Review

Biocomposites Using Whole or Valuable Component-Extracted Microalgae Blended with Polymers: A Review

Gyu Min Kim 1,*, Won-Seok Chang 2 and Young-Kee Kim 1,*

1 Faculty of Food Biotechnology and Chemical Engineering, Research Center of Chemical Technology, Hankyong National University, Anseong 17579, Gyeonggi-do, Korea; gyumin@hknu.ac.kr
2 Frontier R&D Institute, Korea District Heating Corp., Yongin-si 17099, Gyeonggi-do, Korea; wschang@kdhc.co.kr
* Correspondence: kim@hknu.ac.kr; Tel.: +82-31-670-5206

Abstract: Global demand for plastics has increased steadily alongside industrial development. Despite their versatility and convenience, environmental pollution caused by plastics are a major issue. With a reduction in the market size of plastics being seemingly impossible, bioplastics may become key to tackle this issue. Among a wide range of sources of bioplastics, microalgae have come into the limelight. While abundant and valuable components in microalgae have the potential to replace preexisting plastics, complex processes and low cost performances have prevented them from entering the market. In this study, we examined techniques for biocomposites in which polymers are blended with microalgae. We focused on microalgae-based biocomposite blending processed from the perspective of functionality and cost performance.

Keywords: microalgae; biomass; biopolymer; biocomposites; bioplastics

1. Introduction

Microalgae are photosynthetic organisms that are widely distributed across the planet thanks to their ability to survive under various environmental conditions (salt water, brackish water, and fresh water). Microalgae have an ability to use carbon dioxide (CO₂), a primary greenhouse gas, in addition to their use as resources, such as ingredients in foods, biofuels, biochemicals and bioplastics. Many research groups have been attracted to the study of microalgae, actively spurred by the value of research and development in this industry [1].

Microalgae only require small spaces for their cultivation and utilize CO₂ 10–100 times faster than terrestrial plants [2]. Algae contain the photosynthetic pigment chlorophyll a, which converts solar irradiation to chemical energy through photosynthesis and is categorized into prokaryotic microalgae (cyanobacteria Chloroxybacteria), eukaryotic microalgae (green algae Chlorophyta), red algae (Rhodophyta) and diatoms (Bacillariophyta) [3,4]. Approximately, half the amount of photosynthesis on Earth is estimated to result from microalgae, in part due to their extremely large quantities. Thus, microalgae are a key player in the control of the concentration of CO₂ in the earth atmosphere [5].

Microalgae have a variety of shapes (rods and spheres) with average sizes of 2–200 µm and are mainly composed of polymeric compounds, such as proteins, lipids, and carbohydrates [3]. Microalgae were initially the focus of the search for renewable energy sources for the production of biofuels (biodiesel, bioethanol, bio-hydrogen, and methane). As a result, their application fields have been expanded to other products, such as pharmaceuticals, cosmetics, and nutrient supplements [6–9]. The size of the food-grade seaweed (algae) product market in 2017 was 216,000 tons and valued at US$568 million per year. In contrast, the value of microalgae trade in the same year was only US$40 million per year, despite their potential application in many industries [10]. Arthrospira (formerly Spirulina), Chlorella, and Dunaliella are the microalgae that are primarily traded in this market [11].
Various attempts have been made to obtain biofuels, as an alternative to fossil fuels, from biomasses. These technologies are divided into 1st generation production technology using grains, 2nd generation production technology using lignocellulosic biomass, and 3rd generation production technology using microalgae. The 1st generation production techniques have resulted in excessive competition for food supplies and a sharp rise in the price of grains. Although the 2nd generation production technique has been suggested, it has another problems due to the complex processes and difficulties associated with the utilization of lignin [12]. In the 3rd generation production technology, the utilization of microalgae has much greater potential compared to other types of biomass. The biofuel production process using microalgae does not use food resources as raw materials, and the process of converting it into energy is relatively simple and low-cost.

Occasionally, valuable components in microalgae are found in the outer part of the cell membranes. However, the majority of the practical ingredients in microalgae that have industrial applications are found inside cells, so complex processes are required for their valorization. Figure 1 depicts the structure of typical microalgae [13]. In general, the requirements for the downstream process after microalgae cultivation are as follows: harvesting (separation), thickening, dehydration, drying, cell disruption, extraction, and purification [14]. Harvesting involves the coagulation, flocculation, and solid-liquid separation (sedimentation, floatation, filtration, and centrifugation) of microalgae biomass [15–17], as well as a variety of harvesting methods [18].

![Figure 1. The structure of inner part of microalgae. Reproduced with permission from [13].](image)

To obtain a high value product from the inner parts of microalgal cells, additional processes, such as cell disruption, extraction, and purification, are required after drying. Cell disruption can be categorized into mechanical and non-mechanical methods, which are used to breakdown the surface of the cell wall to acquire metabolites from the within the cell. Bead mills [19], homogenizers [20], high-pressure presses [21], ultrasound [22], and autoclaving have been suggested as mechanical methods. As the non-mechanical methods, organic solvents [23], osmotic shock [24], supercritical fluid [25], and enzyme-assisted methods [26] have been developed. Extraction is a separation method used for the extraction of valuable metabolites, such as lipids, fatty acids, pigments, proteins, and polysaccharides, from disrupted microalgal biomass. Recently, the trend of extraction method has shifted to economically beneficial and efficient methods, such as supercritical fluid extraction, pressurized liquid extraction, microwave-assisted extraction, ultrasound-assisted extraction, surfactant-assisted extraction, and pulse electric field extraction [27]. The additional downstream processes (e.g., cell disruption, extraction, and purification) obtaining the valuable components from microalgae is complex and costly, so a method that is able to
exploit entire microalgae without additional complex processes is required. Microalgae are composed of polymeric materials (proteins, lipids, polysaccharides), and the primary content is protein. Methods for blending dried microalgae biomass with other polymeric materials for producing bioplastics have been developed to utilize these polymeric compounds. The amount of bioplastic produced in 2020 is estimated to reach 2.111 million tons per year, and that of bioplastics in 2025 is expected to reach 2.871 million tons per year [28]. Microalgae-based bioplastics are microalgal biomass and polymer blended products, which are processed to final products through molding and extruding. The bioplastics are primarily used in the packaging industry, recording 0.998 million tons per year. Packaging materials from bioplastics account for 47.3% of the entire bioplastics industry, followed by consumer goods, textiles, agriculture and horticulture, automotive, and transport [28]. 

*Spirulina* and *Chlorella* are the main microalgae used to produce bioplastics because complex treatments are not required [29]. To effectively exploit microalgal biomass as ingredients of bioplastic, plasticization, which is a process to improve flexibility and durability by adding non-volatile organic compounds, such as glycerol, triethylene, and glycol, is essential. In addition, the blending of microalgal biomass with compatible polymers, such as poly(vinyl alcohol), polyethylene, and ethylene-vinyl acetate, to improve the stability of blended polymers through changes in the interfacial properties is also necessary [30].

In this review, we discuss recent studies on composite technologies for the production of microalgae-based bioplastics.

2. Major Components in Microalgae

Although the ratio of main components, such as proteins, carbohydrates, and lipids, of microalgae depends on the cultivation conditions as well as microalgal species, the major component is usually protein. The production characteristics of these components in different microalgae are summarized in Table 1.

**Table 1.** Composition of microalgal species (all data are % on a basis of dried biomass).

| Species                  | Composition (%) | Ref. |
|--------------------------|-----------------|------|
|                          | Proteins        | Carbohydrates | Lipids |
| *Chlorella vulgaris*     | 41.51           | 20.99      | 15.67  | [31]  |
| *Chlorella vulgaris*     | 29.0            | 49.5       | 19.7   | [32]  |
| *Spirulina platensis*    | 49.23           | 31.20      | 11.20  | [33]  |
| *Chlorella sorokiniana*  | 18.81           | 35.67      | 9.90   | [34]  |
| *Scenedesmus obliquus*   | 30.38           | 13.41      | 4.66   | [35]  |
| *Dunaliella tertiolecta* | 61.32           | 21.69      | 2.87   | [36]  |
| *Chlamydomonas reinhardtii* | 64.76     | 22.64      | 12.60  | [37]  |
| *Nannocloropsis oculata* | 39              | 20         | 17     | [38]  |
| *Nannochloropsis oceanica* | 19.1      | 22.7       | 24.8   | [39]  |

2.1. Proteins

Protein is the major content in microalgae compared to lipid and carbohydrate. For example, *Spirulina* and *Chlorella*, major microalgae used for bioplastics, take up 30–75 wt% of proteins under nutrient-rich conditions [40]. The specific protein contents depend on the species of microalgae (Table 1). In addition, different cultivation environments and nutrient conditions result in different amounts of protein in the same species. Nitrogen is the main factor involved in protein production. Thus, the supply of high levels of nitrogen leads to the accumulation of protein. Microalgae are able to produce all types of amino acids. Due to their abundance and diversity of amino acids, microalgae have drawn attention as a major protein resource [41,42]. The amount of amino acids depends on the species, and the amount determines the type of protein [43,44].
2.2. Carbohydrates

Carbohydrates are essential biocomponents, acting as energy carriers in metabolism. The amount of carbohydrates in microalgae depends on the cultivation and nutrient conditions, as well as the microalgal species (Table 1). Generally, carbohydrate content accounts for 20–60 wt% [10,44,45]. Microalgae that contain high levels of carbohydrates can be used to produce bio-alcohols, such as ethanol, and high value-added metabolites, such as alginates [46].

2.3. Lipids

Microalgal lipids are intracellularly accumulated in fatty acid complex forms during microalgae growth. The amount of lipids produced by microalgae accounts for 5–30% of the total mass of dried microalgae (Table 1). The specific amount of lipids depends on the species, cultivation conditions, and nutrient composition [10,44]. Lipids consist of storage lipids (triacylglycerides as a major component) and membrane lipids. In general, the amount of lipid (especially, storage lipids) produced from microalgae is not high under optimized growth conditions [47].

3. Microalgal Biomass-polymer Blends

Since the invention of plastics and the development of mass production, plastic demand has increased exponentially annually [48]. Despite their easy processability and economically viable merits, the management of plastic waste has always been a contentious issue due to their non-biodegradable properties, resulting in significant damage to the environment. Although the share of bioplastics in the plastic market remains low, eco-friendly and abundant amounts of bioplastics are considered to be sufficient alternatives to replace preexisting plastics [49]. *Chlorella* and *Spirulina* are the primary sources for bioplastics from microalgae due to their easy processability [29,50,51]. Although the replacement of artificially synthesized existing plastics with 100% microalgal bioplastics could be ideal when it comes to environmentally friendly plastics, the physical and mechanical properties, such as tensile strength, glass transition temperature, and elongation at break, of 100% bioplastics are inferior to those of commercially available plastics. Another option to tackle these issues is to blend microalgae with polymers, namely microalgal biomass-polymer composites [52,53]. These blended composites are hybrid-type plastics that have both properties of each component. The general properties of these blends depend on the ratio between the amount of microalgae biomass and those of the polymer. In general, a higher polymer content in biomass-polymer composites results in better performance, especially in terms of tensile strength and elongation at break [54]. The required level of biomass contents in authorized bioplastics depends on individual national regulations. Korean government suggest that the percent of biomass in biomass-polymer composites should be over 30 wt% to be considered as an eco-friendly bioplastic. According to our investigation, the contents of microalgae in most composites remain less than 30 wt%, implying that further studies to increase the proportion of microalgae in the composites should be conducted to boost the commercialization of microalgae-based biocomposites.

Another important factor is whether valuable refined biocomponents, such as proteins or lipids, extracted from microalgae by several processes, or whole microalgal biomass are used to make the blended composites. Although the physical properties of composites are easily improved by relatively pure components from microalgae using special extraction methods blended with polymers, high costs devalue the development of biocomposites [54,55]. From an economical point of view, whole microalgae without any extraction process blended with polymers has a lower overall cost; however, the relatively lower quality of the final products has hindered its commercialization. Here, we address microalgal biomass-based composite products using dried whole microalgae without any processes and valuable components-extracted microalgae.
3.1. Composites with Poly(vinyl alcohol)

Lipids, one of the most valuable components in microalgae, can be extracted using simple methods that induce direct physical forces, such as microwaves and sonication [56–58]. Despite their simplicity, small amounts of lipids from microalgae hinder their utilization in industry. Lipids extracted from the microalgae of *Nannochloropsis salina* lead to the mass production of oil from algal biomass [59,60]. In this method, lipid-extracted microalgae are often used as the filler to make composites with polymers. Tran et al. attempted to blend lipid-extracted microalgae with poly(vinyl alcohol) (PVA). PVA is one of rare water-soluble synthesized polymers. In contrast to the direct blending method, which involves blending microalgae with a heated polymer by increasing the temperature to the glass transition temperature of the polymer, PVA can be dissolved in water to mix microalgae. PVA is easily dissolved in protic solvent at 90°C. The characterization of functional groups for microalgae is essential to check whether microalgae is compatible with petroleum polymer. The measurement of infrared (IR) spectrum in Figure 2 reveals that lipid-extracted microalgae have strong peaks at 3285 cm\(^{-1}\), 2919 cm\(^{-1}\), and 2851 cm\(^{-1}\), which are assigned to O–H, CH\(_2\), and CH stretching vibration, respectively [54]. The use of PVA, which has exactly same functional groups, leads to relatively homogeneous mixing with lipid-extracted microalgae by chemical interaction between polymeric metrics. The resulting biocomposites displayed enhanced thermal stability and mechanical properties when the portion of lipid-extracted microalgal biomass to PVA was 20%. However, the relatively high cost of extracting specific components from *N. salina* may not be adequate for the ultimate commercialization of these biocomposites.

![Figure 2. IR spectrum of lipid-extracted microalgae. Reproduced with permission from [54](#).](image-url)

The Dianursanti group also reported on blends of microalgae with PVA. They focused on using whole microalgae (*Spirulina platensis*) to mix with PVA. *S. platensis*, which contains a large portion of protein (approximately 60 wt%), has a positive effect on elongation at break when it forms biocomposites with PVA. They used 56% of microalgae to make composite and added glycerol as a plasticizer, which led to further improvements in the tensile strength [61]. The use of whole microalgae with PVA resulted in enhanced plastic properties of composite and cost performance, minimizing the processing costs. In addition, the limitations of conspicuous enhancement of properties prevents them from competing...
with preexisting plastics in markets. In addition, they treated PVA with maleic anhydrate as compatibilizer to make maleic anhydrate-grafted PVA (PVA-g-MAH), and PVA-g-MAH was blended with *Chlorella vulgaris* for fabricating biocomposite to overcome the above mentioned drawbacks [62]. PVA-g-MAH was synthesized using a simple and economical method by mixing maleic anhydrides, dimethyl sulfoxide, and potassium persulfate with PVA. The biocomposites composed of *C. vulgaris* with PVA-g-MAH increased the elongation at break and tensile strength. Furthermore, elasticity was also improved, in contrast with that achieved using other methods. Another simple method to form biocomposites is the sonication of *Chlorella*, followed by mixing with PVA [63]. However, despite slight improvements in tensile strength and elongation at break, the degree of improvements compared to other methods was marginal.

### 3.2. Composites with Polyethylene or Polypropylene

Polyethylene (PE) and polypropylene (PP) are poly(olefins) used in a variety of products owing to their rigidity, easy processability, and low cost. The application of these polymers to microalgae to form biocomposites has been attempted at the very beginning of research on biocomposites. The use of whole microalgae rather than extracted components from microalgal biomass was dominant to blend with PE and PP [29,64]. Despite their easy accessibility and viable processes, the intrinsic structural differences of these polymers lead to incompatibilities, in particular for *Chlorella*. Further studies on enhancing compatibility will be needed.

So far, the purpose of using microalgae blended with polymers has mainly focused on mechanical properties improvement. However, a recent report regarding the use of microalgae in PP has emphasized the stabilization effects [65]. They reported that the stabilization effects by adding *Chlorella vulgaris* and *Spirulina platensis* in PP. Microalgal biomass acted as agents to protect the degradation of PP, primarily caused by polyphenols in microalgae. Tafreshi et al. also reported that polyethylene glycol (PEG), which is chemically different from PE, combined with *C. vulgaris* significantly improved the stress against gamma irradiation [66]. These recent studies have demonstrated the potential of biocomposites with simple polymers (such as PE and PP), with a focus on stability issue.

### 3.3. Composites with Poly(vinyl chloride)

Poly(vinyl chloride) (PVC), which has a high density, hardness, and durability, has also been used to fabricate biocomposites with microalgae. A simple method to blend PVC with microalgae involves pressurized heating by increasing the temperature to 190°C [67]. However, the application of relatively high temperatures to PVC blended with *Chlorella* may have negative effects, leading to weight loss of *Chlorella* due to the volatilization and degradation of chlorophyll in microalgal biomass. Despite these drawbacks, by handling with care, the addition of *Chlorella* to PVC enhances the tensile strength. In their study, the weight ratio of *Chlorella*, as filler, to PVC was less than 20% to meet the requirements for rigid PVC products.

### 3.4. Composites with Polyurethane

Polyurethane (PU) is a polymer synthesized by reacting isocyanate and polyol groups. Despite their superior flexibility, their relatively low hardness and strength serve as a barrier to their use with microalgae. The applications of PU in biocomposites have focused on biomass with high lignin content because of the limited properties of PU [68]. The actual use of PU blended with microalgae has recently been studied [69]. A mixture of PU and *Chlorella* treated with sonication improved the mechanical properties of the biocomposites. The increase in the ratio of *Chlorella* to PU enhanced the tensile strength and elongation at break, similar to those of other polymer blends. Large amounts of *Chlorella* (up to 70 wt%) were used with the help of PEG as a model polyol, which is the highest content compared to other reports regarding biocomposites. The optimization of biocomposites using PU and microalgae as biofillers will be needed to further improve their applications.
The further characteristics of biocomposites mentioned above are summarized with respect to pros and cons in Table 2.

**Table 2. Summary of various microalgae-based biocomposites.**

| Microalgae Blended Polymer | Pros | Cons | Ref. |
|---------------------------|------|------|------|
| Lipid extracted *Nannochloropsis salina* PVA | - Enhanced thermal stability - High tensile strength | - Extraction process required - Plasticizer needed | [54] |
| *Chlorella vulgaris* PVA-g-MAH | - Enhanced tensile strength and elongation properties | - Complex compatibilizer required | [62] |
| *Chlorella vulgaris* and *Spirulina platensis* PP, PE | - High cost performances - Easy processability | - Incompatibility especially with *Chlorella* | [29] |
| *Chlorella* PVC | - High tensile strength due to rigidity of PVC - Superior mechanical properties due to interactions with isocyanate group | - High sensitivity to water content in microalgae | [67] |
| *Chlorella* PU | | - Complex process requiring a coupling reagent | [69] |

3.5. Biodegradable Bioplastics

In terms of biodegradability of polymers, poly(butylene succinate) (PBS) is considered as eco-friendly polymer. Although its thermoplastic properties are similar to those of PE, allowing for blending with microalgae using high temperatures, studies on composite with PBS have rarely been conducted, presumably due to technical issues [53]. They attempted to form maleic anhydride-grafted PBS (PBS-g-MAH), similar to PVA-g-MAH conducted by Dianursanti and Khalis [62]. As a compatibilizer, PBS-g-MAH was found to improve the mechanical properties of eco-friendly composites when blended with *Spirulina*.

Polyhydroxyalkanoate (PHA) is a polyester that is widely known as a biodegradable plastic. Poly-3-hydroxybutyrate (PHB) is a type of PHA with properties similar to those of PP and PE with self-degradable effects. Recently, it has been reported to the extraction of PHB from microalgal biomass [70–72]. In addition to *Chlorella* and *Spirulina*, other types of microalgae, such as *Chlorogloea fritschii*, have been used to extract PHB [70]. In general, valuable components extracted from microalgae are not used unilaterally but are blended with other materials (mainly polymer). As PHB can solely be utilized as a plastic because of its similarity to commonly used plastics, the extraction of PHB from microalgae has been an important focus of the production of biodegradable polymers.

4. Conclusions

Biocomposites consisting of various types of microalgae blended with different polymers have been comprehensively investigated in this study. Especially, the methodologies regarding fabrication of biocomposites have been extensively reviewed. Through recent investigations on efficient blending methods, the mechanical properties of biocomposites consisting of microalgae and petroleum polymers have been gradually enhanced. The mechanical properties of final bioplastics are generally improved by enhancing tensile strength and thermal stability by blending with most petroleum polymers introduced above. Thus, it is reasonable to choose polymer for bioplastic based on processing conditions. For manufacturers that only require low temperature processing, water-soluble PVA could be good option as it can be processed under boiling temperature of water. Though poly(olefins), such as PP and PE, are melted at relatively high temperature, simple fabrication condition without liquid water is possible. The use of PU with microalgae can take advantage of superior mechanical properties while it requires complex process, which possibly increases costs. Bioplastics using microalgae could be good alternative to following the trend of eco-friendly materials.
Despite its progress, commercialization and industrialization still lag behind due to immature technologies related to scale up. In addition, as most high performance biocomposites mentioned-above still need additives, the application of biocomposites to food and pharmaceutical packaging is still restricted. In this regard, the direction of research should be focused on more broad usage of biocomposites by optimizing mass production system and reducing additives, which will boost them to enter eco-friendly market.

Author Contributions: Conceptualization, G.M.K., W.-S.C. and Y.-K.K.; methodology, G.M.K., W.-S.C. and Y.-K.K.; investigation, G.M.K., W.-S.C. and Y.-K.K.; resources, Y.-K.K.; writing—original draft preparation, G.M.K. and Y.-K.K.; writing—review and editing, G.M.K. and Y.-K.K.; supervision, Y.-K.K.; project administration, G.M.K.; funding acquisition, W.-S.C. and Y.-K.K. All authors have read and agreed to the published version of the manuscript.

Funding: This study was supported by “Carbon to X” project (Project No. 2021M3H7A1026228) through the National Research Foundation (NRF) funded by the Ministry of Science and ICT, Korea and Korea Environment Industry & Technology Institute (KEITI) through the program for the management of aquatic ecosystem health, funded by Korea Ministry of Environment (MOE). (202000300001).

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Aliyu, A.; Lee, J.; Harvey, A. Microalgae for biofuels via thermochemical conversion processes: A review of cultivation, harvesting and drying processes, and the associated opportunities for integrated production. Bioresour. Technol. Rep. 2021, 14, 100676. [CrossRef]

2. Wang, B.; Li, Y.; Wu, N.; Lan, C.Q. CO2 bio-mitigation using microalgae. Appl. Microbiol. Biotechnol. 2008, 79, 707–718. [CrossRef][PubMed]

3. Phwan, C.K.; Ong, H.C.; Chen, W.-H.; Ling, T.C.; Ng, E.P.; Show, P.L. Overview: Comparison of pretreatment technologies and fermentation efficiencies of bioethanol from microalgae. Energy Convers. Manag. 2018, 173, 81–94. [CrossRef]

4. Sambusiti, C.; Bellucci, M.; Zabaniotou, A.; Beneduce, L.; Monlau, F. Algae as promising feedstocks for fermentative biohydrogen production according to a biorefinery approach: A comprehensive review. Renew. Sust. Energ. Rev. 2015, 44, 20–36. [CrossRef]

5. Moroney, J.V.; Ynalvez, R.A. Algal Photosynthesis. Encycl. Life Sci. 2018. [CrossRef]

6. Abd El-Hack, M.E.; Abdelhour, S.; Alagawany, M.; Abdo, M.; Sakr, M.A.; Khafaga, A.F.; Mahgoub, S.A.; Elser, S.S.; Gebriel, M.G. Microalgae in modern cancer therapy: Current knowledge. Biomed. Pharmacother. 2019, 111, 42–50. [CrossRef]

7. Chen, C.-Y.; Kao, P.-C.; Tsai, C.-J.; Lee, D.-J.; Chang, J.-S. Engineering strategies for simultaneous enhancement of C-phycocyanin production and CO2 fixation with Spirulina platensis. Bioresour. Technol. 2013, 145, 307–312. [CrossRef]

8. Ho, S.-H.; Chan, M.-C.; Liu, C.-C.; Chen, C.-Y.; Lee, W.-L.; Lee, D.-J.; Chang, J.-S. Enhancing lutein productivity of an indigenous microalga Scenedesmus obliquus FSP-3 using light-related strategies. Bioresour. Technol. 2014, 152, 275–282. [CrossRef]

9. Irshad, M.; Hong, M.E.; Myint, A.A.; Kim, J.; Sim, S.J. Safe and Complete Extraction of Astaxanthin from Haematococcus pluvialis by Efficient Mechanical Disruption of Cyst Cell Wall. Int. J. Food Eng. 2019, 15, 20190128. [CrossRef]

10. De Carvalho, J.C.; Magalhaes, A.I., Jr; de Melo Pereira, G.V.; Souza Vandenberghe, L.P.; Soccol, V.T.; Soccol, C.R. Microalgal biomass pretreatment for integrated processing into biofuels, food and feed. Bioresour. Technol. 2020, 300, 122719. [CrossRef]

11. Viganì, M.; Parisi, C.; Rodriguez-Cerezo, E.; Barbosa, M.J.; Sijtsma, L.; Ploeg, M.; Enzing, C. Food and feed products from micro-algae: Market opportunities and challenges for the EU. Trends Food Sci. Technol. 2015, 42, 81–92. [CrossRef]

12. Zhu, L.; Nugroho, Y.; Shakeel, S.; Li, Z.; Martinkauppi, B.; Hiltunen, E. Using microalgae to produce liquid transportation biodiesel: What is next? Renew. Sust. Energ. Rev. 2017, 78, 391–400. [CrossRef]

13. Safi, C.; Zebib, B.; Merah, O.; Pontalier, P.-Y.; Vaca-Garcia, C. Morphology, composition, production, processing and applications of Chlorella vulgaris: A review. Renew. Sust. Energ. Rev. 2014, 35, 265–278. [CrossRef]

14. Pierobon, S.; Cheng, X.; Graham, P.; Nguyen, B.; Karakolis, E.; Sinton, D. Emerging microalgae technology: A review. Sustain. Energy Fuels 2018, 2, 13–38. [CrossRef]

15. Lee, D.-J.; Liao, G.-Y.; Chang, Y.-R.; Chang, J.-S. Coagulation-membrane filtration of Chlorella vulgaris. Bioresour. Technol. 2012, 108, 184–189. [CrossRef][PubMed]

16. Ramanan, R.; Kannan, K.; Deshkar, A.; Yadav, R.; Chakrabarti, T. Enhanced algal CO2 sequestration through calcite deposition by Chlorella sp. and Spirulina platensis in a mini-raceway pond. Bioresour. Technol. 2010, 101, 2616–2622. [CrossRef]

17. Zheng, H.; Gao, Z.; Yin, J.; Tang, X.; Ji, X.; Huang, H. Harvesting of microalgae by flocculation with poly (γ-glutamic acid). Bioresour. Technol. 2012, 112, 212–220. [CrossRef]

18. Chen, C.-Y.; Yeh, K.-L.; Aisyah, R.; Lee, D.-J.; Chang, J.-S. Cultivation, photobioreactor design and harvesting of microalgae for biodiesel production: A critical review. Bioresour. Technol. 2011, 102, 71–81. [CrossRef]
Catalysts 2022, 12, 25

19. Greenwell, H.C.; Laurens, L.; Shields, R.; Lovitt, R.; Flynn, K. Placing microalgae on the biofuels priority list: A review of the technological challenges. J. R. Soc. Interface 2010, 7, 703–726. [CrossRef]

20. Doucha, J.; Livansky, K. Influence of processing parameters on disintegration of Chlorella cells in various types of homogenizers. Appl. Microbiol. Biotechnol. 2008, 81, 431–440. [CrossRef]

21. William, P.; Laurens, L. Microalgae as biodiesel and biomass feedstock: Review and analysis of the biochemistry, energetic and economics. Energy Environ. Sci 2010, 3, 554–590. [CrossRef]

22. Halim, R.; Rupasinghe, T.W.; Tull, D.L.; Webley, P.A. Mechanical cell disruption for lipid extraction from microalgal biomass. Bioresour. Technol. 2013, 140, 53–63. [CrossRef]

23. Cooney, M.; Young, G.; Nagle, N. Extraction of bio-oils from microalgae. Sep. Purif. Rev. 2009, 38, 291–325. [CrossRef]

24. Mercer, P.; Armenta, R.E. Developments in oil extraction from microalgae. Eur. J. Lipid Sci. Technol. 2011, 113, 539–547. [CrossRef]

25. Mendes, R.L.; Rei, A.D.; Palavra, A.F. Supercritical CO2 extraction of γ-linolenic acid and other lipids from Arthrospira (Spirulina) maxima: Comparison with organic solvent extraction. Food Chem. 2006, 99, 57–63. [CrossRef]

26. Wang, D.; Li, Y.; Hu, X.; Su, W.; Zhong, M. Combined enzymatic and mechanical cell disruption and lipid extraction of green alga Neochloris oleoabundans. Int. J. Mol. Sci. 2015, 16, 7707–7722. [CrossRef]

27. Harris, J.; Viner, K.; Champagne, P.; Jessop, P.G. Advances in microalgal lipid extraction for biofuel production: A review. Biofuel Bioprod. Biorefin. 2018, 12, 1118–1135. [CrossRef]

28. European Bioplastics. Bioplastics market development update 2020. In Proceedings of the European Bioplastics Conference, Berlin, Germany, 2 December 2020; p. 10117.

29. Zeller, M.A.; Hunt, R.; Jones, A.; Sharma, S. Bioplastics and their thermoplastic blends from Spirulina and Chlorella microalgae. J. Appl. Polym. Sci. 2013, 130, 3263–3275. [CrossRef]

30. Dixon, C.; Wilken, L.R. Green microalgae biomolecule separations and recovery. Bioresour. Bioprocess. 2018, 5, 24. [CrossRef]

31. Wang, K.; Brown, R.C.; Homay, S.; Martinez, L.; Sidhu, S.S. Fast pyrolysis of microalgae remnants in a fluidized bed reactor for bio-oil and biochar production. Bioresour. Technol. 2013, 127, 494–499. [CrossRef]

32. Xu, L.; Brilman, D.W.W.; Withag, J.A.; Brem, G.; Kersten, S. Assessment of a dry and a wet route for the production of biofuels from microalgae: Energy balance analysis. Bioresour. Technol. 2011, 102, 5113–5122. [CrossRef][PubMed]

33. Jena, U.; Das, K.; Kastner, J. Effect of operating conditions of thermochemical liquefaction on biocrude production from Spirulina platensis. Bioresour. Technol. 2011, 102, 6221–6229. [CrossRef]

34. Chen, W.-H.; Huang, M.-Y.; Chang, J.-S.; Chen, C.-Y. Thermal decomposition dynamics and severity of microalgae residues in torrefaction. Bioresour. Technol. 2014, 169, 258–264. [CrossRef]

35. Chen, W.-H.; Wu, Z.-Y.; Chang, J.-S. Isothermal and non-isothermal torrefaction characteristics and kinetics of microalgae Scenedesmus obliquus CNW-N. Bioresour. Technol. 2014, 155, 245–251. [CrossRef]

36. Shuping, Z.; Yulong, W.; Mingde, Y.; Chun, L.; Junmiao, T. Pyrolysis characteristics and kinetics of the marine microalgae Dunaliella tertiolecta using thermogravimetric analyzer. Bioresour. Technol. 2010, 101, 359–365. [CrossRef]

37. Mahdy, A.; Mendez, L.; Ballesteros, M.; Gonzalez-Fernandez, C. Enhanced methane production of Chlorella vulgaris and Chlamydomonas reinhardtii by hydrolytic enzymes addition. Energy Convers. Manage. 2014, 85, 551–557. [CrossRef]

38. Du, Z.; Mohr, M.; Ma, X.; Cheng, Y.; Lin, X.; Liu, Y.; Zhou, W.; Chen, P.; Ruan, R. Hydrothermal pretreatment of microalgae for production of pyrolytic bio-oil with a low nitrogen content. Bioresour. Technol. 2011, 102, 5113–5122. [CrossRef][PubMed]

39. Cheng, J.; Huang, R.; Yu, T.; Li, T.; Zhou, J.; Cen, K. Biodiesel production from lipids in wet microalgae with microwave irradiation and bio-crude production from algal residue through hydrothermal liquefaction. Bioresour. Technol. 2014, 151, 415–418. [CrossRef][PubMed]

40. Al Rey, C.V.; Mayol, A.P.; Ubando, A.T.; Biona, J.B.M.M.; Arboleda, N.B.; David, M.Y.; Tumlos, R.B.; Lee, H.; Lin, O.H.; Espiritu, R.A. Microwave drying characteristics of microalgae (Chlorella vulgaris) for biofuel production. Clean Technol. Environ. Policy 2016, 18, 2441–2451.

41. Phong, W.N.; Show, P.L.; Ling, T.C.; Juan, J.C.; Ng, E.-P.; Chang, J.-S. Mild cell disruption methods for bio-functional proteins recovery from microalgae—Recent developments and future perspectives. Algal Res. 2018, 31, 506–516. [CrossRef]

42. Spolaore, P.; Joannis-Cassan, C.; Duran, E.; Isambert, A. Commercial applications of microalgae. J. Biosci. Bioeng. 2006, 101, 87–96. [CrossRef]

43. Guldhe, A.; Ansari, F.A.; Singh, P.; Bux, F. Heterotrophic cultivation of microalgae using aquaculture wastewater: A biorefinery concept for biomass production and nutrient remediation. Ecol. Eng. 2017, 99, 47–53. [CrossRef]

44. Kannah, R.; Kavitha, S.; Karthikeyan, O.P.; Rene, E.R.; Kumar, G.; Banu, J.R. A review on anaerobic digestion of energy and cost effective microalgae pretreatment for biogas production. Bioresour. Technol. 2021, 332, 125055. [CrossRef]

45. Khan, M.I.; Shin, J.H.; Kim, J.D. The promising future of microalgae: Current status, challenges, and optimization of a sustainable and renewable industry for biofuels, feed, and other products. Microb. Cell Factories 2018, 17, 36. [CrossRef][PubMed]

46. Khanra, S.; Mondal, M.; Halder, G.; Tiwari, O.; Gayen, K.; Bhomvik, T.K. Downstream processing of microalgae for pigments, protein and carbohydrate in industrial application: A review. Food Bioprod. Process. 2018, 110, 60–84. [CrossRef]

47. Ahn, B.; Park, S.E.; Oh, B.K.; Kim, Y.K. Effect of nanoparticle on cellular growth and lipid production in Chlorella vulgaris culture. Biotechnol. Prog. 2018, 34, 929–933. [CrossRef][PubMed]

48. Gourmelon, G. Global plastic production rises, recycling lags. Vital Signs 2015, 22, 91–95.

49. Venkatachalam, H.; Palaniswamy, R. Bioplastic world: A review. J. Adv. Sci. Res. 2020, 11, 43–53.
