AIMS Energy, 10(1): 45–63.
DOI: 10.3934/energy.2022003
Received: 04 November 2021
Revised: 18 January 2022
Accepted: 23 January 2022
Published: 08 February 2022

http://www.aimspress.com/journal/energy

Research article

Bioenergetic valorization of *Sargassum fluitans* in the Mexican Caribbean: The determination of the calorific value and washing mechanism

José A. Sosa Olivier[1,*], José R. Laines Canepa[1], David Guerrero Zarate[2], Anabel González Díaz[3], Donato A. Figueiras Jaramillo[4], Heidi K. Osorio García[5] and Berenice Evia López[1]

[1] Pilot Plant 3 solid waste and atmospheric treatment, Academic Division of Biological Sciences, Universidad Juárez Autónoma de Tabasco, Mexico
[2] Chemistry Laboratory, Jalpa de Méndez Multidisciplinary Academic Division, Universidad Juárez Autónoma de Tabasco, Mexico
[3] Coprocessing Laboratory. Geocycle® SA. of CV., Mexico
[4] Characterization Laboratory, Academic Division of Engineering and Architecture, Universidad Juárez Autónoma de Tabasco, Mexico
[5] Technological Institute of the Morelia Valley, Mexico

* **Correspondence:** Email: aurelio.sosa@ujat.mx, ing-jaso@hotmail.es; Tel: (+52) 9931940812.

Abstract: The advent of large volumes of *Sargassum sp.* on the Mexican Caribbean coast has become an emerging issue for the Mexican population. The most frequent action is harvesting, but a correct treatment or energy recovery strategy is still missing. This work aimed to evaluate the energy potential of *Sargassum fluitans*, through elemental calculations and direct measurements, considering the effect of its washing. The calorific value determined by the direct method was 9.24 ± 0.28 MJ/kg and 12.64 ± 0.18 MJ/kg for dirty and washed *Sargassum*, respectively. The washing effect increased the calorific values in *Sargassum fluitans* by 36.80%. The washing effect increased the calorific values determined by indirect methods, increasing 10.10% and 41.04%, each method, respectively. The content of toxic metals was lower in both materials than that established for non-woody biomass from energy use, concerning the ISO 17225:2014 standard. The unit energy cost of *Sargassum fluitans* is $0.007 and $0.011 per MJ for dirty and washed conditions, respectively. Finally, the results of this work indicate that the *Sargassum* wash provides better characteristics to be considered an

alternative fuel option in combustion systems such as thermo-electric plants (based on carbon), sugar mills, and cement kilns with co-processing of solid waste. Attending from a bioenergetic approach, *Sargassum's* emerging seasonal problem affects the Mexican Caribbean coast.

Keywords: alternate fuel; bioenergy; biomass; calorific value; *Sargassum*; seaweed

Abbreviations: % mol: percent mol; ℃: degrees Celsius; ®: trademark; ~: approximate symbol; ≤: equal or minor; ø: diameter; C/N: carbon-nitrogen relation; C/P: carbon-phosphorus relation; cm^{-1}: Wavenumber; g: gram; GWh: Gigawatt hora; h: hours; HHV: Higher Heating Value; J/g: Joule per gram; kg: kilogram; km: kilometer; L: liter; m^3: cubic meter; mg/g: milligram per gram; mg/kg: milligram per kilogram; mg: milligram; MJ/kg: Mega Joule per kilogram; mm: millimeter; MPa: Megapascal; mS/cm: milli siemens per centimeter; MXN$: Mexican peso; t: tons; TWh: Terawatt hora; US$: American dollar

1. Introduction

During 2019 worldwide, primary energy consumption had an annual growth rate of 1.30%. As a consequence, the carbon emission from energy use increased 0.50% (almost 50% less than in 2018), the main sources of electricity generation were coal (36.38%), natural gas (23.32%), and renewable energies (10.39%), the latter is the source of energy generation with the highest growth (41%), the geothermal and biomass group, represent 6% of renewable energy sources [1]. In Mexico, the electricity demand grew at an average annual rate of 2.50%, with a generation of 329.71 TWh [2]. Nevertheless, 78.90% of the energy in the country is produced through conventional technologies, and the remaining 29.50% comes from clean technologies, including biomass that represents only 0.92%. The use of biomass is divided between cane bagasse (0.75%) and biogas (0.17%), with a growth of 28.60% and 24.20%, respectively, in addition to the existence of 79 plants that use biomass [3]. Biomass is considered a source of clean and renewable energy due to the ability to absorb CO_2 from the atmosphere, which helps reduce the greenhouse effect [4], and due to its abundance, large distribution and carbon neutrality are considered a potential substitute for fossil fuels [5]. In Mexico, there are small advances in the use of biomass as a source of clean energy, perhaps the best example is the cane bagasse in the sugar mills. The Santa Rosalia sugar mill (Tabasco, México) generates 100% of the electrical energy from the bagasse generated as a byproduct in sugar production, avoiding the use of fuel oil or any other fossil fuel. Surplus electricity is sold to the Federal Electricity Commission, which is responsible for producing, distributing, and billing electricity in Mexico and industrial customers [6]. The calorific value of cane bagasse varies from 7.53–17.58 MJ/kg, hence using other biomass with similar potentials could be a fuel alternative in combined cycle plants or other combustion power generation systems [7–9].

Aquatic biomass is one of the most abundant renewable energy sources and will be an essential component of a more sustainable energy system [9]. Nevertheless, in recent years an atypical phenomenon has been unleashed, such as the arrival of large volumes of seaweed, on some shores of the Atlantic Ocean. In 2011, the massive influx of brown seaweed occurred, denominated "*Sargassum*" in the eastern Caribbean, from Trinidad and Tobago to the Dominican Republic, and on the west coast of Africa, from Sierra Leone to Ghana [8]. In 2012, the massive arrival of *Sargassum* on the coast of

Cuba [10], in 2014, many other islands and countries of the Caribbean were affected, including the Mexican Caribbean. These travel routes were verified by Franks et al. [11] when conducting experiments using drift buoys with satellite location, with a 60% similarity. In Mexico, the excessive arrival of the *Sargassum* has impacted nearly 1,000 km of the Mexican Caribbean coast [12], reaching volumes of up to 2 m^3 per linear meter of the beach [13]. During the periods 2017 [13], 2018 [14,15], and 2019 [16], the government of Mexico invested 22.30 million dollars in the collection and management of around 701.67 thousand tons of *Sargassum* collected off the coast of Quintana Roo. According to DrecKmann & Sentíes [17], the arrival of this biomass in the state of Quintana Roo mainly affects Cancun and Puerto Morelos. It is presumed that this phenomenon originates from the natural detachment of aggregations of free-living species such as *Sargassum fluitans Børgesen* and *Sargassum natans Gaillon*, endemic to the Sargasso Sea in the Atlantic Ocean [18]. Subsequently, the hypothesis that originated in northeastern Brazil emerged [19]. It is important to mention that one of the hypotheses of greater debate is the interference of high nutrient loads [20], due to the mouth of the Mississippi rivers (west of the Gulf of Mexico) and the Amazon (southern Ecuador). In the case of the Amazon River, the concentration of inorganic nitrogen is reduced below the detection limit about 200 km from the mouth [21,22], but a higher growth rate has been observed in these neritic zones than in the center of the Sargasso Sea [23]. These nutrients have altered aquatic resources and various economic activities such as tourism, fishing, and shipping, of the coastal areas. Hernández-Zanuy [24] points out that the large accumulation of this material and its natural decomposition causes an increase in the chemical and biochemical oxygen demand, anoxia alters the quality of the sand, affects coastal ecosystems, and generates greenhouse gases (GHG). Lapointe et al. [23] indicate that a low C/N and C/P ratio is attributable to the rapid growth of the *Sargassum*. The use of macroalgae biomass for direct combustion has been studied by various researchers [25–28]. Sudhakar and Premalatha [29] indicate that the calorific value of macroalgae biomass is in the range of 4.35–20.10 MJ/kg, relatively lower than the biomass values of terrestrial crops with ranges of 14–20 MJ/kg. The chemical composition of marine biomass (Table 1) is very different from terrestrial biomass due to lower carbon (C) values, hydrogen (H), and oxygen (O), concerning higher values of nitrogen (N) and sulfur (S) [30].

The complexity causes inconsistencies in the stoichiometric calculations of the calorific value of the *Sargassum* [32]. Although the combustion of macroalgae is economically viable, the technical dimension remains debatable due to the high content of ash and moisture, which reduces its energy efficiency. Sudhakar et al. [34] pointed out that some technical problems are the handling of ash and the presence of alkali metals such as sodium (Na), potassium (K), and halogens, which cause problems of corrosion and saturation of conductive lines. Algae naturally, including *Sargassum sp*. they can absorb metal ions, such as lead (Pb II), copper (Cu II), and nickel (Ni II), its average removal capacity is 113.50 mg/g, with a range of 10.60 to 357 mg/g [35]. The European Environmental Agency [36] reported that the anthropogenic emission of toxic metals such as arsenic (As), Cadmium (Cd), chrome (Cr), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn), it is due to the thermal conversion of fuels, for the generation of energy and heat. For this reason, determining the presence or absence of compounds that may pose a risk of pollution to the atmosphere in materials that can be used as fuels must be necessary. Jagustyn et al. [37] mentioned the level limited based on ISO 17225-1, the limits of metals in solid biofuels, particularly for non-woody biomass, both in pellets and briquettes. Some authors highlight the valorization of *Sargassum* in multiple sectors such as pharmaceuticals, cosmetic, food, and biorefineries, due to the high content of carbohydrates in the form of sulfated alginates and polysaccharides, the presence of metals and high amounts of ash reduce its use in the food or fertilizer

sector and biofuel production, respectively [38]. Other authors highlight its use in the biosorption and bioaccumulation of pollutants [39]. Thompson et al. [40] mention that the use of *Sargassum* in digestion systems, like monodigestion, is not very efficient, but the use of cosubstrates improves the high C/N ratios, but the lack of energy policies, financial and financing in the Caribbean area, this strategy is hindered. Thus, the objective of this work is to determine the calorific value of *Sargassum sp*. off the coast of the Mexican Caribbean. Three methods are evaluated, two calculable stoichiometric, and a direct method with a calorimeter pump, considering the washing of the *Sargassum*, as a factor of influence. Moreover, this research aims to outline the presence and concentration of the main toxic metals in the seaweed.

Table 1. Characteristics comparison between Sargassum fluitans and others sargassum species.

Characteristics	Units	*Sargassum tenerrimum*	*Sargassum sp.*	*Sargassum sp.*	*Sargassum horneri*	*Sargassum fluitans* Dirty	Wash
Moisture		5.70	6.70	9.80	10.46	5.08 ± 0.31	6.34 ± 0.37
Ash		26.50	6.60	21.20	29.29	40.52 ± 1.24	16.67 ± 1.17
Volatile Matter		61.50	54.70	43.90	48.85	52.18 ± 0.79	76.81 ± 1.31
Fixed Carbon		6.30	32.00	25.10	11.60	7.31 ± 1.90	6.52 ± 0.14
Carbon	%	32.10	40.30	25.50	48.93	27.01 ± 1.14	39.05 ± 0.18
Hydrogen		4.70	5.40	3.81	6.22	3.70 ± 0.08	5.00 ± 0.11
Oxygen		60.72	51.80	-	42.16	26.07 ± 0.76	36.72 ± 0.86
Nitrogen		0.93	2.50	1.37	0.92	1.45 ± 0.26	1.65 ± 0.19
Sulphur		1.55	-	-	1.77	1.04 ± 0.19	0.79 ± 0.04
Chlorine		-	-	-	-	0.20 ± 0.00	0.12 ± 0.00
Calorific values	MJ/kg	-	-	14.70	15.44	9.82 ± 0.52*	13.85 ± 0.19*
						13.87 ± 3.22**	15.27 ± 0.18**
						9.24 ± 0.28***	12.71 ± 0.07***
Author		[5]	[31]	[32]	[33]	This Work	

*Note: * Dulong method; ** Chaniwala method; ***Calorimetric pump method.

2. Materials and methods

2.1. Obtaining and characterizing Sargassum sp.

The material was naturally dehydrated, out of the water, and exposed to the sun, subsequently transferred to pilot plant 3 of Air and Solid Waste Treatment of the Academic Division of Biological Sciences (DACBiol) of the Juarez Autonomous University of Tabasco (UJAT) in México. A sample of *Sargassum sp*. was hydrated for 24 h with distilled water to be observed under the microscope and to determine the morphological characteristics of the species. It 1.10 kg of *Sargassum fluitans* was manually sieved on a # 10 sieve (2 mm ø). The biomass was placed in a 19 L container and filled with 12 L of drinking water to reduce the sand and salts content. It was mixed manually for 5 min to wash the material, and the process was repeated up to 10 times. In each wash cycle, 250 mL of drinking water (start) and wash water (end) were sampled. Thus, the electrical conductivity was measured in mS/cm with the help of measuring equipment. Finally, the material was left to dry in an oven at 105 ℃ for 10 h.

2.2. Proximal and ultimate characterization

Samples were taken to perform the proximal analysis determining the gravimetric content (mass loss) by the action of temperature and time, according to the American Society of Testing Methods (ASTM). The humidity was determined at 105 ℃ for 24 h, volatile matter at 550 ℃ for 2 h, and ashes at 800 ℃ for 1 h, based on ASTM D-2974 [41]. Further, the ultimate analysis was carried out, determining the content of C, H, N, and S (elemental composition). Each determination was performed in quadruplicate, using a Perkin Elmer PE2400 CHNS/O Elemental Analyzer (PerkinElmer, Waltham, MA, USA). The presence of O is achieved by the arithmetic difference of the sum of the elements and ash at 100%.

2.3. Content of toxic metals

The presence of toxic metals such as As, Cd, Cr, Pb, Ni, and Zn was determined according to the United States Environmental Protection Agency. Samples were ground and pretreated, based on the ASTM 5468-02 [42] and analyzed US EPA 6010-B [43] method, using a Plasma Atomic Emission Spectrometer Perkin Elmer® Optima 5300 (PerkinElmer, Waltham, MA, USA) for metal arrest heavy and a Leco® AC-500 kit for PC analysis. These analyses were carried out in the coprocessing laboratory at the Macuspana plant of the Geocycle® Company.

2.4. Characterization of functional groups by FT-IR

Fourier Transform Infrared (FT-IR) spectrophotometer was used to identify the functional groups present in each sample. Specimens of both types were first mixed with KBr at an approximate ratio of 1/100 (sample/KBr) and then ground in an agate mortar. The resulting mixture was pressed at 10 tons for 5 min to form the pellet, which was characterized using an FT-IR spectrometer Shimadzu IRAffinity-1 (Shimadzu Scientific Instruments, Columbia, MD, USA). Eighty scans and 2 cm^{-1} resolutions were applied in the range of 4500–500 cm^{-1} for recording the spectra. The background obtained from a scan of pure KBr was automatically subtracted from the sample spectra.

2.5. Determination of the calorific value using the calorimetric pump method

The calorific value was determined on a semi-automatic oxygen bomb calorimeter A4000 from Heedding. The calibration of the oxygen bomb is made with standard benzoic acid (calorific value 26433 J/g). For the *Sargassum* samples, weighed a mass close to 1 g in an analytical balance VE-204 from VELAB (precision 0.1 mg); in the bottom of the reaction vessel, was added 10 ml of deionized water and fill the vessel with reactive degree oxygen (purity greater than 99.50% mol) up to a pressure of 3 MPa, to achieve an oxygen-excess atmosphere. All the measurements are carried out in triplicate.

2.6. Higher heating value (HHV)

The calorific value of a material such as biomass is equal to the sum of the calorific value of the simple elements that form it, multiplied by the mass quantity of the elements present. The calorific

value can also be determined by calculating the HHV, which is an important characteristic of fuels, and this can be calculated from their elemental composition (C, H, N, O, and S) [44] and their respective combustion products [45]. Two equations with multiple citations were used to determine HHV, employing the stoichiometric composition of *Sargassum.*

2.7. HHV by Dulong method

The equation proposed by Dulong [44] expresses the HHV (MJ/kg) of dry fuel solid or liquid, containing C, H, and S in its composition.

$$HHV\ Dulong\left(\frac{MJ}{kg}\right) = \left[(0.3383 * C) + \left[1.443 * \left(H - \frac{O}{8}\right)\right] + (0.0942 * S)\right] \quad (1)$$

2.8. HHV by Channiwala method

The equation reported by Channiwala et al. [44] determines the HHV (MJ/kg) considering a higher number of components such as O, N, and ash.

$$HHV\ Channiwala\ \left(\frac{MJ}{kg}\right) = (0.3491 * C) - (1.1783 * H) + (0.1005 * S) - (0.1034 * O) - (0.0151 * N) - (0.0211 * Ash) \quad (2)$$

2.9. Ash-free calorific value (AFCV)

An adjustment was made to analyze the effect of washing on removing impurities such as ash. The ash-free calorific value (AFCV) was calculated by applying the following equation reported by Wang et al. [45] for each calorific value method.

$$AFCV = \frac{100 * calorifc\ value}{100 - Ash} \quad (3)$$

2.10. Analysis of results

Analysis of variances was performed to determine the statistical similarity between the calorific value determination methods in response to the washing factor. This factor was also analyzed using linear regressions. The analyses were carried out using the statistical package Statgraphics® Centurion XVIII.

To have knowledge for the precision of the methods used, a relative error analysis was carried out using the calorific values calculated, thereby determining the mean percentage error (MPE) and the mean absolute percentage error (MAPE), using Eqs 4 and 5, reported by Huang and Lo [46].

$$MPE = \frac{1}{n}\sum_{i=1}^{n}\frac{HHV_c - HHV_D}{HHV_D} * 100\% \quad (4)$$

$$MAPE = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{HHV_c - HHV_D}{HHV_D}\right| * 100\% \quad (5)$$

Where HHV_C is the calorific value calculated (Dulong and Channiwala), and HHV_D is the calorific value determined (calorimetric pump). A positive MPE value indicates overestimation, and a negative value suggests underestimation in the method used. For its part, the MAPE helps us to know the proximity of the calculated value of the determined one. The lower the MAPE, the greater the precision.

2.11. Unit Cost

The unit cost per ton of pretreated biomass and the cost of calorific value per ton were estimated. Therefore, the costs of the inputs required in three stages of pretreatment, collection, washing, and crushing of *Sargassum Fluitans* were estimated. The costs were obtained by calculating the consumption of inputs on a small scale in the laboratory and scaled to one metric ton. Investment and equipment acquisition costs were not considered.

3. Results and discussion

Figures 1 A) and B) show the most characteristic difference between the species *Sargassum fluitans* and *Sargassum natans*, which is the upper spine of the air bladder. In Figure 1C, it can be seen that the gas bladders of *Sargassum sp*. analyzed under the microscope lack the upper column in the air bladder, which indicates that it is *Sargassum fluitans* as reported by Oyesiku & Egunyomi [47].

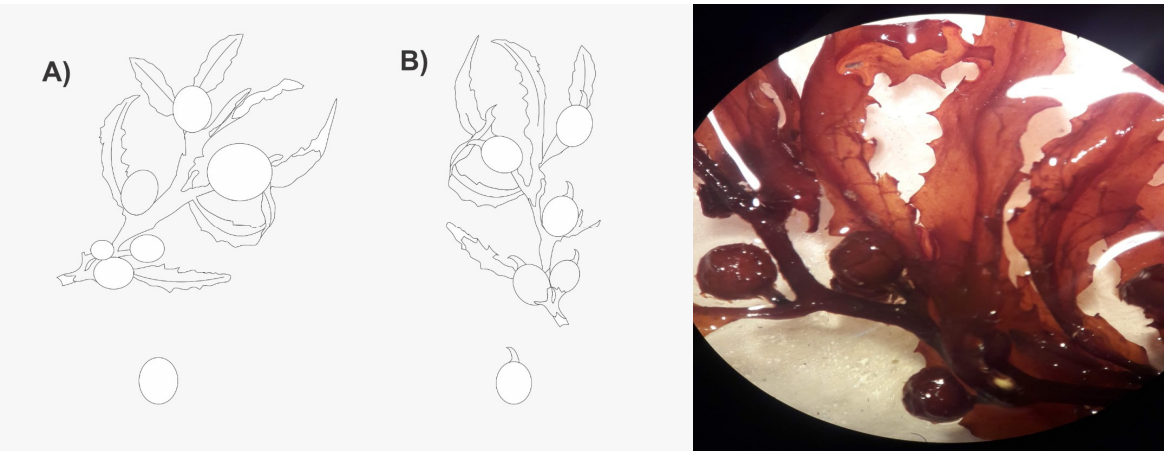

Figure 1. Characteristics of *Sargassum sp*. A) *Sargassum fluitans*; B) *Sargassum natans* (Own image, based on Oyesiku and Egunyomi [47]); C) *Sargassum fluitans* observed under a microscope.

3.1. Washing

In Figure 2, see the decreasing electric conductivity (EC) for the wash water, regarding drinking water, during the *Sargassum* wash.

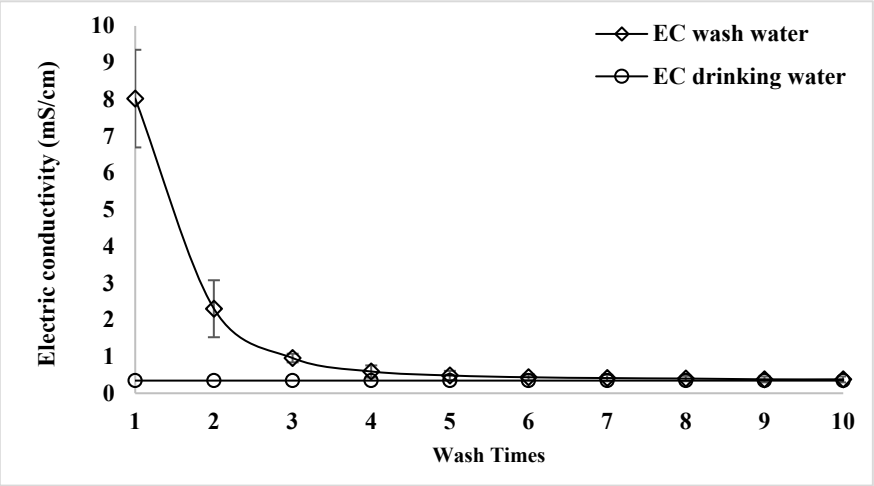

Figure 2. Decreased EC due to washing effect.

The EC measure of the water of the first washing of the material reached 8.02 mS/cm, concerning 0.34 mS/cm, that had drinking water before its use. After each washing session, it was possible to notice a reduction until reaching an average value of 0.38 mS/cm after 10 wash times. In the first two wash times, the reduction was 88%. Finally, the washing ratio was 0.25 L to 10 g of *Sargassum* to achieve similar EC values. This process differs from reported by Milledge [48], those who have washed the material for 30 seconds in running water.

3.2. Elementary characterization, metal content, and washing effect

The results of the proximal and ultimate characterizations and calorific values for the three theoretical methods are shown in Table 1.

The results of the proximal analysis ranged according to the reported by Li et al. [31], Ali & Bahadar [32], Biswas et al. [5] and Li et al. [33]. Nevertheless, the effect of washing is noticeable since the ash content was reduced and it was increased volatile matter significantly; this is attributed to reducing the content of sand and salts and the manual removal of shells from mollusk and waste plastic.

The elemental analysis results also showed an improvement in the effect of washing. The element values of C, H, and N of dirty *Sargassum fluitans* are similar to those reported by Ali & Bahadar [32]. No higher proportions were observed in N and S, concerning the content of C, H, and O, as indicated by Ghadiryanfar et al. [30]. In washed *Sargassum*, the results of C, H, O, and N are very similar to those reported by Wei et al. [31], with the use of *Sargassum sp*. Significant differences were found in the elemental results reported by Biswas et al. [5]; this could be because of the use of *Sargassum tenerrimum* or that they did not report a previous separation of the sands as in this work, they only mention washing with water. The notable increase in the elemental proportions is due to the elimination of sand, waste, and impurities in the screening and washing steps, which is related to the reduction of ashes mentioned above.

The determined content of the metals is observed in Table 2.

Table 2. Reported values of heavy metals content and regulatory limit (mg/kg)

Toxic metals	ISO 17225:2014	Microalgae *Nanno chloropsis gaditana*	Sea balls	Dirty	Wash
Ar	≤1	<1	>10	<0.1	<0.1
Cd	≤0.5	<0.5	<0.5	<0.1	<0.1
Cr	≤50	<10	20	<0.1	<0.1
Cu	≤20	10	<10	-*	-*
Pb	≤10	<10	<20	<0.1	<0.1
Ni	≤10	<5	<10	<0.1	<0.1
Zn	≤100	<100	<50	<0.1	<0.1
Ba	-	-	-	10.2	5.67
Mn	-	-	-	14.2	<0.1
	[49]	[37]		This work	

*Note: * Not determinated.

The low presence of toxic metals is evident regarding the limits of the ISO 17225-1 [49]. Nevertheless, a difference in barium (Ba) and manganese (Mn) values could be observed since Mn is not soluble in water, unlike Ba, the effect is attributed to the cleaning of the material, both sand removal, and the washing. In general terms, the concentration of toxic metals in biomass is below the limits reported by Jagustyn et al. [37].

3.3. The Fourier Transform Infrared Spectroscopy (FT-IR)

The spectra in Figure 3 show typical absorption bands of *Sargassum fluitans.*

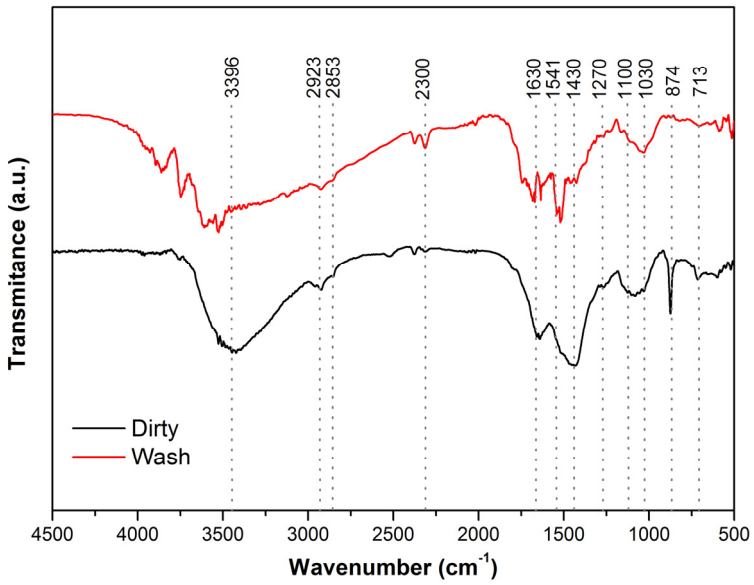

Figure 3. Functional groups detected by FT-IR.

The strong absorption bands around 3200–3600 cm^{-1} may be attributed to the stretching vibrations of hydroxyl groups (-OH) in the hydrogen bond of the molecules [50], which can also be attributed to

the overlapping of -OH and -NH stretching bands [49,50]. Weak bands around 2900 cm^{-1} are due to C-H stretching vibrations [48,51]; the bands at ~2923 and ~2853 cm^{-1} are due to the stretching vibration of -CH_3 and -CH_2- groups, respectively. The absorption peak of weak bands around 2300 cm^{-1} may correspond to the C-O stretching band [54]. In both spectrums, the absorbance at wavenumber around 1640 and 1420 cm^{-1} correspond to stretching vibrations of carbonyl double bond ($\upsilon_{C=O}$) and carbon-oxygen single bond (υ_{C-O}), respectively [51]. However, in the spectrum of the dirty sample, more intense signals were observed at ~1630 cm^{-1} corresponded to carboxylate O-C-O asymmetric, stretching vibration and to C=O asymmetric stretching vibrations of uronic acids and band at ~1430 cm^{-1} can be attributed to C-OH deformation vibration [48,51,53]. In this regard, it is important to mention that it is possible to identify carboxylate bands (COO-) in natural *Sargassum sp*., related to carboxylic acid groups bound to metal ions (nickel and copper) in the 1635 and 1427 cm^{-1} regions [56]. In the spectrum of the washed samples, weak bands around 1541 cm^{-1} represent C=C stretch vibration indicative of the lignin were observed [54]. The absorption band at ~1246 cm^{-1} and ~1270 cm^{-1} are due to S=O (sulfate esters) [52,53]. These wide bands around 1200 cm^{-1} were observed with greater intensity in the spectrum of the dirty sample. They were attributed to sulfonate salts resulting from the formation of salts of the sulfonic acid of polysaccharides [56]. The absorption bands at ~1100–1030 cm^{-1} in the fingerprint region indicate several modes such as C-H deformation or C-O or C-C stretching, pertaining to carbohydrates and polysaccharides [48,52]. In the dirty sample, strong absorption bands were observed at approximately 1400 and 874 cm^{-1}, the calcium carbonate ($CaCO_3$) shows strong bands in these regions. The sharp band at ~874 cm^{-1} corresponded to the symmetric deformation of the CO_3 group. The wideband centered at ~1400 cm^{-1} corresponded to an asymmetric stretch of the CO_3 group. The peak at ~713 cm^{-1} was due to bending vibration [55,56]. In this regard, the presence of crystals biominerals that have been reported in algal samples was quantified based on the specific λ_{max} referred from the existing literature for calcite, 706–716 cm^{-1}, 869–877 cm^{-1}, 1414–1439 cm^{-1}, and 2920–2952 cm^{-1} [57].

3.4. Directly and theoretical calorific value

The calculated and measured calorific value results are shown in Table 1. The calorific values are slightly similar to those reported by Li et al. [33]. The increase in the values is noted due to the effect of the *Sargassum fluitans* washing, increasing to 41.04%, 10.09%, and 36.80% in the Dulong, Channiwala, and Calorimetry pump methods, respectively. This increase is attributed to the decrease in the content of sand and salts, which do not add calorific value to the biomass.

The results of the AFCV applying equation 3 on the calorific values of dirty *Sargassum fluitans* showed an increase of these, being slightly higher than the calorific values of washed *Sargassum fluitans*, 16.58 MJ/kg and 17.36 MJ/kg, in the Dulong methods. and Channiwala, respectively. This contributes to the hypothesis that the content of impurities removed in the washing process has a positive impact on increasing the calorific values of the biomass. However, in the calorific values of the direct method (calorimetric bomb), the AFCV obtained was significantly higher, reaching 22.81 MJ/kg. The great difference with the values of the direct method responds to the overestimation of the values of the stoichiometric methods, as shown in Figure 5.

3.5. Statistical analysis

Figure 4 A) and B) show the ANOVA tests for each type of *Sargassum fluitans* (dirty and washed) and compare the three calorific value methods. The lowercase letters at the top indicate differences or similarities, depending on their repetition.

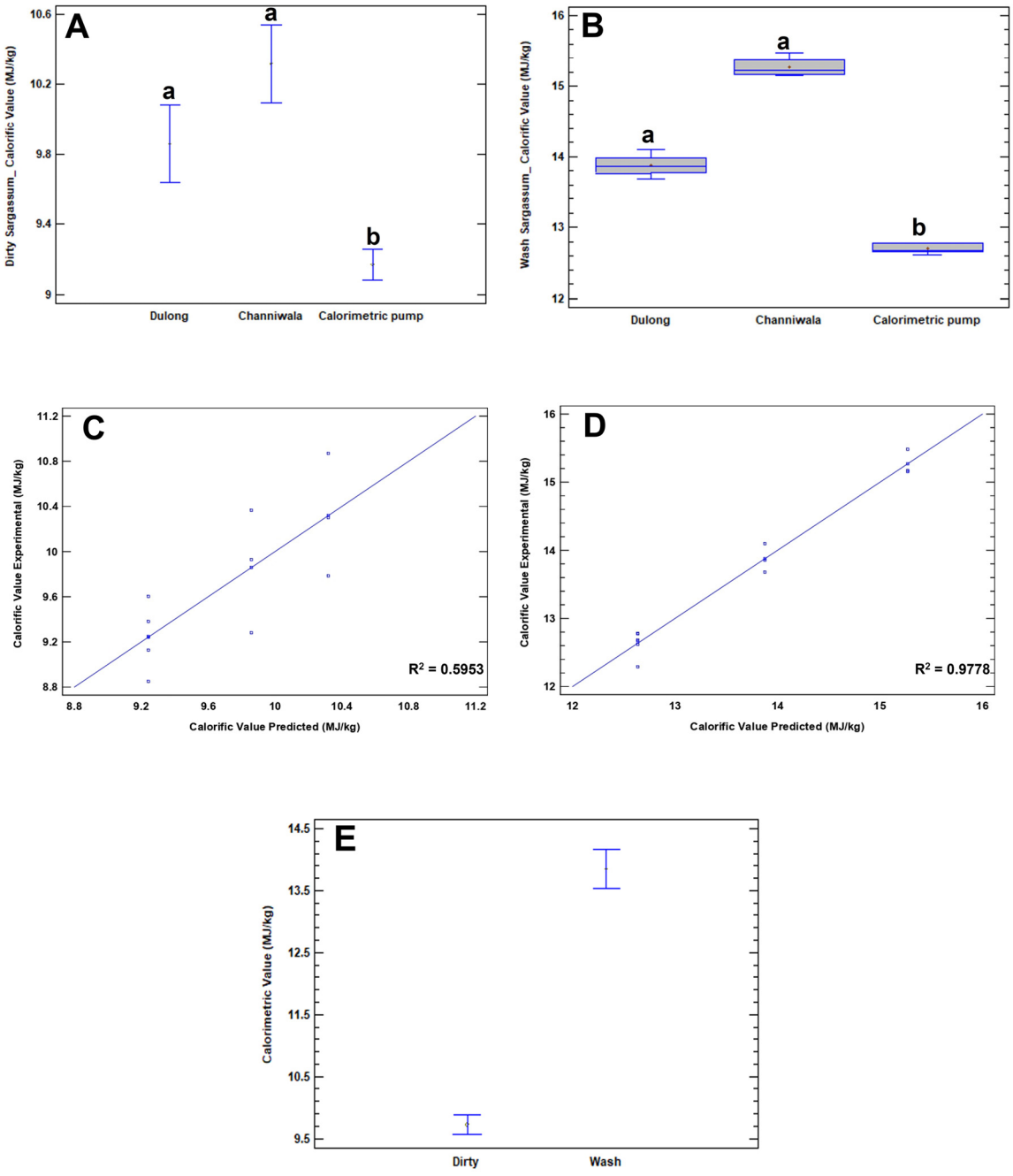

Figure 4. ANOVA graphics of calorific values, A) Dirty *Sargassum fluitans*, B) Wash *Sargassum fluitans*. Linear regression graphics, by the interaction between methods, C) Dirty *Sargassum fluitans*, D) Wash *Sargassum fluitans*, E) ANOVA graphic by groups.

The results indicate that there are statistically significant differences in both materials. Applying a Tukey test (Figure 4A), a dirty *Sargassum* p-value = 0.0028 was obtained. Using a Kruskal-Wallis test (Figure 4B) in the washed *Sargassum* values, a p-value = 0.0047 was obtained. It is noteworthy the similarity in the stoichiometric methods' calorific variables and the differences with the direct method. It is possible to miss the mistake of inferring that the Channiwala method offers us a better result. These inequalities refer to overestimations in the calculations, which are best described in the relative and absolute error analysis.

The linear regression analyses performed, shown in Figure 4 C) and D), indicate the trends of the models used. The R^2 values of the adjusted model explain 59.53% (Figure 4C) and 97.78% (Figure 4D) of the variability of each factor. The washing effect promotes a better adjustment of the calorific values of *Sargassum fluitans*, demonstrating the importance and possible need to implement this pretreatment.

In Figure 4 E), the ANOVA graphic performed at calorific values by combining groups is shown, all dirty and all wash. The results indicate statistically significant differences; the p-value = 0.00001 was obtained by applying a Bonferroni test. A statistically significant effect on the two conditions of use of *Sargassum* can be demonstrated in the methods to determine the calorific values. These results would be similar to those reported by Choi et al. [59], who used different proportions and washing times with *Saccharina Japan.*

3.6. Relative and absolute error analysis

Figure 5 shows the results of the analysis of percentage error (MPE) and absolute percentage error (MAPE).

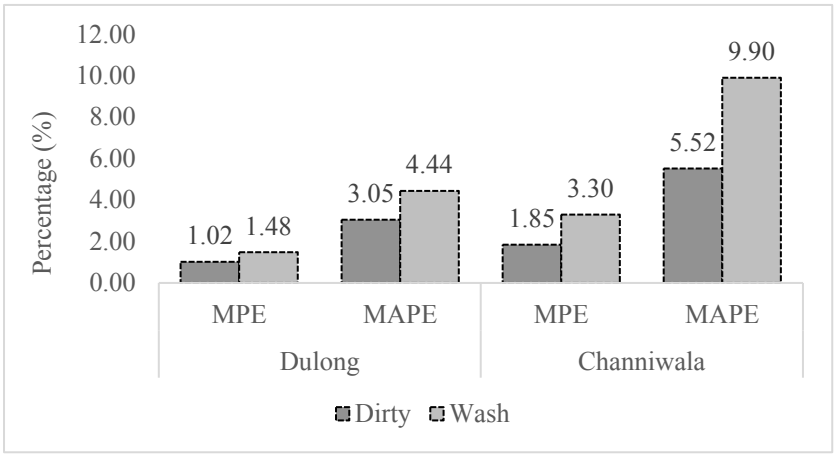

Figure 5. Relative error graphic by each method.

Both methods present a slight overestimation (MPE), being the Dulong equation the one with the lowest MPE. However, the MAPE values indicate an important difference between the calculated and determined values, of 9.90% for the Channiwala method and 4.44% for Dulong. This indicates that the Dulong method would be most similar to the values determined with the bomb calorimetric method. The MAPE obtained from both methods is different from those reported by Huang and Lo [46], who reported 6.73% in Dulong and 2.49% in Channiwala; however, the authors use these methods in lignocellulosic biomass. Although authors such as Channiwala and Parikh [44] also reported 6.94%

for the Dulong method, authors such as Vardon et al. [9] used this method to determining HHV of three species of marine algae. It would be important to obtain a greater number of results (n > 100), as mentioned by Huang and Lo [46], to analyze the overestimation of calorific values more effectively. Although there are differences in each method (Dulong and Channiwala), both equations at a practical or pilot level are useful, specifically in determining the value of the gross calorific value, based on the elemental composition of the biomass, like the *Sargassum fluitans.*

3.7. Unit cost

The cost of collecting *Sargassum fluitans* was estimated by relating the annual expenditure reported by the Mexican government with the amounts collected per year (2017–2019). The cost of washing was determined based on the water consumed in the process. The cost per grinding was determined by the time of electrical consumption by using an electrical mill at a certain amount of dough. Finally, the quantities were extrapolated to a base quantity of one ton, and the costs were integrated (Table 3).

Table 3. Unit cost analysis integration.

Activity (inputs)	Unit	Quantity per t	Price ($)	Cost ($)	
				Dirty	*Wash*
Recollection	t	-	31.75	31.75	31.75
Water (washing)	m^3	96*	0.74	-	71.04
Electricity (grinding)	kW	32.40**	1.09	35.21	35.21
Cost per ton				66.96	138.00
Cost per calorific value					
Dirty (9,242 MJ/t)				0.007***	-
Wash (12,705 MJ/t)				-	0.011***

*Note : * Costs of the industrial tariff in water consumption (10 m^3) of the Potable Water and Sewerage Commission of Quintana Roo; ** Average costs of medium voltage electricity tariff (25 kW) from Mexico's Federal Electricity Commission (CFE); *** The quotient obtained between the calorific value and the price per ton.

The cost of US$ 0.007 per MJ of dirty *Sargassum fluitans* is similar to the US$ 0.006 per MJ reported by Tauro et al. [60] with the use of sawdust pellets. The cost of US$ 0.011 per MJ of washed *Sargassum fluitans* is similar to the US$ 0.013 per MJ reported by Tauro et al. [60] in cane bagasse pellets. Park et al. [61] report a price of US$ 0.010 per MJ of LPG, which is very similar to the price per MJ of the washed *Sargassum fluitans* used in this research. BP [1] reports a price of US$ 57.16 per t of coal in North America, with dirty *Sargassum* being the closest to this price. The cost of *Sargassum fluitans* with only two wash times (Figure 2) could be reduced to US$ 84.80 per t. Costs in dollars were calculated at an exchange rate of MXN$ 20.00 per USD.

4. Conclusions

The washing mechanism had favorable effects on the bioenergetic characteristics of *Sargassum fluitans.*

- Removing sand, salts, and residues reduce the ash content by 58%. Volatile matter increased by 47%. There was an increase in the percentage content of C, H, O, and N and a reduction in the

content of S and Cl. A decrease in the concentration of heavy metals was observed at levels below international standards. In addition, the decrease in the concentration of Ba and Mn.

- The reduction of the impurity content allowed the calorific values to increase by 36.80% in the direct measurement by the calorimetric pump. The MPE and MAPE analysis in the indirect methods indicate a slight overestimation and lower proximity in washed *Sargassum*. Dulong's method showed the least overestimation and the greatest proximity. It is very important to standardize the washing process. Improving the screening process with the use of mechanized equipment could substantially improve the elemental and calorific value characteristics and reduce wash times.
- The calorific value of *Sargassum fluitans* that reaches the shores of the Mexican Caribbean could be compared to other types of biomass used as fuels. It could be used as an input in combustion processes, being a potentially economical option in already proven systems such as sugar mills or cement kilns with co-processing of solid waste, especially given the emerging need to remove it from the coast and while developing methods and technologies of better application, efficiency, and profitability.

Authors' contributions

José Aurelio Sosa (ORCID: https://orcid.org/0000-0001-6786-0521): Ph.D. student, performed the calculations of calorific values and statistical analysis. aurelio.sosa@ujat.mx ; ing-jaso@hotmail.es.

José Ramón Laines (ORCID: https://orcid.org/0000-0002-6770-5596): Research Professor, performed the proximal analysis. josra_2001@yahoo.com.mx.

Donato Antonio Figueiras: Laboratorian, performed the heavy metal content analysis. donato.figueiras@geocycle.com.

Anabel González (ORCID: https://orcid.org/0000-0002-6855-788X): Laboratorian, performed the FTIR analysis and elementary mapping. anaiq86@hotmail.com.

David Guerrero (ORCID: https://orcid.org/0000-0002-7762-0246): Research Professor, performed the calorimetry tests. iqguerrero@gmail.com.

Heidi Kimberly Osorio García and Berenice Evia López: Environmental engineering students carried out the washing material tests and the ultimate analysis. kim159h@gmail.com (Osorio), bereniceevialopez@gmail.com (Evia).

Acknowledgments

We are grateful for the collaboration of the co-processing laboratory of the company Geocycle® S.A de CV.

We acknowledge and appreciate the support received by Dr. Alejandro Padilla (University of Calgary, Canada).

Conflicts of interest

The authors have no conflicts of interest to declare relevant to this article content.

References

1. British Petroleum (2020) Statistical review of world energy 2020 | 69th edition, 2020. Available from: https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2020-full-report.pdf.
2. Secretary of energy of Mexico (2018) Electric sector prospect 2018–2032, 2018. Available from: https://base.energia.gob.mx/Prospectivas18-32/PSE_18_32_F.pdf.
3. Secretary of energy of Mexico (2018) Renewable Energy Prospect 2018–2032, 2018. Available from: https://base.energia.gob.mx/Prospectivas18-32/PER_18_32_F.pdf.
4. Ross AB, Biller P, Kubacki ML, et al. (2010) Hydrothermal processing of microalgae using alkali and organic acids. *Fuel* 89: 2234–2243. https://doi.org/10.1016/j.fuel.2010.01.025
5. Biswas B, Fernandes AC, Kumar J, et al. (2018) Valorization of Sargassum tenerrimum: Value addition using hydrothermal liquefaction. *Fuel* 222: 394–401. https://doi.org/10.1016/j.fuel.2018.02.153
6. Beta San Miguel Group (2019) Environmental responsibility, environmental responsibility, 2019. Available from: http://www.bsm.com.mx/resp_ambiental.html.
7. Henkel C, Muley PD, Abdollahi KK, et al. (2016) Pyrolysis of energy cane bagasse and invasive Chinese tallow tree (Triadica sebifera L .) biomass in an inductively heated reactor. *Energy Convers Manage* 109: 175–183. https://doi.org/10.1016/j.enconman.2015.12.013
8. Smetacek V, Zingone A (2013) Green and golden seaweed tides on the rise. *Nature* 504: 84–88. https://doi.org/10.1038/nature12860
9. Vardon DR, Sharma BK, Blazina GV, et al. (2012) Thermochemical conversion of raw and defatted algal biomass via hydrothermal liquefaction and slow pyrolysis. *Bioresour Technol* 109: 178–187. https://doi.org/10.1016/j.biortech.2012.01.008
10. Moreira Á, Alfonso G (2013) Unusual arrival of *Sargassum fluitans* (*Børgesen*) in the center-south coast of Cuba. *Rev Investig Mar* 33: 17–20. Available from: http://hdl.handle.net/1834/5248.
11. Franks JS, Johnson DR, Ko DS (2016) Pelagic Sargassum in the Tropical North Atlantic. *Gulf Caribb Res* 27: 6–11. https://doi.org/10.18785/gcr.2701.08
12. Fernández F, Boluda C, Olivera J, et al. (2017) Prospective elemental analysis of the algal biomass accumulated on the coasts of the Dominican Republic during 2015. *Cent Azucar* 44: 11–22. Available from: http://scielo.sld.cu/pdf/caz/v44n1/caz02117.pdf.
13. Secretary of the navy of Mexico (2017) Arrival of sargassum on the coasts of Quintana Roo, 2017. Available from: https://digaohm.semar.gob.mx/oceanografia/SargazoSEMAR.html.
14. Secretary of ecology and environment of Quintana Roo (2018) Sargazo harvesting activities report, 2018. Available from: http://sargazo2018.semaqroo.gob.mx/.
15. Espinosa LA, Li Ng JJ (2020) BBVA research, The risk of *Sargassum* for the economy and tourism of Quintana Roo and Mexico, 2020. Available from: https://www.bbvaresearch.com/wp-content/uploads/2020/02/Riesgo_Sargazo_Big_Data.pdf.
16. Secretary of the environment and natural resources of Mexico (2021) Semarnat, technical and management guidelines for attention to the contingency caused by Sargasso in the Mexican Caribbean and the Gulf of Mexico, 2021. Available from: https://www.gob.mx/semarnat/acciones-y-programas/plan-sustentable-ante-arribazon-anormal-de-sargazo.

17. DrecKmann K, Sentíes A (2013) Seaweed 'arribazones' in the Mexican Caribbean: natural biological event or trash on the beaches. *Biodiversitas* 7–11. Available from: https://docplayer.es/9653723-Las-arribazones-de-evento-biologico-natural-o-basura-en-las-playas.html.
18. Webster R, Linton T (2013) Development and implementation of Sargassum Early Advisory System (SEAS). *Shore & Beach* 81: 1–6. Available from: http://www.sargassoseacommission.org/storage/Webster_et_linon_2013_1.pdf.
19. Gower J, Young E, King S (2013) Satellite images suggest a new Sargassum source region in 2011. *Remote Sens Lett* 4: 764–773. https://doi.org/10.1080/2150704X.2013.796433
20. Johnson DR, Ko DS, Franks JS, et al. (2012) The Sargassum invasion of the Caribbean and dynamics of the Equatorial North Atlantic. Proceedings of the 65th Gulf and Caribbean Fisheries Institute. Available from: https://nsgl.gso.uri.edu/flsgp/flsgpw12004/data/papers/65-17.pdf.
21. Weber SC, Carpenter EJ, Coles VJ, et al. (2017) Amazon River influence on nitrogen fixation and export production in the western tropical North Atlantic. *Limnol Oceanogr* 62: 618–631. https://doi.org/10.1002/lno.10448
22. Brooks MT, Coles VJ, Hood RR, et al. (2018) Factors controlling the seasonal distribution of pelagic Sargassum. *Mar Ecol Prog Ser* 599: 1–18. https://doi.org/10.3354/meps12646
23. Lapointe BE, West LE, Sutton TT, et al. (2014) Ryther revisited: nutrient excretions by fishes enhance productivity of pelagic Sargassum in the western North Atlantic Ocean. *J Exp Mar Bio Ecol* 458: 46–56. http://dx.doi.org/10.1016/j.jembe.2014.05.002
24. Hernández-Zanuy AC (2018) Ecosystem-based adaptation: alternative for the sustainable management of Caribbean marine and coastal resources. CYTED Network 410RT0396. (E. Book). Editorial Institute of Oceanology, Havana. 171 pp. Available from: http://www.cyted.org/sites/default/files/adaptacion_basada_en_ecosistemas._2018.pdf.
25. Lamare MD, Wing SR (2001) Calorific content of New Zealand marine macrophytes. *New Zeal J Mar Freshw Res* 35: 335–341. https://doi.org/10.1080/00288330.2001.9517004
26. Yu LJ, Wang S, Jiang XM, et al. (2008) Thermal analysis studies on combustion characteristics of seaweed. *J Therm Anal Calorim* 93: 611–617. https://doi.org/10.1007/s10973-007-8274-6
27. Wang S, Jiang XM, Han XX, et al. (2009) Combustion characteristics of seaweed biomass. 1. Combustion Characteristics of Enteromorpha clathrata and Sargassum natans. *Energy Fuels* 23: 5173–5178. https://doi.org/10.1021/ef900414x
28. Bruhn A, Dahl J, Nielsen HB, et al. (2011) Bioenergy potential of Ulva lactuca: Biomass yield, methane production and combustion. *Bioresour Technol* 102: 2595–2604. https://doi.org/10.1016/j.biortech.2010.10.010
29. Sudhakar K, Premalatha M (2015) Characterization of micro algal biomass through FTIR/TGA /CHN analysis: Application to Scenedesmus sp. *Energy Sources, Part A* 37: 2330–2337. http://dx.doi.org/10.1080/15567036.2013.825661
30. Ghadiryanfar M, Rosentrater KA, Keyhani A, et al. (2016) A review of macroalgae production, with potential applications in biofuels and bioenergy. *Renewable Sustainable Energy Rev* 54: 473–481. http://dx.doi.org/10.1016/j.rser.2015.10.022
31. Li W, Tan S, Shi Y, et al. (2015) Utilization of sargassum based activated carbon as a potential waste derived catalyst for low temperature selective catalytic reduction of nitric oxides. *Fuel* 160: 35–42. http://dx.doi.org/10.1016/j.fuel.2015.07.045

32. Ali I, Bahadar A (2017) Red Sea seaweed (Sargassum spp.) pyrolysis and its devolatilization kinetics. *Algal Res* 21: 89–97. http://dx.doi.org/10.1016/j.algal.2016.11.011
33. Li J, Qiao Y, Chen X, et al. (2019) Steam gasification of land, coastal zone and marine biomass by thermal gravimetric analyzer and a free-fall tubular gasifier: Biochars reactivity and hydrogen-rich syngas production. *Bioresour Technol* 289: 121495. https://doi.org/10.1016/j.biortech.2019.121495
34. Sudhakar K, Mamat R, Samykano M, et al. (2018) An overview of marine macroalgae as bioresource. *Renewable Sustainable Energy Rev* 91: 165–179. https://doi.org/10.1016/j.rser.2018.03.100
35. Gupta VK, Nayak A, Agarwal S (2015) Bioadsorbents for remediation of heavy metals: Current status and their future prospects. *Environ Eng Res* 20: 1–18. http://dx.doi.org/10.4491/eer.2015.018%0AReview
36. Yan J, Karlsson A, Zou Z, et al. (2020) Contamination of heavy metals and metalloids in biomass and waste fuels: Comparative characterisation and trend estimation. *Sci Total Environ* 700: 134382. https://doi.org/10.1016/j.scitotenv.2019.134382
37. Jagustyn B, Kmieć M, Smędowski Ł, et al. (2017) The content and emission factors of heavy metals in biomass used for energy purposes in the context of the requirements of international standards. *J Energy Inst* 90: 704–714. http://dx.doi.org/10.1016/j.joei.2016.07.007
38. Amador-Castro F, García-Cayuela T, Alper HS, et al. (2021) Valorization of pelagic sargassum biomass into sustainable applications: Current trends and challenges. *J Environ Manage* 283: 112013. https://doi.org/10.1016/j.jenvman.2021.112013
39. Saldarriaga-Hernandez S, Hernandez-Vargas G, Iqbal HMN, et al. (2020) Bioremediation potential of Sargassum sp. biomass to tackle pollution in coastal ecosystems: Circular economy approach. *Sci Total Environ* 715: 136978. https://doi.org/10.1016/j.scitotenv.2020.136978
40. Thompson TM, Young BR, Baroutian S (2020) Pelagic Sargassum for energy and fertiliser production in the Caribbean: A case study on Barbados. *Renewable Sustainable Energy Rev* 118: 109564. https://doi.org/10.1016/j.rser.2019.109564
41. American Society of Testing Methods (2002) ASTM D-2974, Standard test methods for moisture, ash, and organic matter of peat and organic soils, 2002. Available from: https://www.astm.org/d2974-14.html.
42. American Society of Testing Methods (2015) ASTM D-5468, standard test method for gross calorific and ash value of waste materials., 2015. Available from: https://www.astm.org/DATABASE.CART/HISTORICAL/D5468-02.htm.
43. Environmental Protection Agency USA (1996) EPA, METHOD 6010B, Inductively Coupled Plasma-Atomic Emission Spectrometry, 1996. Available from: https://www.epa.gov/sites/production/files/documents/6010b.pdf.
44. Channiwala SA, Parikh PP (2002) A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel* 81: 1051–1063. https://doi.org/10.1016/S0016-2361(01)00131-4
45. Wang C, Deng X, Xiang W, et al. (2020) Calorific value variations in each component and biomass-based energy accumulation of red-heart Chinese fir plantations at different ages. *Biomass Bioenergy* 134: 105467. https://doi.org/10.1016/j.biombioe.2020.105467
46. Huang Y-F, Lo S-L (2020) Predicting heating value of lignocellulosic biomass based on elemental analysis. *Energy* 191: 116501. https://doi.org/10.1016/j.energy.2019.116501

47. Oyesiku O, Egunyomi A (2014) Identification and chemical studies of pelagic masses of Sargassum natans (Linnaeus) Gaillon and S. fluitans (Borgessen) Borgesen (brown algae), found offshore in Ondo State, Nigeria. *African J Biotechnol* 13: 1188–1193. https://doi.org/10.5897/AJB2013.12335
48. Milledge J, Nielsen B, Sadek M, et al. (2018) Effect of freshwater washing pretreatment on Sargassum muticum as a feedstock for biogas production. *Energies* 11: 1771. https://doi.org/10.3390/en11071771
49. International Organization for Standardization (2014) ISO 17225-1. Solid biofuels—Fuel specifications and classes. 56. Available from: https://www.iso.org/standard/59456.html.
50. Flórez-Fernández N, Domínguez H, Torres MD (2019) A green approach for alginate extraction from Sargassum muticum brown seaweed using ultrasound-assisted technique. *Int J Biol Macromol* 124: 451–459. https://doi.org/10.1016/j.ijbiomac.2018.11.232
51. Liu H, Yang F, Zheng Y, et al. (2011) Improvement of metal adsorption onto chitosan/Sargassum sp. composite sorbent by an innovative ion-imprint technology. *Water Res* 45: 145–154. http://dx.doi.org/10.1016/j.watres.2010.08.017
52. Wang Y, Li Y, Zhao FJ (2014) Bisorption of chromium(VI) from aqueous solutions by Sargassum thunbergii Kuntze. *Biotechnol Biotechnol Equip* 28: 259–265. http://dx.doi.org/10.1080/13102818.2014.907028
53. Jesumani V, Du H, Pei P, et al. (2019) Unravelling property of polysaccharides from Sargassum sp. as an anti-wrinkle and skin whitening property. *Int J Biol Macromol* 140: 216–224. https://doi.org/10.1016/j.ijbiomac.2019.08.027
54. Kannan S (2014) FT-IR and EDS analysis of the seaweeds Sargassum wightii and Gracilaria corticata (red algae). *Int J Curr Microbiol Appl Sci* 3: 341–351. Available from: https://www.ijcmas.com/vol-3-4/S.Kannan.pdf.
55. Chale-Dzul J, Pérez-Cabeza de Vaca R, Quintal-Novelo C, et al. (2020) Hepatoprotective effect of a fucoidan extract from Sargassum fluitans Borgesen against CCl4-induced toxicity in rats. *Int J Biol Macromol* 145: 500–509. https://doi.org/10.1016/j.ijbiomac.2019.12.183
56. Barquilha CER, Cossich ES, Tavares CRG, et al. (2019) Biosorption of nickel(II) and copper(II) ions by Sargassum sp. in nature and alginate extraction products. *Bioresour Technol Reports* 5: 43–50. https://doi.org/10.1016/j.biteb.2018.11.011
57. Arunkumar K, Buvaneswari B, Murugan M (2014) Quantification of carbonate crystals using FTIR technique in some calcareous algae occurring along the southeast coasts of India. *Indian J Geo-Marine Sci* 43: 2289–2297. Available from: http://nopr.niscair.res.in/bitstream/123456789/34601/1/IJMS%2043%2812%29%202289-2297.pdf.
58. Samanta A, Chanda DK, Das PS, et al. (2016) Synthesis of nano calcium hydroxide in aqueous medium. *J Am Ceram Soc* 99: 787–795. https://doi.org/10.1111/jace.14023
59. Choi JH, Kim S-S, Ly HV, et al. (2017) Thermogravimetric characteristics and pyrolysis kinetics of high-density-aquacultured Saccharina Japonica : Effects of water-washing. *Fuel* 193: 159–167. https://doi.org/10.1016/j.fuel.2016.12.041
60. Tauro R, García CA, Skutsch M, et al. (2018) The potential for sustainable biomass pellets in Mexico: An analysis of energy potential, logistic costs and market demand. *Renewable Sustainable Energy Rev* 82: 380–389. http://dx.doi.org/10.1016/j.rser.2017.09.036

61. Park K, Shin D, Yoon ES (2011) The cost of energy analysis and energy planning for emerging, fossil fuel power plants based on the climate change scenarios. *Energy* 36: 3606–3612. http://dx.doi.org/10.1016/j.energy.2011.03.080

AIMS Press