CHAPTER

11

Towards a greener future: biorefinery approaches for sustainable algae-based products

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11.1 Introduction

Macroalgae can convert solar energy into chemical forms through photosynthesis. They also are capable of producing economically-valuable compounds like nutraceuticals, biofertilizers, and bioenergy, assisting in wastewater treatment, nitrogen-fixing, as well as wastewater treatment, nitrogen-fixing, and CO_2 mitigation, respectively. They were used as feedstock for renewable biofuel production, including bioelectricity, methane produced by anaerobic digestion of the algal biomass, bioethanol, biohydrogen produced under aerobic conditions, and biodiesel derived from microalgae oil (Fernandes et al., 2019). The valorization of all biomass and coproducts of other compounds for the feed, food, cosmetic, and medical industries is desirable. Interest in macroalgae biorefinery can solve environmental and economic drawbacks. Reviews on the ability of macroalgae as biorefinery feedstock are available and focused on current trends, conversion pathways, economic considerations, the challenge of large-scale production, and the role of seaweed biorefineries in sustainable bioeconomy (Álvarez-Viñas et al., 2019). Over the last

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years, there has been a growing demand for natural antioxidants, synthetic molecules in food and pharmaceuticals. Marine macroalgae, which include chemical structures, are used to produce functional foods. The use of marine macroalgae in food products accounts for approximately 83%–90% of the current global value. However, they play a key role in generating both energy and valuable bioproducts (Filote et al., 2021). Macroalgae contain varying levels of nutrients depending on species, season of harvest, geographic origin, and environmental conditions. The protein and essential amino acid content can be rather low and variable, especially in brown macroalgae, when considered against the amino acid requirement of most aquacultural and terrestrial animal species. The challenges of using macroalgae in animal feed include the high content of recalcitrant polysaccharide components such as alginates, which are not digested to any extent by monogastric animal species. This reduces the nutritionally available energy content of macroalgae and most algae-derived products. In the early 2000s, the complex carbohydrates in macroalgae were recognized as having a prebiotic effect when used at low levels to supplement animal diets. Marine macroalgae are rich in bioactive compounds that can be converted to a variety of secondary metabolites with a broad spectrum of biological activities (Øverland et al., 2019). On the basis of recent development on algae cultivation, they are not limited to only photoautotrophic cultivation mode, under which they only can utilize inorganic carbon (CO_2) and not to organic carbon to enhance their growth using dual pathway photosynthesis and oxidative phosphorylation. Thus a new cultivation strategy of microalgae has to grow as it is very important to remove the economic constraints and their effective exploitation for obtaining higher biomass. Moreover, another advantage is that algae is the most promising in carbon capture and utilization (CCU) technology. They are used for increased CO_2 mitigation rates mainly due to their higher productivity than any other plant. These attributes along with the mixotrophic cultivation mode can greatly reduce challenges that are related with their biomass harvesting, self life extension, and constrained industrial viability. Recent advances in macroalgae research could be helpful toward the exploitation of high throughput screening techniques to sort out potential strains, especially desirable, high-yielding products for health applications (Patel et al., 2021). Nowadays, we have to focus on waste-free techniques, as a sustainable bioeconomy and a suitable production system would create these. Biorefinery is the best way to decrease negative impacts on the environment and create products with higher added value to get more economical and environmental benefits (Balina et al., 2017). The chapter discusses the baseline for the biorefinery concept with the utilization of marine macroalgae that evaluates the significant synergies identified among commercial actors, stakeholders, and private investors. Moreover it is the

identification of prerequisites for better available of valuable biorefinery feedstocks within bioeconomy extensive outlook. This would play a vital role in targeting the low-carbon economy, higher sustainability, and optimal bioresource. Thus deals with the production of biorefinery biofuels through the marine macroalgae and describes the innovation in the techniques and the advances regarding an integrated approach are also highlighted (Balina et al., 2017; Filote et al., 2021; Linares et al., 2017).

11.2 Role of marine macro/microalgae in biorefineries

The concept of biorefinery deals with the network of facilities that integrates biomass conversion processes and equipment to produce transportation fuels, electricity, and chemicals from biomass. On the other hand, bio-refineries are used for the utilization of affordable and sustainable raw materials, some of which would otherwise be discarded as waste. A biorefinery, ideally, can valorize all types of biomass—such as wood, agricultural crops, organic waste, industrial and domestic wastes, and aquatic biomass (Linares et al., 2017). Seaweed biorefineries adhere to the norms of sustainable development, bioeconomy key principles, mainly food security, clean energy and technologies, economic growth, resource use efficiency, responsible consumption and production, and climate action (Álvarez-Viñas et al., 2019).

In the past decade, seaweeds—red, green, and brown—have attracted a lot of interest, as raw material inputs to biorefineries. Red seaweed with its higher protein content, vis-a-vis their brown and green cousins, dominates with 61% of the total global seaweed production, and are source for the extraction of agar and carrageenan, inter alia (Álvarez-Viñas et al., 2019). In Asian countries, most of the seaweed is cultivated in algacultural facilities, set up specifically for the purpose of catering to market demands (Álvarez-Viñas et al., 2019; Filote et al., 2021). Green seaweed has higher growth rates when compared to terrestrial crops, and is tolerant to temvariations in marine environments. They have unique SPs that design the chemical composition of green seaweed biomass and the nutritive value derived from high-soluble dietary fiber, high-quality proteins, and higher free radical scavenging properties than terrestrial crops. This abilities shows that green seaweed is the most alternative biorefinery feedstocks (Zollmann et al., 2019). The mineral content is higher in seaweed than in terrestrial plants and animal products. High mineral content and low fat content represent a suitable feedstock for food and feed. Polysaccharides found in seaweed make them attractive for the food and pharmaceutical sectors. Fucoidans and laminarin found in brown algae show various biological activities with health benefits (Balina et al., 2017).

The main objectives of biorefineries (Aristizábal-Marulanda & Cardona Alzate, 2019), can be listed hereunder.

Biorefineries have been classified in different ways. According to the reference, the classifications are:

1. Systems or models.
2. Status of technological implementation.
3. Size.
4. Feedstocks, platforms, processes, and products.

Biorefinery is not a new concept because industries such as sugar, starch, and pulp uses technologies which is similar to biorefinery approaches. There are economic and environmental factors that guides the development of the concept of biorefinery.

11.3 Taxonomy and composition

11.3.1 Marine macro/microalgae: types and biochemistry

Algae is also known as the polyphyletic group of organisms which means they do not have the same origin, but are multiple which include both unicellular and multicellular as well as prokaryotes and eukaryotes, which can capture light energy. The idea of using macroalgae for biofuel production is not new and it was already developed in the year 1940s–1950s. In 1970s the large scale production of macroalgae has been done for producing liquid fuels (Linares et al., 2017). Marine macroalgae represent a group of multicellular organisms with 1549 species which is identified in Europe. The macroalgae have common cellulosic cell wall and their structure represents with *chlorophyll a*, each have the presences of pigments that give different colors with specific group names. It is very important to consider the development of marine macroalgae biorefinery based on the algal feedstock. The cultivation and harvesting of macroalgae is the most expensive and energy-consuming process (Filote et al., 2021). Macroalgae is also a protein source that depends on the yields and functional properties. Macroalgae as a food protein shows the individuality of the algae proteins that censoriously depend on the extracted protein yields. It is important to maintain the protein functions to achieve nutraceutical, pharmaceutical, and cosmeceutical properties. The challenges faced during the extraction process are the complex, adhering, and often charged macroalgae cell wall with the extracellular matrix, to overcome we need proper biorefinery designs. Osmotic shock, mechanical grinding, high shear force, ultrasonic treatment, acid and alkaline pretreatment, and polysaccharide-aided digestion and their combinations have been used to increase the extraction yields which involves mostly in chemical

procedures, which would literally affects the functions of proteins and peptides (Polikovsky et al., 2016). There are several factors of macroalgae, which make them engaging feedstock for food ingredients, biofuels, and industrial chemicals. First, they grow faster than terrestrial plants. Second, usually macroalgae do not occupy arable land and also do not consume fresh water, thus they do not compete with traditional food agriculture. Third, normally macroalgae does not contain lignin, eliminating the energy-intensive lignin removal step in pretreatment processes (Lehahn et al., 2016). Macroalgae can also perform as a sustainable aquafeed ingredient. Like terrestrial plants, the macroalgae is highly variable between divisions, genus, and species which describes its nutritional compositions. Seasonality and geographic locality can also play an important role in the nutritional composition (Wan et al., 2019). The production of marine macroalgae accounts for nearly 30% of global aquaculture production, with an output around 30 million tons per year that is worth more than $6 billion. Nearly 90% of all cultivated seaweeds are produced in China and Indonesia. Macroalgae targets on the high-value applications, recent developments have revealed the bioremediation capacity of both seaweeds and freshwater macroalgae and their sources are nutrient-rich waste water from agriculture, aquaculture, municipal wastewater treatment, and power generation (Hua et al., 2019). Aside from the potential use for biorefinery, macroalgae is a good source of protein and bioactive compounds. Thus contains inorganic nonprotein which includes nitrogen, ammonia, and nitrite (Fernandes et al., 2019; Øverland et al., 2019). The protein content in macroalgae reported different studies that there can be difficult in owing to methodological properties and for estimating protein, spectroscopy methods are often used. But many proteins from macroalgae is difficult to extract and contain colored substance and specifically for this reason the analysis of nitrogen and the conversion of nitrogen to protein is recommended (Øverland et al., 2019). Protein content is variable and have the highest contents which are generally found in green and red seaweeds in comparison to brown seaweeds. Phospholipids and glycolipids are the major classes of lipids found in seaweeds, which occupy about 1%–5% of cell composition (Rodrigues et al., 2015). Macroalgae in mesophotic coral ecosystems are generally understudied compared to corals and fishes yet may be more abundant than coral-dominated reefs given their lower depth limits and ability to grow over soft and hard bottom habitats. Mesophotic macroalgae are important as habitat and performs as seedbanks for environmental stress. Abiotic factors influences the abundance and distribution of mesophotic macroalgae that include temperature, water clarity, nutrients, and currents. In general, threats include rhodolith mining, oil spills, sedimentation, ocean acidification, invasive species, bottom trawling, and eutrophication (Spalding et al., 2019). Macroalgae are commonly described from intertidal and shallow subtidal

marine environments, but are less well known from mesophotic environments given the technical difficulties of accessing depths greater than 30 m (Spalding et al., 2019). It is noted that the composition of macroalgae of the same species can also differ. Local conditions at the collection site, such as light, salinity, nutrients, temperature, pollution, and water motion, can considerably influence the metabolite levels and bioactive compound contents (Gordalina et al., 2021).

11.4 Cultivation strategy

The growth characteristics and configuration of macroalgae are known to notably depend on the cultivation strategies (Chen et al., 2011). Two types of cultivation systems are widely executed for the cultivation of microalgae namely raceway pond and photobioreactor. In order to generate maximal biomass, outdoor cultivation system involve open or closed raceway pond, laboratory scale cultivation using photobioreactor should be developed. There are other different cultivation where organic and inorganic carbon sources used. Organic carbon sources like glucose, glycerol, sodium acetate, and sucrose and inorganic carbon sources like CO_2, bicarbonates, etc., for high productivity (Kumar et al., 2021). Most domestic wastewater also contains organic carbon, nitrogen, phosphorus, and other compounds, which makes them suitable for micro/macroalgae cultivation. Wastewater is capable of offering possible conditions for bacterial growth and decomposition of organic matter by oxygenation yet, bacteria are less efficient in the removal of inorganic nutrients such as phosphorus, which is usually the main cause of eutrophication of freshwater ecosystems (Kumar et al., 2021). Three different types of wastewater are used for macroalgal growth and which are the primary wastewater, secondary wastewater and the centrate wastewater also it plays as a supporting information. During the production period the wastewater are sampled and tested in order to remove the undesirable particulate matter (Ge & Champagne, 2017). Macroalgae have the ability to synthesis the biodiesel under suitable conditions for that it includes number of factors like temperature, nutrients, pH, and the microbial elements. The cultivation strategy using wastewater or gases is displayed in Fig. 11.1.

11.4.1 Photobioreactors

It refers to a cultivation system which is designed for growing photoautotrophic organisms using artificial light or solar light inorder to facilitate photosynthesis. They are mostly used in microalgae, macroalgae, cyanobacteria, and some mosses. Photosynthesis represents a unique process of

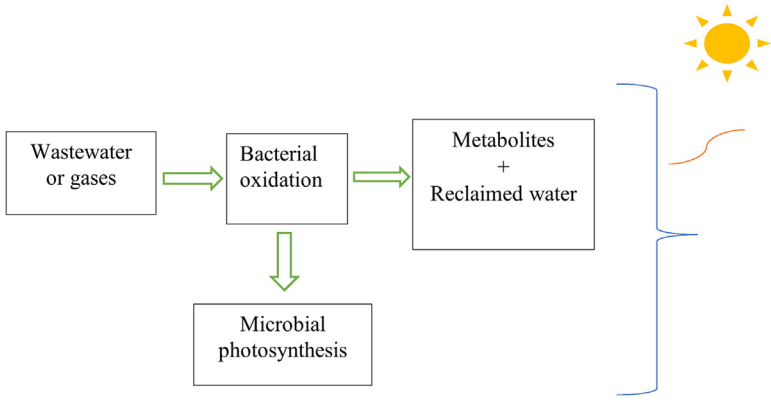


FIGURE 11.1 Cultivation process based on the wastewater treatment.

sunlight energy conversion. In this process, inorganic compounds and light energy are converted to organic matter by photoautotrophs (Lee et al., 2013). Microalgae biomass production performance is often limited by the light energy supplied and the cell concentration. Hence, various photobioreactors have been constructed and designed to improve light supply and microalgae biomass production performance (Chen et al., 2011). These bioreactors lose less water by evaporation and CO_2 into the atmosphere.

They can have different configurations:

1. Vertical column reactors (bubble columns or air-lift).
2. Tubular reactors.
3. Flat-plate reactors.

Open ponds are the most applied to cultures at commercial scale as it presents low capital and operating costs. On the other hand, closed system can have high biomass productivity due to there better controlling system (Pires et al., 2017). The performance of these outdoor open pond photobioreactors is usually poor, due to its difficult in controlling the culture conditions, direct exposure to UV irradiation, contamination, low light intensity and uneven distribution, day–night cycles, and the need for a large area of land (Chen et al., 2011). The bioprocessing of macro-microalgae for the biofuel production is depicted in Fig. 11.2.

Algal biodiesel is produced using a transesterification process, transforming triglycerides into methyl esters and glycerol using alcohol and a catalyst. Biodiesel production from algae is based on their rich lipid content, and micro-macroalgal biofuels are economically attractive (Kumar et al., 2021). Suppose the right microalgae species are chosen, and the growing circumstances suit the task. In that case, micro-macroalgae-based biorefineries enable the continuous production of microalgae biomass enriched in a specific macromolecule and high-added and low-value

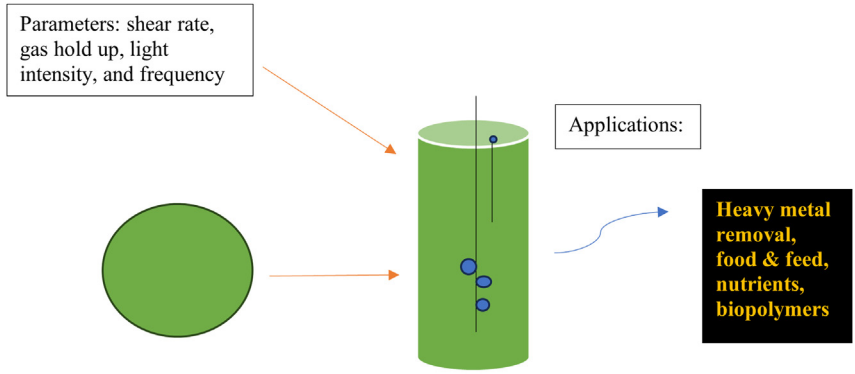


FIGURE 11.2 Shows the involvement of bioprocess in the production of biofuel using micro- macroalgae.

TABLE 11.1 Pigments and bioactivities: extraction methods.

Characters	Red algae	Brown algae	Green algae
Pigment	Phycoerythrin + Phycocyanin	Xanthophyll pigment fucoxanthin	Chlorophyll
Cell wall	Cellulose + Pectin + Phycocolloids + Calcium carbonate	Cellulose + Algin	Cellulose
Proteins	10%–47%	3%–15%	9%–26%
Carb	30%–60%	30%–50%	25%–50%
Storage	Floridean starch as stored food	Mannitol as stored food	Excess energy as starch

products (Olguín et al., 2022). Organic compounds are transformed into biofuels by the microbiological processes of anaerobic fermentation and by thermochemical processes of pyrolysis. When organic matter is heated without oxygen, the process is called pyrolysis (Suutari et al., 2015).

11.4.2 Pigments and bioactivities: extraction methods

The different pigments and their extraction methods are shown in Table 11.1.

11.4.3 Chemical composition

11.4.3.1 Under seasonal conditions

The chemical composition of different algae is shown in Table 11.2.

TABLE 11.2 Chemical composition of different algae.

	Energy	Protein	Carbon	Nitrogen
Corallina pilulifera	S	=	W	S
Hapalospongidlon gelatinosum	W	W	W	=
Hildenbrandia rubra	S	S	W	=

"W" represents that the component is more abundant during the winter, "S" represents the component more abundant during the summer, and " = " represents no quantitative difference between the seasons (Kaehler & Kennish, 1996).

TABLE 11.3 Parameters of mannitol.

Characters	Mannitol
Concentration range	1.50–50.00
Chlorophyta	34.80
Slope	0.0363
Rhodophyta	34.70
Correlation coefficient	0.9919

Values are expressed as mean distribution (Pereira et al., 2011).

TABLE 11.4 Lipid content of macroalgae species.

Species	Total lipid
Chondrus ocellatus (RA)	13
Analipus japonicus (BA)	49.6
Callophyllis sp. (RA)	6.59
Ulva fasciata (GA)	36
Codium fragile (GA)	15
Iridaea cordata (RA)	15.1
Fucus sp. (BA)	9.75

RA, Red algae; *BA*, brown algae; *GA*, green algae (Suutari et al., 2015).

11.4.3.2 Parameters for mannitol

The different parameters of mannitol is given in Table 11.3.

11.4.3.3 Lipid content of macroalgae species

Lipid content available in different macro algae species is shown in Table 11.4.

11.5 Biorefinery process

The current population size has resulted in maximum utilization of available resources with biorefinery process for developing sustainable agricultural practices (Yaashikaa et al., 2022). The development of an integrated biorefinery process capable of producing multiple products is crucial for commercialization of microalgal biofuel production (Dong et al., 2016). Efficient extraction methods must be introduced into biorefineries early on to enable extraction prior to additional processing if their production is to be profitable as represented on Fig. 11.3 (FitzPatrick et al., 2010).

11.5.1 Micro/macro biorefinery for industrial application

In order to control the cost, natural resources like light, carbon dioxide, water, and inorganic salts are used to grow. The use of macroalgae in the biofuel industry is still under development, and even recent results on this topic are widely based on laboratory or mesoscale operations, as shown in the Fig. 11.4 (Suutari et al., 2015).

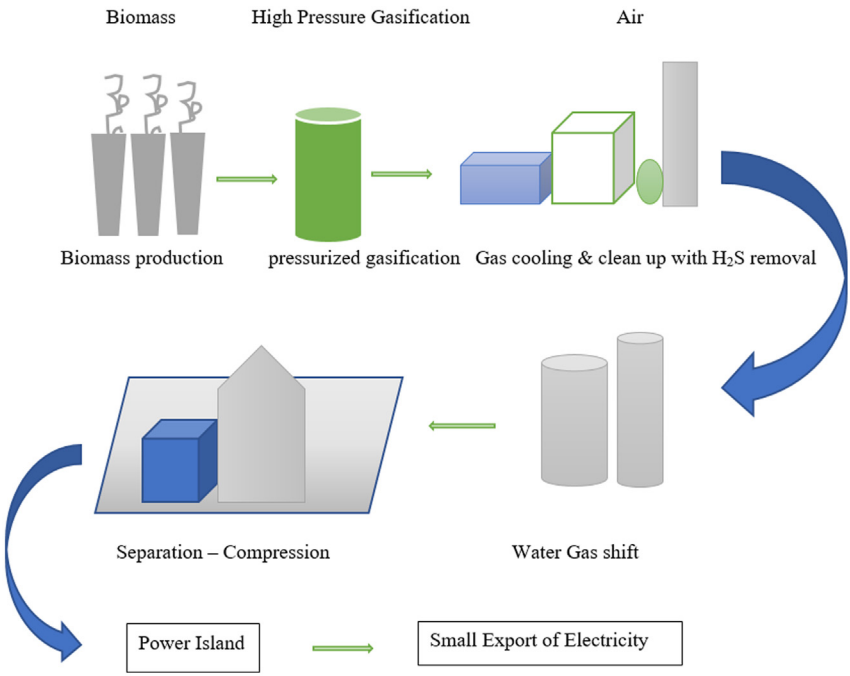


FIGURE 11.3 Shows the flowchart of biorefinery using high pressure gasification.

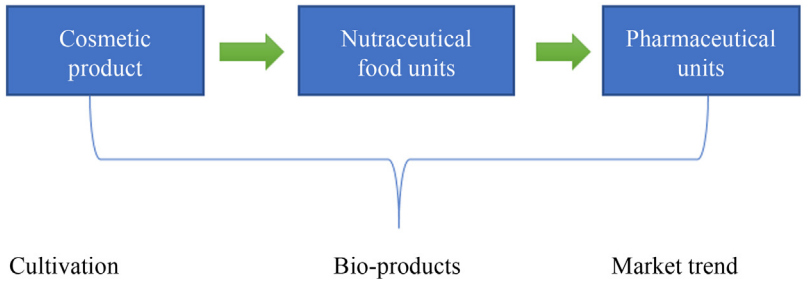


FIGURE 11.4 Shows the different stages of biorefinery production.

11.6 Feasibility and sustainability

Micro/macroalgae are biorefineries that use renewable, sustainable, and cost-effective feedstock to manufacture biofuels and green agrochemicals. Microalgae can be a sustainable solution for energy and the environment since they can contribute to reducing CO_2, wastewater treatment, bioactive substances, and creating other compounds (Ahmad et al., 2021). In the modern era, micro-macroalgae have strong scientific disciplines, wide applications with biofuel compounds and valuable bioresources in food, nutraceuticals, and pharmaceuticals (Saravana et al., 2023). Microalgae, in general and marine form a richest sources of known bioactive compounds including toxins. Recent advances in bioactive compounds from marine organisms and development of high value products produces a valuable products and their chemical perspectives with 33 wide pharmaceutical applications (Chakraborty & Joy, 2018). Value-added products have been synthesized within biological species, benefiting plant, animal matter, and microorganisms (FitzPatrick et al., 2010). The production of biomass at a large scale becomes more economically feasible when it is part of a biorefinery designed within the circular economy concept (Olguín et al., 2022).

11.7 Challenges and future directions

Macro-microalgae give a practical exhibition explanation of biotechnology's potential as a vital source of various macromolecules (Olguín et al., 2022). Environmental factors, such as light, temperature, and minerals, affect lipid metabolism, play essential roles, and present many challenges. In most algae, high light intensity increases the content of storage lipids (Suutari et al., 2015). Microalgae-bioactive compounds are potential health-promoting agents for the prevention and therapeutic application. They are closely connected to infectious, chronic, and degenerative

diseases such as viral, fungal, and bacterial infections, diabetes, metabolic, cardiorespiratory, cancer, inflammatory, and neurodegenerative, among other pathologies. Algal health-promoting microalgae-bioactive compounds have shown a significant role in therapeutical bioactivities for the prevention or treatment of diseases, as proven by animal functional studies (Olguín et al., 2022). *Cultivation* is an essential aspect that must be borne and coordinated to develop large-scale sustainable macroalgal biorefineries (Kostas et al., 2021). Challenges in the field of seaweed occurred in 2010. However, it was overcome as it was developed in many areas for environmental improvement (Kim et al., 2019). There is a need for methodologies for economic and detailed examination of novel bioeconomy technologies, taking into account environmental side effects and physical and economic unsureness. Farmers growing cellulosic energy crops face significant revenue uncertainty due to production and price uncertainties (Palatnik & Zilberman, 2017). Globally, extensive efforts are currently undertaken to preserve and increase biodiversity, farmlands, and environmental friendliness of the systems and processes required for a functioning society (Tardy et al., 2023).

11.8 Case studies and prospects

Various microalgae harvesting techniques, such as flocculation, centrifugation, filtration, and floatation, have been well established on an industrial scale, along with various combinations of the available techniques in this study (Lim et al., 2022). The literature reports show a wide range of growth rates for microalgae, and the few business case studies show mixed results regarding production frontier and profitability considerations (Palatnik & Zilberman, 2017). Much literature on growing various microalgae species for biodiesel production has further opened the opportunity of carbon dioxide fixation as this significance to a new milestone (Rajkumar & Sobri Takriff, 2016).

One of the emerging trends in biorefinery is carried out by SABA (Saudi Arabia Biorefinery from Algae). The primary mission is to develop the Algae-based biorefineries, which is viable solutions for green chemistry bio-products. The SABA methodology is demonstrated in Fig. 11.5.

Though microalgae and macroalgae are potential organisms with biotechnological, industrial, and environmental application, still the production cost of algal fuel remains higher than the fossil based fuels. For reducing the nutrient cost and other mechanical equipment, waste water and flue gases has been used (Kumar et al., 2021).

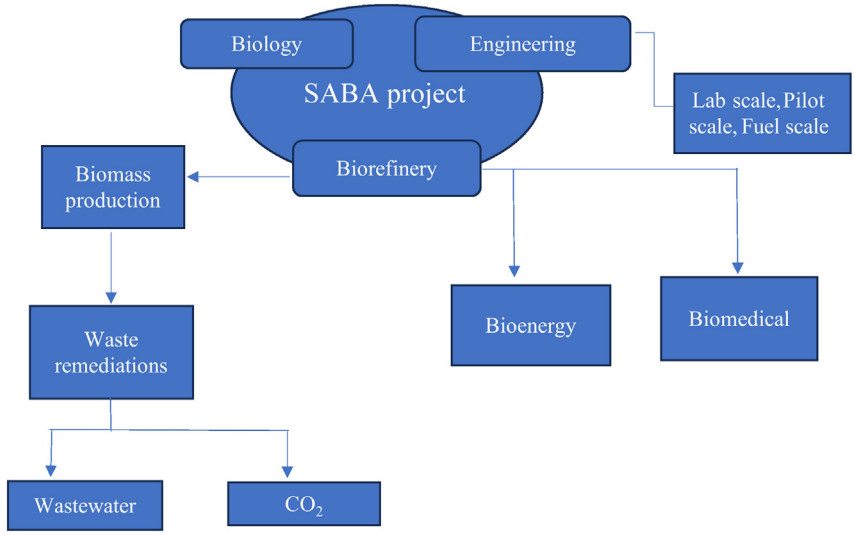


FIGURE 11.5 Demonstration of SABA project.

11.9 Conclusion and discussion

The seaweed biorefinery can make a significant development to the sustainable conversion of any biomass within a biotechnology perspective; this is the reason why seaweed techniques are very rich in the field of biotechnology, particularly in areas like biofuels, cosmetics, food supplement production, and also have an essential role in pollution removal (Balina et al., 2017). The unique perspective of marine algal biorefineries derives from the wide variety of products like animal-fed food energies. There are additional hurdles to seaweed biorefineries. These include seaweed feedstock availability and monoculture's unsustainability with high capital costs (Zollmann et al., 2019). There are many possible ways to produce biofuels, but through continuous studies, it is found that marine macroalgae contribute a significant portion in the biorefineries (Allen et al., 2018). The successful implementation of biofuel projects will require detailed modeling and simulation, which are present in the integrated design of biorefineries combined with the thermodynamic model (Golberg et al., 2014). The protein levels and potentially limiting essential amino acids in macroalgae vary greatly, and protein digestibility may be affected by species-specific polysaccharides and phenolic compounds (Øverland et al., 2019). In this context, there is a need for more research and studies in future for the utilization of macroalgae to develop the biorefinery infrastructure and efficient sources that are required for human society.

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