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Sustainable Process Technology to Extract Biochemicals from Microalgae: A Mini-Review

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In this work, we propose a mapping of suitable feedstock, products, and technologies used in various stages of algae biorefinery, including cultivation, harvesting, dewatering, drying, cell disruption, and extraction. The current technologies at each interval are studied and compared with each other. To set up, compare and select the most promising production pathways, a superstructure is proposed. A superstructure of algae biorefinery based on a literature review is developed and presented. Due to the significant impact of the environment on compositions and the number of microalgae, the effect of two factors i.e., light intensity and nutrient composition, on biomass production efficiency are critical. We will further demonstrate the potential application of algae as source for various products such as cosmetic ingredients, nutraceuticals (e.g., carotenoids and proteins), energy carriers (e.g., biodiesel, bioethanol, biohydrogen, biogas) and fertilizer.

1. Introduction

Algae-based (third-generation) feedstocks have received a lot of attention. Algae can be grown in wastewater available during a year at a low price and does not need sizeable fertile land. Algae have a short harvesting time that allows for multiple or continuous harvests. Algae can grow quickly and contain vast amounts of neutral lipids as compared to other types of biomass (Fernández-Linares et al., 2017).

Microalgae are single-cell marine organisms growing in wastewater or seawater with artificial/sun light, carbon dioxide, water, and nutrients. Microalgae can produce valuable compounds such as pigments, proteins, antibiotics in addition biofuel. The concentrations of each of these added-value products vary according to the species and stage of development. As microalgae contain many interesting component, the industrial application area is very broad (Laurens et al., 2014).

Microalgae can be used to produce biofuels but they also have use as food, pharmaceutical, and cosmetic ingredient. For instance, Arthrospira and Chlorella can be used as nutraceuticals or added to functional meals which help prevent tissue damage and disease due to their high protein and amino acid content (Santhosh et al., 2016). Algae can be used in the medical- and cosmetic industries as a source of Omega-3. The Schizochytrium, Crypthecodinium, hraustochytrium, Phaeodactylum, Chlorella, and Monodus are the microalgae that can produce omega-3 bypassing specific separation process (Harris, 2010).

The technologies applied determine the price of added-value products and the biorefinery efficiency. However, algal biorefineries are not cost-competitive with conventional ones and large-scale applications are a significant issue (Rizwan et al., 2015). This challenge attracts the attention of the scientific community and there are studies conducted to identify the most cost-effective technologies and boost economic viability.

Davis et al. (2011) did a cost study of algal lipid production by comparing two alternative cultivating methods (open pond and tubular photobioreactor). According to their research, the cost of lipid production to obtain a 10 % return was 2,242.1 ($/m³) for open ponds and 4,788.3 ($/m³) for tubular photobioreactor. Rizwan et al. (2015) suggested a generic superstructure of eight main stages to produce biodiesel, bio-oil, and biogas from algal residues. Capital costs were not considered in this study. Galanopoulos et al. (2019) proposed an integrated algal biorefinery superstructure to produce bioethanol, levulinic acid, and biofuel. Their approach can be used to determine processing methods that reduce the cost of manufacturing biodiesel from algae.

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Microalgae biomass cultivating and processing alternatives are critical to find cost-effective pathways for producing biodiesel and other added-value products. Investigation of extracting biochemical instead of only biofuel is important highlighted of this mini-review study. The main technologies for extracting bio components from algal biomass are discussed. Different technologies are compared based on techno-economic aspects. A superstructure representation is given that maps the alternatives and will aid process systems engineers to select the optimum upstream and downstream processes for various bioproducts. The superstructure with more than 500 production pathways are developed and presented.

2. Research methodology

This mini-review addresses to resume the up-to-date technologies needed to extract biochemical from microalgae. The focus is to produce added-value products required for various industries. First, literature has been chosen from recent research (since 2010). These studies investigate various technologies used in different steps of biorefinery (cultivation, harvesting, and extraction). The focus of these studies is considering the techno-economic aspects of each of these alternatives. Some measurements parameters (energy requirements and cost operation and efficiency) of each method helps to compare them better. This approach is guidelines for this review that consequently improve scale-up biorefinery. Second, the critical role of process system engineers and previous efforts to find cost-effective production pathways are mentioned.

3. Biorefinery

Algae pass multiple steps in a biorefinery to produce added-value products, as shown in Figure 1. Cultivation, dewatering, harvesting, drying, pigment extraction, lipid extraction, transesterification, lipid production, and remnant treatment are essential steps. Various technologies can be used in each step.

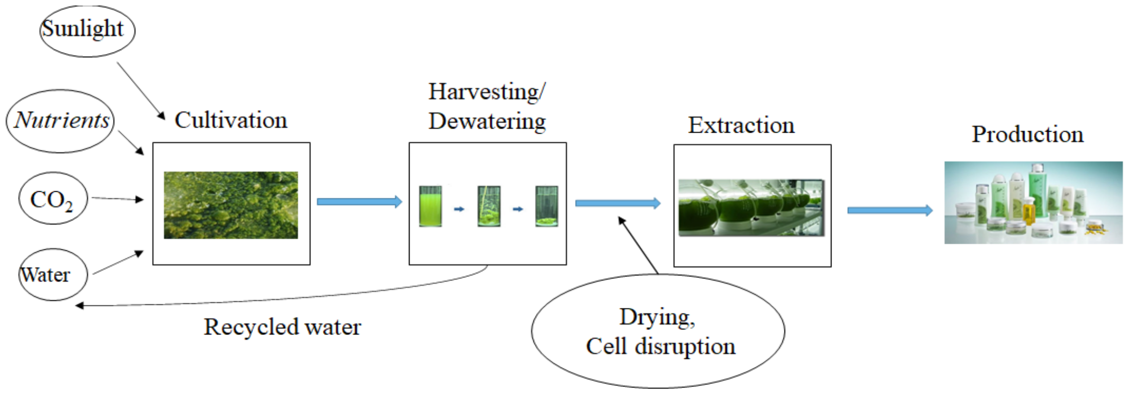

Figure 1: Conceptual figure of microalgae biorefinery. The focus is to define significant steps (Cultivation, dewatering, harvesting, drying, and extraction)

3.1 Cultivation

Microalgae cultivation is the initial step in the algae biorefinery. Microalgae use light, carbon dioxide, water, and nutrients to grow in extremely dilute water suspensions under autotrophic conditions and release oxygen. The type of conditions required to produce the microalgae leads to a variety of cultivation options. Open ponds and photobioreactors are the two main cultivation technologies.

Open ponds consist of a lake or pond in which microalgae can be grown with sunlight and air. These cultivating systems require less investment, energy, and regular maintenance compared to photobioreactors. Open ponds have difficult-to-control growing conditions (e.g., light, temperature). For most microalgal strains, the changes of temperature, pH, and salinity make it a hostile environment.

Photobioreactors are closed systems which control growth conditions and can be utilized indoors or outdoors. These provide a regulated environment for producing high-value biocomponent since they can manage culture parameters (e.g., light, temperature). These reactors have significant energy requirements and capital costs. These drawbacks have slowed down their use at an industrial scale. Table1 lists the advantages and disadvantages of open ponds and photobioreactor (Dickinson et al., 2017).

Table 1: Advantages and disadvantages of open ponds and photobioreactor (Dickinson et al., 2017)

Cultivation methods	Advantages	Disadvantages
Open ponds	Low energy requirement and capital costs, heat dissipated easily	Contamination risk; efficiency depends on the environment/ location of the pond; limitation growth time; necessitates a vast amount of land and high harvesting costs
Photobioreactor	Larger specific surface area ratio to increase algae production; optimizing growth conditions to enhance microalgae density; applying artificial light instead of sunlight; low harvesting costs	High capital costs and energy requirements; oxygen accumulation risk; high shear stress in flat plate photobioreactors; CO_2 depletion or pH fluctuation in turbo photobioreactor

Photobioreactors are divided into flat plate photobioreactors, turbo column photobioreactors, and bubble column photobioreactors. These designs can enhance the quantity of available light and nutrients while reducing dangers such as oxygen accumulation. However, as reactor designs become more complex, the cost of the reactor also rises (Pruvost, 2019).

3.2 Harvesting and dewatering

After cultivating microalgae, the cells must be harvested from a very dilute solution with a cell density of 300–1,000 (g/m³) (Barros et al., 2015). This is one of the most costly steps in the biorefinery. The harvesting and dewatering account for 20–30 % of the total production costs (Barros et al., 2015). Various technologies can be used, including gravity sedimentation, filtration, centrifugation, flocculation, and flotation. The combination of two or more technologies is occasionally used to boost results even further.

Centrifugation and gravity sedimentation are common and straight forward separation methods used in bioprocessing. One advantage of centrifugation is that the microalgae are not contaminated. However, centrifugation is currently too energy-intensive and costly to be a viable choice to separate microalgae from water (Kim et al., 2013). Flotation is a method of transporting microalgae to the culture's surface, where the biomass can be harvested. This technique requires less energy and has lower capital cost as compared to centrifugation. Sometimes a flocculant is used to improve aggregation. In flocculation, free-floating unicellular microalgae cells coalesce to create bigger particles by removing the surface charge of the cells. Physical flocculation methods and chemical flocculants methods are the two main categories of this technique. Chemical flocculants such as iron and aluminum are inexpensive and widely accessible (Bracharz et al., 2018). Microalgae may be harvested using various types of filters. Filtration can extract a high concentration of cells. The variety of filter pore sizes allows the system to adapt to the needs of various microalgae and manage the more delicate species that are susceptible to shearing damage. As filtration is prone to fouling and clogging, it requires frequent cleaning in the short term and replacement of new filters or membranes in the longer term, increasing the processing cost strongly (Tan et al., 2020).

3.3 Drying

Although the harvesting step decreases the biomass concentration, microalgae are grown in an aqueous substrate, and more effort is needed to separate them from the water. The drying process consumes large amounts of energy. At least 3,347 joule of energy is necessary to evaporate 1 kilogram of water and produce biomass with concentration of 90 % (Chen et al., 2015). Unfortunately, this stage might be an economic bottleneck in the overall process due to high energy usage. Thus, choosing an appropriate alternative has a vital role in the final price of products.

Freeze-drying, drum drying, spray drying, and sun-drying are the most prevalent drying processes used in the biorefinery. Among them, spray drying is the most common drying method that is used for many microalgae species (Hosseinizand et al., 2018). Spray drying provides several benefits, including high adaptability, the ability to pack immediately, to generate powder without the need for grinding and the simplicity of processing control, which allows product quality to stay consistent (uniform) throughout the process. However, the biggest downsides are the hefty capital and energy/operating expenses (Chen et al., 2015).

3.4 Cell disruption

To recover intracellular microalgae components, the algae’s cell walls might be disrupted. The cell is disrupted by mechanical methods (e.g., pressing, bead mill, and high-pressure homogenization), physical methods (such as sonication and microwave), biological methods (enzyme degradation), or chemical methods including bases, acids, supercritical fluids. Energy requirements, operation cost, and increased capacity are critical factors in considering various cell disruption methods for industrial application. These factors are evaluated for different cell disruption techniques qualitatively and summarized in Table 2. They are classified based on high, medium, and low difficulty. Kim et al. (2013) compared three cell disruption techniques (bead mill, high pressure homogenization, microwave). Among them, bead mill requires more energy to prevent the degradation of products. The energy requirements and efficiency of different chemical solvents were compared with other alternatives. Depend on the types of solvents, operation cost and capacity are varied (Brennan and Owende, 2010). Vast amounts of biomass are needed in pressing technique compared to others (Mubarak et al., 2015). Although mechanical methods use a lot of energy, these offer the benefit of easy scale-up (Menegazzo and Fonseca, 2019).

Table 2: Comparison between different cell disruption techniques (H: high, M: medium, L: low)

Cell disruption methods	Energy requirements	Operation cost	Increase capacity	References
High pressure homogenization	L-H	M-H	L	(Kim et al., 2013)
Bead mill	H	L-M	L	(Kim et al., 2013)
Pressing	L	L-M	L	(Mubarak et al., 2015)
Ultrasound	H	M-H	L	(Menegazzo and Fonseca, 2019)
Microwave	M-H	M-H	L	(Menegazzo and Fonseca, 2019)
Osmotic shock	L-M	H	L-M	(Menegazzo and Fonseca, 2019)
Enzymatic breakdown	L-M	H	M-H	(Menegazzo and Fonseca, 2019)
Chemical breakdown	L	M-H	M-H	(Brennan and Owende, 2010)

3.5 Extraction

Most types of microalgae have been known to contain a large number of pigments and lipids that can be extracted with chemical solvents or supercritical fluids. Pigment extraction with organic solvents depends on temperature and might result in solvent-component interactions, which are the result of chemical interaction between the molecules in the system. Carotenoids, a well-known pigment, are low-polarity chemicals that are soluble in low-polarity solvents like hexane and acetone (Mezzomo and Ferreira, 2016). Hexane and n- butanol are two common solvents used for extraction lipids. Due to environmental and economic issues with solvent recovery, supercritical carbon dioxide is an alternative solvent in the extraction of carotenoids and lipids (Galanopoulos et al., 2019).

Lipids of microalgae consist of various components such as polyunsaturated fatty acids and saturated fatty acids. Instead of converting them via transesterification into biofuels, different lipids can be separated to produce added-value products such as omega-3 and glycerol before biodiesel production. The benefit of this approach is the larger economic value of the components as compared to biodiesel. The combined utilization of microalgae into added-value chemicals and fuels may be a cost-effective strategy (Stokes et al., 2020). The remaining parts of microalgae cells can been converted in to additional products such as biogas or fertilizer in the remnant treatment section (Galanopoulos et al., 2019).

3.6 Role of Process System Engineering (PSE)

In the design and operation of algae biorefineries the role of PSE has been increasing in the last years. Especially with regard to the identification and selection of appropriate process pathways from many alternatives to minimize feedstock, energy consumption capital, and operating expenditures environmental impacts. Life cycle assessment and techno-economic assessment are employed as two systematic PSE approaches. Often the first step in the economic- environmental evaluation of process pathways is by developing a superstructure. Figure 2 is the proposed superstructure for nine algae biorefinery steps to produce omega-3, glycerol, biogas, biodiesel, carotenoids, fertilizer. Each block is related to one technology described in the previous sections. The next step is converting this superstructure to a mathematical model as a mixed integer non-linear program (MINLP). The MINLP comprises mass- and energy balances, economic equations and logical constraints. Zondervan et al. (2011) proposed an MINLP model of a biorefinery, considering 72 process options.

Various optimization strategies to solve MINLPs are now in use. Luus and Jaakola (1973) applied a direct search or adaptive random search as solution method. Holaysan et al. (2015) modified this random search procedure by a line-up competition algorithm to design an integrated algal bioenergy system.

The PSE community has a set of tools for advanced decision-making that aids in the design and operation of the algae biorefinery. However, some challenges for establishing algal biorefineries are available such as lack of physical/chemical information, insufficiency of the numerical method, rare of actual data for comparison (Wu and Chang, 2019). With the PSE approach, microalgae provide nearly limitless opportunities for establishing a contemporary bioeconomy.

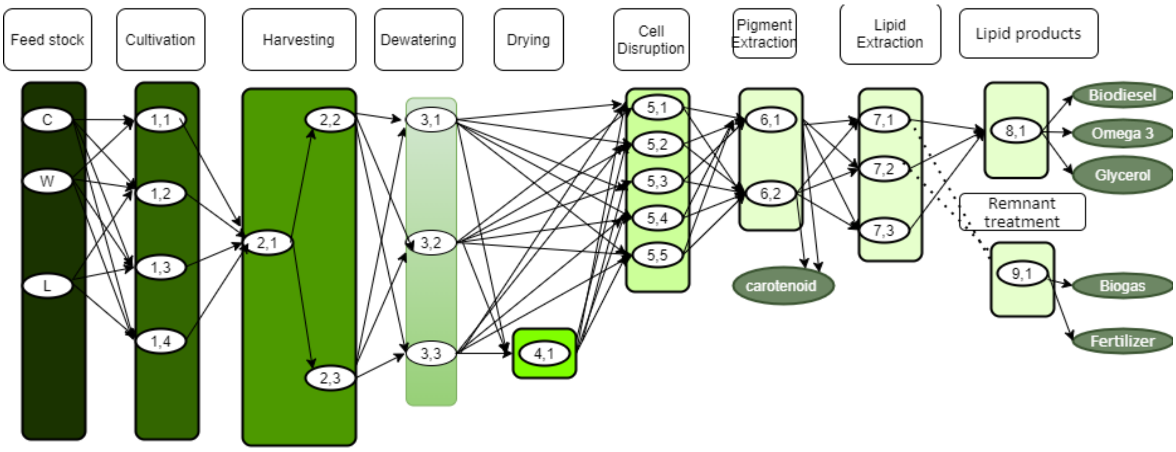

Figure 2: microalgae superstructure(c: carbon dioxide; w: wastewater; L: light; 1,1: open pond; 1,2: flat plate photobioreactor; 1,3:turbo column photobioreactor; 1,4:bubble column photobioreactor; 2,1:gravity sedimentation; 2,2:flotation; 2,3:filteration; 3,1:flocculation; 3,2:centrifugation; 3,3:filter press; 4,1: dryer; 5,1: bead beating; 5,2: high pressure homogenization; 5,3: microwaving; 5,4: sonication; 5,5: hydrothermal liquefaction; 6,1: organic solvent based pigment extraction; 6,2: supercritical carbon dioxide pigment extraction; 7,1: hexane based lipid extraction; 7,2: n- butanol based lipid extraction; 7,3: supercritical carbon dioxide lipid extraction; 8,1: transesterification and purification; 9,1: anaerobic digestion and fertilizer)

4. Conclusions

Various bioproducts such as biogas, omega-3, fertilizer, and carotenoids should be extracted in addition to biodiesel to have an efficient microalgae biorefinery. Different technologies of each step of biorefinery (cultivation, dewatering, harvesting, cell disruption, and extraction) are techno-economically compared with each other. To develop technical and economical feasible production pathways, superstructure optimization is a promising tool for decision-making. The first steps to work superstructure optimization has been made to map feedstocks, technologies, and products.

References

Barros A.I., Gonçalves A.L., Simões M., Pires J.C.M., 2015, Harvesting techniques applied to microalgae: A review. Renewable and Sustainable Energy Reviews, 41, 1489–1500. DOI:10.1016/j.rser.2014.09.037

Bracharz F., Helmdach D., Aschenbrenner I., Funck N., Wibberg D., Winkler A., Bohnen F., Kalinowski J., Mehlmer N., Brück T.B., 2018, Harvest of the oleaginous microalgae scenedesmus obtusiusculus by flocculation from culture based on natural water sources. Frontiers in Bioengineering and Biotechnology, 6. DOI:10.3389/fbioe.2018.00200

Brennan L., Owende P., 2010, Biofuels from microalgae—A review of technologies for production, processing, and extractions of biofuels and co-products. Renewable and Sustainable Energy Reviews, 14, 557–577.

Chen C.L., Chang J.S., Lee D.J., 2015, Dewatering and Drying Methods for Microalgae. Drying Technology, 33, 443–454. DOI:10.1080/07373937.2014.997881

Davis R., Aden A., Pienkos P.T., 2011, Techno-economic analysis of autotrophic microalgae for fuel production. Applied Energy, 88, 3524–3531. DOI:10.1016/j.apenergy.2011.04.018

Dickinson S., Mientus M., Frey D., Amini-Hajibashi A., Ozturk S., Shaikh F., Sengupta D., El-Halwagi M.M., 2017, A review of biodiesel production from microalgae. Clean Technologies and Environmental Policy, 19, 637–668. DOI:10.1007/s10098-016-1309-6

Fernández-Linares L.C., Guerrero Barajas C., Durán Páramo E., Badillo Corona J.A., 2017, Assessment of Chlorella vulgaris and indigenous microalgae biomass with treated wastewater as growth culture medium. Bioresource Technology, 244, 400–406. DOI:10.1016/j.biortech.2017.07.141

Galanopoulos C., Kenkel P., Zondervan E., 2019, Superstructure optimization of an integrated algae biorefinery. Computers and Chemical Engineering, 130, 106530. DOI:10.1016/j.compchemeng.2019.106530

Gong J., You F., 2014, Optimal design and synthesis of algal biorefinery processes for biological carbon sequestration and utilization with zero direct greenhouse gas emissions: minlp model and global optimization algorithm. Industrial and Engineering Chemistry Research, 53, 1563–1579. DOI:10.1021/ie403459m

Gong J., You F., 2017, Optimal processing network design under uncertainty for producing fuels and value-added bioproducts from microalgae: Two-stage adaptive robust mixed integer fractional programming model and computationally efficient solution algorithm. AIChE Journal, 63, 582–600. DOI:10.1002/aic.15370

Coates P.M., Betz J.M., Blackman M.R., Cragg G.M., Levine M., Moss J., White J.D., 2010, Encyclopedia of dietary supplements, London: Informa Healthcare.

Holaysan S.A.K., Razon L.F., Tan R.R., 2015, Development of a modified luus-jaakola adaptive random search algorithm for design of integrated algal bioenergy system. Chemical Engineering Transaction, 45. DOI:10.3303/CET1545272

Hosseinizand H., Sokhansanj S., Lim C.J., 2018, Studying the drying mechanism of microalgae Chlorella vulgaris and the optimum drying temperature to preserve quality characteristics. Drying Technology, 36, 1049–1060. DOI:10.1080/07373937.2017.1369986

Kim J., Yoo G., Lee H., Lim J., Kim K., Kim C.W., Park M.S., Yang J.W., 2013, Methods of downstream processing for the production of biodiesel from microalgae. Biotechnology Advances, 31, 862–876. DOI:10.1016/j.biotechadv.2013.04.006

Laurens L.M.L., Van Wychen S., McAllister J.P., Arrowsmith S., Dempster T.A., McGowen J., Pienkos P.T., 2014, Strain, biochemistry, and cultivation-dependent measurement variability of algal biomass composition. Analytical Biochemistry, 452, 86–95. DOI:10.1016/j.ab.2014.02.009

Luus R., Jaakola T.H.I.,1973, Optimization by direct search and systematic reduction of the size of search region. AIChE Journal, 19, 760–766. DOI:10.1002/aic.690190413

Menegazzo M.L., Fonseca G.G., 2019, Biomass recovery and lipid extraction processes for microalgae biofuels production: A review. Renewable and Sustainable Energy Reviews, 107, 87–107. DOI:10.1016/j.rser.2019.01.064

Mezzomo N., Ferreira S.R.S., 2016, Carotenoids functionality, sources, and processing by supercritical technology: a review. Journal of Chemistry, 2016, 1–16. DOI:10.1155/2016/3164312

Mubarak M., Shaija A., Suchithra T.V., 2015, A review on the extraction of lipid from microalgae for biodiesel production. Algal Research, 7, 117–123. DOI:10.1016/j.algal.2014.10.008

Stokes J., Tu R., Peters M., Yadav G., Fabiano L.A., Seider W.D., 2020, Omega-3 fatty acids from algae produced biodiesel. Algal research, 15, 102047. DOI: 10.1016/j.algal.2020.102047

Pruvost J., 2019, Cultivation of algae in photobioreactors for biodiesel production. in biofuels: alternative feedstocks and conversion processes for the production of liquid and gaseous biofuels. Elsevier. DOI:10.1016/B978-0-12-816856-1.00026-9

Rizwan M., Lee J.H., Gani R.,2015, Optimal design of microalgae-based biorefinery: Economics, opportunities and challenges. Applied Energy, 150, 69–79. DOI:10.1016/j.apenergy.2015.04.018

Santhosh S., Dhandapani R., Hemalatha N., 2016, Bioactive compounds from microalgae and its different applications- a review. Advances in Applied Science Research, 7, 153–158.

Tan J. Sen Lee S.Y., Chew K.W., Lam M.K., Lim J.W., Ho S.H., Show P.L., 2020, A review on microalgae cultivation and harvesting, and their biomass extraction processing using ionic liquids. Bioengineered, 11, 116–129. DOI:10.1080/21655979.2020.1711626

Wu W., Chang J.S., 2019, Integrated algal biorefineries from process systems engineering aspects: A review. Bioresource Technology, 291, 121939. DOI:10.1016/j.biortech.2019.121939

Zondervan E., Nawaz M., de Haan A.B., Woodley J.M., Gani R.,2011, Optimal design of a multi-product biorefinery system. Computers and Chemical Engineering, 35, 1752–1766. DOI:10.1016/j.compchemeng.2011.01.042