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Evaluation of ethanol concentration and yields from different types of macroalgae

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Abstract*– Energy consumption represents the main source of greenhouse gas emissions, which brings serious problems to the environment and human health. Biofuels are one of the significant renewable energy sources to reduce the environmental impact produced by these emissions, highlighting bioethanol extracted from biomass like macroalgae (due to their high amount of hydrolysable carbohydrates and low lignin content). The present article focuses on the evaluation of ethanol concentration and yield obtained from different types of macroalgae. For this purpose, a bibliographic review and a classification of the information according to the algae taxonomy (brown, green, and red) was conducted, followed by a comparison of the chemical composition, the yields, and the amount of ethanol produced from the algae. According to the results of the research, red algae presented a higher ethanol yield and concentration than those of algae from other species, positioning this taxonomy as the ideal one for the extraction of this fuel. However, this conclusion is not definitive, since red algae do not always obtain higher concentrations and yields than algae of other species. It is necessary to analyze other variables and conditions that establish the best scenario for ethanol production from macroalgae, such as pretreatment, hydrolysis, and fermentation.

Keywords*-- Bioethanol, Macroalgae, Gracilaria, Taxonomy, Yield.

I. Introduction

Globally, energy use is the largest source of greenhouse gas (GHG) emissions, being responsible for approximately one third (34%) of total emissions. These emissions result from the combustion of fossil fuels for electricity and heat generation, which are used in various sectors including energy systems, industry, buildings, and transportation. In 2019, energy use worldwide led to the production of 20 gigatons (Gt) of GHG emissions (in CO_2 equivalents). Additionally, the transport sector alone contributed 8.7 Gt, amounting to 49% of that year's global GHG emissions [1]. Specifically, 64% (38 ± 3.0 Gt CO_2) of the 59 Gt global net anthropogenic GHG emissions in 2019 can be attributed to fossil fuel and industry (Fig. 1). These fossil fuels emissions are the main cause of global climate change and are associated with dangerous effects such as temperature increases, droughts, rising sea levels, more frequent and severe natural disasters, and depletion of polar ice, which are effects well known by the public, and have been largely documented by the scientific community.

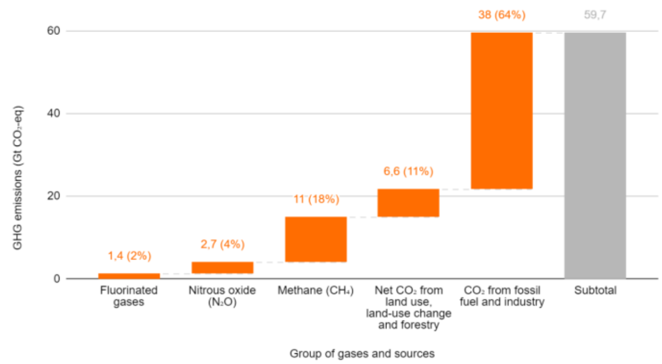

Fig. 1 Global net anthropogenic GHG emissions in 2019, by group of gases and sources. Adapted from Reference [1].

Given this scenario, and to mitigate climate change, there has been an increasing global transition towards sustainable energy sources in recent years. The development of new renewable energy sources (as well as alternative fuels that can meet the world's growing energy needs with the least environmental impact possible) has become crucial.

One of the most important renewable energy sources used to tackle this problem are biofuels, among which bioethanol produced from biomass stands out as one of the most promising options to replace petroleum-based liquid fuels, specially gasoline [2].

Bioethanol is a liquid fuel produced by microbial fermentation of monomeric sugars, which contains 35% oxygen and can be obtained from different carbohydrate sources. First generation bioethanol is produced from edible food crops (such as corn, sugar cane, and soybeans); second generation bioethanol is produced from lignocellulosic crops (such as grass, algae, and wood), and finally third generation bioethanol is produced from algae crops [2]. Bioethanol's biodegradability and carbon neutrality make it a promising fuel, since the amount of GHG emissions generated by its combustion is the same amount previously absorbed by biomass sources during photosynthesis [3].

In order to obtain bioethanol, first and second generation energy crops need to be subjected to a series of processes, including pretreatment, acid or enzymatic hydrolysis, fermentation, ethanol extraction, and purification [4]. The first two stages of this process are crucial for lignin removal and reducing sugars extraction. However, those are the most expensive and the least environmentally friendly steps, due to the use of toxic reagents (concentrated acids) and very aggressive thermochemical conditions (temperatures above 200 °C) [5]. Besides, along with the high cost of enzymes, reagents, detoxification, and recovery of extracted ethanol, the whole process becomes economically unfeasible [3]. Among other things, the production of first and second generation energy crops requires extensive use of fertilizers, causes soil erosion, transforms vulnerable ecosystems in energy crops, and could disrupt the global food supply [6]. Considering these drawbacks, one proposed solution is the use of marine algae biomass, particularly macroalgae, for the extraction of bioethanol.

Macroalgae are multicellular eukaryotic organisms of various shapes and sizes, ranging from a few centimeters to several meters long, and can be divided into three main taxonomic groups: brown algae (Phaeophyta), green algae (Chlorophyta), and red algae (Rhodophyta) [5]. Macroalgae have a carbohydrate content in the range 25-70% of dry weight [7], and between a 2-10% dry weight content of cellulose and hemicellulose. Only a few species have up to 3% lignin content. They also have other chemical components like lipids, proteins, and minerals in smaller amounts [8]. However, this composition is variable and depends on macroalgae species and development stage, season, geographical location, light intensity, sea currents, day length, salinity, nutrient concentration, and temperature [9].

Macroalgae are a promising biomass source for bioethanol production due to their high hydrolysable carbohydrate content [10] and low lignin content, which reduces high pretreatment costs and simplifies the fuel extraction process [11]. Furthermore, they do not compete for resources with food crops, are fast growing, have high productivity, higher yield per unit area, and do not need fertilizers to be cultivated [5], [12]. In addition, the residues obtained from the bioethanol extraction process can be used to produce high added-value products, such as fertilizers, bio adhesives, fish feed, biofuels, biomass for biogas production, and feed for agriculture and livestock [13]. This approach, called biorefinery, again demonstrates the suitability of algae as a feedstock for biofuel production.

Despite all the advantages mentioned above, for macroalgae as a suitable feedstock for bioethanol, its use for large-scale ethanol production is not yet popularized, because extraction methods and technologies, as well as the determination of the ideal macroalgae species for the process, are still under investigation [14]. Therefore, establishing the best conditions for bioethanol production within the existing macroalgae processing alternatives becomes necessary, to determine those species able to provide the highest bioethanol concentration and yields. One way in which this can be accomplished is to determine which one of the three main macroalgae species is the most suitable for bioethanol production, studying different bioethanol concentrations and yields obtained from the three macroalgae taxonomies. This approach is a first step and a closer approach to improve bioethanol yields at the end of the process, since macroalgae species can affect final ethanol yields because of the polysaccharides content in its biomass.

Therefore, in this paper, a literature review is conducted to compare the concentrations and yields of ethanol extracted from different types of macroalgae. In the end, the macroalgae species with the greatest potential for bioethanol production amongst the three main taxonomies is established, and a closer approach to determining one of the ideal conditions for the extraction of this fuel is provided.

II. Materials and Methods

To conduct bibliographic review, research and review articles were obtained from databases such as ScienceDirect, Springerlink, Scopus, PubMed, Google Scholar, ResearchGate, Semantic Scholar, Taylor & Francis online, and Redalyc. The period chosen for the review were the last 6 years (between 2017 and 2022), consulting articles in English, Korean, and Spanish languages, with no geographical delimitation defined, so publications from all over the world were included in the revision. The keywords used were "Bioethanol", "Macroalgae", "Gracilaria", "Acid Hydrolysis", and other related ones. Keywords were inserted by themselves in search engines or combined by implementing AND/OR Boolean connectors.

The studies chosen for the review had obtained bioethanol from fresh or processed macroalgae, macroalgae residues from economic and industrial processes or other sulfated and non-sulfated polysaccharides derived from macroalgae, such as carrageenan, agar, alginate, mannitol, ulvan, cellulose, or starch. Selected studies where those that reported the obtained bioethanol yields in grams per liter (g/L) or in grams of fuel per gram of dry biomass, grams of fuel per biomass moisture content, grams of fuel per spent biomass, or grams of fuel per specific substrate or polysaccharide (g EtOH/g algae – g EtOH/g substrate – g EtOH/g agar, for example). To compare bioethanol yields between macroalgae species, the results were converted to g EtOH/g algae as far as possible. The conversions were made according to other data reported in the articles, namely:

- If bioethanol yields were given in g EtOH/g monosaccharide, the yields of g monosaccharide sugars/g algae were used if they were also included in the article.
- If bioethanol yields were given in g/L of ethanol, the amount of algae powder used by the authors was sought in the volumes of the hydrolysis or fermentation samples, and the corresponding conversion factor was used.
- If bioethanol yields were given in g/L of ethanol and percentage, the article was skimmed to see if the authors had reported a formula to calculate the ethanol yield, and if so, the available data were replaced in the formula and solved for the amount of

dry biomass per volume of solution, or the amount of ethanol per amount of initial monosaccharides, or any other variable that allowed the amount of g EtOH/g algae to be calculated through simple operations. Then, the relevant conversion factors were used.

- If the results were given in units other than grams or liters, or in other concentration units in general (%w/w or %v/v), the relevant conversion factors were used.

To identify whether an article met the inclusion criteria, it was read in its entirety and evaluated according to whether it reported its yields in g/L or g EtOH/g dry algae or substrate or polysaccharide. If so, the article was summarized in a reference table.

The results of the review were collected through tables, where the yields of ethanol, sugars and carbohydrates produced from different species of macroalgae were compared. In the end, seventy (70) articles were found, and were classified according to the type of algae (taxonomy) from which ethanol was extracted. Among them, the chemical composition of the algae, the yields and the amount of ethanol produced were compared, and the respective conclusions were drawn.

III. Results and Discussion

In the bibliographic review conducted, articles from different countries of the world were found, such as Thailand, China, India, Mexico, the United Kingdom, and Chile. The complete geographical distribution of the studies, according to the United Nations (UN) geoscheme, is shown in Fig. 2. This graph shows how more studies were found from East, Southeast, and South Asia than from other subregions of the world. This geographical distribution can be explained because a large part of the territory of these nations is surrounded by oceans (Pacific and Indian). In addition, the identified coasts are rich in nutrients and have hard substrates, a vital condition for the growth of these macroalgae [6].

Most of the studies found green, brown, and red algae species used for ethanol production (85.54%), and fewer of them used macroalgae mixtures (5.71%) or compared the yields of several species at the same time (8.57%). The most common species found in each taxonomy were *Ulva sp*. for green algae, *Sargassum sp*. for brown algae, and *Gracilaria sp*. for red algae. Table 1 shows a more detailed comparison of bioethanol yields, concentrations, and chemical composition (carbohydrates) from the reviewed studies, distributed according to the three macroalgae species. Those studies from which bioethanol concentrations and yields were impossible to express in the corresponding units (g EtOH/g algae and g/L ethanol), were left out when calculating the percentages of articles that reported yields and concentrations within a certain range of values, as shown in the next paragraphs.

From the review, it was found that most green algae (86%) had bioethanol yields between 0.0001 and 0.14 g EtOH/g of dry algae, and most ethanol concentrations (79%) went around 0.01 and 12 g/L of ethanol. This species had relatively low yields compared to those of the other taxonomies, considering that most of its numbers were between 0.001 and 0.01 g EtOH/g dry algae (Table 1). For instance, Reference [15] produced acetone, butanol, and ethanol (ABE) from the algae *Rhizoclonium sp*., studying various pretreatment, hydrolysis, and fermentation conditions.

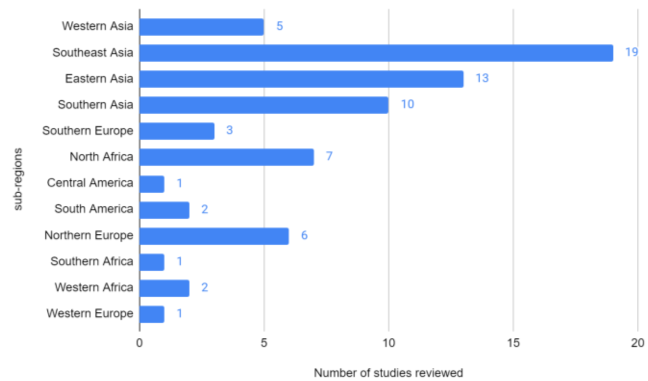

Fig. 2 Geographical distribution of the reviewed studies on bioethanol obtained from macroalgae.

The study found that this species had a composition of 65.88% carbohydrates, and produced 1.06 g/L of ethanol, which translated into 0.0216 grams of ethanol per gram of dried algae. Reference [16] obtained bioethanol from the macroalgae *Ulva lactuca*, optimizing the conditions of the acid hydrolysis performed and fermenting the hydrolysate. They found that this species had a concentration of 74.82% carbohydrates and produced about 11.44 g/L of ethanol. Other authors like Reference [17] implemented two environmentally friendly pretreatments to produce ethanol from the algae *Ulva rigida* and *Ulva intestinalis*, achieving 0.74 g/L of ethanol at the end of the process and having a yield of 0.007 g EtOH/g of dry *Ulva intestinalis*. However, despite these small values, the highest concentration of the bioethanol found in the studies for green algae were 48.2 g/L [18] and 65.43 ± 18.13 g/L [19], the latter concentration being the highest of the documents reviewed to date for this and the other taxonomies.

In the category of brown algae, it was found that most of the reported ethanol yields (80%) went from 0.01 to 0.2 g EtOH/g dry algae, and most ethanol concentrations (78%) went around 0.5 and 14 g/L, being the 27.93 g/L and 22.62 g/L concentrations reported by Reference [20] the highest among the reviewed studies. Bioethanol yields and concentrations found for this taxonomy were slightly higher than those found for green algae. Reference [21] used directly the alga *Saccharina latissima* for the production of ethanol, by means of an enzymatic hydrolysis. The species turned out to have a yield of 0.132 g EtOH/g dry algae, and a concentration of 13.02 ± 0.61 g/L ethanol could be obtained, reaching a fermentation efficiency of 84% of the theoretical yield.

TABLE I

ETHANOL YIELDS AND CONCENTRATIONS OF SOME ALGAE SPECIES

Green algae (Chlorophyta)				
Algae	Ethanol yield (g EtOH/g dried algae)	Amount of ethanol produced (g/L)	Sugars/ algae carbohydrates (Chemical composition)	Reference
Ulva lactuca	-	11.44 g/L	74.82 % v/v	[16]
Ulva sp.	0.042 g/g	-	0.22 g/g (Sugars)	[22]
Codium tomentosum (waste)	-	4 ± 0.33 g/L	58.7%	[23]
Spirogyra sp. and *Oedogonium sp.* (Mixture)	0.072 g/g*	-	-	[24]
Ulva rigida	0.12 g/g	11.92 ± 0.1 g/L	53% dry weight	[25]
Ulva lactuca	-	3.52 g/L	16.47% dry weight	[26]
Rhizoclonium sp.	0.0216 g/g	1.06 g/L	60.41% dry weight	[15]
Ulva sp.	0.00467 g/g	-	-	[27]
Ulva intestinalis	0.003 g/g	0.73 g/L	-	[17]
Ulva prolifera	-	11.40 g/L	-	[28]
Brown algae (Phaeophyta)				
Algae	Ethanol yield (g EtOH/g dried algae)	Amount of ethanol produced (g/L)	Sugars/ algae carbohydrates (Chemical composition)	Reference
Sargassum latifolium	0.056 g/g	-	20.1% dry weight	[29]
Sargassum horneri	0.113 g/g	2.89 g/L	1.37 g/L (Reducing sugars)	[30]
Turbinaria ornata	-	1 g/L	0.477 g/g (Sugars)	[31]
Ecklonia kurome	-	2.1 g/L	44.13 g (Sugars)	[32]
Sargassum sp.	-	1.97 g/L	55.88% dry weight	[33]
Laminaria digitata	-	3 g/L	46.6% dry weight	[34]
Saccharina latissima	0.132 g/g	13.02 ± 0.61 g/L	58% dry weight	[21]
Sargassum angustifolium	0.187 g/g	4.9 g/L	36.2-50% dry weight	[35]
Sargassum sp.	-	19.9 g/L	45% dry weight	[36]
Padina tetrastromatica	0.161 g/g*	-	-	[37]
Red algae (Rhodophyta)				
Algae	Ethanol yield (g EtOH/g dried algae)	Amount of ethanol produced (g/L)	Sugars/ algae carbohydrates (Chemical composition)	Reference
Gracilaria chilensis	-	8.9 g/L	20 g/L (Sugars)	[38]
Kappaphycus alvarezii	0.102 g/g	20.90 g/L	71.22 % dry weight	[39]
Gracilaria manilaensis	0.111 g/g	18.16 g/L	59.68% dry weight	[39]
Gracilaria verrucosa	0.242 g/g	29 g/L	66.95% dry weight	[40]
Gloiopeltis furcata	0.224 g/g	26.8 g/L	61.33% dry weight	[41]
Gelidium elegans	0.120 g/g	13.27±0.47 g/L	49.6% dry weight (Sugars)	[42]
Kappaphycus alvarezii	0.263 g/g	-	-	[43]
Gelidium amansii	0.217 g/g	-	-	[43]
Gracilaria sp.	-	28.7 g/L	56% dry weight	[36]
Euchema Spinosum (Industrial waste)	0.1 g/g	36.6 g/L	50.2% dry weight [a]	[44]

*Refers to grams of ethanol extracted per gram of algal biomass used for lipid extraction, since ethanol was extracted from the residue of biodiesel production with algae in this article.

[a]Cellulose and organic matter content.

Similarly, Reference [30] studied the effect of temperature, fermentation time, pre-hydrolysis time, and cellulase loading on ethanol yield obtained from the seaweed *Sargassum horneri*. The species released a concentration of 2.89 g/L of ethanol, with a yield of 0.113 g EtOH/g biomass. Reference [29] carried out different types of hydrolysis with the seaweed *Sargassum latifolium* to optimize the production process, and fermented it with two different yeast strains. The species had a composition of 20.1% total carbohydrates, and 0.29 g EtOH/g total reducing sugars were obtained.

Finally, for red algae, most bioethanol yields (67%) were between 0.1 to 0.3 g EtOH/g dry algae, and most concentrations (65%) oscillated between 10 to 40 g/L ethanol, being 51.10 g/L and 56.26 g/L the highest ethanol concentrations among the reviewed studies for this taxonomy overall [45]. Reference [40] obtained bioethanol from the alga *Gracilaria verrucosa* by means of combined hydrolysis and fermentation with two different yeast strains adapted to high concentrations of galactose, which produced the highest ethanol yields. The algae turned out to have 67% carbohydrates and produced 29 g/L of ethanol with a yield of 0.5 g EtOH/g of sugar used. On the other hand, Reference [41] obtained bioethanol from the alga *Gloiopeltis furcata* by means of genetically modified yeasts to maximize the yield of ethanol production. The hydrolysis conditions were optimized, and the algae were fermented with genetically modified yeasts, comparing the amounts of ethanol obtained with those produced by the original unmodified strains. In the end, the algae turned out to have 61.33% carbohydrates, and, under the best conditions, 26.8 g/L of ethanol were produced with a yield coefficient of 43%. Reference [38], made a batch fermentation for the alga *Gracilaria chilensis* and measured the metabolic kinetic parameters of the yeast used for fermentation, optimizing the process with different initial carbohydrate loads. In the end, the highest ethanol concentration of 8.9 g/L was obtained with a 20 g/L load of initial carbohydrates.

With this information, and taking into account the values reported on Table 1, it can be concluded that the macroalgae that had the highest yields and concentrations of ethanol were red algae (*Rhodophyta*), which is explained because they have a higher carbohydrate content than other species [7]. These carbohydrates (consisting mainly of agar, carrageenan, and cellulose) are easily hydrolysable and can release monomeric sugars like glucose and galactose, which are used by fermentation microorganisms for ethanol production [46]. In fact, from the red algae taxonomy evaluated, algae of the genus *Gracilaria sp.* are particularly suitable for bioethanol production, because they have high carbohydrate content, are easy to grow in terrestrial ponds, and are abundant in several parts of the world [47]. This type of algae has carbohydrate contents of about 62-77% [7], which are significantly greater than those of the same and other macroalgae taxonomies (like the *Ulva*, *Sargassum*, *Laminaria*, and *Rhodymenia* genus, with carbohydrate contents of 42%, 33%, 39.3%, and 44.5%, respectively) [48]. Besides, *Gracilaria sp.* has a high growth rate and high productivity when grown in inland ponds, giving it the potential to be a profitable energy crop [49].

Regarding released sugars and bioethanol yields obtained in hydrolysis and fermentation, *Gracilaria sp.* tends to generate greater amounts than those of other algae from the same and different genus. For example, Reference [50] managed to produce an aqueous compound with 59.1% (w/w) of cellulose from the alga *Gracilaria verrucosa*, after a basic pretreatment and bacterial hydrolysis. Under the best fermentation conditions, it was possible to obtain a higher sugar content and, consequently, a higher bioethanol concentration (2.26 g/L or 7.7% ethanol, with a yield of 0.033 g EtOH/g cellulose) than the ones obtained from another red algae used by the authors (*Eucheuma cottonii*, which turned out to have 48.9% w/w of cellulose and produced 7.2% ethanol). On the other hand, Reference [45] showed that the alga *Gracilaria manilaensis* managed to produce a greater amount of ethanol (56.26 ± 1.10 g/L) than the red algae *Kappaphycus alvarezii*, from which 51.10 ± 1.21 g/L of ethanol were obtained. Reference [51] also reported that the fresh algae *Gracilaria corticata* and *Gracilaria edulis* produced concentrations of 1.96 g/L and 2.42 g/L of ethanol respectively, which were higher than the 1.90 and 2.22 g/L of ethanol obtained from the brown algae *Sargassum wightii* and *Sargassum ilicifolium*, respectively. Similarly, Reference [36] managed to obtain, with acid and enzymatic hydrolysis, 28.7 g/L of ethanol from the alga *Gracilaria sp.*, which was a higher concentration than the 19.9 g/L of ethanol obtained from the algae *Sargassum sp*.

Some examples of the superiority of the genus *Gracilaria sp.* in obtaining sugars and ethanol, compared with other macroalgae species, are shown in Table 2.

Given this information, it could be concluded that red algae, especially those of the genus *Gracilaria sp*., produce greater amounts of ethanol than algae of other species, which would position them as a very suitable taxonomy for obtaining this biofuel. Reference [18], for example, found that ethanol concentrations of the red alga *Porphyra umbilicalis* (4.23 and 5.68 g/L) were higher than those produced by the brown algae *Laminaria digitata* and green *algae Ulva linza*. Reference [52] also showed, in a comparison of different ethanol yields, that red algae (such as *Kappaphycus alvarezii* or *Gracilaria sp.*) had higher ethanol yields than some algae of other taxonomies (0.51 - 0.53 vs. 0.1 - 0.4 g EtOH/g sugars, respectively).

Among other things, algae of the *Rhodophyta* category are ideal for obtaining this biofuel, since macroalgae use and commercial production worldwide is mainly based on red and brown algae. This suggests that obtaining ethanol from said taxonomy seems to be the most feasible and optimal option in terms of efficiency [46], [53] However, these conclusions are not definitive. Reference [6] concluded that green algae are more suitable than red or brown algae for bioethanol production, since they have higher cellulose contents (necessary to obtain ethanol), shorter nursery periods and higher growth rates than the latter.

TABLE 2
COMPARISON OF SUGAR AND ETHANOL YIELDS AND CONCENTRATIONS OBTAINED FROM MACROALGAE OF THE GENUS GRACILARIA SP. WITH THOSE OF OTHER MACROALGAE SPECIES

Sugar and ethanol yield and concentrations obtained from macroalgae of the genus *Gracilaria sp.*			Sugar and ethanol yield and concentrations obtained from other macroalgae species			References
Species	Released sugars	Obtained ethanol	Species	Released sugars	Obtained ethanol	
Gracilaria dura	-	0.411 g/g	*Palmaria palmata*	-	0.0173 g EtOH/g algae	Adapted from Reference [5]
			Kappaphycus alvarezii	-	0.262 g EtOH/g alga	
Gracilaria verrucosa	-	0.48 g/g	*Laminaria japonica*	-	0.4 g EtOH/g reducing sugars	
			Eucheuma cottonii	-	0.33 g EtOH/g reducing sugars	
			Gelidium amansii	-	0.38 g EtOH/g reducing sugars	
Gracilaria sp.	-	28.7 g/L	*Eucheuma cottonii*	-	11.7 g/L	
			Ecklonia kurome	-	2.1 g/L	
Gracilaria verrucosa	-	0.43 g EtOH/g sugars	*Saccharina japonica*	-	0.41 g EtOH/g sugars	Adapted from Reference [21]
			Sargassum sagamianum	-	0.38 g EtOH/g sugars	
			Saccharina japonica	-	0.17 g EtOH/g sugars	
			Kappaphycus alvarezii	-	0.39 g EtOH/g sugars	
			Laminaria japonica	-	0.41 g EtOH/g sugars	
			Kappaphycus alvarezii	-	0.37 g EtOH/g sugars	
			Gelidium amansii	-	0.38 g EtOH/g sugars	
			Saccharina japonica	-	0.41 g EtOH/g sugars	
			Ulva pertusa	-	0.38 g EtOH/g sugars	
			Alaria crassifolia	-	0.28 g EtOH/g sugars	
			Gelidium elegans	-	0.38 g EtOH/g sugars	
			Sargassum sagamianum	-	0.13 - 0.23 g EtOH/g sugars	
Gracilaria gigas	9.7 g/L glucose	3.56 g/L	*Kappaphycus alvarezii*	0.78 g/L glucose	1.5 g/L	Adapted from Reference [54]
Gracilaria fisheri	7.76 g/L glucose	-	*Gelidium amansii*	0.81 g/L glucose	0.66 g/L	
Gracilaria tenuistipitata	4.58 g/L glucose	-	*Gelidium latifolium*	2.40 g/L glucose	-	
Agar residue (Gracilaria verrucosa)	14.3 g/L glucose	5.52 g/L	Carrageenan residue	-	5.47 g/L	
Agar residue (Gracilaria latifolium)	16.2 g/L glucose	10.83 g/L	Agar industrial waste	-	2.34 g/L	
			Alginate industrial waste	-	2.60 g/L	

Moreover, green algae are evenly distributed throughout most of the world and have high annual productivity and good tolerance to adverse environmental conditions. On the other hand, Reference [55] suggest that brown algae are the most suitable feedstock for bioethanol production, due to their high carbohydrate content and ease of mass cultivation. In fact, among the reviewed studies, Reference [56] found that the green algae *Ulva lactuca* produced a higher ethanol concentration (7.8 g/L) compared to the 5.4 g/L ethanol obtained from the red alga *Dilsea carnosa*, and stated that the results were consistent with the nature of the polysaccharides content in these two species; green algae, being the closest to land plants, have high cellulose and hemicellulose contents, while red algae have less cellulose and are formed mostly by unique polysaccharides such as agarose and carrageenan. Similarly, Reference [57] showed that the green alga *Ulva lactuca* had a higher ethanol yield (5.27 g EtOH/g total solids) than the total solids yield obtained from the red alga *Gelidium sesquipedale (*3.51 g EtOH/g).

The conclusion that can be drawn from this analysis is that red algae do not always obtain higher concentrations and yields than algae of other species, although in most cases they are better than the latter for bioethanol production. To make a complete comparison, other variables and conditions that establish the best scenario of ethanol production from macroalgae must be considered, such as those of pretreatment, hydrolysis, and fermentation, which are beyond the scope of this article but will be explored in further studies.

Making bioethanol from macroalgae has a lot of potential because this type of algae grows fast. They also need no farmland and have a high carbohydrate and sugar content. However, there are still some challenges for high scale collection, since growing and harvesting macroalgae on a large scale can have a high cost. The sustainability of collecting residual macroalgae on the shorelines depends on seasonal variability and marine currents that affect macroalgae location and abundance. Natural factors such as water temperature, solar radiation and nutrients availability, which are also seasonal dependent, can make it a challenge to keep a continuous supply of raw material. The carbon footprint of macroalgae-based bioethanol is comparable to that of fuels made from corn or sugarcane, although the values depend on the energy needed to collect, process, and transport the macroalgae. Finally, while macroalgae are a clean and promising option, there is still need to improve growth, collection, and processing technology in order to make this solution actually sustainable.

IV. Conclusions

Globally, energy use represents the largest source of GHG emissions, which are related to fossil fuel burning and constitute the main cause of climate change around the world. In the upcoming energy transition trend, developed to offset the adverse effects of this phenomena with non-conventional renewable energy sources, biofuels, such as bioethanol, have become a great alternative to replace fossil fuels. Considering all the environmental drawbacks related to first and second generation bioethanol, macroalgae are considered as a novel and more suitable feedstock for bioethanol production than other food or lignocellulosic crops. However, treatments and procedures for bioethanol production from macroalgae are still under investigation, so determining the best processing conditions, like the most ideal macroalgae taxonomy, is crucial to make the most use out of this biomass.

In this review, it was found that red algae tend to be more suitable for ethanol production (with most yields between 0.1 and 0.3 g EtOH/g of dry algae and most concentrations ranging from 10 to 40 g/L) than green algae (which reported values between 0.0001 and 0.14 g EtOH /g of dry algae, and concentrations around 0.01 and 12 g/L of ethanol), and brown algae (with yields between 0.01 to 0.2 g EtOH/g of dry algae and concentrations around 0.5 and 14 g/L of ethanol), which is explained because this taxonomy has a higher proportion of easily hydrolysable carbohydrates for fermentation than the other taxonomies. In fact, within the red algae species, algae of the genus *Gracilaria sp.* are especially suitable for bioethanol production, since they tend to generate higher sugars and ethanol yields than other algae of the same and different genus, thanks to their ubiquity, high carbohydrate content (62-77%), rapid growth, and high productivity. However, red algae do not always obtain higher ethanol concentrations and yields than algae of other species, so it cannot be established with certainty that they are the ideal taxonomy to obtain the biofuel in all cases. In order to determine the optimal conditions to produce the highest bioethanol concentrations and yields from macroalgae at the end of the process, further studies in the remaining treatment steps (like pretreatment, hydrolysis, and fermentation) need to be conducted.

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