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Hydrothermal systems to obtain high value-added compounds from macroalgae for bioeconomy and biorefineries

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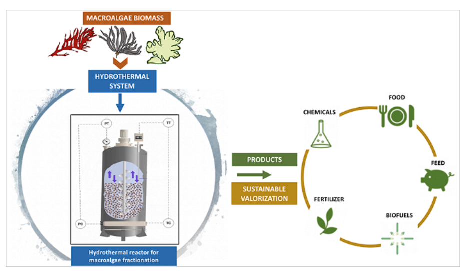
HIGHLIGHTS

- Hydrothermal systems are a potential technology for high-value compounds recovery.
- Operational conditions play an important role on the macroalgae target compounds.
- Energy savings in hydrothermal treatments make them a sustainable alternative.
- Macroalgae processing allows to enhance its application under biorefinery concept.

GRAPHICAL ABSTRACT



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ABSTRACT

The search of sustainable and environmentally friendly alternatives to obtain compounds for different industrial sectors has grown exponentially. Following the principles of biorefinery and circular bioeconomy, processes in which the use of natural resources such as macroalgae biomass is prioritized are required. This review focuses on a description of the relevance, application and engineering platforms of hydrothermal systems and the operational conditions depending on the target as an innovative technology and bio-based solution for macroalgae fractionation in order to recover profitable products for industries and investors. In this sense, hydrothermal treatments represent a promising alternative for obtaining different high value-added compounds from this biomass; since, the different variations in terms of operating conditions, gives great versatility to this technology compared to other types of processing, allowing it to be adapted depending on the objective, whether it is working under sub/super critical conditions, thus expanding its field of application.

1. Introduction

Macroalgae valorization, has demonstrated to offer several advantages over lignocellulosic and agro-industrial biomasses, due to its significant growing up world production from 10.6 million tonnes in 2000 to 32.4 million tonnes in 2018 of wild-collected and cultivated species, where farmed macroalgae represented 97.1 % (FAO, 2020). Moreover, macroalgae crops and wild collection has several advantages

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over other biomass sources, which include the requirement of zero inputs to grow, there is no competition with food supply, is an important source of unique compounds with a large variety of biological activities, there are no requirements of arable land, freshwater and fertilizer for their cultivation and the higher yields per unit, derived in faster growth rates, compared with terrestrial biomasses (Fasahati et al., 2015; Ruiz et al., 2015; Cervantes-Cisneros et al., 2017).

Despite the high abundance of inherent species of green, brown and red macroalgae around the world and the potential for sustainable cultivating and harvesting in the majority of the western countries these aquatic plants are an underutilized resource that could potentially be incorporated into different bio-based industries. In the last decade, great efforts have been made in order to develop technological innovations that can assist in improving macroalgae cultivation and biomass conversion process efficiencies on a commercial scale (Siller-Sánchez et al., 2019; Kostas et al., 2020).

The National Marine Fisheries Service (NOAA Fisheries, 2020) in US and FAO, (2020) has reported that macroalgae farming has been a fastest-growing aquaculture sector that bring benefits to farmers, communities, and the environment, mostly dominated by countries in East and Southeast Asia. In the last years, macroalgae cultivation are principally focused on kelp, *Kappaphycus alvarezii, Eucheuma* spp., *Undaria pinnatifida*, *Porphyra* spp and *Caulerpa* spp. species that are used as food and pharmaceutic products, ingredient in cosmetics, animal feed and fertilizer (FAO, 2020). Moreover, macroalgae farms are a sustainable and environmentally friendly industry that benefit communities and the environment because help to improve water quality and buffer the effects of ocean acidification in surrounding areas by the ability of macroalgae to absorb nutrients and carbon dioxide to growth (Xiao et al., 2021). Algal biomass is considered a promising source of various high-value products as well as biofuels not only because of its rapid growth capacity but also because of the ability to fix atmospheric carbon dioxide, which contributes significantly to the reduction of greenhouse gases (Yu et al., 2017). This contribution is quite considerable since this gas contributes approximately 52% to global warming, algae being photosynthetic organisms have a greater capacity even than terrestrial plants to take advantage of it and convert it into glucose for growth which can later be transformed into different types of biofuels, by using mainly their carbohydrates in fermentation processes replacing conventional sources of carbohydrates such as simple sugars or lignocellulosic biomass (Cheah et al., 2015, Chew et al., 2017).

The overexploitation of natural resources and economic development has representing the enormous emerging and critical problems around the world as: climate change, global warming, and hunger which are directedly related with overpopulation and the instability of the economic model (Lara-Flores et al., 2018, Pinales-Márquez et al., 2020). The Sustainable Development Goals of the UN has stablished that the main challenge for the society today is a sustainable way of living, meaning the implementation of economic changes such as bio-based industries, to mitigate pollution and environmental damages.

The implementation of third generation biorefineries implies the conversion of aquatic biomass (such as macroalgae, microalgae, and cyanobacteria) by diverse environmental and economically friendly technologies, such as hydrothermal process. In order to obtain a broad spectrum of high value-added compounds (chemicals, new materials, and renewable energies) with minimal emissions and wastes, including the minimal or no use of corrosive and contaminant reagents. The biomass macroalgae can be considered as a sustainable source in terms of biorefinery and bioeconomy by processing it using hydrothermal treatments (Fig. 1) (Ruiz et al., 2013; Aparicio et al., 2021; Lara et al., 2020; Kostas et al., 2021). A detailed description of the relevance, application and engineering platforms of hydrothermal systems as an innovative technology and bio-based solution for macroalgae fractionation in order to recover profitable products for industries and investors, under the principles of sustainability and circular economy, are described in the present review.

2. Macroalgae as a sustainable source of valuable compounds

Macroalgae are macroscopic, multicellular organisms usually classified into three groups Rhodophyta, Phaeophyta and Chlorophyta, according to their content of characteristic pigments, chlorophylls, carotenoids and phycobilins. The composition is species dependent, highly influenced by seasonal and geographical factors as well as processing conditions, polysaccharides being the most abundant fractions and are characteristic of each algal type. Brown macroalgae contain alginate, a polymer of guluronic acid and mannuronic acid, commercially used due to its high viscosity and gelling properties. Fucoidans, sulfated heteropolysaccharides with fucose as the major constituent, are attracting interest due to their biological properties, some of them are also exhibited by laminarins, which are beta-glucans (Holdt and Kraan, 2011; Cervantes-Cisneros et al., 2017; Abdul Latif et al., 2019; Torres et al., 2019; Cabello-Galindo et al., 2020). Agar and carrageenan, formed by polysaccharides of galactose and anhydrogalactose, containing sulfate and other groups, are major polysaccharides characteristic to red algae species and commonly extracted for commercial purposes. Ulvan, characteristics of green algae, are composed of xylose, glucose, rhamnose, iduronic acid, glucuronic acid and smaller amounts

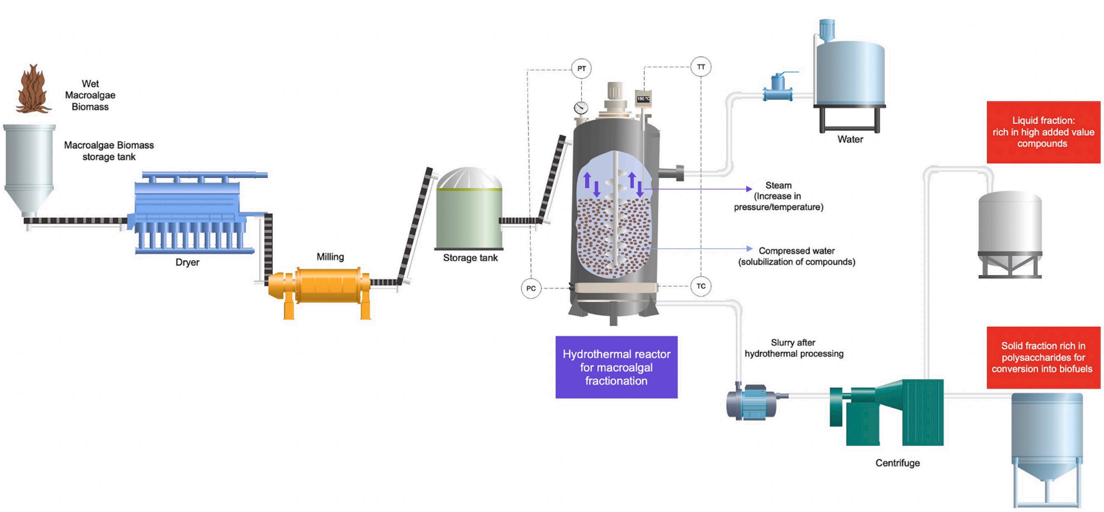

Fig. 1. Macroalgae biomass as a sustainable source in terms of biorefinery and bioeconomy using hydrothermal processing.

of galactose. Protein content is higher in red macroalgae and present all the essential amino acids. Brown macroalgae contain the highest amounts of phenolic compounds, mainly phlorotannins, a specific highly complex and diverse group of phloroglucinol derivatives. Also, flavonoids, bromophenols and phenolic acids can be present (Argüello-Esparza et al., 2019). The lipid content of macroalgae is low, but they show a highly unsaturated profile, with large proportions of arachidonic acid and eicosapentaenoic acid in brown and red macroalgae, respectively, and docosahexaenoic acid in green macroalgae (Trivedi et al., 2016; Gereniu et al., 2017; Yang et al., 2020). A summary of components and their major activities are presented in Table 1. Macroalgae also contain pigments, the major being chlorophylls, carotenes and phycobiliproteins, with a variety of properties, including antioxidant and antiproliferative (Holdt and Kraan, 2011).

Sustainability is becoming one of the main current society challenges, with a major objective of complying with the growing demand for food, feed, chemicals and fuels. Marine macroalgae is a widely available biomass feedstock requiring no arable land, freshwater or fertilizers and with faster growth rate, higher productivity, and photosynthetic efficiency compared to terrestrial plants (Raikova et al., 2019; Aparicio et al., 2020). Macroalgae cultivation offers additional advantages since they can aid in reducing carbon dioxide in the atmosphere, supplying oxygen to the sea, and can remove heavy metals from water (Goh and Lee, 2010). For a continuous supply, macroalgae cultivation is preferred, and the integrated aquaculture could significantly reduce the costs. Similarly, utilization of low-cost biomass, such as algae from eutrophication, algal blooms and invasive species, could prevent negative ecological impacts and provide sustainability of coastal environments. However, their development indicates an imbalance in the ecosystem that should be prevented and would require additional considerations for sustainable business models (Filote et al., 2021).

The complete valorization of this renewable resource is recommended in different scenarios: i) the industrial exploitation for hydrocolloids usually leaves an important part of the raw material as a residue and ii) the exclusive energetic valorization for relieving the pressure on fossil resources (Raikova et al., 2019; Abdul Latif et al., 2019; Mahadevan, 2015; Goh and Lee, 2010) can lack economic viability and the utilization of non-energy bioproducts and bioactive molecules could improve the final economy. Therefore, a biorefinery perspective with zero-waste is suggested for an integrated production of biofuels and value-added co-products for successful and cost-effective utilization of macroalgal biomass in an environmentally friendly way (Jung et al., 2013; Aparicio et al., 2020). In such a multistage cascading process the extraction of the macroalgae products should prioritize those with the highest value, such as bioactive or functional compounds (Kostas et al., 2017).

The process sustainability requires an approach based on an adequate selection of optimal technologies. Systems as hydrothermal or green solvent extraction of natural compounds complies with the consumers demand, the need for safe nontoxic solvents and with the design of efficient processes providing high yields and high-quality products with low energy and time requirements. Actually, innovative extraction methods include intensification strategies to reduce the costs and improve the yields and/or selectivity, such as hydrothermal or pressurized-hot-water extraction systems, pressurized solvents, microwaves, ultrasound or pulsed electric fields (Torres et al., 2019; Filote et al., 2021).

Table 1
Major components and fractions in macroalgae and their major functional and biological properties.

Fraction and components	Content(%, brown/ green/red)	Functional and biological properties[1]	Reference
Carbohydrate	38–67 / 42–67 / 36–70		Jin et al., (2013); Gereniu et al., (2017); Yang et al., (2020)
Agar/ carrageenan	- / - / 20–36	AV, G, Pr	Gereniu et al., (2018); Machmudah et al., (2019)
Alginate	11–40 / - / -	G, Pr, WH	Holdt and Kraan, (2011); Bordoloi and Goosen, (2020a)
Fucoidan	17–30 / - / -	AI, AC, AO, AT, IM, Pr	Holdt and Kraan, (2011); Aparicio et al., (2021)
Laminaran	4–30 / - / -	AB, AC, AI, AO; AP, AV, Pr	Holdt and Kraan, (2011)
Ulvan	- / 8–50 / -	AC, AI, AO, AP, AV	Trivedi et al., (2016); Shi et al., (2017)
Mannitol	20–30 / - / -	AO, Di, Sw	Holdt and Kraan, (2011)
Proteins and peptides	1–15 / 2–32 / 4–40	AH, AI, AM, AO; E, Fo	Holdt and Kraan, (2011); Gereniu et al., (2017); Jin et al., 2013; Yang et al., (2020)
Minerals	12–40 / 11–38 / 7–37	F, Bs	Gereniu et al., (2017); Polikovsky et al., (2020); Yang et al., (2020)
Lipids	0.3–5/2–5/ 1–20	AI, AM, IM	Trivedi et al., (2016); Gereniu et al., (2017); Yang et al., (2020)

[1] AO: antioxidant; AC: anticoagulant; AH: anti-hypertensive; AI: anti-inflammatory; AM: antimicrobial; AP: antitumoral; AV: antiviral; Bs: biostimulant; E: emulsifying; Di: diuretic; F: fertilizer; Fo: foaming; G: gelling; IM: immunomodulatory; Pr: prebiotic; Sw: sweetener; WH: wound healing

3. Current challenges for the cultivation and extraction of high-value compounds from macroalgae

The growing need for food, feed, energy and many more due to the exponential growth of the population represents great challenges in various factors. Macroalgae production is currently a multi-billion industry, at least 291 species are cultivated around the world including green, brown and red species. The production of these has shown an annual growth of around 10% (Krastina et al., 2017). In the last ten years, the brown and red macroalgae were cultivated in much larger quantities than green macroalgae, the global total production reached 30.1 million tonnes wet weight in 2016 with a value over USD 11.7 billion, and projections have been made that by 2027 more than 200,000 tons will be produced for food, feed, biofuel and other uses (Tan et al., 2020); However, not all countries have direct access to the sea for the cultivation and harvest of macroalgae, which represents a challenge for the present and future use of this biomass. On the other hand, climate change due to intense human activity has caused a serious alteration in the marine ecosystem, the world's largest green and yellow tide caused by the macroalgae blooms causing significant economic losses (Xing et al., 2019). The collection of these macroalgae for other uses contributes in a certain way to counteract the problem and make these activities more sustainable.

The main groups of high added value compounds that can be obtained from macroalgae are biofuels, carbohydrates and antioxidants; However, currently the processes for obtaining them are considered under development and most of the alternatives are still carried out on a laboratory or pilot scale (Tan et al., 2020), so one of the main challenges for obtaining compounds of interest from macroalgae is to be able to develop processes possible on an industrial scale so that a considerable impact can truly be observed.

4. Engineering principles of hydrothermal systems to obtain high value-added compounds

Hydrothermal treatments from an engineering point of view can be described as supplying energy to increase the temperature and pressure in a system. The energy source can be very diverse, from traditional forms such as superheated steam to the use of new technologies such as ultrasound and microwave. This type of treatment can have multiple applications in different sectors. However, this section focusing on its use to obtain high value-added compounds from macroalgae. During processing by hydrothermal treatments, operating parameters such as temperature, pressure, particle size, water to solid ratio, and resident time should be considered, since their effectiveness will depend on these (Aguilar-Reynosa et al., 2017a; Cervantes-Cisneros et al., 2017; Ruiz et al., 2017; Ruiz et al., 2020).

As can be seen in Fig. 2, depending on the objective and the type of product to be obtained, hydrothermal treatments can be classified into 3 different processes (Ruiz et al., 2017; Abdul Latif et al., 2019; Aparicio et al., 2020).

1. Carbonisation: generally carried it out in a temperature range from 150 °C to 230 °C and pressures from 2 MPa to 4 MPa, and the main products obtained are char, and some carbohydrates (Koks, 2016). According to Marzbali et al., (2021) the carbonisation improve significantly the energy density of the hydrochar obtained making it convenient as a secondary fuel/coal substitute.

Recently, carbonisation has been used for the valorization of macroalgaes as *S. latissima* and *F. serratus* by obtaining hidrochars, and biomethane (Brown et al., 2020); although, for years this method has also been used in *Laminaria digitata*, *Laminaria hyperborean*, and *Alaria esculenta* to production of bio-coal, bio-methane and fertilizer (Smith and Ross, 2016).

2. Liquefaction: it can be described as the thermochemical conversion of different types of biomass such as macroalgae into liquid fuels mainly (Elliott et al., 2015). This conversion occurs through the breakdown of the biopolymeric structures present in the biomass due to the effect of temperature and pressure ranging from 230 °C to 330 °C and at pressures of 4 MPa up to 15 MPa respectively, which are considered subcritical (Abdul Latif et al., 2019). In this mentioned temperature range, it is possible to obtain phenolic compounds, hydrochar and even biocrude.

In recent years, liquefaction processes have proven to be convenient for the treatment of macroalgae to obtain high-value products. *Ulva prolifera*, *Sargassum tenerrimum* and *Gracilaria corticate* have been used to obtain bio-oil (Yan et al., 2019; Ma et al., 2020; Biswas et al., 2020; Li et al., 2021) and *Mesoporous* by-product to produce biochars (Parsa et al., 2019). Ong et al., (2019) concluded that hydrothermal liquefaction is highly recommended to bio-oil production from macroalgae (*Caulerpa lentillifera*, *Gracilaria coronopifolia*, and *Chaetomorpha linum*) because their high moisture content (80% approximately) increase the efficiency in combination with microwave technology.

3. Gasification: it refers to the most severe process since for this it is necessary to reach temperatures ranging from 330 °C to 550 °C and pressures between 15 MPa and 23 MPa (Abdul Latif et al., 2019). This type of thermochemical conversion it is particularly suitable for the exploitation of macroalgae due to the content of inorganic metals, which achieve a catalytic effect in the process (He et al., 2020). Gasification can be used for the production of high-value compounds under different atmospheres such as air, steam, O_2, CO_2, etc. (Ren et al., 2019).

Gasification has been used in macroalgae to obtain various products, to mention some C. *glomerata* as bioresource for hydrogen-rich gas production (Safari et al., 2016), *Kappaphycus alvarezii* to obtain biohydrogen (Jayaraman et al., 2021); being the production of hydrogen so important, special attention has also been given to the optimization of the process conditions Okolie et al., (2021) has made a compilation of the mathematical models that have been developed for this purpose, which is quite useful in saving resources.

Even the combination of the hydrothermal liquefaction and supercritical water gasification process have been studied for a better use of macroalgae biomass, obtaining various products such as crude bio-oil, solid, gas, and water-soluble products; demonstrating, that the integration of both of them could improve energy recovery from algal biomass in comparison to each process individually (Duan et al., 2018).

One of the key points in hydrothermal treatments is energy expenditure, as in any other process. In order to achieve the necessary conditions (temperature and pressure) for the different variants of hydrothermal treatments, it is necessary to supply energy to the system. This energy can come from different sources, which can be conventional as steam and heat conduction. However, since the 1990 s technologies such as microwaves and ultrasound took the rise mainly because it favors that the processes are more sustainable due to a considerable reduction in energy and cost spent.

On the other hand, the effectiveness of hydrothermal treatments is essential for the viability of using them. One way to evaluate the hydrothermal treatment effectiveness is the severity factor, although it has been most used for the study of the effectiveness in lignocellulosic biomass that describes the degree of solubilization of compounds present in the cell wall (Silverstein et al., 2007; Aguilar-Reynosa et al., 2017b; Aguilar et al., 2018), is fully applicable to the effect on macroalgae (Aparicio et al., 2021). In a recent publication, Ruiz et al. (2021) described in detail the relevance and operational correlation of the severity factor, which is an index that represented by a numerical value the degree of hydrolysis effectiveness by the changes of time and

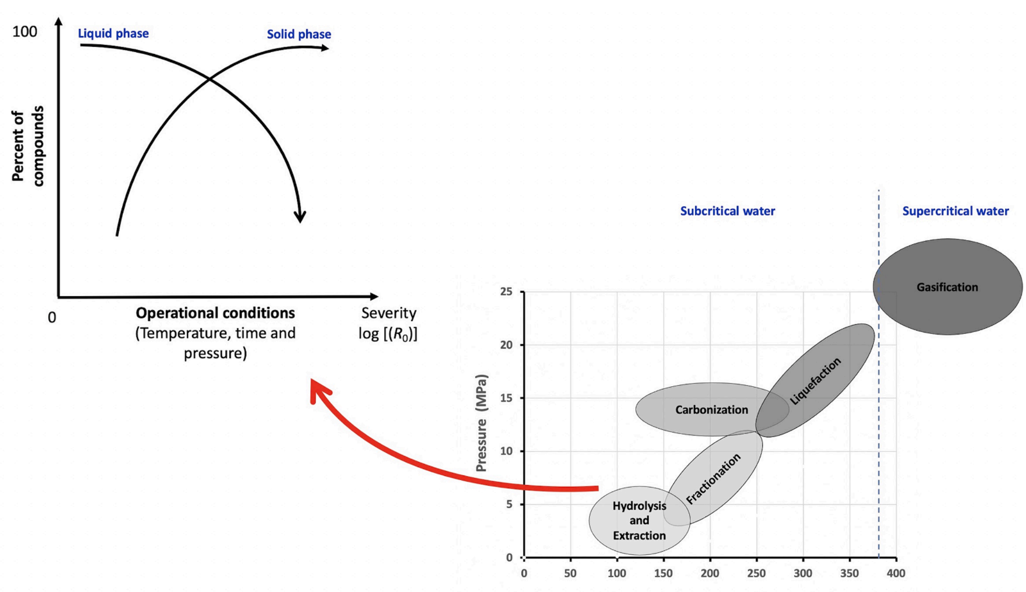

Fig. 2. Hydrothermal treatment variations according to the operational conditions (pressure and temperature).

temperature, and its mathematical modeling representation is described by the equation 1. The relationship between the temperature and the time of the hydrothermal treatment, allowing this value to be used as an indicator of the degree of fractionation and hydrolysis over the different biomasses and the target compounds that can be produced and valorized. The equation to calculate the severity factor considers the entire process from the beginning of the heating process (time it takes to reach a specific temperature), the isothermal stage (time the desired temperature is maintained), to the cooling time (time it takes to lower the temperature until reaching the initial temperature), which is the basis of hydrothermal treatments in any of its variants (Pedersen and Meyer, 2010; Chornet and Overend, 2017).

$$log\,R_o = [R_0 Heating] + [R_0 Isothermal\,process] + [R_0 Cooling]$$

$$log\,R_o = \left[\int_0^{t_{max}} \frac{T(t) - 100}{\omega}\right] + \left[\int_{ctrl}^{ctrf} exp\left[\frac{T(t) - 100}{\omega}\right] dt\right] + \left[\int_0^{t_{max}} \frac{T'(t) - 100}{\omega}\right]$$

The severity factor was determined taking into account the heating-up and cooling profiles and the isothermal section of the process. Where $[log\,R_0]$ is the severity factor, t_{max}(min) is the time demanded to reach the peak of temperature, $T(t)$ and $T'(t)$ are the profile of temperature in heating and cooling steps, *ctrl* and *ctrf*(min) are the period needed for the overall heating–cooling process, and ω is an empirical number with a value of 14.75 (Pino et al., 2019; Aparicio et al., 2021).

In addition to severity factor equation, there are some other forms of the equation that adapt to other representations related to the effectiveness of treatments.

Hydrothermal treatments seem to be convenient and effective alternative for obtaining high value compounds; However, the operational conditions should not be neglected, since depending of the pressure and temperature ranges, different products can be obtained, and the optimization of these operational conditions is essential for their sustainability. Also, the valorization of macroalgae biomass represents an alternative with advantages as an organic source of endless compounds, and even the humidity and composition of macroalgae favors hydrothermal processes, so this impulse that has been taken in recent years will surely continue and the generation of knowledge in this sector will bring enough economic and environmental benefits (Ruiz et al., 2021).

5. High-value added compounds from macroalgae obtained with hydrothermal treatments

It is well known that macroalgae are rich in minerals and dietary fibers, as well as other types of compounds such as fatty acids, polyphenols, sterols, proteins, sulfated polysaccharides, antioxidants, pigments, to name a few (Zhao et al., 2018; Argüello-Esparza et al., 2019) as is mentioned above. All of these are considered high added value compounds and various methodologies can be used to obtain them. However, in this review we are focusing on hydrothermal treatments. In addition to this, it is important to mention that there is also the production of biofuels from macroalgae by hydrothermal treatments that, although under different conditions, can be obtained solid, liquid and gas biofuels (Jin et al., 2013; Aparicio et al., 2020). Hence, the particular interest for a macroalgae biorefinery is based in the hydrothermal systems sustainability for aquatic biomass valorization and fractionation to high value and high commercial compounds combined with biofuels production (Fig. 3) (Ruiz et al., 2013; Ruiz et al., 2015).

The effect of hydrothermal treatment to obtain compounds of interest also depends on the type of algae and harvest time. Abeln et al., (2019) evaluated the hydrothermal pretreatment in 12 different types of macroalgae, observing that under rapid hydrothermal microwave pretreatment carbon efficiencies increase. However, a large fraction of this carbon remained locked in polysaccharides, and under more severe condition the degradation of polysaccharides has been favored, which increases the effectiveness in subsequent fermentations, which is reflected in a higher conversion of biomass.

One of the categories with the greatest boom in terms of compounds obtained by hydrothermal treatments are polysaccharides, because the particular physicochemical properties and the biological activity. The polysaccharides content it depends on the macroalgae type. a) Brown macroalgae: laminarin, alginate, and fucoidan. b) Red macroalgae: floridean starch, and carrageenans. c) Green macroalgae: agar, xylan, mannan, ulvan, xylan, mannan, and starch (Cervantes-Cisneros et al, 2017; Saravana and Chun, 2017). The increase demand of hydrocolloids in the industry has fostered the search for better methods of obtaining them. In this sense, the extraction conditions are a function of the target hydrocolloid. Respect to the temperature, above than 85 °C for agar, 80–90 °C for ulvan; on the other hand, the pH to alginate, which must be above the pKa, or the solubility in the case of carrageenan, which can be

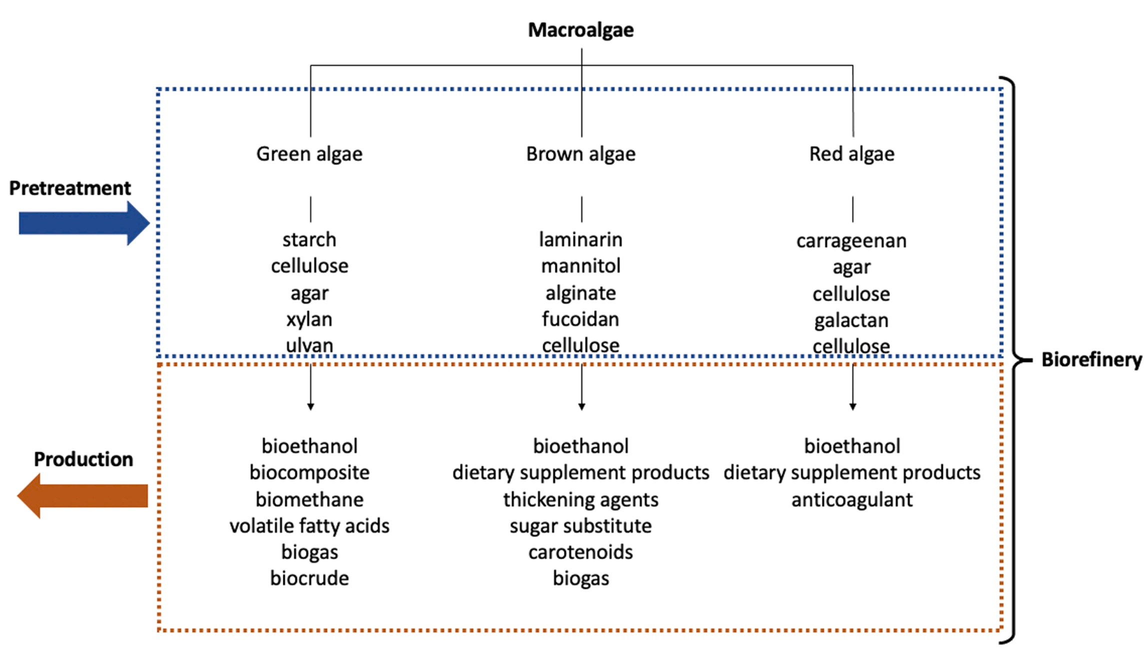

Fig. 3. Macroalgae high value-added products under the biorefinery principle.

both in cold and hot water.

Another large group is that of compounds that are characterized by their bioactivity, among which polyphenols and flavonoids stand out, as well as some proteins, peptides, and although fucoidan has already been mentioned in the polysaccharides group it must also be included in this group due to the bioactivity it possesses (Plaza et al., 2010; Balboa et al., 2013; Rodríguez-Jasso et al., 2013; Gereniu et al., 2017; Pangestuti et al., 2019; Flórez-Fernández et al., 2021; Trigueros et al., 2021).

Finally, there is the obtaining of sugars by hydrolysis that is later used in fermentations with different objectives, among which the production stands out. For this, most of the cases focus on applying the hydrothermal treatment to the macroalgal biomass in order to hydrolyze the main components of the cell wall that favors the release and hydrolysis of polysaccharides. So, that the simple sugars are increased, subsequent processes them are used as a carbon source for different microorganisms in order to obtain mainly bioethanol and hydrochar (del Río et al., 2019; Greiserman et al., 2019; Polikovsky et al., 2020; Steinbruch et al., 2020; Aparicio et al., 2021).

Nowadays, hydrothermal treatments that involve the use of microwaves, ultrasounds, high pressures are considered the most promising processes, since they improve extraction performance, considerably reducing time and energy consumption, making them more sustainable (Gomez et al., 2020).

Based on the above, within hydrothermal processes, most of the obtaining of compounds of interest is carried out under subcritical conditions, which are characterized by keep the water temperature above its boiling point (100 °C/273 K, 0.1 MPa), and below its critical point of (375 °C/647 K, 22.1 MPa) in order to keep it in a liquid state (Saravana and Chun, 2017).

Table 2 shows some examples of the outcomes obtained for different type of compounds from macroalgae and the hydrothermal treatment conditions. In this way, the great potential of the use of hydrothermal processes to obtain compounds with high added value is evident, and it is a fact that the exploration of how to optimize these processes depending on the type of macroalgae and the compound of interest to be obtained will continue in the next years.

6. Potential of hydrothermal systems to obtain valuable compounds from macroalgae

Hydrothermal processing with water under subcritical conditions can be proposed either as a fractionation tool, based on the extraction and depolymerization of the major components to be further separated and valorized, or for the thermochemical transformation into final products, usually with chemical and energetic applications. A survey of both applications is presented in this section.

6.1. Extraction of macroalgae compounds and fraction with biological properties

6.1.1. Phenolics, protein and saccharidic compounds

Hydrothermal treatment at temperatures close to 200 °C has proved optimal for the extraction of phenolic, protein and saccharidic compounds from macroalgae (Balboa et al., 2013; Flórez-Fernández et al., 2019; Alboofetileh et al., 2019; Sarmiento-Padilla et al., 2021) in shorter times (20–40 min) than conventional extraction. Further reduction of the extraction time can be achieved using microwave heating (Rodriguez-Jasso et al., 2011; Quitain et al., 2013; Ponthier et al., 2020) or combination with ionic liquids (Vo Dinh et al., 2018).

Hydrothermal processing with subcritical water is promising for the extraction and hydrolysis of protein (Álvarez-Viñas et al., 2021). Trigueros et al., (2021) processed the *Gelidium sesquipedale* industrial wastes in a semicontinuous fixed-bed reactor for the solubilization of phenolic and proteinic fractions, maximum in the protein extraction was achieved at 185 °C. However, most studies deal on the possibility of extracting the polysaccharidic fraction, also, the simultaneous

Table 2
Examples of hydrothermal processing of seaweeds.

Seaweed	Treatment conditions	Outcomes	Reference
Ecklonia maxima	180 °C, LSR 30 mL/g, 23.7 min (phenolics), 120 °C, 5 min (polysaccharide)	Extraction of alginate, sulfated fucoidans and phenolic compounds with antioxidant activity	Bordoloi and Goosen, (2020b)
Entermorpha prolifera and *Spirulina platensis*	LSR 9.5, 340 °C, 40 min	Co-liquefaction of microalgae and macroalgae	Jin et al., (2013)
Fucus vesiculosus	MAE; LSR 25, 172 °C, 1 min, MAE	Extraction of fucoidan	Rodriguez-Jasso et al., (2011)
Fucus vesiculosus	LSR 25, 180 °C, 20 min	Extraction of fucoidan	Rodríguez-Jasso et al., (2013)
Gelidium sesquipedale agar extraction waste	Semicontinuous fix-bed reactor, 2 mL/min, 185 °C	Extraction of protein, polyphenolics, peptides and free amino acids. Ash in solid residue for fertilizers	Trigueros et al., (2021)
Hypnea musciformis	LSR 50, 210 °C	Extraction of sugar, protein, phenol, and flavonoids with antioxidant and thermostable emulsifying properties	Pangestuti et al., (2019)
Himantalia elongata	ASE 200 °C, 20 min	Phenolics with antiradical and antimicrobial properties	Plaza et al., (2010)
Himantalia elongata	NI (160 °C) (alginate, sulfated fucoidan), 220 °C (phlorotannins)	Extraction of sulfated fucoidans and phlorotannins with antiradical and cytotoxic effects against lung, ovarian and breast carcinoma cells	Cernadas et al., (2019)
Kappaphycus alvarezii	LSR 40, 150–300 °C, 1 MPaSugar (150 °C, 1 MPa) Polyphenol and protein (270 °C/8 MPa)	Extraction of sugars, phenolics and proteins and the products showed antiradical and emulsifying properties (270 °C/8 MPa)Sugar and foaming and emulsifying properties	Gereniu et al., (2017)
Kappaphycus alvarezii	LSR 80, 150 °C, 1% BMIMAc	Depolymerization of κ-carrageenan, and enhancement of bioavailability and properties (gel strength, viscosity, emulsification, antioxidant)	Gereniu et al., (2018)
Kappaphycus alvarezii	LSR 160, 130 °C, 200 rpm, 5 min	Isolation of κ-carrageenan for the preparation of nanoemulsions with fucoxanthin rich seaweed oil	Saravana et al., (2019)
Laminaria japonica	LSR 40, 115 °C, 1 h	Extraction of low molecular weight low viscosity fucoidans wih bile acid-binding capacity	Gao et al., (2017)
Mastocarpus stellatus	MAE; LSR 30, 170 °C, 6 min (carrageenan), 190 °C, 3 min (phenolics)	Extraction of carrageenan and phenolics with antioxidant properties	Ponthier et al., (2020)
Nizamuddinia zanardinii	LSR 20 mL/g, 150 °C, 29 min	Extraction of fucoidan with antiradical, reducing, antitumoral and immunomodulatory properties	Alboofetileh et al., (2019)
Saccorhiza polyschides	Distilled water, LSR 10, 180 °C,	Essential macroelements (K, Na, S, Ca, and Mg),	Soares et al., (2020)

(continued on next page)

Table 2 (*continued*)

Seaweed	Treatment conditions	Outcomes	Reference
	30 min, agitation frequency 3 Hz	micronutrients (Zn, B, Cl, P, Mo, V, Se, and I), low levels of Ni, Cd, and Pb for biofertilizer	
Saccharina japonica de-oiled by sc-CO_2	LSR 10, 240 °C	Antibacterial activity on Gram-negative and Gram-positive bacteria	Meillisa et al., (2013)
S. japonica	LSR 25, 180 °C, 1% formic acid	Depolymerization of alginate, extraction of sugars and antioxidants	Meillisa et al., (2015)
Saccharina japonica	LSR 25, 180 °C	Extraction of amino acid, mineral, and monosaccharides, low heavy metals content	Saravana et al., (2016)
Saccharina japonica	175 °C, [C4C1im][BF4]	Phenolics with radical scavenging and reducing properties	Vo Dinh et al., (2018)
Sargassum muticum	NI: alginate, fucoidans (150 °C), phlorotanins (170 °C)	Extraction of fucoidan and phenolics, utilization of solid for biogas production	Balboa et al., (2013); Flórez-Fernández et al., (2019)
Sargassum muticum	NI (150 °C)	Enhance enzyme susceptibility for ethanol production	del Río et al., (2019)
Sargassum muticum	NI (190 °C)	Enhance enzyme susceptibility for ethanol production	Aparicio et al., (2021)
Ulva sp.	Seawater, LSR 11.5, 180 °C, 40 min	Two-step fermentation (*S. cerevisiae* and *E. coli*) of the liquid phase to ethanol and hydrochar formation	Polikovsky et al., (2020)
Ulva sp.	170 °C, 20 min, 38 g/L salinity, LSR 19	Production of polyhydroxyalkanoates (with *Haloferax mediterranei*) and biochar	Ghosh et al., (2021)
Ulva sp.	LSR 11.5, 180 °C, 40 min; seawater (salinity 38.2 g/L)	Production of monosaccharide, hydrochar, and polyhydroxyalkanoates by fermentation	Steinbruch et al., (2020)
Ulva sp	LSR 19, 170 °C, 40 min, seawater	Hydrolysis to fermentable sugars with minimum formation of 5-HMF and carbonization to hydrochar	Greiserman et al., (2019)

MAE: microwave assisted extraction; NI: non isothermal heating up to a maximum temperature (T)
[C4C1im][BF4]: 1-butyl-3-methylimidazolium tetrafluoroborate; BMIMAc: 1-Butyl-3-methylimidazolium acetate

depolymerization could serve to prepare lower molecular weight compounds, with enhanced bioavailability and bioactivity (Rodríguez-Jasso et al., 2014; Gao et al., 2017; Flórez-Fernández et al., 2019). Alboofetileh et al., (2019) reported on the subcritical water extraction of fucoidan from *Nizamuddinia zanardinii* produced polysaccharides with lower molecular weights than conventional and enzyme assisted extraction, but less depolymerized than those from acidic extraction, ultrasound or microwave assistance techniques (Fig. 4).

Hydrothermal technology proved also suitable for the depolymerization of fucoidan previously extracted from macroalgae (Saravana et al., 2018a,b; Morimoto et al., 2014).

In general, an increase in the hydrolysis efficiency was observed as the temperature increased. A high temperature decreases the solvent viscosity, facilitating solvent penetration and diffusion stages, but also the disruption of the interactions between solutes and matrix. The highest hydrolysis efficiency ranged from 70 to 97% showing a consistent increase with increasing temperature and pressure conditions (Balboa et al., 2013; Gereniu et al., 2017; Cernadas et al., 2019; Pangestuti et al., 2019; Flórez-Fernández et al., 2019). However, excessive depolymerization and desulfation occurring at higher severity (usually above 150–180 °C) should be avoided (Balboa et al., 2013; Alboofetileh et al., 2019; Gereniu et al., 2017; Flórez-Fernández et al., 2019). The initial pH, usually neutral, gradually decreased (3–6.8) (Greiserman et al., 2019; Pangestuti et al., 2019; Steinbruch et al., 2020; Aparicio et al., 2021) due to the auto-ionization of water causing the release of hydronium ions from water and the sulfate groups from polysaccharides, and then due to degradation of sugar into organic acids, which maintain the autocatalytic process. The color of the extracts could be affected, with a progressive darkening due to pigments (Alboofetileh et al., 2019) and Maillard products (Saravana et al., 2016; Saravana et al., 2018a; Pangestuti et al., 2019; Plaza et al., 2010; Gereniu et al., 2017; Yang et al., 2020). The addition of catalyst was proposed to aid in the solubilization of different polysaccharides. Gereniu et al., (2018) proposed the use of 1% 1-Butyl-3-methylimidazolium acetate during subcritical water extraction of κ-carrageenan from *Kappaphycus alvarezii* at 150 °C and 5 MPa. Gel strength and viscosity were minimal, but emulsification index was relatively high.

The need for different conditions depends on the final target product and the severity required increased in the order carbohydrate, phenolic and protein fractions. Some examples can illustrate this behavior. Bordoloi & Goosen, (2020b) found the maximum extraction yield from *Ecklonia maxima*, phenolic content and antioxidant activity operating at 180 °C and 23.75 min, whereas for alginate and sulfated polysaccharide fractions optimal conditions were 120 °C for 5 min. Pangestuti et al., (2019) reported a similar trend for *Hypnea musciformis*. The phenolic acids and flavonoid content increased reaching maximum values at 210 °C, a trend that might correlate with the protein content, emulsifying and antioxidant properties. Gereniu et al., (2017) have observed that the sugar content and foaming properties from *Kappaphycus alvarezii* were optimal at 150 °C, but the polyphenol and protein content, and the antiradical and emulsifying activities were favored at 270 °C. These trends have been reported for different brown macroalgae processed under non isothermal conditions, i.e. for *S. muticum*, 175 °C was preferred for fucoidan and 210 °C for phenolics (Balboa et al., 2013), for *Saccharina japonica* maximal monosaccharides, mannitol and amino acids levels were reported at 180 °C (Saravana et al., 2016), for *Himantalia elongata* the highest crude sulfated fucoidan and biopolymer-based compounds were found at 160 °C, whereas phlorotannins at 220 °C (Cernadas et al., 2019), for *Laminaria ochroleuca* the maximal fucose content was attained at 180 °C, sulphate and alginate at 160 °C, and phenolic, protein and antioxidants at 220 °C (Flórez-Fernández et al., 2019). Compatible conditions for pressurized hot water extraction of carrageenan and phenolic compounds from *Eucheuma cottonii* at 200 °C have been reported (Machmudah et al., 2019).

Previous washing, drying and defatting to remove the non-target materials both with conventional solvents (Gao et al., 2017; Alboofetileh et al., 2019) and with supercritical carbon dioxide (Meillisa et al., 2013 and 2015; Setyorini et al., 2018) has been reported.

6.1.2. Minerals

The influence of the hydrothermal treatment on the mineral fraction has been reported. Soares et al., (2020) proposed the subcritical water processing of *Saccorhiza polyschides* at 180 °C to obtain essential macro and trace elements, with potential application as a biofertilizer. As a general trend, increasing extraction temperature leads to higher mineral concentration in the final extract, containing macronutrients (K, Na, S, Ca, and Mg) and micronutrients (Zn, B, Cl, P, Mo, V, Se, and I), but low levels of toxic compounds. Saravana et al. (2016) observed increased Mg, Ca, K, and Na contents from *Saccharina japonica* with increased temperature between 180 °C and supercritical conditions, whereas the Al content decreased with temperature.

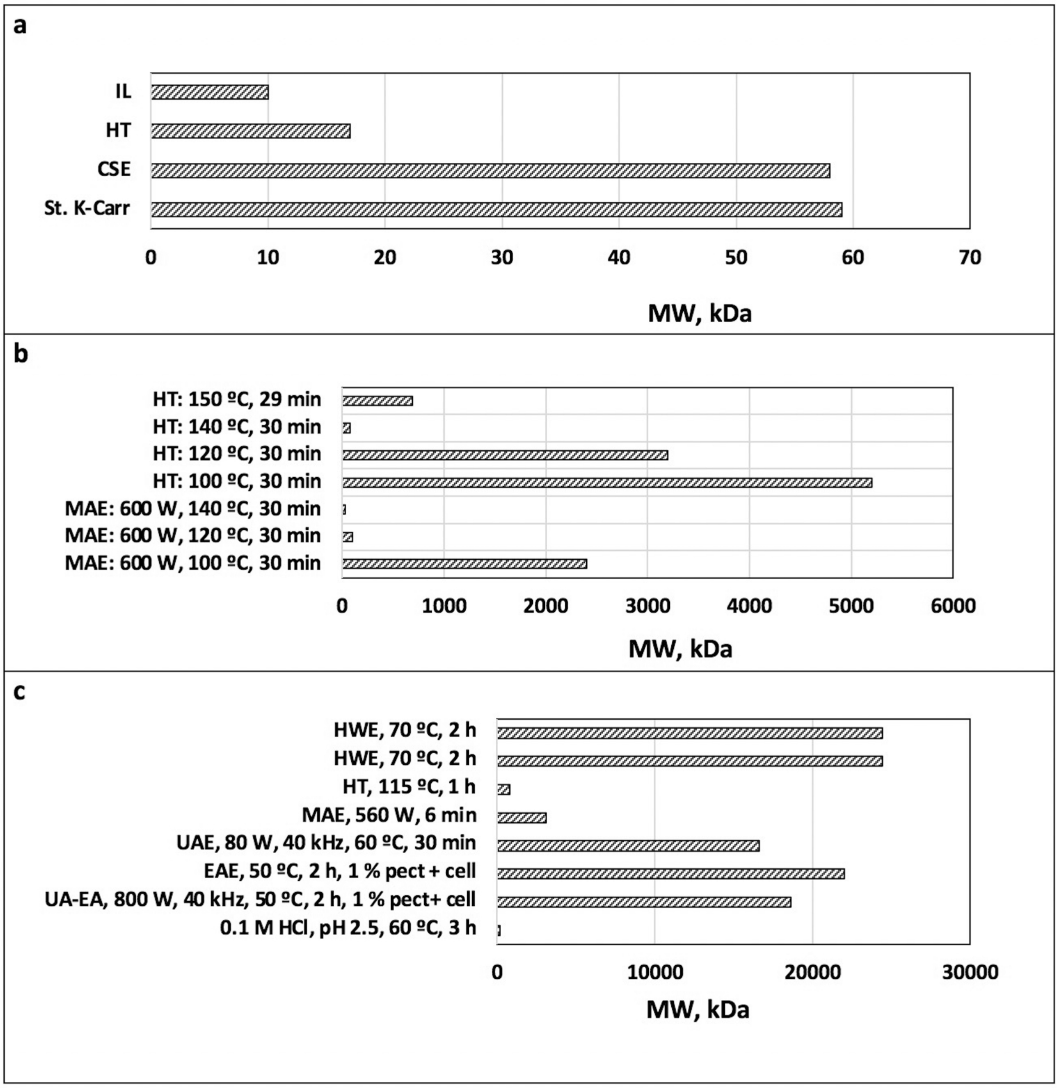

Fig. 4. Influence of the hydrothermal treatment on the molecular weight of a) of carrageenan obtained from *Kappaphycus alvarezii* with conventional solvent (CSE, 107 °C) and for hydrothermal extraction (150 °C) with water (HT) and with ionic liquid (IL) as catalyst in comparison with standard carrageenan (Gereniu et al., 2018); b) fucoidan from *Undaria pinnatifida* extracted by hydrothermal extraction with conventional heating (HT, 100–140 °C) and with microwave assistance (MAE) and extraction of fucoidans from *Nizamuddinia zanardinii* at 150 °C (Alboofetileh et al., 2019); c) extraction of *Laminaria japonica* polysaccharides with different technologies, ultrasound (UAE), microwave (MAE), enzymes (EAE), ultrasound-enzymes (UA-EA) (Gao et al., 2017).

6.2. Bioconversion to chemicals and biofuels

Macroalgae are a potential feedstock to replace fossil resources in the production of biofuels, plastics and chemicals through thermochemical and biochemical pathways (Abdul Latif et al., 2019; Greiserman et al., 2019). Before macroalgae bioconversion an important step is the separation of the polysaccharide fraction and further depolymerization into metabolizable components (Steinbruch et al., 2020).

6.2.1. Pretreatments before biochemical processes

Compared to terrestrial sources, the lack of lignin facilitates the first stage, and the heterogeneity of most polysaccharides facilitates the degradation stage of complex carbohydrates to fermentable sugars (Greiserman et al., 2019). Macroalga are also attractive feedstocks to formulate media for microbial bioconversion, since they can provide highly bioavailable nutrients, such as protein and free aminoacids (Polikovsky et al., 2020). In this context, subcritical thermal hydrolysis is an alternative to acid or enzymatic hydrolysis for deconstruction of complex macroalgae carbohydrates (Ghosh et al., 2021; Greiserman et al., 2019). Compared to other technologies, hydrothermal pretreatments offer advantages derived from the low capital investment, environmental impact and generation of inhibitory compounds (Aparicio et al., 2021).

Temperature is a key factor for the release of sugars but also for the formation of microbial inhibitors, such as 5-hydroxymethylfurfural (5-HMF), formic acid, lactic acid, acetic acid, and levulinic acid. Other relevant variables are salinity, solid load, and treatment time (Greiserman et al., 2019).

The hydrolysates can be used for bioconversion processes to produce biofuels and other bioproducts (Ghosh et al., 2021). Furthermore, the hydrothermal treatment enhanced the enzymatic susceptibility of the solid phase, which can be further converted into fermentable sugars. *Sargassum muticum* biomass pretreatment has been applied before the production of bioethanol. del Río et al., (2019) have reported that 10% glucan was solubilized as oligomers in the liquid phase and the 90% remaining in the solid phase, was quantitatively converted to glucose and further into ethanol. Aparicio et al., (2021) obtained glucan enriched pretreated solids, highly susceptible to the enzymatic hydrolysis stage, which could be performed in a pre-simultaneous saccharification and fermentation strategy to produce bioethanol. The beneficial effect of this pretreatment on the biogas production from the solid fraction was probably due to the removal of phenolic compounds, and the effect of pretreatment breaking the biomass structures (Flórez-Fernández et al., 2019).

6.2.2. Thermochemical transformation of whole biomass

Thermochemical processing is relatively simple and utilizes the organic fraction, including lipids, proteins, and carbohydrates. Of the two main routes to produce biocrude from biomass, pyrolysis requires dried biomass whereas hydrothermal liquefaction can be used to process directly the wet biomass. Hydrothermal liquefaction is a relatively low-energy technique occurring at high temperature high pressure in liquid state water (Raikova et al., 2019). The most important product is bio-crude oil, consisting of aliphatic and aromatic hydrocarbons, having the potential to be refined as crude oil in fossil refineries. Depending on the severity, different terms are used, hydrothermal carbonization (under 250 °C) to produce a hydrochar, hydrothermal liquefaction (up to 374 °C) yielding a biocrude and gasification is dominant at higher temperatures resulting in the production of a synthetic fuel gas (Elliott et al., 2015). The processes occurring under subcritical conditions are briefly discussed.

6.3. Hydrothermal liquefaction

Optimal conditions for maximizing either bio-crude production or bio-crude energy content, typically fall in the range 10–20% solid loading, 350 °C and 5–60 min with heating rates of 5–100 °C/min (Raikova et al., 2019). Microwave assistance accelerates the process, showing high yields and purity with minimum side-products, but are more difficult to control and present risks derived from the use of closed containers (Abdul Latif et al., 2019).

The possibility of using high moisture biomass during hydrothermal liquefaction saves the dewatering costs (Jin et al., 2013; Elliott et al., 2015; Raikova et al., 2019; Abdul Latif et al., 2019). Due to its high ash and moisture content, macroalgae is more suited to hydrothermal liquefaction than to pyrolysis and combustion, where could cause problems of slagging and fouling. Since the salt content in marine biomass could present a challenge regarding equipment corrosion and the lowered energy content of biomass, their extraction could be proposed in an initial stage, but the possibility of replacing water by seawater could be even more attractive. During microwave assisted hydrothermal liquefaction of red macroalgae, Yang et al., (2020) did not find influence of NaCl concentration in terms of biocrude yield and quality.

In order to provide high bio-oil yield and quality, preventing side reactions, Wang et al., (2021) proposed the conversion of *Enteromorpha clathrata* into bio-oil through hydrothermal liquefaction in a two-step reaction, at 200 °C and at 300 °C, both during 30 min.

Jin et al., (2013) developed a strategy to alleviate the severe reaction conditions and they carried out the co-liquefaction at 340 °C and 40 min of microalgae (*Spirulina platensis*) and macroalgae (*Entermorpha prolifera*) in 1:1 mass ratio without affecting the molecular composition although the relative amount of each component differed.

6.4. Hydrolysis and carbonization

The subcritical water hydrolysis at 180–260 °C leads to hydrothermal carbonization of macroalgae biomass, causing an increase in the carbon fraction of the solid residue (hydrochar) due to the release of water molecules from carbohydrates, thus improving the calorific value compared to the value for the untreated biomass. Greiserman et al. (2019) proposed the subcritical water hydrolysis and carbonization of the biomass for co-generation of two energy streams from *Ulva* sp. (fermentable sugars and solid hydrochar). The maximal release of total sugars under minimum formation of 5-HMF occurred at 170 °C and 40 min in seawater.

Steinbruch et al., (2020) compared the direct hydrothermal processing of *Ulva* sp. to the processing of separated starch granules and cellulose, for monosaccharide, hydrochar, and polyhydroxyalkanoates (PHA) production. The extraction of the starch fraction was preferred for releasing glucose, whereas cellulose was the best for hydrochar production. The pretreatment of the whole macroalgae was preferred for PHA production by *Haloferax mediterranei*, because the hydrolysate contained other nutrients. The optimal conditions for maximal content of monosaccharides differ from 180 °C and 40 min for glucose, galactose and fructose, 177 °C and 20 min for rhamnose and xylose. Lower temperatures have been reported by Ghosh et al., (2021), who proposed operation at 170 °C during 20 min in a media containing 38 g salinity/L for the production of PHA and biochar with a yield of 20% from *Ulva* sp. The revenue generated from the biochar by-product could make it suitable for co-combustion in thermal power plants, reducing the total emissions in 0.106 kg CO_2 eq/kg macroalgae.

Polikovsky et al., (2020) confirmed that the multiple product strategy provided higher revenue than other strategies. They processed *Ulva* sp. at 180 °C during 40 min for the production of biochar with a yield of 21% and double heating value than the initial biomass. A two-step fermentation with *Saccharomyces cerevisiae* and with *Escherichia coli* increased the ethanol yield in the second stage.

7. Perspectives

Macroalgae are important marine bioresources, traditionally used as fertilizers, food and feed products, or for the extraction of hydrocolloids. Moreover, they can be regarded as a renewable source of bioactive phytochemicals, which can be destined to the food, pharmaceutical and cosmetic sectors or as raw material for the chemical and energetic industries. Therefore, this resource has high potential for the development of a circular bioeconomy.

Some recommendations for achieving the biorefinery approach have been suggested by Ruiz et al., (2015); Aparicio et al., (2020) and Filote et al., (2021), including the development of markets for non-conventional co-products, optimization of purification steps for different bioactives, the incorporation of innovative extraction techniques, the application of environmental impact studies to provide a wider perspective regarding the overall process, and the possibility of comparing different scenarios in terms of costs and sustainability and finally, large-scale studies are also required.

In this context, hydrothermal processing with water under subcritical conditions is a valuable innovative tool for addressing both the extraction and depolymerization of some bioactives without requiring drying stages and also serving as an efficient pretreatment to enhance bioconversion or for the thermochemical valorization of the whole solids. The possibility of tuning the process selectivity by carefully choosing the severity conditions converts it in a unique and promising technique to develop rapid, flexible, efficient and greener chemical-free macroalgae biorefineries. The possibility of directly using macroalgae without previous drying stages, makes this technique more competitive than the traditional sun drying and conventional oven drying, which require time and energy and can affect some bioactives. Furthermore, the use of seawater for the hydrothermal processing proved suitable and is especially attractive for the marine biorefineries.

8. Conclusions

Hydrothermal treatments are a technology with wide potential for obtaining high-value compounds from macroalgae biomass. The compatibility with this type of biomass allows to be more sustainable processes under the principles of circular bioeconomy, wet processing can be done, avoiding additional energy costs during the macroalgae drying process. The current global problem, regarding the lack of resources coupled with the increase demand for a great product diversity is the main incentive to continue in the search for more efficient alternatives, so the optimization of hydrothermal treatments in macroalgae biomass bioconversion will continue to be a priority for the sectors involved.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Author Contributions

Rosa M. Rodríguez-Jasso and Herminia Domínguez contributed to design, conceptualization, and compilation of the review manuscript. Rosa M. Rodríguez-Jasso, Herminia Domínguez, and Blanca E. Morales-Contreras, Noelia Flórez-Fernández, M. Dolores Torres, and Héctor A. Ruiz contributed to writing (including tables and figures) and revision of the manuscript. All the authors read and approved the submitted version of the manuscript.

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