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6 The role of bioprocess systems engineering in extracting chemicals and energy from microalgae

Abstract: In this study, the role of process systems engineering in enhancing the algae economy is highlighted. First, basic characteristics of the various strains of microalgae are presented. In addition, the beneficial extracted bioproducts and their applications are reviewed. Then, an overview of the various technologies available in each step of biorefinery to produce added-value products and biofuels from microalgae is provided. These technologies are compared in terms of required energy and efficiency. Different perspectives of the algae industry, from molecule to enterprises scale where process systems engineering can have a role, are addressed. Subsequently, the roles of process systems engineering in process and product design, process control, and supply chain of the algae biorefinery are discussed. It is found that process systems engineering can play an important role in the biobased economy, especially by applying sustainability and economic concepts in the decision-making process for selecting the best feedstock, processing pathways, and desired products. Tools such as market analysis, techno-economic analysis, life cycle assessment (LCA), and supply chain (SC) analysis can be applied to design sustainable algae biorefinery. There are, however, several challenges such as the lack of data, the complexity of optimization, and validation that should be addressed before using these tools.

Keywords: bioproduct; biorefinery; microalgae; process systems engineering.

6.1 Introduction

During World War II, medical emergencies prompted microalgae as a possible supply of protein and antibiotics. In the 1950s, the use of microalgae for the generation of hydrogen and methane began [1]. Later, the energy crises of the 1970s encouraged the use of this microorganism to generate renewable energy.

The Aquatic Species Initiative (ASP) was the first research and development program focused on producing biodiesel by microalgae. It was started in 1978 by the US

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National Renewable Energy Laboratory (NREL) and continued until 1996 [2]. However, Nihon pioneered the first large-scale cultivation of Chlorella species in the 1960s [3].

More recently, research has been conducted to use algae for treating wastewater and capturing carbon dioxide [4]. In addition, different studies have been done to design microalgae to produce essential products which have a crucial role in the global economy.

Although some progress has been made towards the medium to large-scale application of microalgae, the technical- and economic-feasibility is not comparable to the use of conventional raw materials and processes that are often fossil-based.

This study addresses the role of process systems engineering in different aspects of the algae industry. First, the essential factors of growth and the potential applications are discussed. Second, the potential bioproducts are described. The possible technologies for each step of algae biorefinery are listed and compared. Then, the procedures of process systems engineering to design and operate algae biorefineries efficiently are explained. The current process systems engineering methodologies implemented to enhance the algae industry are addressed. Finally, the challenges and limitations of these tools are highlighted.

6.2 Microalgae

Algae are marine creatures utilized as primary feedstocks of the third generation of biorefineries (first and second-generation biorefineries use other types of biomass such as sugar cane and animal fats, and lignocellulosic, respectively). They grow with the help of sunlight, water, carbon dioxide (CO_2), and nutrients like nitrogen and phosphorus in wastewater or seawater. They are either single-cell or multicellular. Some of them do not have any roots, stems, or leaves and no sterile protection around reproductive cells [5]. Depending on the size, they divide into microalgae and macroalgae [6]. Macroalgae are made up of several cells; conversely, microalgae are a diverse community of microscopic photosynthetic species, several of which are found in unicellular form and various environments. Since ancient times, coastal populations have used macroalgae for multiple purposes, including food, feed, medical treatment, and fertilizer.

Microalgae can be classified into prokaryotic cyanobacteria, which lack nuclear structures, and eukaryotic algae, which have nuclear structures [7]. Green algae, red algae, and diatoms are the three main types of eukaryotic alga [5]. With over 200,000 species of algae described, including 50,000 microalgae, these organisms have a greater diversity than all terrestrial plants [8].

Microalgae biomass has several advantages over plant-derived biomass [9–11]. Most significantly, microalgae do not need (fertile) land and can be grown in (waste) water. The most significant benefit of utilizing (waste)water is that it is readily available throughout the year and inexpensive [12]. In addition, microalgae can be used to capture CO_2. Typically, 1.83 kg of CO_2 is needed to produce 1 kg of microalgae biomass [13]. They transfer around 3.8% of absorbed solar energy during cellular metabolism, compared to 0.5% for terrestrial crops. Microalgae have higher photosynthetic productivity than plants in general. Microalgae can grow at a much higher rate and reproduce more consistently compared to plants. As compared to soybean (0.4 ton ha^{-1} y^{-1}), rapeseed (0.7 ton ha^{-1} y^{-1} [13]), microalgae-derived biomass is usually higher in lipids (4.5–7.5 ton ha^{-1} y^{-1} [14]). Another benefit of this microorganism is the short harvesting time (between 1 and 10 days depending on the process), which allows for multiple or continuous harvests [15].

6.2.1 Microalgae characteristics

Microalgae can develop in various environments, including autotrophic, heterotrophic, and mixotrophic. Depending on these, they use CO_2/organic culture medium and light/organic medium as carbon and energy sources, respectively [16, 17]. The autotrophic microalgae absorb energy from natural or artificial light and utilize photosynthesis to generate organic matter while bio-fixing CO_2. In heterotrophic cultivation, microalgae grow in a dark environment by using an external source of organic matter. Eventually, mixotrophic means that the microalgae use photosynthesis and other carbon sources during their lifetime [18]. Many microalgae strains with different characteristics are available in each category.

Since the cellular contents (compositions of lipids, proteins, pigments, etc.) and growth behaviors of different microalgae strains are diverse, it is critical to choose the right one depending on the application. For instance, carotenoids, free fatty acids, and proteins are abundant in Chlorella [8, 19]. Due to their high lipid content (14–63% of dry weight), they are also a promising source for biofuel processing. Therefore, specific

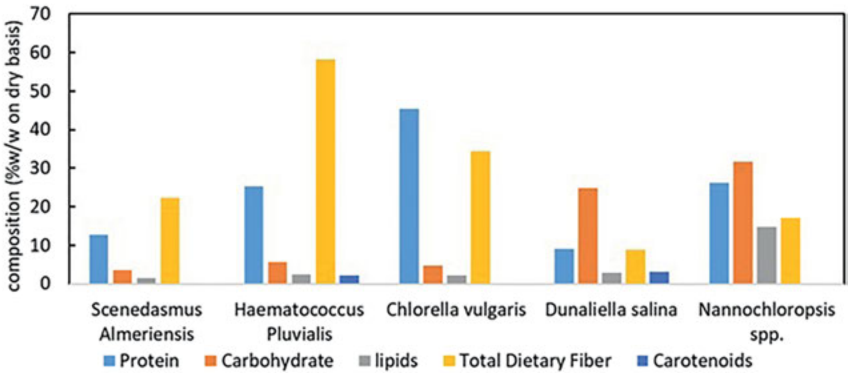

Figure 6.1: Compositions of different kinds of microalgae [21].

microalgae characteristics such as the concentration of lipid and other different added-value components, growth rate, optimal growth conditions, and scale-up capacity should be considered when applying them at industrial scales [20]. Figure 6.1 compares the composition of five kinds of microalgae.

6.2.2 Environmental conditions for microalgal biomass production

Some nutrients are essential for growing microalgae. They should be provided in smaller or larger quantities to the culture medium to ensure species development and higher biomolecule synthesis. Carbon, phosphorus, nitrogen, and micronutrients are essential nutrients for guaranteeing a minimum of microalgae growth conditions [17, 21]. One study estimated the required nutrients for 29 species. It was claimed that ratio C:N:P:S should be 132:18:1:0.99 [22].

Carbon is an essential nutrient for growing microalgae since it is a necessary component for forming all organic substances produced by the cell, such as proteins and carbohydrates. It can be delivered in salts (bicarbonate) or by infusing carbon dioxide. CO_2 must be solubilized before microalgae can use it for photosynthesis [23]. Also, nitrogen is an important building block for structural and operating proteins, second only to carbon because concentrations of carotenoids, proteins, and chlorophyll are related to these components. In addition, phosphorus plays an essential role in cellular metabolism. Pigment accumulation in certain microalgae may be caused by phosphorus deficiency, but the effect is less than that of nitrogen deficiency. Because of iron's role in the transport of electrons during photosynthesis, this component is an essential trace element for microalgae growth. Besides those, potassium, silica, sulfur, metals, and vitamins are needed to cultivate microalgae [24].

One of the most important physical factors affecting microalgae growth is temperature. It affects cell composition. As the temperature drops, the degree of lipid unsaturation increases and as the temperature rises, the pigment concentrations rise, but the concentration of oxygen radicals rises as well. If microalgae do not grow at their optimal temperature, the need for carbon and nutrients to maintain the same pace of growth becomes more critical [24, 25]. Furthermore, the cellular composition of microalgae is affected by light. Generally, the best temperature (between 20 and 30 centigrade) and the light irradiance (between 33 and 400 μ mol/m^2/s) are reported for different algae species [26–28]. Light intensity, temperature, nitrogen sources, minerals, pH, and salinity, in addition to the intrinsic ability of algal species, influence the concentration of lipid and proteins in the microalgae.

6.2.3 Significant compounds produced by microalgae

6.2.3.1 Carotenoids

Although more than 750 types of carotenoids have been already discovered; only a small number have been economically marketed, and the most prevalent are *β*-carotene, astaxanthin, and lycopene [29]. The primary benefit of employing microalgae as a source of carotenoids is their good influence on human health, as many other antioxidant chemicals are found in algal cells.

Astaxanthin, as one of the non-provitamin A carotenoids, has lately attracted interest due to its antioxidant properties. This component can scavenge free radicals, protects against cancer, and has been linked to inflammatory processes and diabetes [30]. The Chlorella, Chlamydomonas, Dunaliella, and Haematococcus spp. can produce more astaxanthin in comparison to other types of microalgae. For instance, Haematococcus spp. can collect xanthophylls outside the plastids in the cytoplasm [31, 32].

One of the non-provitamin A carotenoids that can be converted to retinol is *β*-Carotene. This vitamin has an important role in reducing the risk of macular degeneration [33]. Chlorella spp., Chlorella Ellipsodea, Coccomyxa Acidophila, Dunaliella Salina, and Scenedesmus Almeriensis are well-known microalgae that can produce these types of carotenoids [34].

Lycopene is a non-provitamin A carotenoid with a wide range of biological functions. Prevention of oxidative DNA damage, probable creation of carcinogen-metabolizing enzymes, decreasing risk for some malignancies, cancer prevention with inhibiting cancer growth, and certain cardiovascular events are all recognized some benefits of these added-value components [35].

6.2.3.2 Sterols

Some microalgae species have been utilized to promote the growth of oysters due to their high sterol content. Sterol levels are high in microalgae like Thalassiosira and Pavlova. Unusual sterols such as sitosterol, brassicasterol, campesterol, and stigmasterol are available in this microorganism. High cholesterol and LDL levels are well known to increase the risk of heart and coronary illnesses, which can be decreased by sterol [34].

6.2.3.3 Proteins and enzymes

Proteins are biopolymers of amino acids that cannot be made by the human body and are provided from external sources such as food. Proteins (smaller peptides and amino acids) have roles related to health and have nutritional advantages. Arthrospira and Chlorella are rich in protein and amino acid content, and they can be utilized as nutraceuticals or added to functional meals to help prevent tissue damage and disease [34].

6.2.3.4 Vitamins

The Haslea/Navicula ostrearia is exceptionally high in vitamin E in addition to marennine, a blue pigment that causes oysters to become green. The Porphyridium cruentum, another microalga, is high in vitamins C, E (tocopherols), and provitamin A (β-carotene). Dunaliella Salina also generates tocopherol, thiamine, nicotinic acid, pyridoxine, biotin, and riboflavin, in addition to β-carotene (provitamin A) [34].

6.2.3.5 Polyunsaturated fatty acids (PUFA)

The two most common polyunsaturated fatty acids are omega-3 and omega-6. These are designated essential fatty acids because they participate in building and maintaining cell membranes. Omega-3 (such as EPA and DHA) has been shown to lessen the risk of cardiovascular strokes and arthritis and decreases blood pressure. Omega-3 also helps reduce cholesterol levels by lowering triglycerides, increasing HDL levels, and acting as an anti-inflammatory agent [36].

Even though marine fish oil is the conventional source of both EPA and DHA, research suggests that algae can provide higher quantities of omega-3. The DHA is found in various species, including Schizochytrium, Crypthecodinium, and Thraustochytrium, and the EPA is discovered in Phaeodactylum, Chlorella, and Monodus [37].

6.2.3.6 Fertilizer

Fertilizer is another bioproduct from algae that can have an important role in the agricultural industries. Algae, in principle, contain the required nutrients for growing plants [38]. For example, dry biomass derived from Acutodesmus Dimorphus can be used as a biofertilizer and increased tomato plant growth [39]. In another study, Chlorella Vulgaris was used as a biofertilizer for growing lettuce plants. The results show that dry powder of microalgae might be employed as plant nutrients for optimal growth since they can increase soil fertility [40]. Furthermore, the effect of two microalgae (Spirulina Platensis and Chlorella Vulgaris) on the production of the maize crop was studied by Kumar et al. According to their findings, maize production and growth can be increased up to 51.1% 60 days after planting [41].

6.2.3.7 Fuels

Three fundamental fuels types can be delivered by microalgae: biomethane, biodiesel, and bioethanol. The simultaneous generation of different biofuels may decrease the cost of a single fuel [42]. In addition, to extract the lipids in biodiesel production, the residual algae biomass can be transferred to an anaerobic digestion plant to produce biomethane. Furthermore, carbohydrates and proteins that are not removed during the biodiesel production process might be utilized to make bioethanol.

Table 6.1 lists several added-value products from microalgae, their application, and the predicted annual global market value. As can be seen, the market of these added values is high enough to attract investors.

Table 6.1: Global market and application of some added value products extracted from microalgae.

Added value products	Application	Global market size (billion USD)
Astaxanthin	– Aging skin – Muscle soreness from exercise and athletic performance – Alzheimer disease	0.2 [44]
Lutein	– Eye diseases	0.23 [45]
B-Carotene	– Source of vitamin A	0.2 [44]
Chlorophyll	– Food industry (Color confectionery, gelatine, and drinks)	1 (Natural food collars markets) [46]
Phycobiliproteins	– Food industry – Pharmaceuticals and cosmetic industry [47]	0.05 [44]
Vitamins, minerals, and nutrition	– Food industry – Pharmaceuticals, cosmetic industry	82 [48]

6.3 Algae biorefinery

The term biorefinery has been utilized in the literature since the 1980s and alludes to the coproduction of a range of added-value products and bioenergy from biomass [43]. Many budgets are specified for various research projects to enhance algae biorefinery. For instance, the US Department of Energy issued a $100 million grant for three organizations to investigate algae biorefineries in December 2009 [44]. Or as an example, the University of Greenwich in the UK with 14 European partners, started one project named ‘D-factory’ in December 2013, which the European commission funded. Approximately 10 million euros were specified for this project to improve Dunaliella microalgae biorefinery [45].

The algal biorefinery approach offers a comprehensive methodology to various products, with the added benefit of using all algae components and creating numerous revenues [46]. Upstream and downstream processing are the two main phases of the microalgae biorefinery. The upstream process consists mainly of microalgae cultivation. Harvesting, extraction, and purification of bioproducts are considered downstream processes [47]. Figure 6.2 shows the overall concept of the algae biorefinery and the possible bioproducts. As can be seen, depending on the type of algae, various products can be extracted simultaneously.

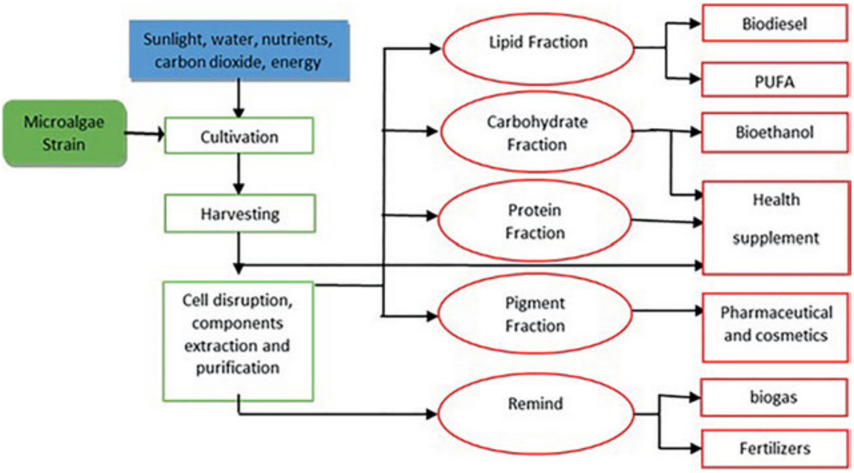

Figure 6.2: The microalgae biorefinery [47].

Cultivating microalgae for biofuels may not be economical, and the microalgal industry must take advantage of markets for added value items such as nutraceuticals and vitamins. The combined extraction of numerous added-value components from a single microalgal slurry with biodiesel moves the general sustainability of the system forward [48, 49].

6.4 Steps in the biorefinery

Various techniques can be employed at each step of the algae biorefinery (cultivation, harvesting, dewatering, cell disruption, drying, extraction, transesterification, and treatment) to produce added-value products and biofuels.

After growing microalgae in the cultivation step, they are concentrated in the following steps: harvesting, dewatering, and drying. The concentrated microalgae substance enters a cell disruption step to break the cell walls and facilitate the valuable components' extraction. Different techniques can be used to extract lipids, pigments, and proteins. The extracted components require further treatment to produce final products. These steps and current techniques of each of them are explained below.

6.4.1 Methods of algae cultivation

Microalgae can be grown at industrial scales in an outdoor or indoor system [13]. The raceway is an outdoor system, while the photobioreactor is an outdoor or indoor system. Although the investment cost of an outdoor system such as a raceway is not

Table 6.2: Comparison of raceway and photobioreactor [51].

Type of cultivation method	Advantages	Disadvantages
Raceway ponds	– Low energy requirements and capital costs – Dissipation of heat with evaporation	– High risk of contamination – Dependency of productivity on the location/environment of the pond – High water evaporation – Large land requirements – High upstream costs
Photobioreactor	– High surface ratio – Controlling growing conditions by adjusting temperature, pH, etc. – Implementing artificial light instead of sunlight – Low upstream cost	– High energy requirements and capital costs – Increase shear stress (flat plate photobioreactor) – Risk of carbon dioxide depletion and oxygen accumulation (tubular photobioreactor), variation of pH (tubular photobioreactor)

high, controlling operational conditions is difficult. Growing efficiency depends on the location and environmental conditions, including temperature and light. Another disadvantage of this type of cultivation system is the large area requirement with a low microalgae concentration [50]. The major advantages and disadvantages of the raceway and the photobioreactor are listed in Table 6.2 [51].

The flat plate photobioreactor, tubular photobioreactor, and bubble column photobioreactor are the three most common types of photobioreactor [52]. Due to high production rates and short harvest periods, the tubular photobioreactor is the most promising technology. It comprises a series of straight clear tubes, often composed of plastic or glass. To catch the most solar light energy, the tube arrays are positioned in various configurations (vertically, inclined, horizontally, or as a helix). The diameter of the solar collector tubes is less than 0.1 m to enable deep light penetration with the presence of thick cultured broth inside the tubes [53].

Although the flat photobioreactor is one of the earliest types of a closed system, it is widely used at a laboratory scale. It is made up of thin glass panels arranged horizontally or occasionally in an inclined orientation. This configuration makes it easier to quantify irradiance at the culture surface [52], but it is challenging to construct at industrial scales [54].

The bubble column photobioreactor is a hollow cylinder reactor made from glass. Due to the structure of the column (long optical paths), the dependence of yield of production on light penetration is very low. Furthermore, this structure increases surface area, allowing for the most algae growth compared to other types of photobioreactors [15].

6.4.2 Methods of separating microalgae biomass

Experimental results show that the algae concentration in the output flow of the cultivation step is typically between 0.1 and 3.0 g L^{-1} [55]. Separating water from the culture medium is necessary, but it accounts for 20–30% of the total production costs. For this reason, the types of technologies used for this purpose have significant effects on the economics of the process [56]. Harvesting/dewatering methods, e.g., gravity sedimentation, filtration, coagulation/flocculation, flotation, and centrifugation, are applied to increase the density of microalgae slurry. Drying methods such as spray drying, solar drying, greenhouse drying, and lyophilization are needed to obtain dried microalgae biomass.

Gravity sedimentation is a straightforward, cheap, and common technology for harvesting microalgae. However, this method also has disadvantages: it is time-consuming, has a high environmental temperature requirement [57], and only used for large algae cells such as spirulina [5].

In flocculation, microalgae cells are aggregated to form flocs, which cause them to settle faster. Although flocculants are needed, the energy requirement for this harvesting method is very low. A flocculating agent can be categorized into chemical flocculants, physical flocculants, and bio-flocculants [51]. A chemical flocculant consists of metal salts, polymers, and/or biopolymers. In electrocoagulation–flocculation, magnetic nanoparticles can be used as physical flocculation methods. In the bio-flocculation method, some microorganisms, such as bacteria with the capacity for autoflocculation are assisted in flocculating microalgae. The flocculation bacteria can proliferate by using the wastewater as a carbon source. Bio-flocculation is a safe and ecofriendly approach with more than 90% harvesting efficiency [58, 59].

Flotation is a process of utilizing air or gas bubbles to transfer the liquid–solid suspension to the surface. These bubbles are generated to aggregate microalgae cells on the surface to separate them from water [60]. Dissolved air flotation, electrolytic flotation, and dispersed flotation are the most common flotation technologies [59, 61]. Generally, the flotation method is very energy-intensive.

Centrifugation is another technique to dewater the algae biomass. A centrifugal force separates microalgae from the culture medium based on the density and size of the components [62]. Although the efficiency of this method is very high (more than 95%), it requires high operational costs and is very time-consuming [11, 63]. Two types of centrifugation are available: fixed wall (e.g., hydrocyclone) and rotary wall (e.g., tubular centrifuges, centrifugal decanters, and disc centrifuges) [61].

Large microalgae cells (>70 µm) can be separated from the cultivation medium by (semi)permeable membrane filtration [5]. The filtration method is prone to fouling and clogging. Thus, it has a high operating cost, and there is a need to replace and clean the filters frequently [56].

Table 6.3: Advantages and disadvantages of various types of dryers [7, 64].

Type of dryer	Advantages	Disadvantages
Freeze dryer	Gentle process	Cost intensive, slow process
Sun dryer	Low running costs and very low capital cost	Weather dependent, slow process
Drum dryer	Fast and efficient	Cost intensive
Spray dryer	Fast and efficient	Cost intensive
Crossflow dryer	Faster than sun dryer and cheaper than drum dryer	High electricity requirements
Vacuum shelf dryer	Gentle process	Cost intensive

Drying is an expensive and energy-intensive part of the biorefinery. Solar and wind dryers are the most economical approaches. However, they require large spaces, and their efficiency depends on environmental conditions such as airflow, temperature, and humidity. Besides natural dryers, many artificial dryers have been proposed for microalgae drying [64, 65]. The spray dryer is the most common one. Although it is costly, its energy and operational efficiency are high. Several advantages and disadvantages of the drying techniques are listed in Table 6.3. The appropriate type of dryer is chosen based on the scale of operation, energy and cost requirements, other downstream processes, and the kind of microalgae [64].

6.4.3 Methods of algae cell disruption

Cell disruption is another crucial step in the biorefinery before extracting pigment, lipid, or other components. An appropriate cell disruption method can reduce the costs for extraction significantly [66]. There are two methods for breaking down algae cell membranes: mechanical and nonmechanical [67]. The nonmechanical methods use enzymes, chemical breakdown, and osmotic shock. The most common mechanical methods are bead mill, ultrasonic, high-pressure homogenization, and microwave. Although the energy consumption for the mechanical methods is higher than the nonmechanical ones, the nonmechanical methods have several other advantages, such as being fast and monitorable for use at industrial scales [67, 68].

In bead milling, a rotating cylinder made of quarts or metal damages microalgae cells within less than minutes without any preparation. However, it must be noted that several factors (such as the shape/size of the cylinder and the stirring speed) affect this method's efficiency and energy consumption. Because this is a high-speed technique with a simple setup, it is often used to extract lipids from microalgae at a large scale [61].

Ultrasonication combines two mechanisms to break the cell walls: cavitation and wave propagation. High energies are needed in this method due to the cooling and power of ultrasound. To have effective cell disruption, the frequency should be in the range of 18–40 kHz or 400–800 kHz. Due to heat dissipation, the temperature should be controlled [61, 67].

High-pressure homogenization is a scalable and straightforward method to disrupt microalgae cells. In this method, the cell is driven through a tiny orifice where mechanical forces such as turbulence, cavitation, and shear stress induce cell lysis. This method's efficiency varies and is directly linked to the type of microalgae [69, 70]. The downsides of this method include long processing times, a substantial amount of cell debris that might create a problem for extraction, and the high energy requirement [51].

In the microwave method, electromagnetic radiation waves (between 0.3 and 300 GHz) break microalgae cells by inducing the interaction of heat and molecules [71]. However, the high temperature could create problems for the biodegradable components in the algae, such as lipid and fatty acids. Another disadvantage of this method is the very high energy requirement on a large scale. Although the microwave method has short extraction times, it might require solvents [72, 73].

Furthermore, solvents, salts, surfactants, nanoparticles, and acids may break the microalgae cell chemically. The efficiency, suitability, and selectivity of these chemical materials strongly depend on the cell wall structure and types of microalgae [67]. Although chemical materials must be used continuously to disrupt the cell, the heat and energy requirements are low compared to mechanical methods.

The osmotic shack is considered a nonmechanical method to disrupt the microalgae cell. In this method, the osmotic pressure balance between the interior and exterior of the cell is disturbed by changing the suspension salt concentration. To damage the cell, two technologies, hyperosmotic or hypo-osmotic stress, increasing or decreasing the concentration of salt outside of the cell, respectively, can be utilized. Although low-cost chemical salts, e.g., sodium chloride and sorbitol, are used in these approaches, a large amount of water is needed for dilution [61].

In addition, biological techniques incorporating suitable lysis enzymes (such as lipase, protease, and cellulase) or algicidal treatment, including bacteria, viruses, and cyanobacteria, can be used to disrupt microalgae cell walls. The biological selectivity, mild operating conditions, and low energy requirements are the main advantages of this technique. However, several challenges exist and prevent large-scale implementation, such as long processing times and the high cost of enzymes [74].

6.4.4 Methods of extraction

An appropriate extraction method would be more selective in extracting certain microalgae components while minimizing contaminants in co-extraction. Extraction of biochemicals has been done in a variety of ways. To extract bio components, two approaches are common: organic solvent extraction and supercritical solvent extraction (e.g., supercritical CO_2).

6.4.4.1 Supercritical solvent extraction

Supercritical fluid (such as CO_2) extraction is a new green technology that has received considerable interest and increased popularity in recent years due to the possibility of replacing highly toxic organic solvents. A supercritical fluid appears to be a suitable extraction solvent for extraction bio components due to high selectivity while it has both gas and liquid properties. In addition, further treatment is not needed after extraction [72]. Carbon dioxide waste from industry might be utilized under supercritical circumstances, saving money and being better for the environment [75]. The main drawback of this technique (compared to organic solvent methods) is that it requires a lot of energy [76].

Lipids of microalgae can be extracted by supercritical carbon dioxide. After extraction, CO_2 evaporates into the atmosphere, and the extracted lipids are precipitated. The performance of this technique depends on the type of microalgae, duration of extraction times, temperature, and pressure of the process. For instance, one study showed that increasing the pressures of supercritical fluids enhances the amount of lipids extracted from Chlorella Vulgaris [77].

Goto et al. considered extraction of astaxanthin from Haematococcus Pluvialis with supercritical CO_2 and ethanol as entrainer under different pressure conditions. The addition of ethanol, which increased the solubility of components in supercritical CO_2, resulted in a considerable improvement in extraction efficiency. Approximately 80% of astaxanthin can be extracted using 5% (v/v) of ethanol under 40 MPa and 40 °C. Although acetone can also be used as an entrainer, ethanol is preferable due to its lower toxicity [78].

6.4.4.2 Organic solvent extraction

Organic solvents can also extract bicomponent such as β-carotene, astaxanthin, and lipids. Hexane, butanol, chloroform, acetone, and methanol are the most common solvents to extract different lipids. The polarity of the solvents defines the types of extracted lipid. For instance, hexane can extract hydrocarbons and triacylglycerols. Due to that, a mixture of solvents (for example, a combination of chloroform, methanol, and water or a mixture of chloroform and methanol) is proposed to extract all lipids classes [61].

The extraction of carotenoids from microalgae has recently been studied using many green solvents such as ethanol and a mixture of organic solvents [79]. Damergi et al. considered carotenoid extraction with ethanol and 2-methyl tetrahydrofuran (MTHF) solvents. 45 and 66% of the total carotenoids can be extracted using pure MTHF and a mixture of ethanol and MTHF (1:1), respectively [80].

The resultant extraction process is a combination of solvents, residual water, biocomponents (lipid, pigment, etc.), and cell debris. A solid–liquid or liquid–liquid separation process is implemented to separate the components in this mixture from each other. Subsequently, some lipids such as triacylglycerol, free fatty acids, and phospholipids can be converted into biodiesel by transesterification reactions [75]. Furthermore, other processes such as liquid–liquid extraction can be utilized to separate omega-3 (methyl eicosapentaenoic acid and methyl docosahexaenoic acid) from biodiesel [81]. Finally, the cell debris is sent to anaerobic digestion to produce biomethane and fertilizers.

6.5 Role of process system engineering

Algae biorefinery, as a burgeoning industry, must be designed and operated effectively and efficiently to survive in today's highly competitive environment. Process systems engineering combines science with engineering to provide the required method that allows this industry to prosper [82]. It offers a molecule to enterprise systems view for the decision-making over the entire algae value chain [83]. In this field, molecular and microscopic (e.g., microalgae cell) discoveries are tied to strategies and logistics for manufacturing and production [82]. Optimizing each element of this chemical supply chain (molecule, process units, plant, supply chain, etc.) is essential. Process systems engineering methodologies and technologies provide the necessary means to produce integrated solutions near the global optimum [84]. Different aspects of the algae industry where process systems engineering can play a role in are shown in Figure 6.3.

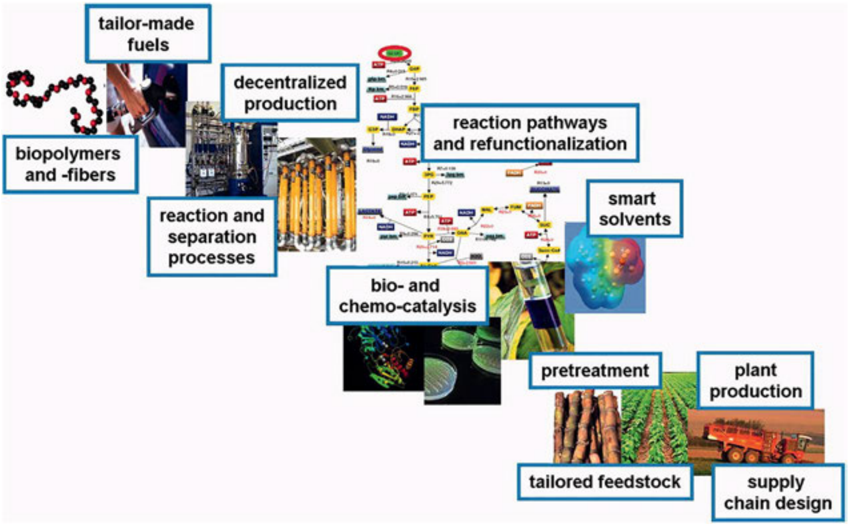

Figure 6.3: Set of interacting systems problems: from biorenewables production to novel generated molecular products (90).

The extensive dependencies between cell composition of microalgae, its pretreatment, processing pathway into target bioproduct, and end bioproduct structure-property relationships necessitate a comprehensive approach [84]. Microalgae cell compositions depend on the selected microalgae strain and cultivation condition (e.g., pH, temperature, etc.). The composition of the cell also depends on the duration of cultivation. It is possible to manage the quality of algae biomass within the ecological restrictions to perfectly fit the valorization process. Optimizing cultivation land area and operation conditions and maximizing usage of carbon dioxide are some issues that can be solved with process systems engineering.

Process systems engineering interlinks decision-making at the molecular level to the process and/or product synthesis and design level. Knowledge-based or heuristics approach can be used as a technique for this purpose [85, 86]. The process synthesis and design trend is to develop computationally efficient models based on mathematical programming for each unit operation to improve efficiency. In product synthesis and design, the current focus is on selecting suitable solvents for various chemical reactions [87].

In addition, process systems engineering supports identifying optimal process configurations, thus contributing to the development of novel process intensification technologies. Process intensification dramatically reduces the energy consumption and processing costs of chemical processes by taking advantage of multiple multifunctional phenomena at different spatial and temporal scales and improving transfer (momentum, mass, and heat) rates. Thus, the configuration and size of different equipments of the process can be optimized by this approach [88].

Process control, as an integral part of process system engineering, traditionally has been limited to regulating key variables (around certain predetermined operating conditions or trajectories) to ensure that products of the required specifications are produced in the presence of disruptions and design errors. With the expansion of its scope, it now deals with economic issues, such as reducing energy consumption and enhancing productivity. It is important to simultaneously think about regulation and economic optimization since this tends to drive the process operation towards an intersection of constraints where precise control is essential for success [82, 87].

Optimization of supply chain and planning is another area where process systems engineering has an important role. To remain competitive, algae biorefinery must now optimize operations across the entire supply chain. Supply chain performance has been improved greatly due to globalization and modern telecommunication technology [89]. Furthermore, supply chain optimization provides various academic research opportunities through industrial needs and fosters and strengthens many industry-academia collaborations since it has strong industrial relevance [90]. For example, the supply chain of algae biorefinery under uncertainty can be studied with the best–worst method (BWM) and mathematical model. In addition, robust optimization is a field of interest that can be used to map uncertainty in demand. In addition, multi-objective optimization aids decision-makers in realizing the trade-off between benefits and investment [85].

Different process systems engineering tools can be applied to design a sustainable algae biorefinery. These tools include market analysis, techno-economic analysis, life cycle assessment (LCA), and supply chain (SC) analysis. They are used to analyze the performance of algae biorefinery from economic, social, and environmental aspects [91].

The market analysis consists of two steps. First, depending on the company's competitive position (e.g., financial status), the possible markets in its area, access to feedstock, current processes, and SC assets, lists of potential bioproducts, processes, and partners are developed. In the second step, these products are ranked with SWOT (strengths, weaknesses, opportunities, and threats) approaches. The ranked products are the result of an analysis study that can be evaluated with other tools such as techno-economic analysis and LCA [91, 92].

The techno-economic analysis considers all possible technologies that can be implemented in algae biorefinery steps to produce targeted bioproducts. Different production pathways are presented by defining various technology options for each step of the biorefinery. These technologies are gathered in a superstructure. The superstructure is optimized based on multiple objectives to propose an appropriate production pathway. The superstructure is a graphical representation of all possible processing pathways and is converted to a mathematical model and solved with the appropriate software (often as a mixed-integer (non) linear programming problem). Pinch analysis can be used to look into possible ways to integrate the biorefinery process into the current company process and consider the effection of process options [91–93].

An LCA can be conducted on the production pathways and related products to assess their environmental impacts. First of all, functional units and system boundaries of the case study are defined based on the goal and scope. Then, the mass and energy quantities of the case study convert to different impact categories such as local, regional, global, etc.; named life cycle impact assessment (LCIA). It is performed by translating the life cycle inventory to environmental impacts. Finally, the results of the environmental impacts on the case study for different criteria such as greenhouse gas emissions are determined for further multi-criteria decision-making [91, 92].

SC analysis considers the price and demand volatility of feedstocks and products and evaluates SC profitability under various market scenarios. The SC indicators have been created to quantify the SC's resilience and adaptability in the face of market volatility in a dynamic market. Robustness metric is calculated to measure each case's resilience under uncertain market conditions. The parameter determines how far the downside profits deviate from the base case profit. Furthermore, flexibility metric was employed to demonstrate how much the production volume deviates from the nominal production rate [91].

Process systems engineering will face different challenges when using these tools for developing and designing commercial-scale algae biorefinery. First, the sustainable design depends on choosing an appropriate feedstock, a product portfolio, a location, and scale, which are all affected by government policies, environmental conditions, and the current market situation. Second, many physical and chemical data are needed to design and simulate the process of algae to bioproduct/biofuel. Due to the varying composition of algae and the complex structure, these data are not available completely and sufficiently. Some of these data should be reported by researchers in other filed (e.g., agriculture); this makes process systems engineering a multidisciplinary field. Third, actual operation data of algae biorefinery are not available due to few available industrial scales of algae biorefinery. Thus, validating the algae biorefinery model/simulation encounters many barriers. Furthermore, numerical methods are needed to optimize algae biorefinery superstructure. Solving these complex models is another critical challenge [92, 93].

6.6 Conclusions

Microalgae are a rich source of added-value components such as pigments and lipids (e.g., omega-3 polyunsaturated fatty acids), with significant health advantages. To extract these bio components, microalgae should pass various steps of algae biorefinery. Different technologies, including raceway, photobioreactor (cultivation), flocculation, centrifugation (harvesting/dewatering), spray dryer (drying), cell mechanical and nonmechanical methods of cell disruption, and green and organic solvent extraction can be implemented. These technologies are compared from different perspectives, such as economics and energy.

To improve the algae industry, process systems engineering considers molecule to enterprise systems view for the decision-making over the entire algae value chain. Different aspects are investigated in this consideration, such as algae cell composition, supply chain design, the performance of technologies, etc. Various process systems engineering tools such as market analysis, techno-economic analysis, LCA, and SC analysis can be applied. Finally, developing sustainable algae biorefinery can be achieved by process control, process operation, supply chain, and product and process design.

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