissions. Furthermore, some algae species can fix N, P and heavy metal ions in waste or polluted water (Zhou et al. 2017; Zhou et al. 2020a). Accordingly, the cultivation of algae combined with polluted/wastewater treatment can relieve both environmental and energy issues (Li et al. 2020; Liu et al. 2020).

The transformation of algae into biofuel has been proven to be a viable way to relieve energy and environmental crises in recent years. High-lipid algae, which contain abundant fatty acids and triglycerides, are suitable for conversion into biofuel. Algal lipids can be extracted and subsequently converted to biodiesel via esterification/transesterification or green hydrocarbons by hydroprocessing (Li et al. 2011; Zhao et al. 2013). In addition, algae with high sugar content are usually utilized to produce bioethanol or biohydrogen by fermentation (Castro et al. 2015; Song et al. 2015). However, there are arguments about cost, energy consumption and commercialization feasibility in the cultivation, harvesting, and conversion process of algae (Foley et al. 2011). In addition to biofuel, algae are also identified as a source of valuable products, which would raise the value of the feedstock via other conversion methods. The concept of biorefinery is defined as the production of bioenergy (including biofuels) and valuable bioproducts via the conversion of biomass in parallel (Laurens et al. 2017; Devadas et al. 2021). Seeking algae-derived high-value products with approaches to achieve the scaled-up conversion process is one of the main aims of recent research. Therefore, processing algae to biofuels via the biorefinery route accompanied by the production of high-value coproducts can relieve economic and energy issues during the cultivation and conversion of algae (Rajesh Banu et al. 2020). The petroleum refinery makes use of every chemical fraction to maximize the value and efficiency of the material. Therefore, algal biorefineries must seek proper ways to effectively utilize all components of algae to find a balance between environmental and economic considerations.

Thermochemical conversion (e.g., pyrolysis, HTL, and gasification) is considered an effective approach to transforming the whole algal cell to liquid fuels. However, the composition of the resulting products is usually complex and has many limits to be directly used as an alternative for fossil fuel (Cui et al. 2020; Zhou and Hu 2020). In addition, it has been shown that the market value of algae biofuels is the lowest (0.3 €/kg), while the application of algae as chemicals, food sources, cosmetics and nutraceuticals is of higher potential value (Ruiz et al. 2016). Therefore, finding ways to produce value-added products such as nutraceuticals, pharmaceuticals, or building block chemicals might be another way to achieve a high profit biorefinery (Foley et al. 2011; Cesário et al. 2018; Davila et al. 2019). Algae are composed of lipids, carbohydrates and proteins, which have some similarity to terrestrial plants (see supplementary material). Therefore, technologies for converting conventional crops are probably suitable for application in algal biorefineries (Foley et al. 2011). To obtain products with simple composition and high selectivity, different components in algae should be fractionated or converted separately. For example, some high-value fatty acids in algal lipids can be extracted selectively, and carbohydrates can be hydrolysed to fermentable sugars or converted to other valuable chemicals, while proteins can be used to produce nitrogen-containing compounds, such as amino acids.

Recently, many studies have focused on the production of biofuels from algae, but the utilization of algal biomass as the source of renewable chemicals and valuable bioproducts has seldom been reported. This review pays primary attention to exploring the potential of algae for valuable product production. Recent advances in algal biochemical (including lipids, pigments, carbohydrates, and proteins) recovery or conversion of algae into high-value chemicals are systematically reviewed. Challenges and future outlooks of algal biorefineries are also proposed.

2. Algae cultivation, biochemical composition, and application

2.1 Microalgae and macroalgae cultivation

Microalgae are unicellular microorganisms living in aquatic environments (freshwater and sea) (Cesário et al. 2018). They have high photosynthetic efficiency and can tolerate high CO_2 concentrations, resulting in approximately 50% of the carbon stored in microalgal cells (Chisti 2007). Generally, over 50,000 microalgae species exist, but not all species are suitable for cultivation (Gnanavel et al. 2019). The species of microalgae suitable for cultivation should have some unique properties, such as high lipid/sugar accumulation, the ability to produce some high-value nutrition bioproducts, or rapid growth rate. Microalgae cultivation is usually more expensive than conventional crops because the growth of microalgae requires appropriate light, CO_2, pH, inorganic salt, and organic nutrition (Yew et al. 2019). Economically, microalgae growth should depend on sunlight and natural water areas (lakes and sea), although daily and seasonal influences might occur. In addition, the cultivation of microalgae can be coupled with wastewater treatment because N (e.g., ammonia) and P (e.g., phosphate) are needed for the growth of microalgae (Lu et al. 2018).

Macroalgae are multicellular aquatic photosynthetic organisms that are also called seaweed. They are more complicated than microalgae and can always be found in marine environments, such as ocean and coastal areas. Additionally, with high photosynthetic efficiency, macroalgae capture CO_2, which is abundantly dissolved in the sea (Sudhakar et al. 2018). In addition, macroalgae have a rapid growth rate, generating sufficient carbohydrates as photosynthates (Tabassum et al. 2018). There are approximately 10,000 species of macroalgae existing on the planet (Sudhakar et al. 2018), which are classified into three major categories by their photosynthetic pigments: green, red, and brown (Jard et al. 2013; Cesário et al. 2018). The different groups of macroalgae grow in different environments: green algae usually appear in bays, estuaries and tide pools; brown algae prefer growing in shallow and cold-water areas and can be found in rocky shores; and red algae are the most abundant and widespread macroalgae, occurring in deep cold waters or in warm shallow waters (Cesário et al. 2018; Sudhakar et al. 2018). Apart from harvesting naturally grown macroalgae, several attempts have been made to cultivate macroalgae offshore to control the life cycle under lab conditions (Fernand et al. 2017).

2.2 The biochemical composition of algae and their possible applications

The biochemical compositions of micro- and macroalgae vary among species. It has been reported that cultivation parameters (e.g., the composition of the growth medium, salinity) influence the composition of algae (Fernandes et al. 2020). Thus, the composition of algae could be controlled to some extent via upstream processes. Because of the growth in natural aquatic environments, the biochemical composition of algae harvested from different seasons also shows different degrees of variation. It was reported that the highest organic fraction (protein, carbohydrates, and lipids) of the three macroalgae species was observed when the strains were collected in spring, while the lowest was obtained in autumn (Khairy and El-Shafay 2013). In contrast to terrestrial biomass, micro- and macroalgae are short in lignin because they grow in water and do not need lignin as the support material. This makes the useful component of algae easier to be extracted and converted to biofuel and bioproducts.

2.2.1 Lipids, pigments and volatiles

The lipid content of microalgae is commonly 20-50 wt% based on the biomass dry weight (Enamala et al. 2018). The high lipid accumulation makes microalgae promising for biofuel production. Recent progress in converting microalgal lipids to biodiesel was reviewed by Goh et al. (Goh et al. 2019). Microalgal lipids can be classified into neutral lipids, polar lipids, hydrocarbons, and phenyl derivatives (Sajjadi et al. 2018). Fatty acids (the main constituents of neutral and polar lipids), generally with 12-22 carbon numbers, are promising for biofuel production (transformation to biodiesel or hydrocarbons). In addition, some algae species contain abundant polyunsaturated fatty acids (PUFAs), which are recognized as valuable bioproducts beneficial to human health (Sun et al. 2018). Microalgae also contain various kinds of pigments, such as chlorophylls, sterols and carotenoids, most of which are lipid-soluble. Therefore, pigments can be recovered by similar methods that are applied in lipid recovery. These compounds have antioxidant activity characteristics and can be used in medicine or nutraceuticals (Khoo et al. 2019b). In addition, some algae species release volatile organic compounds (VOCs) with potential value to be used in pharmaceutical and natural product industries (Zuo 2019). Thus, finding ways to selectively recover these compounds could be beneficial for bioprocessing.

The lipid content of seaweed is usually below 5 wt%, but some macroalgae species have a high fraction of PUFAs (usually above 50% of total fatty acids) (Santos et al. 2017; Dellatorre et al. 2020). Previous studies have found that red seaweed has high contents of oleic acid, eicosapentaenoic acid (EPA) and arachidonic acid (ARA) (Santos et al. 2017). Green seaweed has a high fraction of linoleic acid and α-linoleic acid, while brown algae have a high percentage of linoleic acid, EPA, ARA and stearidonic acid (Dellatorre et al. 2020). These PUFAs add value to the limited lipids stored in macroalgae.

2.2.2 Carbohydrates

The carbohydrate content of microalgae varies from 15 to 50 wt% (Chew et al. 2017). The common forms of carbohydrates in microalgae are cellulose, starch, and other complex polysaccharides (Chew et al. 2017; Cesário et al. 2018). Cellulose is the main component of the microalgal cell wall, whereas starch is stored in algal cells. Apart from cellulose and starch, other polysaccharides, such as heteropolymers of glucose, mannose and xylose, also exist in microalgae cells (Cesário et al. 2018). In recent decades, efforts have been made to ferment microalgal biomass to produce bioethanol or biohydrogen, reviewed by Nagarajan et al. (Nagarajan et al. 2017) and Silva (de Farias Silva and Bertucco 2016). In addition to biofuel purposes, the polysaccharides of microalgae can be transformed to value-added chemicals such as 5-hydroxymethylfurfural (HMF) and levulinic acid.

For macroalgae, carbohydrates are the most abundant components, accounting for 25-60 wt% of the whole algal biomass. The abundant carbohydrates and lack of lignin make macroalgae suitable for fermentation to bioethanol or transformation to high-value chemicals. The fermentation of macroalgae to bioethanol was summarized by Ramachandra et al. (Ramachandra and Hebbale 2020), while that to biohydrogen was reviewed by Kim et al. (Kim et al. 2019). In contrast to terrestrial biomass, macroalgae not only have polysaccharides such as cellulose and starch but also other original and more complicated polysaccharides such as ulvan in green seaweed, agar in red seaweed, and alginate, fucoidan and laminarin in brown seaweed (Cesário et al. 2018; Ramachandra and Hebbale 2020). These complicated polysaccharides are heteropolymers of monose such as glucose, galactose, mannose, xylose and rhamnose. These special polysaccharides in seaweed have many special characteristics to be applied in food and pharmaceuticals. Some macroalgal polysaccharides (such as ulvan and agar) have antioxidant, antiviral and antibacterial bioactivity and can be used in medicine (Wang et al. 2018). In addition, the saccharification of macroalgae produces a variety of monosaccharides, such as glucose, galactose or rhamnose.

2.2.3 Proteins

Proteins are one of the major components of microalgae, accounting for 50-70 wt% of dry biomass weight, and can be hydrolysed to amino acids (Chew et al. 2017). For macroalgae, proteins are also the major component. In terms of different categories, green macroalgae have 9-26 wt% of proteins, brown algae 3-15 wt%, and red algae a high protein content (10-47 wt%) (Cesário et al. 2018; Sudhakar et al. 2018). The proteins in macroalgae are composed of abundant essential amino acids and bioactive peptides, which are beneficial for human beings (Gajaria et al. 2017). Therefore, both microalgae and seaweed are important sources of proteins and amino acids, which are utilized for human and animal nutrition. Generally, algal proteins are applied as nutrients for creatures, such as biofertilizers (Becker 2007). Since the composition and structure of proteins are complicated, it is difficult to produce a single kind of amino acid or other high purity products. However, biocrude oil-containing mixtures of nitrogenous compounds obtained from the thermochemical conversion of algal proteins are usually used for fuel purposes after denitrogenation.

3. Algal lipids, pigments and volatiles as a source of valuable products

Algal lipids are complex mixtures, including glycerides, phospholipids, glycolipids, hydrocarbons, sterols and free fatty acids (Laurens et al. 2017). In addition, algae are abundant in lipid-soluble pigments, such as chlorophylls and carotenoids, discussed in this section. The abundant triglyceride/fatty acid content makes algae an attractive feedstock for biofuel or biochemical production. For biofuel production, lipids/oils are recovered from algal cells, followed by transesterification/esterification to fatty acid alkyl esters (i.e., biodiesel) or hydrogenation to fuel-like hydrocarbons (Chisti 2007; Zhao et al. 2013). Furthermore, algal lipids have higher values beyond biofuel. For example, triglycerides are made up of glycerol and fatty acids. The fatty acid fraction can be hydrogenated to fatty alcohols with higher value, while some algae strains contain high amounts of PUFAs, which have high commercial value because of their bioactivity (Chew et al. 2017; Laurens et al. 2017). In addition, lipid-soluble pigments, such as chlorophylls, astaxanthin, lutein and β-carotene, have high value for application as food additives or nutraceuticals (Hu et al. 2018). Since the method of valuable pigment extraction is similar to the extraction of lipids, pigment recovery is reviewed in this section. The overall utilization of algal lipids and pigments as fuel or valuable products is shown in Fig. 1. This section mainly focuses on the discussion of algal lipids or pigments as a source of high-value products instead of biofuels. Strategies to enhance the lipid/pigment yield via extraction are also included.

3.1 Strategy to enhance lipid yield via extraction

To utilize algal lipids, the method of extraction is applied. Lipids are commonly stored in algal cells, with the cell wall wrapped outside. The rigid cell wall comprises double- or triple-layered complex polysaccharides, such as cellulose and mannose, which maintain the stability of algal cells (Kim et al. 2016). Hence, other compounds, such as solvent molecules, have difficulty to permeate the cell wall, making it difficult to extract valuable components from algal cells. To extract intracellular molecules more efficiently, various cell wall disruption strategies, which can be categorized into chemical, physical and biological disruption methods, have been developed. Cell disruption is preferably conducted under mild conditions to reduce energy consumption and maintain intracellular biomolecule structures (Halim et al. 2012). After disruption, intracellular hydrophobic components can be extracted more easily by organic solvents or ionic liquids. Commonly, Soxhlet extraction, the Bligh and Dyer method, and the Folch method using $CHCl_3$ and MeOH are used for algal lipid extraction (Folch et al. 1957; Manirakiza et al. 2001). To simplify the process, algal cell wall disruption and lipid extraction can be performed simultaneously (Kim et al. 2016). Recent studies on algal cell wall disruption and lipid extraction are summarized in Table 1.

Physical methods, including mechanical methods, can break the cell wall by various physical forces, such as shear forces, microwaves, ultrasound or electric fields (Kim et al. 2016; Lee et al. 2017). Although a high degree of cell disruption is achieved, the high requirement of energy input might affect the scale-up of the technologies. Solvent extraction of lipids is usually conducted simultaneously or after the physical disruption. Recently, many studies have focused on microwave- or ultrasound-assisted lipid extraction due to the high efficiency and low energy consumption of the techniques (Garoma and Janda 2016; Zhou et al. 2019). To achieve highly efficient cell disruption, a combined mechanical method is applied. Bensalem and coworkers investigated the effect of pretreatment using a combined method of pulse electric field (PEF) and mechanical compression on the lipid extraction efficiency of microalga *Chlamydomonas reinhardtii* (Bensalem et al. 2018). The PEF created pores on the microalgal cell wall, and the mechanical force placed further pressure on it, resulting in a high degree of disruption. Consequently, an enhanced lipid yield was achieved.

Chemical disruption methods use chemicals such as organic solvents, ionic liquids, acids, oxidants, or supercritical fluids to directly interact with algal cell walls. Chemical methods are considered energy-efficient and low-cost and can be applied on an industrial scale. However, chemical toxicity problems or the reaction of chemicals with intracellular compounds should be considered (Kim et al. 2016). The choice of chemicals for cell wall disruption should also satisfy the green and sustainable standard. Green or renewable solvents, such as biomass-derived solvents (e.g., FAMEs or ethyl lactate), supercritical fluids (e.g., $scCO_2$), ionic liquids and switchable solvents, have been developed in recent years to achieve a renewable and sustainable biorefinery. In addition, chemical and mechanical disruption can be combined to enhance lipid extraction efficiency. Hua et al. investigated the effects of a Ti_4O_7-based reactive electrochemical membrane (REM) on microalgae harvesting and cell disruption (Hua et al. 2016). The treated microalgal sample was extracted with CH_2Cl_2/MeOH (2:1, v/v) under 400 W microwave irradiation for 45 min. The lipid yield rose from 15.2 wt% (untreated sample) to 23.4 wt% (REM-treated algae).

Biological methods are also a viable and green way to disrupt the algal cell wall. Usually, enzymes such as cellulase and hemicellulase are used in such processes (Wu et al. 2017). Enzyme-assisted cell wall disruption is conducted under mild conditions, resulting in low consumption of energy. Additionally, wet algal biomass can be used in enzyme-assisted lipid extraction because the hydrolysis of the cell wall by enzymes requires water. However, the cost of enzymes is usually higher than that of other methods, and the enzymes used can hardly be recycled (Lee et al. 2017). Qiu and coworkers conducted enzyme-assisted cell disruption and lipid extraction from wet *Nannochloropsis* (Qiu et al. 2019). Under the optimum conditions, a maximum total fatty acid (TFA) yield (90.4%, based on the TFAs in microalgae biomass) was obtained.

Overall, the disruption methods can destroy the algal cell wall to enhance the lipid extraction efficiency, but whether the process is energy- and cost-efficient needs to be considered. Therefore, disruption methods with high energy and cost consumption should be avoided. In addition, high toxicity solvents (e.g., MeOH and $CHCl_3$) are always used for solvent extraction after cell disruption of algae, which is harmful to human health. Nevertheless, other greener solvents, such as hexane/EtOH, $scCO_2$ or dimethyl carbonate, seem to extract fewer lipids than chloroform/methanol mixtures. Thus, strategies for green and efficient lipid extraction methods should be developed.

3.2 Polyunsaturated fatty acids

Some kinds of polyunsaturated fatty acids (PUFAs, ≥ two double bonds) with more than 20 carbon atoms cannot be synthesized by the human body, but are essential for human health (Saini and Keum 2018). Therefore, PUFAs are of high value and must be obtained from other sources. Among the PUFAs, omega-3 fatty acids, such as eicosapentaenoic acid (EPA, 20:5n-3) and docosahexaenoic acid (DHA, 22:6n-3), are important compounds for human health. Some algae species, such as *Crypthecodinium*, *Thraustochytrium* and *Schizochytrium*, contain high DHA contents, while the species *Phaeodactylum*, *Chlorella* and *Monodus* contain high amounts of EPA (Dhanya et al. 2020).

Since PUFAs are high-value bioproducts, strategies have been made to enhance PUFA production from algae. In addition to improving the fatty acid extraction yield (Section 3.1), studies have also been focused on enhancing PUFA production by screening algae strains, genetic/metabolic engineering and optimization of cultivation conditions (Wang et al. 2019). Wang and coworkers investigated the adaptive evolution of *Phaeodactylum tricornutum* and its engineered strains under hyposalinity treatment (Wang et al. 2019). The results showed that 70% salinity had the potential to enhance the PUFA content. The highest PUFA content (EPA: 13.9%, ARA: 4.19% and DHA: 1.82%) was obtained in the presence of 15 mg/L fulvic acid. This work provides a viable strategy for biotechnologically improving microalgae strains.

After cultivation and harvesting, extraction and purification are needed for the production of PUFAs from algae. Omega-3 fatty acids are usually found in the polar lipid fraction (i.e., phospholipids and glycolipids) of algae, so nonpolar solvents are not effective for extracting PUFAs (Ryckebosch et al. 2012). The commonly used extraction methods for PUFAs are mechanical disruption-assisted solvent extraction and supercritical fluid extraction (Li et al. 2019b). The details of the disruption and extraction methods can be found in Section 3.1. After extraction, purification is required to obtain food-grade PUFAs. The steps included in the purification process are degumming, refining, bleaching and deodorizing. Some techniques, such as distillation, high-performance liquid chromatography, and urea fractionation, efficiently remove impurities (Dhanya et al. 2020). Downstream processes might require considerable energy and financial costs. Therefore, evaluation and simplification of these processes are necessary.

3.3 Algal lipids as a source of oleochemicals

Natural oils or fats are important sources for producing valuable oleochemicals, which could be used to substitute the chemicals generated from fossil resources. Oleochemicals mainly include fatty acids, fatty alcohols, fatty esters and fatty amines, as well as glycerol (Laurens et al. 2017; Rincon et al. 2019). Because of their abundant lipid content, microalgae are also potential feedstocks for oleochemical synthesis. However, there are few works about the conversion of microalgae-derived fatty acids/triglycerides into oleochemicals. Studies have mainly focused on transforming model compounds (e.g., fatty acids) to other oleochemicals. This section provides potential routes for the generation of oleochemicals from microalgae lipids.

The conversion of algae-derived fatty acids to various oleochemicals by chemical catalytic routes is depicted in Fig. 2. Chemical conversion is usually applied in oleochemistries, such as hydrogenation, transesterification and epoxidation. To obtain fatty alcohols, fatty acids should be hydrogenated in the presence of a hydrogen source with catalysts. Commonly, conventional Cu-Cr-based catalysts are used for the hydrogenation of fatty acids to related fatty alcohols. However, the severe reaction conditions (250-350 °C and 10-20 MPa) and the toxicity of Cr make Cu-Cr catalysts less attractive (Martínez-Prieto et al. 2019). Other heterogeneous catalysts, such as noble metals (e.g., Pd and Pt) and nonnoble metals (e.g., Ni and Co), are also proved to be efficient for the hydrogenation of fatty acids to fatty alcohols (Zhou et al. 2020c; Zhou et al. 2021). Fatty alcohols can be used to produce solvents, lubricants, detergents, defoamers, shampoos, skin emollients, emulsifiers, lotions, cosmetic creams, thickeners, and so on (Sánchez et al. 2017). Since microalgae are abundant in fatty acids, the production of value-added fatty alcohols from microalgae seems viable.

Algae have been widely used to produce fatty esters (biodiesel) in recent decades. The triglycerides in algal lipids are transesterified with an alcohol (usually MeOH or EtOH), forming fatty esters and glycerol (Fig. 2). Glycerol, is generated as the main by-product, known as crude glycerol, in high amounts from biodiesel production (Remón et al. 2018b), and it is a widely used chemical as a humectant, solvent, and sweetener in the food industry (Monteiro et al. 2018). In addition, glycerol is the building block chemical proposed by the US DOE, which can be transformed into other value-added products via chemical and biological conversion (Werpy and Petersen 2004). For example, glycerol can be transformed to 1,2-propanediol, 2,3-butanediol, n-butanol, PUFAs (EPA and DHA) and poly(hydroxyalkanoates) (PHA) via biological conversion. The chemical conversion of glycerol obtains acrolein, lactic acid, other mono- or polyglycerides, polyols, and polyglycerol with the aid of catalysts. A detailed summary of glycerol conversion to valuable chemicals was reviewed by Luo et al. (Luo et al. 2016).

To obtain fatty amines, fatty nitriles are first produced by the reaction of fatty acids with NH_3 followed by dehydration (Fig. 2) (Gunstone and Hamilton 2001). Subsequently, the fatty nitriles are hydrogenated to primary amines. The two steps are usually performed with the aid of catalysts (e.g., ZnO for nitriles, Ni or Co for amines) (Gunstone and Hamilton 2001). Primary fatty amines are mainly applied in the mining industry, lubricants and corrosion inhibitors. In addition, many other amines and derivatives are originating from fatty acids, such as secondary and tertiary fatty amines and polyamines, which are value-added chemicals with numerous applications (Gunstone and Hamilton 2001).

The unsaturated fatty acid (UFA) fraction of microalgal lipids can be oxidized into products with greater functionality (Foley et al. 2011). For example, UFAs can undergo ozonolysis or oxidative cleavage to form one monocarboxylic acid and another dicarboxylic acid (Enferadi Kerenkan et al. 2016). Dicarboxylic acids are important building block chemicals because of their polymerizable ability (Hill 2000). Dicarboxylic acids can be copolymerized with amine or alcohol to produce polyamides (nylon) and polyester, which have many enhanced characteristics, such as low melting point and great hydrophobicity, to be used as lubricants and plasticizers (Enferadi Kerenkan et al. 2016).

3.4 Algal pigments

Natural pigments are high-value components in algae due to their strong antioxidant characteristics (Ruiz et al. 2016). Because of the specific growth conditions, different kinds of pigments exist in algae, which can be classified into chlorophylls, carotenoids and phycobiliproteins (Nwoba et al. 2020). The various pigments can adsorb different wavelengths of light and subsequently transform the optical energy to chemical energy stored in algae. Among pigments, β-carotene, astaxanthin, and c-phycocyanin are of high value for human nutrition, health care and feed markets (Nwoba et al. 2020).

Chlorophylls are the most abundant pigments in natural plants and algae due to their photosynthetic growth. Microalgae such as Chlorella are promising feedstocks for chlorophyll production due to their high growth rate and total content of over 45 mg/g dry algae weight under optimum culture conditions (Christaki et al. 2015). Chlorophylls are commercially used as colourants in the food, feed, pharmaceutical and cosmetic industries (Christaki et al. 2015). For the production of chlorophyll from algae, the conventional organic solvent extraction method is applied because of the lipophilic character of chlorophyll.

Carotenoids, which are found in photosynthetic organisms (plants and algae) or nonphotosynthetic bacteria and fungi, are the second most abundant natural pigments on earth (Hu et al. 2018). Most carotenoids have isoprene units with up to 40 carbon atoms, which are usually lipid-soluble and in orange or red colour. Carotenoids can be used as natural food colourants because of their inherent colour, bioactivity and antioxidation character (Liu et al. 2021a). To utilize the carotenoids of microalgae, an extraction method was applied. However, carotenoids are stored in algal cells; therefore, pretreatments are needed to deconstruct the cell walls before solvent extraction. The methods of pretreatment and carotenoid extraction from algae are listed in Table 2.

β-carotene, also known as pro-vitamin A, is a common carotenoid used in the food and health care market and is beneficial for preventing night blindness and liver fibrosis and improving the immune system (Dufossé et al. 2005). The microalga *Dunaliella salina*, able to grow in salt water at high concentrations, is an excellent source of β-carotene. Recent studies show that cultivation conditions (light, pH, salinity, temperature and nutrition) influence the biosynthesis of β-carotene in algae. Therefore, studies have been conducted on enhancing β-carotene from *Dunaliella salina* by screening the cultivation conditions (Dufossé et al. 2005). Zhu et al. studied the cultivation of *Dunaliella salina* in seawater desalination concentrate medium for the production of β-carotene (Zhu et al. 2018). Under the optimum conditions, 14.3 g β-carotene was recovered from 300 g microalgae in a 1 m^3 desalination concentrate.

Astaxanthin is another valuable algal carotenoid, also known as 3,3′-dihydroxy-β,β′-carotene-4,4′-dione. It is a carotenoid with pinkish colour commonly used in the fields of food, feed, nutraceuticals and pharmaceuticals (Khoo et al. 2019b). Astaxanthin has strong antioxidant activity even greater than vitamin E, vitamin C and β-carotene, resulting in its anticancer properties and the ability to prevent diseases (Khoo et al. 2019b). Among the different species of algae, *Haematococcus pluvialis* has been investigated by many researchers for the production of astaxanthin because of its high astaxanthin accumulation potential (3.8-5.0 wt% of dry algae) (Khoo et al. 2019b). To effectively extract astaxanthin from *H. pluvialis*, pretreatment of cell wall disruption is needed. In addition, the pretreatment and extraction process should avoid toxic organic solvents under mild conditions because astaxanthin might be degraded and reconstructed under severe conditions (Kaczor and Baranska 2011). Choi and coworkers developed a highly efficient method using room-temperature ionic liquid mixed with water to disrupt the cell and extract astaxanthin from *H. pluvialis* (Choi et al. 2019). Under the optimum conditions (6.7% ionic liquid concentration in water, 30 °C, 1 h), over 99% astaxanthin recovery and approximately 82% lipid extraction were achieved.

Some algae species have photosynthetic pigments made up of proteins and chromophores (phycobilins), called phycobiliproteins, which are stored in the algal chloroplast (Nwoba et al. 2020). Phycobiliproteins can be classified into two major classes by their colours, phycocyanin (blue) and phycoerythrin (red). Because of their unique colours and some bioactive characteristics, phycobiliproteins are of high value for use in the fields of pharmaceuticals, cosmetics and food colourants (Nwoba et al. 2020). Usually, phycoerythrin can be found in *Porphyridium* sp., while phycocyanin is stored in *Spirulina* sp. (Li et al. 2019a). Growth conditions, such as light, nitrogen sources, temperature, pH, carbon source, and salinity, influence phycobiliproteins production from microalgae (Pagels et al. 2019). Phycobiliproteins are water-soluble and can be recovered via extraction and purification processes. Mechanical, chemical and biological methods are used to disrupt the cell wall, such as French press, ultrasonication, ionic liquid, liquid nitrogen or enzymatic assisted method (Saluri et al. 2019; Sharma et al. 2020). Extraction is commonly performed in aqueous solvents (e.g., phosphate buffer) due to the hydrophilicity of phycobiliproteins.

3.5 Volatile organic compounds

Aquatic algae, especially cyanobacterial water blooms, release a wide variety of volatile organic compounds (VOCs), such as terpenoids, furans, alkanes, alcohols, aldehydes, ketones, esters and sulfo compounds, contributing to the foul source-water odour in polluted water area (Zuo 2019). These VOCs are released to transfer information between algal cells, or protect against predators (Zuo 2019). Because of the bioactivities of some kinds of algal VOCs (e.g., terpenoids), such as anti-microbial, anti-inflammatory, anticancer and antidiabetic, they have potential to be used in natural product and pharmaceutical industries. It has been reported that environmental factors such as light, temperature, nutrition conditions and abiotic stress can affect the type and amount of VOCs released. Zuo et al find that increasing temperature and light irradiation caused an increase in β-cyclocitral production from cyanobacteria (Zheng et al. 2020). In addition, separating VOCs from complex algal metabolites might be an existing challenge. Dai and coworkers successfully separated three kinds of terpenoids by high-speed countercurrent chromatography combined with preparative high-performance liquid chromatography with the purity all above 95% (Nie et al. 2021).

4. Algal carbohydrates as a source of valuable chemical products

Algal carbohydrates exist in the polymer forms of hexose and pentose (Chia et al. 2018). Therefore, the carbohydrates in algae are used to produce fermentable sugars, which can be subsequently converted to bioethanol or biohydrogen. In addition, carbohydrates also have the potential to be transformed into valuable products. The US DOE provided a list of building block chemicals that could be obtained from biomass conversion (Werpy and Petersen 2004). Recently, it was proven that the carbohydrates in lignocellulosic biomass could be converted to chemicals via chemical and biological routes (Alonso et al. 2017; De Clercq et al. 2017). This provides clues for the production of value-added chemicals from algae. For the utilization of algal carbohydrates, dissolution or extraction processes are needed. The dissolution and conversion of carbohydrates can also be conducted simultaneously. In this section, the extraction of algal carbohydrates and their conversion to value-added chemicals are mainly discussed.

4.1 Extraction of algal carbohydrates and the production of monosaccharides

To obtain monosaccharides, pretreatment and hydrolysis are required. Prior to extraction, pretreatment of algal cells is needed to disrupt the rigid cell wall (de Farias Silva and Bertucco 2016; Dave et al. 2019). Similar to lipid extraction, disruption pretreatment can be classified into physical, chemical and enzymatic methods. Commonly, the three pretreatment methods can be combined to obtain a higher monosaccharide yield. Physical pretreatment generally includes drying, milling, sonication, or hydrothermal liquefaction (Dave et al. 2019). After physical pretreatment, the particle size of algae decreased, increasing the reaction efficiency in the following process. For chemical pretreatment, diluted acid or alkali is used (Nagarajan et al. 2017). Once pretreated with acid or alkali, the algal cell wall is broken down, releasing intracellular polysaccharides and hydrolysing them into monosaccharides. KOH and NaOH solutions are the most frequently used alkali, while diluted sulfuric acid is usually used in acid pretreatment (Harun et al. 2011; Jeong et al. 2015b). However, enzymatic hydrolysis might be required after acid/alkali treatment because of the incomplete hydrolysis of polysaccharides. In addition, there might be a side reaction of forming HMF, formic acid, and levulinic acid via acid pretreatment, which affect the following process if the hydrolysates are used for fermentation

(Remón et al. 2018a). Furthermore, enzymatic pretreatment requires commercial enzymes such as cellulase, agarase and amylase (Dave et al. 2019). Generally, enzymatic pretreatment is considered to be promising due to the mild operating conditions, high monosaccharide yield and absence of side reactions. Nevertheless, problems still exist because of the high cost and unrecyclability of enzymes. An overview of monosaccharide production from algae by different pretreatment methods is summarized in Table 3.

4.2 Biological conversion of algal carbohydrates to value-added chemicals

Algal carbohydrates are mainly composed of hexose units, which are suitable for converting to a variety of value-added chemicals via biological conversion beyond fermentation to bioethanol. Fig. 3 shows various chemicals from the biological conversion of algal carbohydrates, including 1-butanol, 2,3-butanediol (2,3-BDO), succinic acid, lactic acid, and pyruvate. Some of these chemicals have been listed in the "Top Value Added Chemical from Biomass" by the US DOE (Werpy and Petersen 2004). Generally, microorganisms such as bacteria and fungi are applied in bioconversion (Laurens et al. 2017; Cesário et al. 2018). A detailed summary of the biological conversion of algal feedstock to value-added chemicals is provided in Table 4. Usually, biological conversion involves the following steps: (1) pretreatment of algal biomass, including drying and milling to powder, (2) dissolution and hydrolysis of algal polysaccharides to reducing sugars or monosaccharides, and (3) fermentation of the algal hydrolysate by microorganisms. In the second step, chemical or enzymatic hydrolysis, or their combination, is used to maximize the monosaccharide yield.

Algal carbohydrates can be fermented to several kinds of alcohols, including ethanol, n-butanol and 2,3-BDO. Butanol is an attractive alternative to ethanol due to its high heating value, low volatility, and low corrosiveness to be used as an additive in gasoline (Wang et al. 2017), while 2,3-BDO can be used as an antifreeze agent because of its low freezing point (Mazumdar et al. 2013). In addition, butanol and 2,3-BDO are building block chemicals that can be applied to produce other chemicals. For example, 2,3-BDO can be dehydrated to methyl ethyl ketone used as a fuel additive or 1,3-butadiene, a monomer for synthetic rubber and other polymer production (Mazumdar et al. 2013). Furthermore, the fermentation of algal carbohydrates to organic acids such as lactic acid, succinic acid and pyruvate is also attractive. Succinic acid (1,4-butanediacid) is in the list of US DOE's top 12 sugar-derived building blocks, while lactic acid is in the list of the top 30 candidate building blocks (Werpy and Petersen 2004). Succinic acid, a diacid with four carbons, is a platform chemical for the synthesis of many commercial products, such as hydrogenation to chemicals (tetrahydrofuran, butanediol, or γ-butyrolactone), reductive amination to pyrrolidinone derivatives, or direct polymerization to fibres (Werpy and Petersen 2004). Lactic acid is commonly applied in the food, chemical, cosmetic and pharmaceutical industries (Overbeck et al. 2016). Additionally, lactic acid can be polymerized to biodegradable poly(lactic acid), a substitute for fossil-based polymers (Kartik et al. 2021). The wide application of poly(lactic acid) in the medical, textile, and plastic industries increases lactic acid value (Castro-Aguirre et al. 2016).

4.3 Chemical conversion of algal carbohydrates to value-added chemicals

Apart from biological routes, chemical conversion methods can also be applied for algal carbohydrate conversion. In recent decades, studies have focused on the chemical conversion of carbohydrates to value-added platform chemicals in lignocellulosic biomass (Besson et al. 2014). Due to the similar structure of polysaccharides in algae to lignocellulosics, the method and catalysts applied in lignocellulosic carbohydrate transformation can also be used to convert algal carbohydrates. Fig. 3 illustrates the valuable chemical products from the chemical conversion of algal carbohydrates.

Regarding the chemical conversion process, solvents and acidic catalysts are used for the dissolution and depolymerization of polysaccharides to monosaccharides. The monosaccharide units of algal carbohydrates include glucose, mannose, galactose, xylose, rhamnose and fucose (Ramachandra and Hebbale 2020). In most algae, hexose polymers are the major components, which can be used as feedstock for 5-HMF or levulinic acid synthesis. HMF is a platform chemical for many commercial chemical products or fuel sources, such as oxidation to 2,5-furandicarboxylic acid (FDCA), hydrogenation to dimethylfuran (DMF) or etherification to ethoxymethylfurfural (EMF) (Heo et al. 2020). These further converted products are of high value in the field of fuels and polymers. Levunilic acid, a "top 12 building block chemical" in the list of US DOEs, also has the potential to be transformed into many chemicals with added value (e.g., 2-methyl tetrahydrofuran, γ-valerolactone, 1,4-pentanediol) (Werpy and Petersen 2004). Some algae containing a high fraction of rhamnose, such as *E. prolifera*, are suitable for the production of 5-methylfurfural (5-MF), which could be in turn hydrogenated to dimethylfuran (DMF) (Chen et al. 2020; Zhou et al. 2020b). In addition, the xylose fraction of algal carbohydrates can be dehydrated to furfurals, a platform molecule for fuels and other useful chemicals (Luo et al. 2019). Additionally, lactic acid is a potential product obtained by chemical conversion with specific catalysts. Except for conversion to furan derivatives or some organic acids, hydrogenation of algal sugars to polyols (such as ethylene glycerol and 1,2-propanediol) is of great significance. Polyols are versatile chemicals because they can be used directly as antifreeze agents or precursors to synthesise polymers (Figueiredo 2020). Since many value-added chemicals can be produced from algal carbohydrate conversion, the selection of the reaction parameters (e.g., temperature, time and atmosphere) and types of catalysts should be carefully considered to achieve high selectivity of desired products. Table 5 lists the detailed reaction conditions and catalysts for the production of chemicals from algal carbohydrate conversion. Usually, Brønsted acid (e.g., H_2SO_4) and Lewis acid (e.g., Sn-beta, HZSM-5) catalysts are applied to convert algal carbohydrates to HMF, furfural, levulinic acid or lactic acid. For the production of polyols, reductive catalysts such as supported transition metal catalysts are used under a H_2 atmosphere.

One potential issue in the conversion of algal carbohydrate is the relatively low carbon balance of formed products. This could be caused by the formation of oligomers or humins via the degradation or dehydration condensation of the formed products (e.g., monosaccharides, HMF, LA) (Zhou et al. 2020b). To enhance the carbon balance, suitable reaction systems and catalysts need to be designed.

5. Algal proteins as a source of N-containing valuable products

Algae are rich in proteins, accounting for 50-70% of microalgae (Chew et al. 2017) and 5-50% of macroalgae (Cesário et al. 2018; Sudhakar et al. 2018), varying in species and cultivation conditions. However, only a few studies have reported the application of algal proteins. After lipid extraction or dissolution of carbohydrates from algae, residues containing a large proportion of proteins usually remain unused or are recognized as waste. To realize a zero-waste biorefinery, it is essential for researchers to seek approaches to utilize algal proteins. Generally, proteins in algae are made up of different kinds of amino acids (glutamic acid, aspartic acid and leucine in high amounts). Therefore, algae could be a potential alternative for protein and amino acid sources.

One potential use of algal proteins is as nutrients for humans or animals. Algal proteins as food or feed are attractive due to the high protein accumulation of algae. Algal proteins show nutritional value due to the bioactivity of proteins and peptides, and the considerable content of essential amino acids (Overland et al. 2019). However, the existence of toxic proteins in some algae species is a problem for application as food or feed (Chew et al. 2017). In addition, the bioactive proteins might be destroyed or decomposed by the extraction process or chemicals when considering the use of the lipid or sugar (extracted residue of algae), and thereby lose their biological functionality (Laurens et al. 2017). Thus, prior to being used for food or feed applications, safety and bioactivity analyses need to be conducted to ensure feasibility. In addition, the waste proteins in aqueous byproducts from hydrothermal liquefaction of algae can be used as nutrition or biofertilizer for the cultivation of crops (Leng et al. 2018).

Another possibility for utilizing algal proteins is hydrolysing to amino acids and subsequently converting them into commercial chemical products. Aspartic acid and glutamic acid, which account for a high proportion of algal proteins (Becker 2007; Gajaria et al. 2017), as platform chemicals, can be transformed to many high-value chemicals or polymers via chemical conversion (Werpy and Petersen 2004). Nevertheless, the problems existing in the utilization of algal amino acids are the diversity of amino acids that make up proteins. Purification is the major challenge for obtaining high purity of one specific amino acid.

6. Future perspectives

Recent algal biotechnology is mainly focused on fuel purposes such as biodiesel or bioethanol. For algae valorisation, techniques related to the production of valuable products should be carefully searched. Recently, algae have been utilized to produce value-added chemicals or products such as PUFAs, pigments, carbohydrate-derived chemicals and so on. However, undiscovered opportunities and challenges still exist in algal biorefineries.

More attention should be given to the utilization of naturally grown algae. Commonly, natural algae have a lower organic fraction but a higher ash content than cultured algae. In addition, daily and seasonal changes influence the productivity and composition of natural algae. However, it is more economical to use natural algae as a feedstock because natural algae do not need to be provided with manual cultivation conditions (light, salt, nutrition). Additionally, some natural algae (cyanobacteria) appear as water blooms in lakes and coastal areas, which harm both human health and the coastal ecosystem due to their harmful toxins. However, these algae blooms also have the ability to produce useful lipids, carbohydrates and proteins (Zuo et al. 2018). Therefore, the utilization of such algae would not only provide resources for biorefineries but also relieve burdens on the environment. However, one major issue of utilizing natural algae as the feedstock is the cost of harvesting. To solve this, energy and cost-effective algae harvesting technologies need to be developed. Recently, studies have reported that the application of magnetic nanoparticles (Fe) and flocculation with the aid of chemicals, microbial agents or electric fields is efficient and economical in algae harvesting (Almomani 2020; Xu et al. 2020). Therefore, coupling these harvesting methods with natural algae utilisation might be cost-effective.

Because of the complexity of algal biomass, algae fractionation, in other words, selective conversion of one constituent (i.e., lipids, carbohydrates, or proteins), is a promising method. Therefore, developing a "lipid-, carbohydrate- or protein-first biorefinery" is important because algae cultivation is always designed for only one specific component. For example, lipids can be recovered initially and subsequently transformed into biofuel or oleochemicals from the lipid-rich algae. The carbohydrate-rich algae can be used to produce value-added chemicals such as HMF and levulinic acid. Algae with high content of proteins can be used as nutritional source for humans and animals or converted to amino acids or other nitrogenous compounds.

During the chemical conversion of algal carbohydrates, some unwanted insoluble dark-brown products known as humins are unavoidably formed. The insoluble humins formed from the condensation of soluble molecules (such as HMF) are hardly converted or utilized (Zhou et al. 2020b). Therefore, the formation of humins, which results in a low carbon balance of products, should be avoided as much as possible. Approaches have been made to limit the formation of humins by seeking effective catalysts, changing the reaction solvents, or adjusting the reaction conditions. However, more efforts should be made to understand the formation of humins and design appropriate reaction systems for carbohydrate-based valuable chemical production.

Strategies related to the utilization of algal proteins should be further developed. Proteins account for a large part of the whole algae, but only limited studies focus on extracting algal proteins to be used as human or animal nutrition. The production of high-value products is promising for the valorisation of algal proteins. As one of the major biofixed nitrogen sources, proteins are regarded as a promising feedstock for N-containing chemical or polymer production. During the thermochemical conversion of algae, fatty amides, fatty nitriles, or some N-heterocycle produced via the interactions of fatty acids, carbohydrates and proteins are found in the liquid products (Liu et al. 2021b). These N-containing compounds with high biodegradability and low toxicity are of high-value in the manufacture of surfactants and lubricants. Therefore, methods of enhancing their yields or separating them efficiently need to be developed.

For commercialization and industrialization, the process of valuable product production from algae should be optimized to minimize energy consumption and simplify the processing procedure. Some conversion processes need to be carried out under severe conditions (e.g., high temperature and pressure), resulting in high energy and equipment costs. More efficient catalysts with high activity, product selectivity and excellent reusability should be developed. In addition, the purification process is usually needed to obtain final products with high purity, which increases the process complexity and energy consumption. Therefore, the development of purification technology should also be considered as a major aspect in future research. In addition, the extraction or conversion process must be conducted on a large scale to achieve commercialization and industrialization.

Based on the abovementioned perspectives, future studies could be focused on the utilization of natural algae coupled with efficient harvesting methods (magnetic nanoparticles, flocculation), enhancing the carbon balance during the conversion process and scaling up the process for industrialization. In addition, a few candidates of products based on algae fractionation are suggested: (1) algal lipids can be directly recovered, or converted to oleochemicals (fatty alcohols, fatty nitriles, glycerol); (2) algal carbohydrates are suggested to be transformed into value-added building block chemicals (HMF, succinic acid, lactic acid, polyols); (3) algal proteins could be transformed into fatty amides, fatty nitriles or N-heterocycles from thermochemical conversion.

7. Conclusions

This review provides a deep understanding of algal biorefineries for the production of renewable chemicals and high-value bioproducts. To maximize the value of algal biomass, the focus should be placed not only on biofuel products but also on other ways to utilize the valuable components originally existed in algal cells or transform them into products with higher values. The production of multiple products from every component of algae is promising to achieve a waste-free biorefinery. Additionally, algal biorefineries should be developed to find sustainable and economical methods that are energy-efficient and suitable to be performed on a large-scale process.

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Figure captions

Fig. 1 Schematic diagram for the utilization of algal lipids as renewable biofuel and bioproducts.

Fig. 2 Conversion routes for algae-derived (A) triglycerides or (B) unsaturated fatty acids to oleochemicals.

Fig. 3 Conversion of algal carbohydrates to various chemicals by fermentation or chemical catalysis and a few of their corresponding products.

Table captions

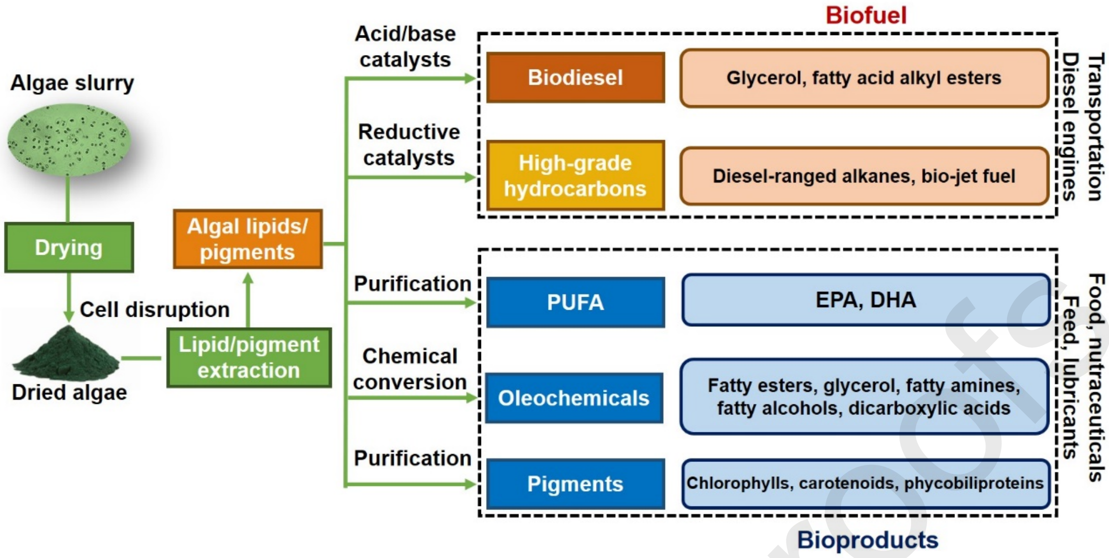
Table 1 Algal cell wall disruption and extraction of algal lipids.

Table 2 Pretreatment of algae and carotenoids recovery.

Table 3 An overview of different pretreatment methods for the production of monosaccharides from algae.

Table 4 Biological conversion of algal carbohydrates to value-added chemicals.

Table 5 Chemical transformation of algal carbohydrates to value-added chemicals.



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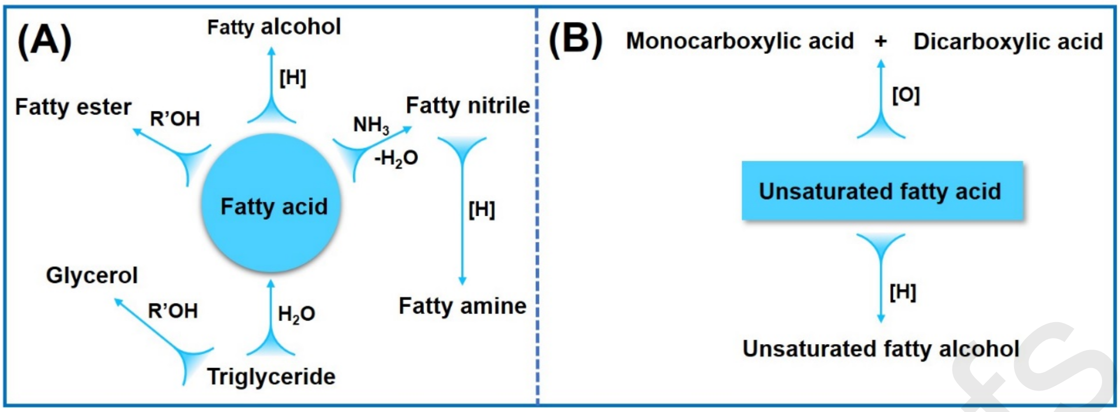
1015 

1016 **Fig. 2** Conversion routes for algae-derived (A) triglycerides or (B) unsaturated fatty
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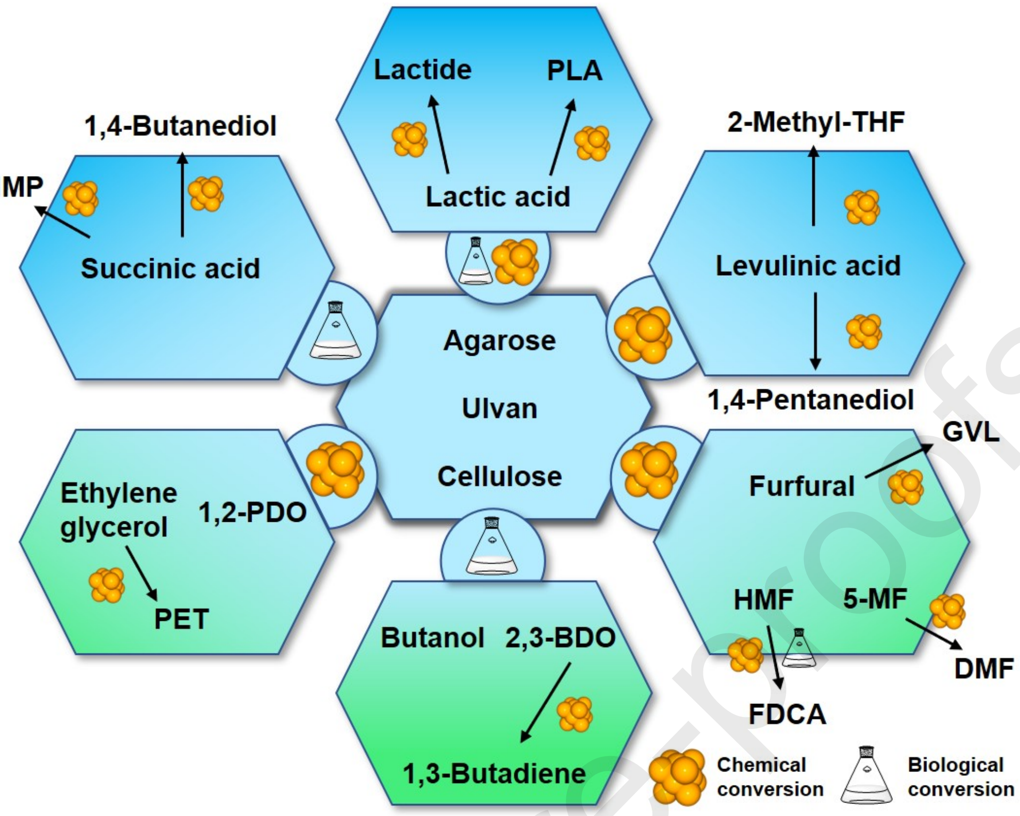

Fig. 3 Conversion of algal carbohydrates to various chemicals by fermentation or chemical catalysis and a few of their corresponding products.

Table 1 Algal cell wall disruption and extraction of algal lipids.

Disruption method	Operating conditions	Extraction solvent	Algae species	Lipid yield (wt %)	Ref.
Physical					
pulse electric field (PEF)	20 kV/cm, 130 Hz, 6 ms PEF at flow rate of 90 mL/min for 3 cycles	$CHCl_3$/MeOH (2:1, v/v)	*C. pyrenoidosa*	12.8	(Han et al. 2019)
Ultrasound	90 W, 10 min	$CHCl_3$/MeOH (2:1, v/v)	*C. pyrenoidosa*	11.4	(Han et al. 2019)
Microwave	300 W, 15 s, 3 times	Liquid CO_2/MeOH	*Scenedesmus* sp.	9.6	(Viner et al. 2018)
Osmotic shock	1:5 biomass: water ratio	Solvent-free	*C. muelleri*	23	(González-González et al. 2019)
Chemical					
Electrochemical oxidation and microwave	500 mA, 0.75 A h; 400 W microwave, 45 min	CH_2Cl_2/MeOH (2:1, v/v)	*S. dimorphus*	23.4	(Hua et al. 2016)
Photocatalysis	TiO_2 catalyst, 990 W/m^2 solar intensity,	H_2O	*N. oculata*	52	(Shwetharani and

	pH=2.5, 1 h				Balakrishna 2016)
Microwave and deep eutectic solvent (DES)	4 mL aDES, 150 °C, 30 min	Dimethyl carbonate	*P. tricornutum*	12.5	(Tommasi et al. 2017)
Ionic liquid	[BMIM]Cl	Hexane/EtOH	*C. pyrenoidosa*	8.7	(Lu et al. 2019)
Acid pretreatment	HNO_2, pH=6, c(NO_2^-)=900 mg/L, 48 h	$CHCl_3$/MeOH (1:1, v/v)	*Tetraselmis striata* M8	21.9	(Bai et al. 2014)
Biological					
Enzyme	NaOH, pH=10.5, 110 °C, 4 h, cellulase, protease, lysozyme, and pectinase, pH=4, 50 °C, 30 min, 200 IU/g.	Chloroform	*Nannochloropsis* sp.	19.9	(Wu et al. 2017)
Bacteria	*Bacillus* sp. K1, 24 h of incubation	$CHCl_3$/MeOH (1:1, v/v)	*Chlorella zofingiensis*	38	(Guo et al. 2017)

1027 **Table 2** Pretreatment of algae and carotenoids recovery. (N/A: not available)

Product	Method	Conditions	Extraction solvent	Algae species	Yield (mg/g algae) [recovery (%)]	Ref.
β-carotene	Ultrasonic	20 kHz, 10 min, ice water	MeOH	*Tetradesmus* sp.	0.67[N/A]	(Singh et al. 2019)
β-carotene	Bead milling	Maximum speed, 2 min	Acetone	*Tetraselmis* sp.	3.21[N/A]	(Schüler et al. 2020)
Carotenoids	Solvent	30 min, 110 °C	2-Methyltetrahydrofuran/EtOH (1:1, v/v)	*Chlorella vulgaris*	0.311[66]	(Damergi et al. 2017)
Lutein	Reduced pressure extraction	850 mbar, 25 min homogenization; 25 °C, 850 mbar, 40 min.	Tetrahydrofuran	*Chlorella sorokiniana*	5.21[99.5]	(Chen et al. 2016)
Astaxanthin	Switchable hydrophilicity solvent	Algae/DMCHA ratio: 5 mg/mL, 24 h of magnetic stirring	Dimethylaminocyclohexane (DMCHA)	*Haematococcus pluvialis*	52.32[87.2]	(Huang et al. 2018)
Astaxanthin	Supercritical CO_2	55 °C, 8 MPa, 15 h	Ethanol/olive oil and $scCO_2$	*Haematococcus pluvialis*	N/A[100%]	(Cheng et al. 2018)

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Table 3 An overview of different pretreatment methods for the production of monosaccharides from algae.

Algae species	Method	Pretreatment conditions	Monosaccharides yield	Ref.
Ascophyllum nodosum	Microwave assisted acid hydrolysis	0.4 M H_2SO_4, 3.13% (w/v) algae concentration, 150 °C, 1 min	127 mg/g	(Yuan and Macquarrie 2015)
Gracilaria verrucosa	Solid-acid pretreatment	Amberlyst-15, 15% (w/v) loading, 140 °C, 3 h, 1:5.7 solid: liquid, 15%	51 g/L	(Jeong et al. 2015a)
Gracilaria verrucosa	Acid hydrolysis	Sulfuric acid, 1.92% and 1.03% for glucose and galactose, 160 °C, 20 min	Glucose: 5.29 g/L, galactose: 18.4 g/L	(Jeong et al. 2015b)
Enteromorpha prolifera	Acid hydrolysis	Formic acid, 0.7% (v/v), 160 °C, 1 h	Rhamnose: 45.2%, xylose: 12.5%, glucose: 9.8%	(Zhang et al. 2019)
Waste water algae	Acid and enzyme treatment	2 M HCl, 120 °C, 10 min, 70 g/L biomass concentration; cellulase, pH=4.9, 50 °C, 300 rpm	53%	(Martin-Juarez et al. 2019)
Gracilaria sp.	Acid and enzyme treatment	4% H_2SO_4, 121 °C, 30 min; cellulase (53 PFU/g) and β-glucosidase (30 U/g), pH=5.0, 50 °C, 300 rpm, 4 h	Reducing sugar: 140.6 mg/g	(Saravanan et al. 2018)

Table 4 Biological conversion of algal carbohydrates to value-added chemicals.

Product	Algal feedstock	Hydrolysis conditions	Microorganism	Product yield/concentration	Ref.
Butanol	Lipid extracted *C. vulgaris*	2% H_2SO_4, 121 °C, 20 min	*Clostridium saccharobutylicum* DSM 13864	8.05 g/L	(Gao et al. 2016)
Butanol	*Chlorella vulgaris*	1% NaOH followed by 3% H_2SO_4, 121 °C, 20 min	*C. acetobutylicum*	13.1 g/L, 0.58 mol/mol sugar	(Wang et al. 2016)
2,3-BDO	*Golenkinia* sp.	1.5 N H_2SO_4, 121 °C, 60 min	Engineered *Klebsiella oxytoca*	2.76 g/L	(Park et al. 2017)
Lactic acid	*Arthrospira platensis*	-	*Lactobacillus plantarum* ATCC 8014	3.7 g/L	(Niccolai et al. 2018)
Succinic acid	*Desmodesmus* sp.	2% (w/w) H_2SO_4, 155 °C, 15 min	*A. succinogenes* 130Z (ATCC 55618)	0.3 g product/g biomass	(Knoshaug et al. 2018)
Succinic acid	*Saccharina latissima*	Cellulase: 40 U g/DM, β-glucosidase: 25 U g/DM, alginate lyase: 10 U g/DM, pH=4.8, 50 °C, 48 h	*A. succinogenes* 130Z	36.8 g/L, 0.919 g/g total sugars	(Marinho et al. 2016)
Pyruvate	*Ulva reticulata*	0.3% (v/v) H_2SO_4, 121 °C, 30 min; 50 IU/g Viscozyme L, 45 °C, 24 h	*Halomonas* sp. BL6	55.23 g/L	(Anh et al. 2020)

Table 5 Chemical transformation of algal carbohydrates to value-added chemicals.

Product	Feedstock	Catalyst	Reaction conditions	Yield (%)	Ref.
HMF	k-Carrageenan	Catalyst free	5% (w/v) substrate, 10 mL IPA:DMSO (70:30), 120 °C, 2 h	50	(Wagh et al. 2019)
HMF	Agarose	Catalyst free	50 mg agarose, 2 mL water, microwave, 180 °C, 10 min	51	(Francavilla et al. 2016)
Levulinic acid	Agarose	H_2SO_4	50 mg agarose, 1% (v/v) H_2SO_4, 2 mL water, microwave, 180 °C, 10 min	64	(Francavilla et al. 2016)
Levulinic acid	*Gracilaria verrucosa*	Methanesulfonic acid (MSA)	10% biomass, 0.5 M MSA, 180 °C, 20 min	36.92	(Park et al. 2018)
Furfural	Alginic acid	12-tungstophosphoric acid hydrate	10 mg reactant, 10 mg catalyst, 1 mL H_2O-THF (5% (v/v) water ratio), 180 °C, 30 min	33.8	(Park et al. 2016)
Furfural	Alginic acid	Amberlyst-15	0.5 wt% reactant, 180 °C, 30 min	18.5	(Jeon et al. 2016)
5-MF	*E. prolifera*	$FeCl_3$	0.0125 mol/L $FeCl_3$, 190 °C, 1 h	19.8	(Chen et al. 2020)
Lactic acid	*Scenedesmus*	Formic acid and Sn-Beta	75 mg formic acid, 300 mg algae, 400 mg Sn-Beta, 210 °C, 2 h, 4 MPa He	83	(Zan et al. 2018)
Polyols	*Chlorococcum* sp.	Ni-MgO-ZnO	0.25 g algae, 0.15 g catalyst, 250 °C, 180 min, 6 MPa H_2	41.5	(Miao et al. 2015)

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

Applications of algae as valuable products instead of biofuel are more profitable.

Algal lipids can be applied for the production of PUFAs and oleochemicals.

Algal sugars can be utilized for the synthesis of value-added platform chemicals.

Algal proteins have the potential to be converted to N-containing compounds.

The realization of zero-waste algal biorefineries valorisation needs to be explored.