



Macroalgal biomass in terms of third-generation biorefinery concept: Current status and techno-economic analysis – A review

K.D. González-Gloria^a, Rosa M. Rodríguez-Jasso^{a,*}, Shiva^a, E. Aparicio^a,
Mónica L. Chávez González^a, Emily T. Kostas^b, Héctor A. Ruiz^{a,*}

^a Biorefinery Group, Food Research Department, Faculty of Chemistry Sciences, Autonomous University of Coahuila, 25280 Saltillo, Coahuila, Mexico

^b The Advanced Centre of Biochemical Engineering, Department of Biochemical Engineering, University College London, Gower Street, London WC1E 6BT, UK

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ABSTRACT

Macroalgae is an emerging third-generation feedstock and promising biomass within the biorefinery context to produce biofuels and high-added value compounds. Biorefinery involves processes and technologies in the context of sustainable bioeconomy.

Throughout the biorefinery process is important not to neglect parameters and conditions that can impact the optimization, such as pretreatment, solid loading in enzymatic hydrolysis and, fermentation. In this case, the techno-economic analysis allows designing a feasible process of macroalgae valorization considering different important parameters for scaling up the process for biofuels and chemicals to approach all these compounds for a future market and commercial. According to these arguments, this review aims to describe the macroalgal biorefinery, applications, and techno-economic analysis to provide the general panorama of economic feasibility for the valorization of macroalgal biomass in terms of biorefinery and circular bioeconomy.

1. Introduction

In the last century, society has over-relied on the dependence on fossil fuels to produce fuels and chemicals. Overconsumption of non-renewable natural resources has caused serious environmental problems, results in high contamination and reducing natural resources. Consequently, it is necessary to search for alternative resources (feedstocks) to develop products with high potential in a biorefinery context (Aguirre-Fierro et al., 2020; Pino et al., 2021). Hence, the valorization of biomass through sustainable processing to obtain renewable energy and high added-value compounds (Ruiz et al., 2017; Lara-Flores et al., 2018).

Macroalgal biomass is a natural resource from the sea with renewable and cost-effective properties. It represents a promising third-generation feedstock for its conversion into sugars and high added-value products in a biorefinery (Aparicio et al., 2020; Aparicio et al., 2021; Kostas et al., 2021; Sarmiento-Padilla et al., 2021). Macroalgae are rich in different compounds such as fucoidan, alginate, and a high content of polysaccharides used in pharmaceuticals, bioenergy, food nutrients, algae chemicals, and biofertilizer (Rodríguez-Jasso et al.,

2013a; García-Vaquero et al., 2017; Kumar et al., 2020; Lara et al., 2020).

The third-generation (macroalgae) biorefinery profits from biofuel production and high added-value compounds by increasing the future transition of an oil-based economy to a bio-economy (Kannah et al., 2021). Third-generation biomass is a promising alternative for bioethanol production by the process of pretreatment, enzymatic hydrolysis, fermentation, and distillation (Aguilar et al., 2018). These procedures are implemented at large scales in a thriving economic and eco-friendly way (Greene et al., 2020). However, there are still some disadvantages (high-cost harvesting biomass) and potential threats holding back the development of industrial bioethanol; therefore, the overall techno-economic analysis of the process is highly important.

This sustainability of macroalgal biorefineries requires to be evaluated by a life cycle assessment study (LCA). LCA is a tool for comparing the whole life cycle process, or cradle-to-grave, environmental impact, transport, distribution, and marketing commercial production (Schroeder et al., 2018; Ubando et al., 2020). The LCA studies depend on algae biomass, the region, and the country for the technical engineering process to scale up and develop products at industrial-scale viability.

* Corresponding author.

E-mail addresses: rrodriguezjasso@uadec.edu.mx (R.M. Rodríguez-Jasso), hector_ruiz_leza@uadec.edu.mx (H.A. Ruiz).

URL: <https://www.biorefinerygroup.com> (R.M. Rodríguez-Jasso), <https://www.biorefinerygroup.com> (H.A. Ruiz).

The study involves each stage in the biorefinery process; thus, third-generation process design, economic, social, and environmental aspects. These parameters require in-depth evaluations through techno-economic analysis that approaches all operational processes by balancing mass and energy in support to obtain a perspective for the cost-effective bioethanol and bioproducts production as an alternative for biofuel and high-added value compounds at industrial or pilot plant level (Gubicza et al., 2016; Hosseinzadeh-Bandbafha et al., 2019; Ubando et al., 2020).

2. Biorefinery and available macroalgal feedstock

Biorefinery refers to the conversion of biomass into high-added value compounds and biofuels; it also refers to a manufacturing process that optimizes and investigates the technologies in a sustainable circular bio-economy way. As third-generation biorefineries, macro- and micro-algae have become important feedstocks for sustainable production (Rosero-Chasoy et al., 2021). Macroalgae are considered a cost-effective and environmentally sustainable source of biomass to synthesize bioproducts (Suganya et al., 2016).

These are mainly found on oceanic coasts or solid surfaces at different depths; macroalgae have also been found floating at sea level near the shores. Currently, a wide variety of different macroalgae species have been identified. Nowadays, several countries worldwide produce macroalgae, including the Philippines, China, Indonesia, Japan, South Korea, Malaysia, France, Ireland, Norway, Spain, Portugal, Argentina, Chile, Brazil, Mexico, and Australia (Siller-Sánchez et al., 2019). *Gelidium*, *Sargassum*, *Laminaria*, *Kappaphycus*, *Gracilaria*, and *Ulva* are the major genera for potential feedstock for biofuel production and high-added value compounds with the potential to be farmed at big scale (Kwon et al., 2016; Lee et al., 2016; Ramachandra et al., 2020). These macroalgae are considered to be relatively available with easy cultivation and harvesting.

Macroalgae are categorized into distinct species based on their color, morphology, and chemical composition (Velazquez-Lucio et al., 2018): Green seaweed (*Chlorophyta*), Brown seaweed (*Phaeophyta*), and Red seaweed (*Rhodophyta*). The different taxonomical groups of macroalgae have different amounts of carbohydrates (25–60%), protein (5–47%), and lipid (<5%). Fig. 1 shows the biorefinery platform from macroalgae

feedstock.

3. Biochemical composition of macroalgae

The macroalgae cell wall mainly contains alginate, fucoidan, cellulose, and other polysaccharides that can be hydrolyzed to sugars and fermented to ethanol (Rajak et al., 2020; Miyashita et al., 2020). The structure and chemical composition can vary during the seasonal period (Cervantes-Cisneros et al., 2017; Praiboon et al., 2018).

Green macroalgae contain identical chlorophyll A and B as plants. This pigment is its characteristic color; there are about 4500 species of green macroalgae, and the main polysaccharide constituents are glucans and ulvan (Siller-Sánchez et al., 2019; Zollmann et al., 2019). There are over 6135 species of red macroalgae, making it the largest macroalgae category that contains the main polysaccharides are carrageenan and agar (Argüello-Esparza et al., 2019).

The main constituents of brown seaweed (Phaeophyta) are alginate, cellulose, laminarin, fucoidan, carotenoids, proteins, lipids, omega-3 fatty acids, and secondary metabolites like polyphenols (Siller-Sánchez et al., 2019; Huang et al., 2021), which could vary in color from olive green to dark brown. The chemical components of the carotenoids are chlorophyll A and C, which provide the green tones, and fucoxanthins provide more yellowish-brown tones (Fasahati et al., 2017; Reboleira et al., 2019; Lamont and McSweeney, 2021). Systematic studies are saying that Brown macroalgae and rockweeds are found together commonly. Human inhabitants in coastal areas have exploited this type of marine algae for food, medicinal uses, and as a source of valuable chemicals (Pozharitskaya et al., 2020).

Alginate is obtained in the form of sodium or calcium salts. It is composed of two monomeric units i.e., β -D mannuronic acid and α -L guluronic acid (Flórez-Fernández et al., 2019). It represents the major component of the cell wall, accounting for up to 40% of the dry weight. Laminarin is a low molecular-weight β -glucan polysaccharide composed of (1,3)- β -D-glucan and some β -(1, 6) intrachain links with a reducing end of mannitol or glucose (Cui et al., 2021). Fucoidan is a sulfated water-soluble polysaccharide composed of sugars such as fucose, glucose, galactose, xylose, mannose, and uronic acid (Rodríguez-Jasso et al., 2013b; Lara et al., 2020).

In recent years, brown seaweed polysaccharides have attracted

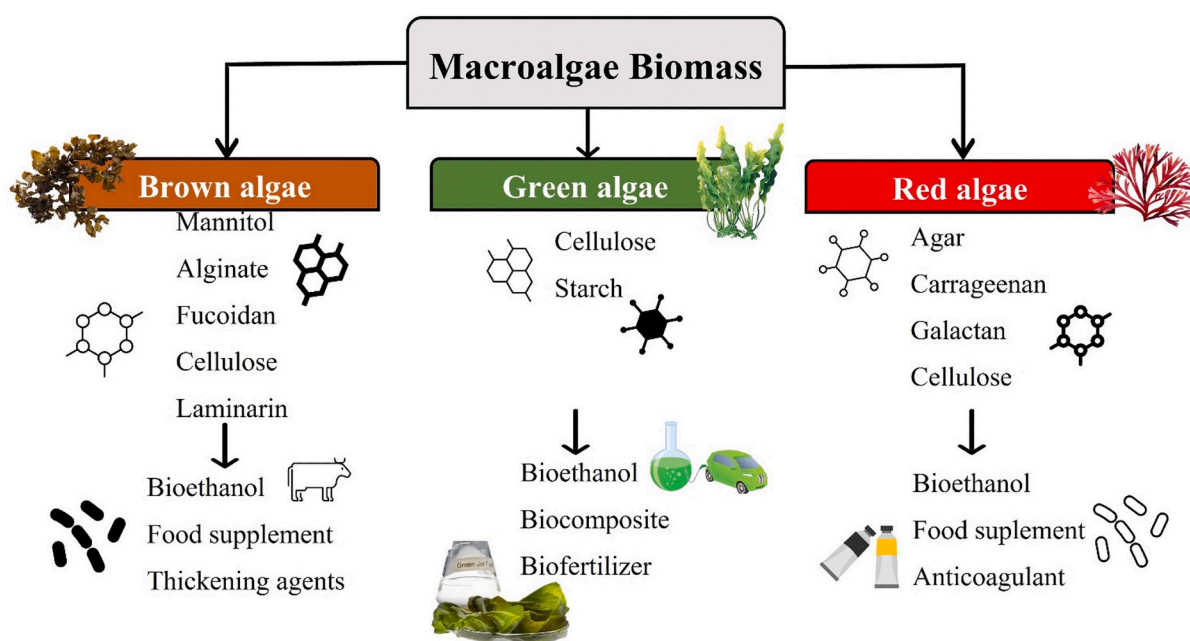


Fig. 1. Biorefinery from macroalgae feedstock and production of high-added compounds.

attention due to their bioactive properties like secondary metabolite's antioxidants (Rodríguez-Jasso et al., 2014; Kazir et al., 2019; Lim et al., 2019). These polysaccharides protect the macroalgae against osmotic stress, pH, and temperature changes (Cabello-Galindo et al., 2019). Furthermore, these compounds have a wide range of applications in many industries such as food and cosmetics, biotechnology, and pharmaceutical (anti-inflammatory, antiallergy, antiviral, antitumoral, anticoagulant activity). Due to these, diversified biochemicals can produce a wide range of commercial bioproducts.

It is important to know that the obtention of macroalgae compounds depends on the geographical location, season, and related environmental factors. For that reason, the composition and physiology change according to the impact of seasonal variation (Praiboon et al., 2018). Solar irradiance, nutrients, pH, temperature, and salinity of seawater are some of the affecting factors that should be carefully considered during the operational process to improve optimal resource utilization (Ometto et al., 2018; Chávez et al., 2020). For example, fucoidan has been found in higher contents in the autumn season for brown macroalgae (Fletcher et al., 2017), and Praiboon et al., 2018 reported the summer season as the best for nutritional composition of brown macroalgae *Sargassum* spp. Saldarriaga-Hernandez et al., 2021 evaluated different factors (season, collection, and extraction) to analyze the biochemical composition of *Sargassum* biomass from the Mexican Caribbean. Studies say that more lipid content in the hottest season, while higher carbohydrates and protein concentrations were found in the wettest season, the metal concentration was high in both seasons. These studies support to be presented in which season is the best to collect as much as possible biomass and save it by knowing the concentration and highly efficient extraction to obtain the interest compounds for future studies to biomass.

4. Bioethanol production from macroalgae

The most common biotechnological steps conversion to bioethanol are pretreatment, enzymatic hydrolysis, fermentation, and anaerobic digestion, which utilizes microorganisms to convert the algae biomass into bioethanol biogas distillation (Khoo et al., 2019; Filote et al., 2020). First, the fermentation step converts sugars to ethanol. Still, before obtaining these sugars, thermochemical processes are needed where cellulose is hydrolyzed by enzymatic hydrolysis process into glucose and subsequently fermented into bioethanol (Pino et al., 2019) (Fig. 2).

However, the ethanol from macroalgae is in the early stages, mainly conducted at a laboratory scale before scale-up. Thus, the bottleneck of third-generation ethanol technology is investigated more comprehensively. In particular, it is necessary to explore algae as an attractive

feedstock and the possibilities of commercially scaling up bioethanol production (Zabed et al., 2017; Borin et al., 2019).

4.1. Pretreatment

Pretreatment is the initial step in the process to obtain polysaccharides and oligomers from macroalgae. Physical, biological, and chemical pretreatments have been used to expose the cell wall components (Cervantes-Cisneros et al., 2017; del Río et al., 2019). Physical pretreatment involves the reduced particle size and milling of raw material. Physical pretreatment is usually combined with chemical pretreatment with the help of dilute acid, base, ionic liquid, ozonolysis, organosol, and other chemicals. Biological pretreatment uses bacteria or fungi to catalyze cellulose enzymes to degrade the biomass and obtain cellulose components (Yun et al., 2016; Ramachandra and Hebbale, 2020; Olguin-Maciel et al., 2020).

Another pretreatment is hydrothermal processing (autohydrolysis) that consists of the action of water at elevated temperature and pressure in a closed reactor (Fig. 3) (Singh et al., 2019, 2021; Ruiz et al., 2013, 2015, 2017, 2020, 2021; Morales-Contreras et al., 2021).

4.2. Enzymatic hydrolysis

The enzymatic hydrolysis (EH), also known as enzymatic saccharification, relies on a chemical interaction of an enzyme-like cellulase or trypsin to deconstruct the cell wall. The hydrolysis of polysaccharides from macroalgae converts them into monomeric fermentable sugars that pass to fermentation for bioethanol production (Pino et al., 2019; Pino et al., 2021). The cellulases (endoglucanase, exoglucanase, and β -glucosidase) are highly specific enzymes that hydrolyze β -1,4 linkages in the cellulose structure, and these enzymes can obtain from commercial Novozyme cellulase (Singhania et al., 2021). These types of enzymes can be synthesized from fungi (*Trichoderma*, *Penicillium*, and *Aspergillus*) and bacteria (*Streptomyces lividans* and *Cellulomonas fimi*) (Singh et al., 2019). The optimal conditions for cellulase activity include a temperature between 45 and 55 °C and a pH value in the range of 4 to 5. At laboratory scale, EH is performed using 10 to 30 FPU/g cellulose for 48 to 72 h, offering an efficient glucose yield. The process begins with the fast liberation of glucose, which degrades roughly half of the cellulase in about 24 h. This procedure is significant in terms of high cost; the cost of cellulase enzymes accounts for 30–50% of overall expenses and, therefore, is a key impediment to lowering the cost of cellulose in the bioethanol process (Yun et al., 2016). The technology development of enzyme production from macroalgae biomass and fermenting microorganisms has been explored with a broad range of substrates in attempts

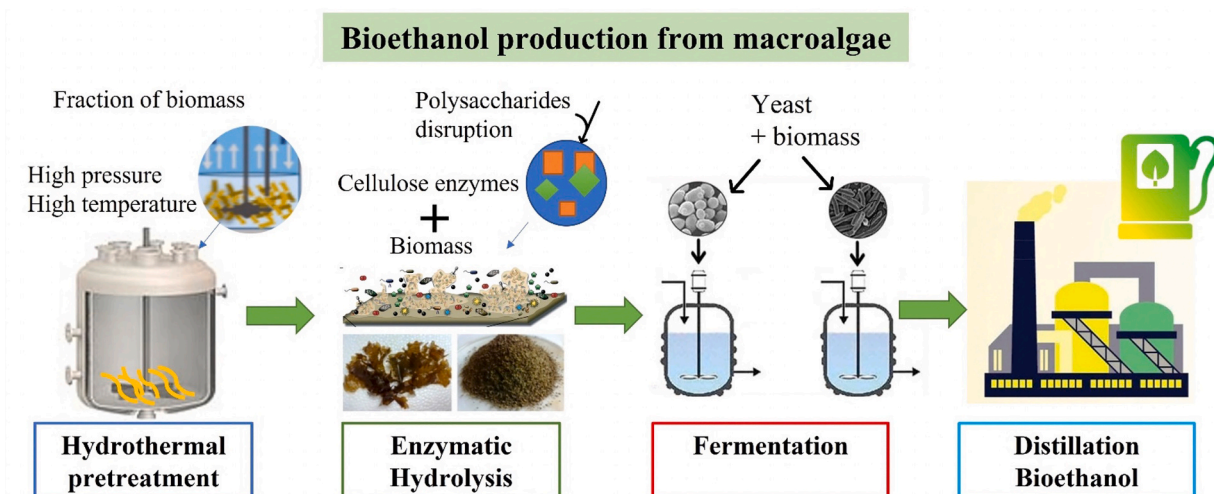


Fig. 2. Bioethanol production process from macroalgae biomass.

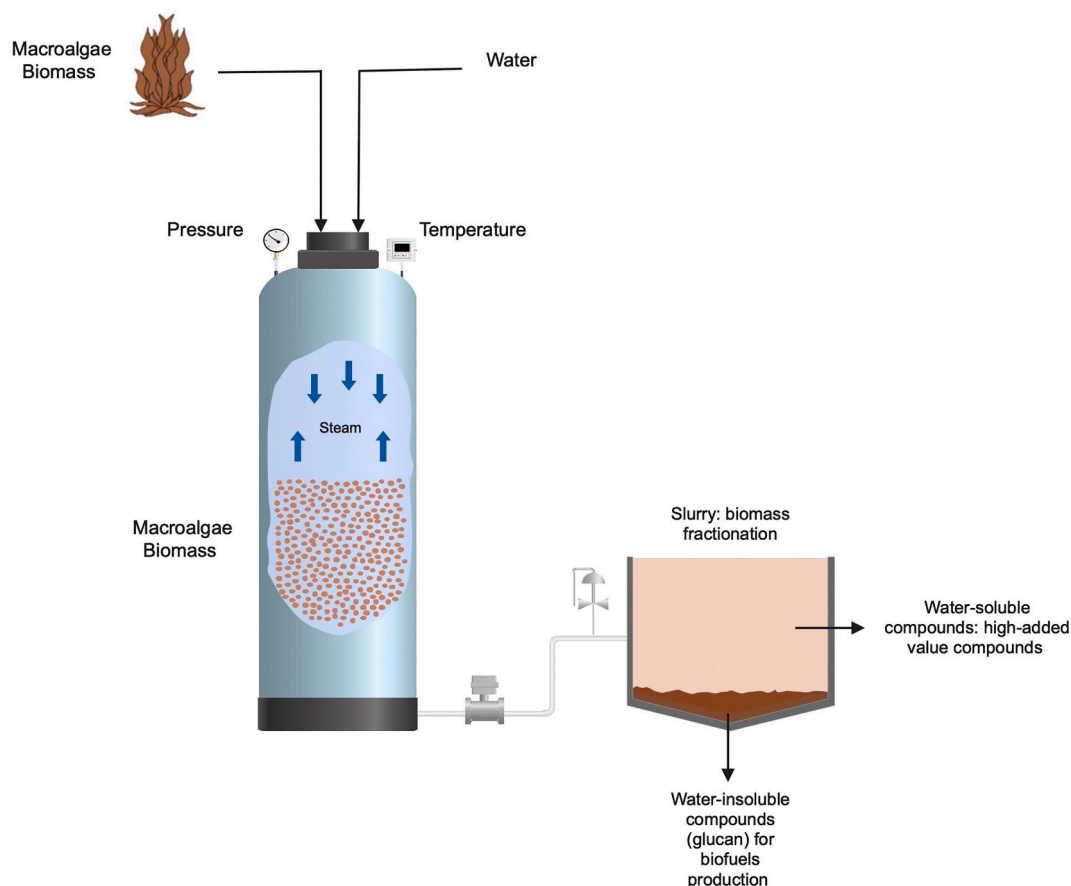


Fig. 3. Pressurized batch reactor for hydrothermal pretreatment using macroalgal biomass (Adapted from Ruiz et al., 2021).

to achieve more efficient processing conditions and reduce the overall costs of the process (Rodríguez-Jasso et al., 2010; Rodríguez-Jasso et al., 2013c).

Pretreatment high-solid loading and low enzymatic loading rate being required for an economically feasible bioethanol production process from algal biomass (Ruiz et al., 2017; Pino et al., 2018).

4.3. Fermentation

The fermentation stage consists of the monomeric sugars obtained from enzymatic saccharification are fermented into ethanol by the action of microorganisms (Rocher et al., 2021). The fermentation process is dependent on the operating conditions and feedstock, and high-temperature-tolerant microorganisms are necessary (Caspeta and Nielsen, 2015). Optimizing fermentation conditions and nutritional and environmental parameters is of primary importance for developing bioprocesses (Dave et al., 2019). Commonly *Saccharomyces cerevisiae* yeast is used for ethanol production by anaerobic conditions. *S. cerevisiae* yeast can ferment simple sugars such as glucose into ethanol. *S. cerevisiae* can not ferment pentoses sugars such as xylose and arabinose (Choudhary et al., 2016). The advantages of these yeasts are the high ethanol yield and maintaining glucose concentrations; it resists low pH and high temperatures (35–40 °C) (Walker and Walker, 2018). Recently, genetically modified microorganisms still challenge the development of cost-effective technologies for processing large amounts of macroalgae due to improvement and conversion efficiency (Camus et al., 2016; Kumar et al., 2020).

Different operating strategies have been developed for the bioethanol production process. Like separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), pre-simultaneous saccharification and fermentation (PSSF), consolidated

bioprocessing (CBP), and simultaneous saccharification and co-fermentation (SSCF). PSSF consists of a pre-saccharification time before the saccharification and simultaneous fermentation; saccharification is carried out at optimal conditions for a short time, between (6–24 h). This strategy helps to decrease the slurry's viscosity at high solid loadings and has higher yields and productivity. Generally, in PSSF, the optimum temperature of pre-hydrolysis and fermentation is found to be 50 °C and 30–37 °C, respectively. An optimum time is recorded as 18–24 h for pre-hydrolysis and 72 h for fermentation (Aguilar et al., 2018). In some studies, PSSF is mostly used due to the efficient ethanol yield (Aguilar et al., 2018; Kumar et al., 2020; Aparicio et al., 2021).

Wargacki et al. (2012) reported enabling bioethanol production directly from macroalgae via a consolidated process. These studies achieved 0.0281 g ethanol/weight dry macroalgae (equivalent to ~80% of the maximum theoretical yield from the sugar composition in macroalgae). The conversion of marine biomass would be developed, contributing to realizing the production of renewable fuels and chemical compounds from sustainable biomass resources (Enquist-Newman et al., 2014).

5. Macroalgae high added-value compounds

Macroalgae biomass is a promising feedstock for a conversion technology that produces high added-value products and chemicals for nutraceutical products by valorizing bioactive compounds such as pigments, peptides, vitamins, and proteins (Gomes-Dias et al., 2020).

5.1. Bioactive compounds from algae biomass

Algae extracts have a market value of almost \$500 million and

include high minerals and vitamins, making them a promising bio-refining source (Griffiths et al., 2016). Macroalgae have a diversity of high-value metabolites that can be converted into bioactive compounds for bioproducts, mainly: lipids, phenolic compounds, and carbohydrates (Esquivel-Hernández et al., 2016). The products that can be obtained from macroalgae in terms of the biorefinery are summarized in Table 1.

Polyphenols are known to have antioxidant and antiviral activities, fungicides with antimicrobial and anti-proliferative functions used as UV- skin protectors, some pigments as fucoxanthin have hepatoprotective, anti-obesity, and anticancer activities. Polyphenols are a group that contains the hydroxyl group (–OH), substituting some of the aromatic hydrocarbons: phenolic acids, flavonoids, phenylpropanoids (Álvarez-Viñas et al., 2021).

Carbohydrates are an important constituent of algae that are divided into oligosaccharides with bioactivity that can modulate the immune response and function as natural antimicrobial owing to their sulfate concentration (Saldarriaga-Hernandez et al., 2020). Agarose and alginate, two of their distinct polysaccharides, are used in a variety of industries (Ruiz et al., 2015).

Lipids are hydrophobic molecules originating from carbanion-based condensations, which are fatty acids, and carbocation-based condensations of isoprene units like carotenoids, sterols, and a terpenoid that are used as anti-inflammatory and skin protector, have several bioactivities applications like food, cosmetic, pharmaceutical (Abeln et al., 2019).

To obtain high-added value compounds, extraction techniques are required. These are based on drying followed by maceration of biomass, processing with or without chemical agents using enzymes, and organic solvents and physical agents, such as ionic liquid solvents, switchable, and supercritical fluid extraction (García-Vaquero et al., 2017). As green technology hydrothermal processing, these technologies are applied to macroalgal biomass because researchers do not use any contaminating reagents; also, these are more environmentally friendly and sustainable. The number of different high added-value compounds for pharmaceutical, food, and biofuel applications that can be recovered from a single feedstock within a biorefinery concept is significantly beneficial to any bioeconomy. A biorefinery attempts to commercialize all the bioactive

compounds of macroalgae is a far greater and more appropriate approach for the exploitation of macroalgae, rather than an approach based only on biofuel production. A cascading biorefinery process to obtain high-added value compounds use different types of treatments and applying for bioproducts; for example, Glasson et al. (2017) reported the extraction of compounds ulvan, and pigments with high content of rhamnose (53.1 mol%) and uronic acid (37.9 mol%) and low content of xylose (5.3 mol%) from same macroalgae *Ulva spp.*. Kostas et al., 2017, 2020 reported different chemicals like lipids, proteins, polysaccharides such mannitol, laminarin, and fucoidans, and phenolics compounds with potential bioactive can be recovered, bioethanol was also produced from the same process using *Laminaria digitata* as feedstock.

6. Opportunities and derived products from macroalgae

Several macroalgae species have been available for biofuels (bioethanol, bio-oil, biodiesel) and the production of high-added value compounds through biotechnology processes (Abomohra et al., 2018). Macroalgae can be used for animal feed, bioremediation, and water treatment industrial effluent (Rahman et al., 2020), due to their high capacity for uptake and accumulation of nutrients and metals being biosorption (Saldarriaga-Hernandez et al., 2020; Thompson et al., 2020). Still, the availability of macroalgae varies throughout the season and year (Zollmann et al., 2019; Lopes et al., 2020;).

The macroalgae global cultivation market was estimated to be USD 16.7 billion in 2020. It has been projecting to reach USD 30.2 billion by 2025. Also, Recently, the high cost of the end product cannot be controlled by the formulation of a single product at a time due to high equipment cost and high processing values, which enhance the economic value.

The different types of compositions of macroalgae directly link to high commercialization in the market how is antioxidants and food (Krishnan and Narayanakumar, 2013; Reboleira et al., 2019). According to the FAO (FAO, 2016), different species of macroalgae have high commercial values, such as principal red (*Eucheuma spp*, *Gracilaria spp*, *Gelidium spp*), and brown (*Sargassum spp* and *Saccharina japonica*) macroalgae, as reported by (Siller-Sánchez et al., 2018). Worldwide consumption of macroalgae has exceeded its natural existence, and such demands promote the advancement of the cultivation industries with an optimum life cycle (Mu et al., 2020). By this mode, cultivation industries are holding up to 90% of market demand via the production of wild industrial macroalgae. The world's leading supplier of the edible macroalgae China, produces approximately 500,000 tons of *Laminaria japonica* on a wet basis, followed by the Republic of Korea produces 800,000 tons of three distinct species such as *Saccharina japonica* (Sea tangle, Dasima), *Undaria pinnatifida* (Sea mustard, Miyuk), and *Porphyra species* (Purple laver, Gim), whereas Japan's output is about 600,000 tons, with *Porphyra species* which is accounting for 75% of total production (Jang et al., 2012; Cervantes-Cisneros et al., 2017). These biomasses, being as a potential feedstock, serves as a good food supplement (Øverland et al., 2019), the nutritional composition of macronutrients: sodium, potassium, sulfur, phosphorus, calcium, and magnesium, and micronutrients: iodine, copper, zinc, manganese, nickel, and vitamins: B12, A, and K; such as *Enteromorpha* that was a nutritional supplement snack in India, which contain high content of calcium and iron, significant amount of proteins, vitamins, and fibers (Kim et al., 2014; Ramachandra and Hebbale, 2020).

Despite the technological interest and the potential of macroalgae production as an innovative sector within the European Union for a bioeconomy, the macroalgae industry's current status in some European countries remains largely unknown (Araújo et al., 2021).

Here are some catalogs of the macroalgae industry; some of these are global commercial macroalgae manufacturers and producers: Cargill, Incorporated (US), DuPont (US), Qingdao Gather Great Ocean Algae Industry Group (China), Seaweed Energy Solutions AS (Norway), The

Table 1

Macroalgae high-added value compounds and potential industry application in terms of biorefinery.

Application area	High-added value products	Potential application	References
Nutraceutical	Astaxanthin,β carotene, chlorophyll, alginates	Food additive, antioxidant	(Rodríguez-Jasso et al., 2013a)
Pharmaceuticals	Omega-3-based chlorophyll, fucoidan, Ulvan, porphyran	Antimicrobial, antiviral, antifungal, And neuroprotective product	(Schroeder et al., 2018)
Hydrocolloids	Agar, alginate and carrageenan	Anticoagulants	(Esquivel-Hernández et al., 2016)
Cosmetics	Alginates, porphyran	Anti-cellulite skin and sensitive skin treatment – algaronic acid	(Gomes-dias et al., 2020)
Bioremediation	Carboxyl groups, fucoidan	Wastewater treatment and	(Saldarriaga-Hernandez et al., 2020)
Biofuels	Sulfated polysaccharides Sugars (glucan, mannitol, galactose)	Nutrient bioasorption Bioethanol, biodiesel	(Aparicio et al., 2020)
Animal feed and fertilizer	Macroalgae biomass, sugars	Aquaculture feed (shrimp shellfish feed).	(Sudhakar et al., 2018)

Seaweed Company (Netherlands), Algea (Norway), Seasol (Australia), Gelymar (Chile), Algaia (France), CEAMSA (Spain), COMPO EXPERT (Germany), Irish Seaweeds (Ireland) and AtSeaNova (Belgium) (Seaweed Cultivation Market, 2021). In December 2020, Qingdao Seawin Biotech Group Co. Ltd. (China) expanded its industrial to produce marine bio-stimulants and tool enzymes from seaweed and marine peptides. In 2019, the Asia Pacific region contributed the projects with the highest share of the seaweed cultivation market attributed to the availability of the raw materials, favorable climatic conditions for the production of seaweeds, availability of cheap labor, and usage of macroalgae directly into the food preparations (Araújo et al., 2021).

More than 50% of these companies produce algae production is still yet dependent on harvesting from wild stocks (68% of the macroalgae producing units), but macroalgae aquaculture (land-based and at sea) is developing in several countries in Europe, currently representing 32% of the macroalgae production units. France, Ireland, and Spain are the top 3 countries in the number of macroalgae production units, while Germany, Spain, and Italy represent the top 3 for microalgae (Araújo et al., 2021; Seaweed Cultivation Market, 2021). These industries are moving into new trends of technologies such as equipment to improve macroalgae production, monitoring, and control of the macroalgal biomass for growth in a future market.

In the pharmaceuticals industries, macroalgae play a significant role due to their medicinal properties, which can be used to prevent or cure some diseases such as cancer, diabetes, and obesity by food. On the contrary, agar, carrageenan, and alginate can be used for thickening and gelling agents in creams and ice cream as dairy products (Ali et al., 2021).

However, biofuel production from algae needs further effort, particularly from the engineering and industrial sides required to make them economically competitive and integrate different production systems, and the use of low-cost feedstocks could help decrease the process's costs (Borin et al., 2019).

The approach of third-generation biorefinery introduces emerging techniques for developing a variety of products by reducing the cost or accomplish more economically feasible all over the world (Hal et al., 2014; Kumar et al., 2020). From an economic point of view, the industry would be more profitable to utilize extractive products (Scown et al., 2021).

7. Techno-economic analysis of macroalgae biorefinery

Biorefinery is the significant production of bio-based products from various biomass utilizing a combination of technologies; this involves developing modern, viable, and competitive for the usual industries and is influential to society to produce technology processes (Zollmann et al., 2019; Ubando et al., 2020). To establish a biotechnological industry is necessary to carry out a techno-economic analysis to have order in the process of logistic operation and, at the end of the process, to achieve a cost-effective biorefinery plant (Ramachandra and Hebbale, 2020; Manhongo et al., 2021). The bioeconomy goal is to create concepts with a long-term sustainability profile; for example, fossil fuels cannot provide the world's energy needs indefinitely. For many biotechnological applications at the industrial scale, technology is necessary to use high-added value chemicals that are inexpensive and easy to obtain. The production of renewable resources from biological feedstock and biomass for conversion into food, bio-based products, or bioenergy is known as a bioeconomy (Gajaria et al., 2017; Kumar et al., 2021). At this moment, The techno-economic analysis concept defines the terms economic and technology, which use for the technological feasibility of the commercial approach (DeRose et al., 2019; Gu et al., 2020). Biorefinery brings alternatives at first glance, a direct cascade that consists of the obtaining of high-added value compounds to the first focus of the process and biofuels by the residues from the production, and in the other hand, the inverse-cascade that prioritizes the production of biofuels and then the reverses of the compounds (Lara et al., 2020; Pinales-Márquez

et al., 2021).

However, new processes developed to improve the economic barrier representing the implementation of technologies applicable to the valorization of macroalgae (Lynd et al., 2017). The latest trend of investigation in the last decade is the use of new technologies (pretreatments, bioprocess strategies) and biomass (Ingle et al., 2020). Researchers are incorporating the algal feedstock in planning, costing, economic, social, and environmental elements of third-generation biofuels and bioproducts and evaluating the life-cycle and feasibility of feedstock (Olofsson et al., 2017; Pinales-Márquez et al., 2021). These can be comprehensively assessed and enhanced by manufacturing significant products, including biofuel production, which could fulfill market quality and pricing standards, to obtain a successful macroalgae biorefinery process is necessary to evaluate techno-economic viability for an industrial design and scale (Konda et al., 2015; Ansari et al., 2020).

7.1. Biorefinery plant design

According to recent studies, biomass logistics is one of the most critical aspects of the growth of the bio-economy. However, further study is needed to build an economically viable macroalgae biorefinery. A design below the technical method of extracting compounds from macroalgae, which may favor the designing economy and pricing of a bio-plant design for different bioproducts derived from marine biomass, is the foundation of the biorefinery concept (Chemodanov et al., 2017; Chong et al., 2020).

There are some barriers to the development, commercialization, and implementation of a biorefinery plant. The present challenge for feedstock is the expense of the manufacturing process, harvesting, and biomass collecting techniques, particularly for raw materials that must be collected at a specified time and has an impact on transportation costs. That is why improving the economic, technical, and environmental elements of establishing a biorefinery in a pilot plant has become a considerable step. It is essential to construct scenarios to investigate and determine the design of a biorefinery plant (Rogers et al., 2017).

Simulator process, Aspen Plus, and SuperPro Designer software are examples of technology platforms and software that can model a design and assist with calculations and simulations (Aziz and Zaini, 2017). The variables and operating costs in the software application are based on raw material and energy balance calculations from process modeling utilizing simulations; these bioprocess simulators construct upstream and downstream processes involved in producing and distillation of biofuels (Hasanly et al., 2017). Table 2 shows the operational conditions and techno-economic analysis studies currently found in the literature.

7.2. The operational process of a techno-economic plant

The techno-economic assessment is an essential practice for evaluating the process of biotechnological biorefineries and quality of production; it aids in controlling and identifying prospective investment and finance processes for the future industry (Bessette et al., 2018).

At the initial stage of the biorefinery process, washing the macroalgae biomass is considered a significant step to eliminate every particle of salt, sand, and ashes that can affect the pretreatment step and improve the biomass quality before further processing. The operational process to get high-value-added compounds followed considerable steps such as biomass cultivation and harvesting, post-harvesting (cleaning, size reduction), pretreatments and treatments, enzymatic hydrolysis, fermentation, distillation (Kern et al., 2017; Khan et al., 2019).

In Fig. 4, the biorefinery model design depicts an industrial-scale process of producing ethanol from fermentable carbohydrates during the pretreatment stage. As a life cycle economy, these methods contribute to the creation of high-added value compounds utilizing a substantial concentration of sugar as an end product, such as hydrolysis and fermentation, followed by separation and distillation to get a high-

Table 2
Macroalgae biorefinery, conditions and techno-economic analysis using different simulation software.

Seaweed Feedstock	Conditions	Software	Ethanol price	Feedstock	References
<i>Saccharina latissima</i>	≥80% yield ≥20% solids loading ≤10 mg/g enzyme loading	SuperPro Designer	\$2.9–7.5/gal	\$50/MT.	Konda et al., 2015
Brown macroalgae	0.68 and 3.7 million tonnes (dry basis)	Economic model MS Excel	0.93 (\$/L).	25 (\$/t dry)	Soleymani and Rosentrater, 2017
<i>Saccharina latissima</i> and <i>Nereocystis luetkeana</i>	13% Macroalgae Solids	–	\$1.35 to \$2.91 Per liter of Gasoline equivalent	\$100 DMT – 1	Greene et al., 2020
<i>Saccharina japonica</i> <i>Eucheuma cottonii</i>	– 20 wt% total solid loading Enzyme loading of 20 mg/g cellulose.	– Aspen Plus V10	– 1.31 \$/gal. \$ 0.54/kg	– 0.127 \$/kg \$72.6 per tonne	Dickson and Liu, 2019 Chong et al., 2020
<i>Saccharina japonica</i>	<i>Saccharomyces cerevisiae</i> Loading of 17.5 mg/mL dry seaweed weight was 29% wt	Aspen Plus	0.589 USD/L	0.07 USD/kg	Brigljević et al., 2018
<i>Laminaria/Gracilaria</i>	EH% solid loading 17.5–20 (80,000 ton/year) (400,000 ton/year)	Aspen Plus	2.39 and 2.85 \$/gal	64.6 and 26 \$/ton	Fasahati et al., 2017

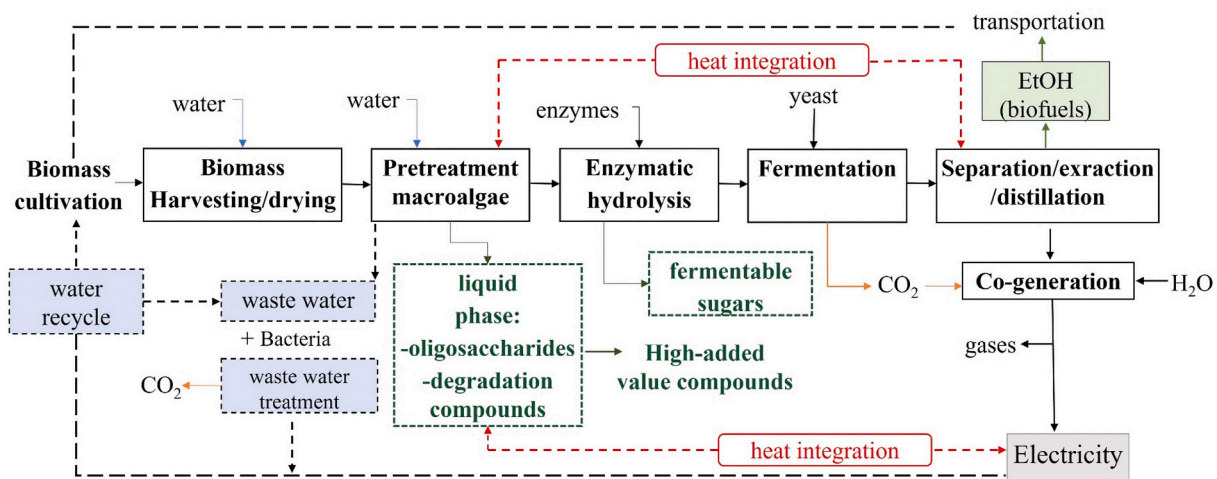


Fig. 4. Simplified block flow diagram of macroalgae biorefinery ethanol process.

added-value molecule along as a life cycle economy by producing electricity for an industrial plant, followed by gases (Alio et al., 2020). The residual water is also recycled to harvest the macroalgae process and the solid residue used for animal feed or fertilizer. To obtain process and operational cost is necessary for the techno-economic analysis to consider a life cycle and environmental process (Sanchez et al., 2014; Konda et al., 2015; Soleymani and Rosentrater, 2017; Brigljević et al., 2018). In a recent work Ruiz et al. (2020) and Singh et al. (2021) reported the process for biofuel production taking into consideration energy integration for second generation biorefineries with the aim of reducing production costs.

The macroalgae biorefinery process starts with biomass cultivation, harvesting, and drying; then, after the pretreatment stage, the next stage is recognized as enzymatic hydrolysis. The alternatives are to obtain enzymes from fungus on-site or purchase (commercial scale); another way is to convert polysaccharides into ethanol by fermentation. These end procedures include releasing CO₂, along with solid, liquid, and gaseous phases (Souza et al., 2021).

Considering the mass balance calculations for the biorefinery process can offer a mid-and long-term view of the structural costs needed for a biorefinery industry to be competitive and economically viable (Juneja and Murthy, 2017). Several cost analysis techniques exist; meeting the economic model assessment is an element of the techno-economic analysis. This model uses an economic model to calculate the equipment, material, and operational costs. One of them is the net present value, which is used to calculate the overall cost of ethanol production

by relating yearly cash flows and the initial investment required by considering an interest rate and several periods. The following formulas were used to calculate the results: equation Eq. (1) (Sanchez et al., 2013; Dickson and Liu, 2019).

$$NPV = \frac{\text{cash flow} \left((1+i)^n - 1 \right)}{i(1+i)^n} + \frac{\text{working capital}}{(1+i)^n} - \text{investment} \quad (1)$$

$$\text{cash flow} = \text{cash flow} - \text{cashout flow} \quad (2)$$

$$\text{cash outflow} = \text{direct production costs} + \text{taxes} + \text{financial costs} \quad (3)$$

$$\text{working capital} = f(\text{production costs}) \quad (4)$$

$$\text{investment} = \text{fixed capital} - \text{borrowing} \quad (5)$$

Where the cash flow is the difference between the inflow of cash and the outflow of cash without income tax or depressurization divided over the entire life of the plant, the cash income is the sum of annual ethanol production multiplied by the total cost of production, the outflow of cash includes all the fixed, and general expenses of the plant, the raw material, inputs, labor, electricity, services, and maintenance costs are considered in the costs of production (Sanchez et al., 2013), where y , n , i , and CF_y show the project year, project lifetime, discount rate, and after-tax cash flow in year y , respectively.

The capacity of a biorefinery plan or industry change depends on the process. This includes the capital investment and operating cost.

7.3. Techno-economic ethanol cost

The market value of the end product, such as ethanol, is directly proportional to the cost of the macroalgae, their growth and harvesting techniques, the origin of feedstock, and cost of transportation, weight yield, equipment, and technologies costs. To build a circular bioeconomy by means green and long-term, one must be demonstrated as economic viability with zero waste, hazardous chemicals, and gases (Somers and Quinn, 2019).

Some studies and research investigating the industrial-scale and pilot plant techniques for ethanol production by developing the ways of techno-economic analysis using different strategies, different solid loadings, contrasting software programs, and types of raw material, like macroalgae, lignocellulosic biomass to demonstrate that can be an alternative to convert biomass to biofuels (Gnansounou and Raman, 2016).

Hasanly et al. (2017) developed a techno-economic analysis of lignocellulosic raw material (wheat straw) into ethanol production by simulation using SuperPro Designer software. The profitability analysis revealed the design is potentially feasible. The simulation showed that 20 million liters of ethanol obtained by 104.22 thousand tonnes of wheat straw per year with the selling price was equal to or greater than 2.57 \$ l⁻¹. Bonfim-Rocha et al. (2018) reported an industrial biorefinery ethanol plant that modeled using Aspen Plus software; as a result, could process 2 to 3.5 mt/y sugarcane in the range of 1136–1988 t of methanol can be produced each year, and the production costs in the range of 0.51–0.62 \$/kg. Another comparative analysis of techno-economic studied by Brigljević et al. (2018) uses brown macroalgae material, economic and environmental implications of microalgae-based biorefinery's simulated in Aspen Plus software. The researcher studied at the industrial scale using *Saccharina japonica* as a raw material with fast pyrolysis. The techno-economical analysis was performed and compared to single conversion pathways such as biochemical and thermochemical. Macroalgae (dry weight) 50,800 flow kg/h and 0.07 Price USD/kg had shown both pathways favorably economically compared to standalone pathways of the same scale. Konda et al. (2015) studied techno-economic analysis of macroalgae using third-generation biorefinery; the cost of all the parameters such as feedstock price of \$100/MT and the minimum ethanol selling price was in a range of \$3.6–8.5/gal, which reduced to \$2.9–7.5/gal with macroalgae priced at \$50/MT. Producing chemicals in the range of €21–47/lb. or €16–40/lb. with macroalgae priced at \$100/MT gives an alternative economics biorefinery. As an alternative response to macroalgae biomass, these studies are based on the capital cost of the fermented products as bioethanol and biofuels like biogas, with estimated to price from \$25 to \$409 MT⁻¹ based on literature cost. Dickson and Liu (2019) reported an optimal biorefinery to produced bioethanol, with a minimum ethanol selling price of 1.31 \$/gal, indicated that biofuel production from *Saccharina japonica* macroalgae is viable. Chong et al. (2020) used Aspen Plus V10 software to conduct a techno-economic analysis of bioethanol produced from a red macroalgae *Eucheuma cottonii* as a cellulosic residue; the study found that obtaining 15,833.3 kg/h of macroalgae biomass was required to produce 7626 kg/h of anhydrous bioethanol with a minimum selling price of \$ 0.54/kg. These recent studies help to standardize and optimize the bioethanol process for biofuels to blend as an alternative with gasoline. At the industrial and plant scales, techno-economical analysis necessitates the use of modern methods and monitoring metrics such as bioconversion processes. This techno-economic analysis demonstrates that it has potential and economic viability for commercial deployment: for example, the mechanism of hydrolysis and fermentation using microorganisms required great understanding and control. On the other hand, this third-generation of biorefinery tries to convert to the real economy by further analysis as an alternative to the biomass conversion sugars source on-site enzyme production that should also determine to reduce raw material cost (Anto et al., 2020).

Most of the techno-economic analysis results are laboratory and scale

tests and need further optimization before full-scale industrial production (Suutari et al., 2015).

7.4. Third-generation biorefinery under socio-economic and bioeconomy

A sustainable biorefinery depends not only on the bioprocess but also on the economic, financial resources, season, environmental, and socio-economically aspects (Thompson et al., 2020). For the bioeconomy, the principles focus on preserving the sustainable use of biomass resources, reducing contamination, and providing food security, creating jobs for humanity. In this way, the macroalgae biomass following these principles strengthens the bioeconomy (Balina et al., 2017). Principal the macroalgae farming is rapidly increasing in north countries, making development in cultivation area and a high yield for sustainability, the principal macroalgae are *Eucheuma* spp. and *Kappaphycus alvarezii* for carrageenan, *Gracilaria* spp. for agar; and *Laminaria japonica* and *Pyropia* spp. all of which are used as food (Buschmann and Camus, 2019). Harvesting can produce considerable ecological, social, and economic consequences if not well managed. From one farming location and collection or transport to another production plant is challenging (Chemodanov et al., 2017). The disadvantage is that invasive macroalgae as *Sargassum* species affect the environment, which is problematic to harvest. For example, the Mexican government invested ~USD 17 million dollars to remove 522,226 tons of *Sargassum* in 2018, and ~USD 2.6 million dollars for the removal of 85,000 tons in 2019 (Chávez et al., 2020). This means that it is a costly process for cleaning and harvesting macroalgae on the coastline, so this has a severe impact on the socio-economic in the society. There are no official policies in countries, but in the USA estimate to challenge that the scale-up of algal biofuel production needed to be sufficient to meet at least 5% of demand for transportation fuels would place unsustainable demands on energy, water, and nutrients with current technologies, first, the macroalgal selection and improvement to enhance desired characteristics and biofuel productivity, then to be an energy that is comparable to other transportation fuels, or at least improving and approaching of other fuels, the use of wastewater for cultivating macroalgae or the recycling of harvest water, and make use of the high-added value compounds and biofuels from macroalgae, after having the economic analysis and how prices are needed to inform the potential amount that could be produced economically in the country. South Korea, Brazil, and Taiwan have major research and development projects with Marine Bioenergy Development Project and Green Growth Via Marine Algal Biomass, focusing on clean energy production from macroalgae biomass. In Mexico, support with Secretaria of Energy and its National Council for Science and Technology supply the majority of funding for macroalgae biofuels research., these were reported in (Laurens et al., 2017) State of Technology Review – Algae Bioenergy 2017.

However, the production of biofuels and products has mainly derived from government policies to reduce oil dependency and increase the share of renewable energy.

The bioprocess and techno-economic analysis can convert the biomass to the implementation of novel technologies to reach sustainable economic growth and market development. This allows maximizing the biomass conversion efficiency and reducing the number of invasive macroalgae waste approaches.

In conclusion, the principal challenge of techno-economic analysis is the standardization of the design model to scale up to pilot demonstration to validate reliable data and prices for the socio-economic development of scalable and cost-effective technologies.

8. Future trends challenges of macroalgae and recommendations

In this approach, the techno-economic analysis for implementing macroalgae biorefinery necessitates biomass conversion and process to a viable and efficient output. However, the high-added value compounds

to food, pharmaceuticals, and the energy industry as a biorefinery concept are dependent on the type of macroalgae species, pretreatments, and enzymatic process. As a result, there is a generosity to optimize and develop more technologies and research to reduce cost and equipment for the process of macroalgae-based biofuels and compounds in the future. For example, the utilization of carbohydrates and polysaccharides fractionated at the fermentation stage and the hydrolysis process generate many organic wastes like proteins, lipids, and other materials used for commercial-scale bioethanol production, thereby increasing the economic value of macroalgae biomass. This could be maximized as a biorefinery approach (Offei et al., 2018). Recent studies state that the energy and bioremediation by macroalgae biomass cultivation combined with bioethanol and biogas can render energetic sustainability using energy and transportation. These procedures also provide appreciable valuable compounds like biofertilizers to the plants, contributing to a sustainable environment for the chemical, agricultural, and fuel industries. However, the high production cost of macroalgal feedstock, productivity, and cost-intensive downstream processing has been the major bottlenecks in developing technology processes for biofuels (Makut, 2021).

As for recommendations of macroalgae biomass, some key of future research:

1. There are advantages of macroalgae biomass over other feedstocks, and these can use to design special reactors and processes to support the large areal requirements. As this field is still in its infancy, it is worth exploring the using macroalgae in biofuels production.
2. Development of the economic analysis and performance-based scale-up of the macroalgae biorefinery process is still required.
3. Applying concepts that explore the possibility of genetic modifications to the cellular biology of algae engineering to improve biorefinery products would be beneficial to the industry and the circular bioeconomy.

9. Conclusion

The valorization of macroalgae biomass is an alternative for processing under a biorefinery concept. In addition to implying a socio-economic to the process, the techno-economic analysis represents an advantage to show the cost, process design, and availability of these macroalgae biomass to develop the scale-up of bioprocess for future products in the market. To conclude, macroalgae biomass can potentially produce an economical and viable alternative to obtaining chemicals that can use for many applications mentioned in the review (antioxidants, pharmaceutical, food), biofuels (bioethanol) converting for bioenergy this from only biomass.

Declaration of competing interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest. There are no conflicts to declare.

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CRedit authorship contribution statement

Karla Daniela Gonzalez Gloria contributed to the design, conceptualization, editing, and compilation of the original manuscript. **Shiva and E. Aparicio**: Contributed to visualization, Review and English language editing, **Monica L. Chavez Gonzalez and Emily Kostas**: Contributed in Review & editing, **Rosa M. Rodríguez-Jasso, and Héctor A. Ruiz**: Contributed in visualization, Review & editing, Supervision, Funding acquisition, Resources, Project administration.

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