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A Prospective Study of the Exploitation of Pelagic *Sargassum* spp. as a Solid Biofuel Energy Source

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Abstract: This study presents a prospective study for the potential exploitation of pelagic *Sargassum* spp. as a solid biofuel energy source. It was carried out in three stages. First we conducted a morphological, physical-chemical, and structural characterization using scanning electron microscopy (SEM), infrared spectroscopy (FTIR), and X-ray diffraction (DRX), respectively. Second we evaluated the material's functional properties as a solid biofuel based on its calorific value and the quantification of polymeric components like hemicellulose, cellulose, and lignin, as well as thermogravimetric and differential analysis to study the kinetics of its pyrolysis and determine parameters like activation energy (E_a), reaction order (n), and the pre-exponential factor (Z). Third we analyzed the energetic potential considering the estimated volume of pelagic *Sargassum* spp. that was removed from beaches along the Mexican Caribbean coast in recent years. Results of the kinetic study indicate that *Sargassum* spp. has an enormous potential for use as a complement to other bioenergy sources. Other results show the high potential for exploiting these algae as an energy source due to the huge volumes that have inundated Caribbean, West African, and northern Brazil shorelines in recent years. As a solid biofuel, *Sargassum* spp. has a potential energy the order of 0.203 gigajoules (GJ)/m^3. In the energy matrix of the residential sector in Mexico, its potential use as an energy source is comparable to the national consumption of firewood. The volume of beachcast *Sargassum* spp. that was removed from ~8 km of coastline around Puerto Morelos, Mexico in 2018–2019, could have generated over 40 terajoules/year of solid biofuel.

1. Introduction

Evidence of contemporary tendencies in the exploitation, production, and use of renewable energy sources have fostered a great interest in processes for diversifying energy generation worldwide to reduce dependence on fossil fuels [1–3]. The inevitable exhaustion of conventional fuels has convinced people of the need for a broad energy transition in light, of the obligation to address the issues that contribute to global climate change [4]. However, any such energy transition must also promote the integration of policies that link social justice and economic equality with sustainable energy sources capable of satisfying the energy needs of all humanity in order, to ensure a sustainable future [5,6], and decrease greenhouse gas emissions [7]. This will require investing in technological innovation to generate alternative energy sources, processes, and approaches to foment the democratization of energy [8].

The generation of energy from renewable sources is increasing yearly in many countries [3], along with the optimization of materials in various processes [9,10]. While Mexico is not an exception, the existing national energy system is still based on fossil fuels that supply over 60% of primary energy, while the figure for renewable energy is still below 20%, a proportion quite similar to the global energy matrix [6,11,12]. It is important to emphasize that developing countries like Mexico maintain a strong dependence on biomass in their matrix of energy consumption in the residential sector, largely due to its local availability and economic affordability [11]. However, biomass is a renewable energy source investigated much recently [13]. The biomass consumed by Mexico's residential sector comes from locally-available species of trees and bushes, while resources from aquatic bodies have rarely been explored even though they constitute an interesting field of study, as in our ongoing research. Energy sources derived from biomass generally come from lignocellulosic materials with great potential, but these have been explored only incipiently [14], while studies of other kinds of bioenergy alternatives have been increasing in frequency. To give one example, solid industrial material in the form of lignocellulosic residues are a massive source of carbohydrates and lignins that exceeds 2×10^{11} t/year worldwide [15]. A recent study in Mexico examined the feasibility of exploiting timber residues to produce briquettes using accessible mechanisms with low environmental impact. This material has been used in cooking by residential sectors in rural communities, demonstrating that the production of solid biofuels can provide an alternative energy source with low environmental impact [16,17]. In this regard, exploring resources and/or residues with bioenergy potential will confer added value, contribute to generating sustainable energy sources, and help construct affordable scenarios for energy security at the local level.

The pelagic *Sargassum* that has invaded the Mexican Caribbean coastline since 2014 is composed mainly of the *S. fluitans* and *S. natans* species [18]. During the peak month (September) of the event in 2015, the average volume of *Sargassum* spp. that arrived to the northern sector of this region was estimated to be ~2.4×10^3 m^3 per kilometer of beach [19]. Massive volumes of beachcast *Sargassum* spp. were also recorded on this coast in 2018, 2019 and 2020 [18]. The massive influx of *Sargassum* spp. is considered an ecological plague that has adverse impacts on coastal ecosystems, fishing, and the tourist industry, which is the base of the economy in the region [20]. These algae, however, could be an energy resource with high potential for exploitation in, for example, biogas and fertilizer production [21–23].

Our study analyzes the potential for energy exploitation of the *Sargassum* spp. that has reached the coasts of the Mexican Caribbean in recent years. It evaluates the material's potential for primary energy exploitation as a solid biofuel through a simple process of drying and compaction. The analyses include a physical-chemical and functional characterizations of *Sargassum* spp. to determine its composition of polymetric compounds and calorific value, and a pyrolithic analysis that provides evidence and

indicators of sustainability for a scenario in which exploiting these algae as an energy source foresees substantial benefits for Mexico's Caribbean region.

2. Materials and Methods

2.1. Characterization

A total of 30 samples of *Sargassum* spp. (500 g each sample), collected from the beach (Figure 1a,b) at three sites (Cancun, Puerto Morelos and Tulum) along the Mexican Caribbean coast in 2019, were employed to conduct the physical-chemical and functional characterizations of the *Sargassum* spp. and to determine the composition of polymetric compounds and calorific value. The *Sargassum* spp. collected were fresh and had no appreciable content of decayed material.

Figure 1. Processing of *Sargassum* spp. (**a**) collection; (**b**) washing; (**c**) open-air drying; (**d**) grinding.

Afterward, in the laboratory, the algae were washed in distilled water to remove impurities and salts (Figure 1b), left to dry under natural solar irradiance (Figure 1c) until it reached a moisture content of 20%, and grounded in an agate mortar (Figure 1d). The density of the *Sargassum* spp. after drying was 136 Kg/m^3.

2.1.1. Thermogravimetric and Kinetic Analyses

A thermogravimetric analysis [24–27] was conducted to determine (i) physical-chemical changes in *Sargassum* spp. at different temperatures, (ii) the kinetics of the pyrolithic process of this material, and (iii) its kinetic parameters. To eliminate the moisture, *Sargassum* spp. samples were oven dried at, a temperature of 25 °C for five days. Once dry, the samples were ground in an agate mortar to a particle size of approximately 400 microns, and dried again at 115 °C, until they reached a constant weight. All the samples remained in storage in the oven until analyses were conducted.

The thermal degradation (TGA-DTG) of the *Sargassum* spp. was determined in a PerkinElmer STA 6000 thermogravimetric analyzer. To perform the thermal process and protect the samples from oxidation, a relative grade inert gas (nitrogen) was utilized at a purity of 99.99% and a flow rate of 20 mL/min. The samples were heated from room temperature (25 °C) to a maximum of 900 °C. For the thermal process, we considered non-isothermal conditions at a heating velocity of 10 °C/min. To reduce errors, complete pyrolysis was performed in three time. Each sample used had an approximate weight of 30 ± 5 mg.

The TGA analysis allowed us to calculate such key parameters as activation energy (E_a), frequency factor (Z), and reaction order (n). Diverse mathematical models have been proposed for studying the kinetics of thermogravimetric processes based on Arrhenius' equation. It is important to note that existing models are of two types: a function of the degree of advance, represented by α; and a function of heating velocity, represented by β. The present study analyzed the pyrolysis of *Sargassum* spp. by considering an inert nitrogen atmosphere using Horowitz and Metzger's method, based on the degree of advance (α) to determine the aforementioned kinetic parameters.

According to various researchers, the complete thermal process of biomass can be simplified as a global mechanism [28–30]. If we consider that the decomposition of the biomass can be obtained in only one step, then the conversion velocity can be represented as a function of *k(T)* [31–33] as follows:

$$\frac{d\alpha}{dt} = k(T) * f(\alpha) \tag{1}$$

Once the degree of conversion is defined, applying Arrhenius' expression makes it possible to proceed with the kinetic analysis. If we consider the initial and final mass (m_i, m_f) as the mass in the sample-holder of the TGA apparatus (aluminum crucible), and the residual mass at the end of the pyrolithic process, respectively, then the degree of conversion, or degree of advance (α), of any mass (m) in the entire temperature range (T), is expressed as:

$$\alpha = \frac{m_i - m}{m_i - m_f} \tag{2}$$

As Equation (3) shows, and considering the *k(T)* term of Equation (1), dependence with respect to temperature can be described as a function of Arrhenius' expression as follows:

$$Velocity\ constant[k(T)] = pre-exponential\ factor\ (A) * e^{\left[\frac{-activation\ energy\ (E_a)}{gas\ constant\ (R)*Temperature\ (K)}\right]} \tag{3}$$

The appropriate kinetic analysis is fundamental for the goals of evaluating pyrolysis and optimizing the thermal transformation of *Sargassum* spp., that is, to obtain the most important parameters of the thermal process. The Horowitz-Metzger method is a simplified form of Coast-Redfern's integral method and, provides an excellent approach towards a straight line, so it is utilized to calculate such kinetic parameters as activation energy (E_a) by analyzing a slope that is obtained by representing a function of the degree of conversion (α) with respect to the temperature of the thermal degradation process [34]. This method also permits the determination of the reaction order (n) by considering the relation between α and the maximum point of conversion velocity with respect to temperature ($d\alpha/dT$) [35].

In general, and according to the Coast-Redfern method, the mathematical expression from which the Horowitz-Metzger method is derived is the following:

$$F(\alpha) = \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E_a}{RT}\right) dT \tag{4}$$

For a first-order reaction, Equation (4) generates:

$$-\ln(1-\alpha) = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E_a}{RT}\right) dT \tag{5}$$

By considering diverse approximations, and by simplifying and integrating the right side of Equation (5), it is possible to arrive at the following expression:

$$-\ln(1-\alpha) = \exp\left(\frac{-E_a\theta}{RT_s^2}\right) \tag{6}$$

For Equation (6), we eventually obtain:

$$\ln\left\{\ln\frac{1}{(1-\alpha)}\right\} = \frac{E_a\theta}{RT_s^2} \tag{7}$$

where α is the degree of advance, *Ts* is the maximum temperature of the derivative of TGA, that is, of DTG; θ is the deviation from the absolute characteristic temperature; that is, the difference between

the temperature (*T*) at any time (t) and *Ts*. E_a is the activation energy, *R* is the constant of the ideal gases. Therefore, if we graph each value of θ vs. ln{ln[1/(1 − *α*)]}, a linear adjustment is feasible at an ample interval of *α* (0.1–0.9) of the degradation reaction, making it possible to calculate the activation energy [29].

As mentioned above, the Horowitz-Metzger method also permits intuiting the reaction order *(n)* by considering the conversion α_m at the point of the maximum velocity of degradation (*dα/dT*). Calculating this requires approximating the following expression:

$$\alpha_m = n^{\frac{1}{1-n}} \tag{8}$$

Considering that in our work we performed a thermal analysis of the *Sargassum* spp. at a constant heating velocity, the factor frequency *(Z)* can be calculated using the following expression [36]:

$$Z = \frac{\beta * (E_a + 2 * R * T_\alpha) * \exp{\frac{E_a}{RT_\alpha}}}{R * T_\alpha^2} \tag{9}$$

where *Z* is the frequency factor (min^{-1}), *β* the heating velocity (°C/min), E_a the activation energy (kJ/mol), *R*, the constant of ideal gases (0.008314 kJ K^{-1} mol^{-1}), T_α the temperature (K) at the point of maximum conversion (*α*); that is, the maximum heating temperature.

2.1.2. Structural, Physical-Chemical, and Functional-Energy Characterization of *Sargassum* spp.

X-ray diffraction analysis (DRX, model D8 Advance Davinci) was conducted to identify the phases present in the compounds that make up the *Sargassum* spp. by identifying planes and crystallographic structures. For this analysis, the following conditions were established: 2θ range of 25–55° with increases of 0.05° and a time of 0.2 s per step, and infrared spectroscopy, performed by using model FTIR Tensor 27 equipment (Bruker, Berlin, Germany) with transmittance spectrum analysis from 500–4000 cm^{-1}. The morphology and elemental composition of *Sargassum* spp. were analyzed under scanning electron microscopy (SEM, model Jeol JSM 7600F with field emission). The chemical composition of the main polymeric components of the *Sargassum* spp. (cellulose, hemicellulose, lignin) was determined by fiber analysis using Van Soest's gravimetric method and a-amylase [37]. For this analysis, 0.5-g samples of the dried algae with a homogeneous particle size (passed through a mesh of 60/40, 0.274/0.516 mm) were used. This step was performed in triplicate for each of the 30 samples, utilizing an ANKOM-200 fiber analyzer [38]. The apparent density of the samples collected was also obtained. The calorific value of the samples was calculated using an isoperibol calorimeter (LECO model AC600) in accordance with the norm IN-14918 [39].

2.2. Study of the Potential Energy of Sargassum spp. Based on Beachcast Volume

The magnitude of *Sargassum* spp. washing up on beaches along the northern sector of the Mexican Caribbean coast was estimated from data obtained in 2018 and 2019 on the volume of *Sargassum* spp. removed monthly from the beach by nine hotels, located between Cancun and Playa del Carmen, with a total beachfront of 8.01 km. The volume of *Sargassum* spp. was calculated by the number of trucks of known capacity (7 m^3 or 14 m^3) that the hotels used for its transportation to disposal sites or by the number of trips that cleaning machines of known capacities did per day. The material removed was mostly composed of *S. fluitans* and *S. natans*, but it could also include sand, seagrasses, and occasionally other macroalgae. To correct for compositional heterogeneity in beachcast material, on the basis of mass-specific components, we used the value provided by Salter et al. [40] who analyzed twelve 1 kg samples of beach-cast material in Puerto Morelos in 2019, and found that *Sargassum* spp. dominated each sample, accounting for, on average 74% of total mass (95% CI: 68–80). The results of the analysis of calorific value allowed us to conduct a prospective study of the potential exploitable energy from

the beachcast *Sargassum* spp. collected in 2018 and 2019, considering that after drying in the sun the pelagic *Sargassum* spp. will loses 85% of humidity, and only 11.1% of the total mass will be used.

3. Results and Discussion

3.1. Thermal Degradation and Kinetic Analysis of Sargassum spp.

The thermogravimetric (TGA) and derivative analysis (DTG) curves of the *Sargassum* spp. are shown in Figure 2. The TGA curve is divided into three main zones (I-III) to coincide with the results of various analyses of the pyrolysis of diverse kinds of marine biomass, including *Sargassum* spp. [41–44]. Zone I shows a very low percentage of loss of mass (≈15%) due to dehydration; that is, the elimination of water and some slightly volatile substances from *Sargassum* spp. This zone is represented by an approximate temperature range of 300–460 K. The following stage (zone II) takes place between 460 and 870 K and displays the largest, most significant mass degradation (≈50%), due to the elimination of diverse amounts of biopolymers from the algae [45]. This zone is characterized by complex chemical reactions fostered by decarbonization and the degradation of important polymers, such as cellulose and hemicellulose [46]. The third zone of mass degradation occurs between 870 and 1150 K.
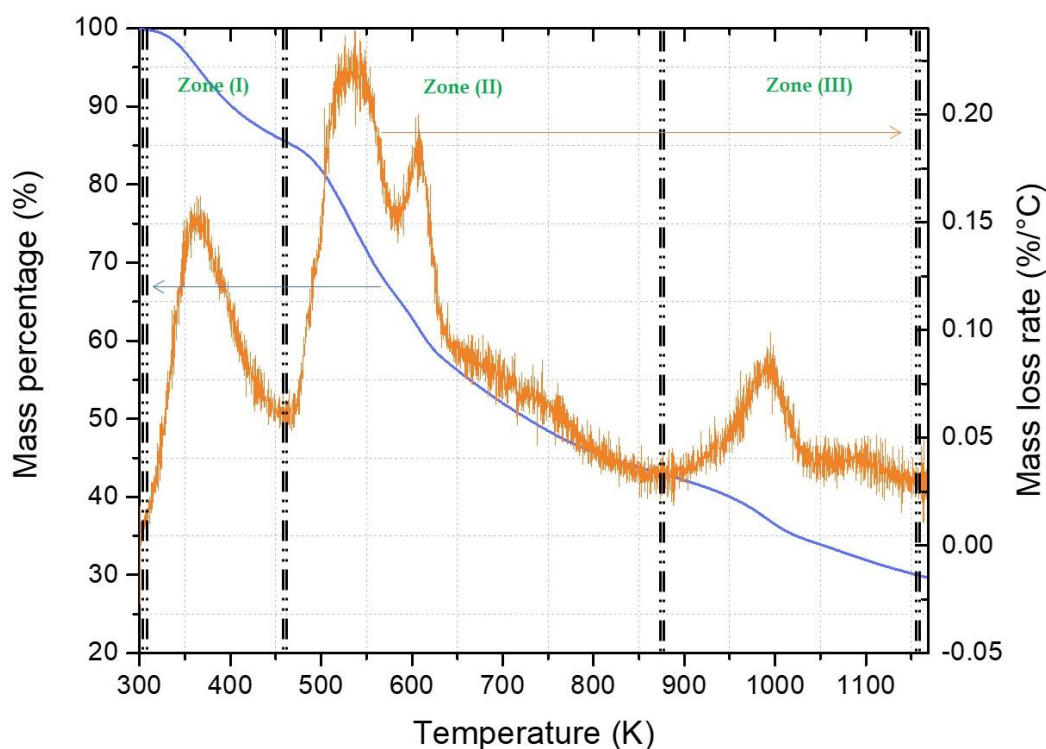

Figure 2. Thermogravimetric (TGA-left *y*-axis) and derivative analysis (DTG-right *y*-axis) curves of *Sargassum* spp. collected on the Mexican Caribbean coast.

The right panel of Figure 2 shows the degradation velocity (DTG), or first derivative of TGA. As a result of the temperature increase, a series of peaks appeared, which that became more pronounced as the temperature rose. According to the literature, the second peak of the DTG graph usually occurs in the range of 460–580 K and represents, principally, the thermal degradation of carbohydrates due to depolymerization and cracking [46]. Following the curve, a third peak appears in the interval between 580 and 625 K. This peak represents the decomposition of the proteins of *Sargassum* spp. [47,48]. Other authors have observed that these two peaks appear in the opposite order, as in the case of *Saccharina japonica (S. japonica)* [49], where the third peak was seen to be higher, indicating differences primarily in carbohydrate content. In this regard, and compared to *S. japonica*, the *Sargassum* spp.

analyzed in the present study presents a second peak that is higher than the third one, suggesting that they contain a larger amount of carbohydrates. Another interesting aspect of the second peak of the DTG of the *Sargassum* spp. marine biomass (Figure 2) is that its temperature at the point of maximum heating velocity is lower than that of terrestrial biomass [50]. One example of this is the cellulose of lignocellulosic materials such as pine trees, which during their initial stage of degradation generally present a larger temperature range after the second DTG peak [51]. This phenomenon can be explained by comparing the degree of devolatilization and primary composition of terrestrial biomass (cellulose, hemicellulose, lignin), which pyrolyzes at a higher temperature than the main components of marine biomass (soluble carbohydrates in H_2O, lipids, proteins), which degrade thermically at a lower temperature [50]. As Figure 2 shows, Zone III becomes visible at around 850 K with a fourth peak that begins at a temperature above 900 K and ends at approximately 1050 K. According to the graph, this transformation occurs at a very low heating velocity. The degradation in Zone III is due mainly to the degradation of inorganic material, such as the thermal transformation of some carbonates and the elimination of certain metals contained in *Sargassum* spp. [47].

To determine the kinetic parameters of *Sargassum* spp., we analyzed the TGA-DTG data in Figure 2. It is well-known that the most important kinetic parameters are activation energy (E_a), reaction order (n), and the frequency factor (Z). Horowitz and Metzger proposed a method for determining the E_a and n of the degradation of biomass [29] that allows to obtain E_a by calculating the slope that results from the T−Ts graph (*x*-axis) vs. $\ln\{\ln[1/(1-\alpha)]\}$ (*y*-axis), as shown in Figure 3.

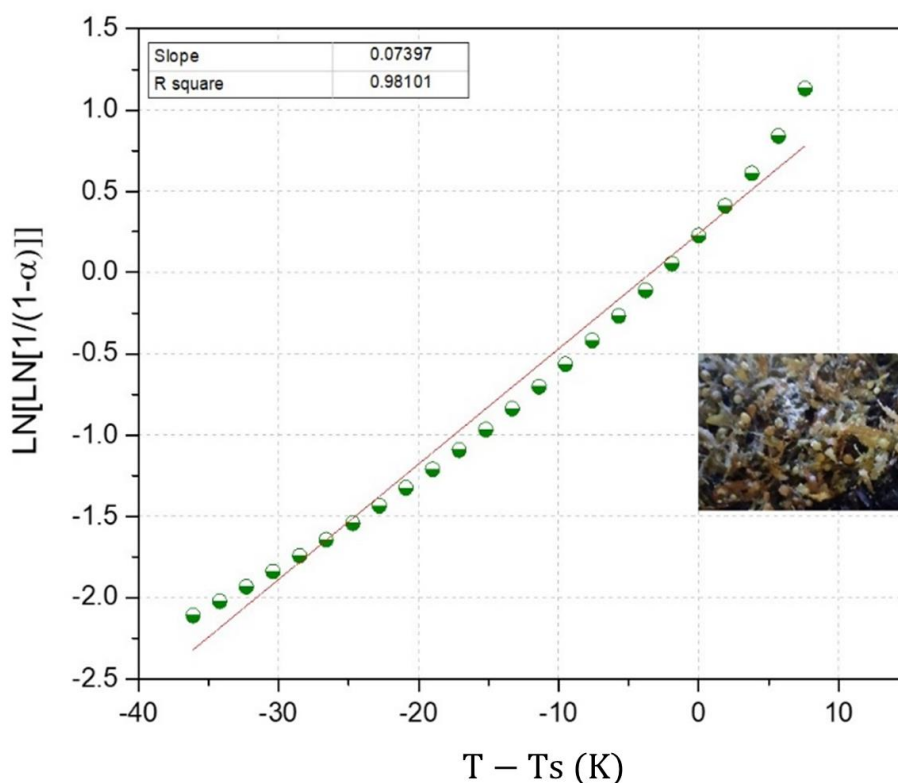| Slope | 0.07397 |
| R square | 0.98101 |

Figure 3. Activation energy (E_a) of *Sargassum* ssp. obtained using the Horowitz and Metzger method.

As Figure 3 shows, there is a good linear adjustment and a slope with a value of 0.07397. Based on Figure 3 and the point of maximum velocity (DTG), we obtained a temperature value of approximately 550 K. Consideration of the constant of ideal gases (R = 8.314 J K^{-1} mol^{-1}) allows the calculation of the activation energy. Our result was an approximate value of 186.03 kJ/mol, which is similar to the figures reported by other researchers who have studied *Sargassum* spp. [45,52,53]. The fact that the correlation coefficient (R^2) presents a value of 0.9810–1 indicates that the Horowitz-Metzger method is acceptable

for predicting both E_a and n. It is important to recall that E_a is the minimum amount of energy required to achieve a reaction, and that as it increases, the reaction velocity decreases. Upon comparing the E_a of *Sargassum* spp. (186.03 kJ/mol) to recent kinetic studies of terrestrial biomass from western Mexico (like *Pinus pseudostrobus, Pinus leiophyllla*, and *Pinus montezumae*, which have average values of 120.84, 140.71 and 147.05 kJ/mol respectively) [52], the E_a of the *Sargassum* spp. studied herein (also from Mexico) was slightly higher. Added to an exploitable energy in the order of 1.24 gigajoules (GJ)/m^3 (see below), this result is acceptable for generating biofuels in a pyrolysis reactor.

Figure 4 presents the graph of the degree of advance (α) vs. $d\alpha/dT$. According to Horowitz and Metzger's method, it is possible to calculate the reaction order by placing the value of α_m at the point of maximum degradation velocity ($d\alpha/dT$). This procedure generated a value of $\alpha_m \approx 0.3637$. Based on the approach in Equation (8) for n, we obtained an n value that approached 1.
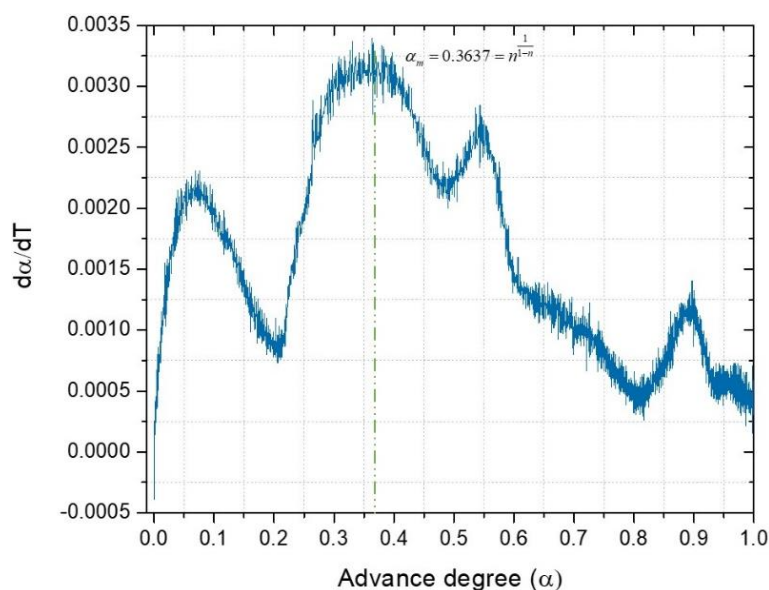

Figure 4. Calculation of the maximum degree of advance (α) at the highest degradation rate to calculate the reaction order (n) of *Sargassum* spp. using the Horowitz-Metzger method.

Another important kinetic parameter is the frequency factor (Z). Using Equation (9), we calculated Z by considering a heating velocity of $\beta = 10$ °C/min, the activation energy of 186.03 KJ/mol, an R value equal to 0.008314 KJ K^{-1} mol^{-1}, and a temperature ($T\alpha$), of 1173 K. This produced an approximate value for Z of 5.76×10^5 min^{-1}. Considering the surface of the study material, reports indicate that the factor Z can vary on the order of magnitude values above six. In the case of a value for the reaction order (n) that is very close to 1, there are reports that the factor Z can vary in a range of 10^5 to 10^{18} s^{-1}. For the *Sargassum* spp. analyzed in our study we obtained a relatively low frequency factor, perhaps due to a reaction that occurred on the surface of the biomass. However, if the surface is not involved, then this magnitude of Z ($<10^9$ s^{-1}) could result from the formation of some –unidentified and more densified structure or compound [54,55].

3.2. X-ray Diffraction and Physical-Chemical Analysis

X-ray diffraction analysis (Figure 5) identified compounds already reported for *Sargassum* spp. in earlier studies, such as calcium carbonate and dolomite (calcium-magnesium carbonate) [56,57]. The planes characteristics of each phase are shown in Figure 5. These compounds were present throughout the anatomy of *Sargassum* spp., from stem to leaves, as was previously recorded in other scientific studies [56–59] and demonstrated in this study using scanning electron microscopy (SEM, Figure 6).
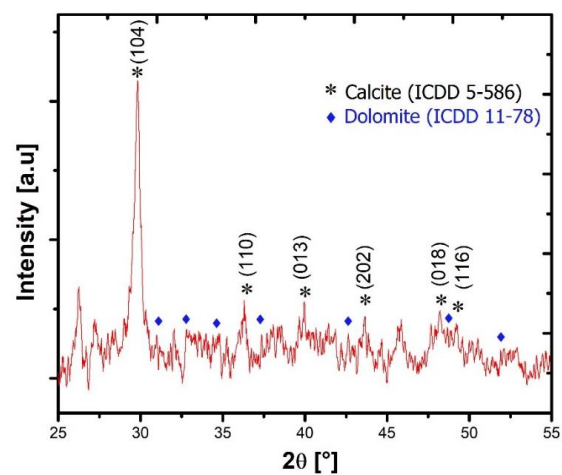
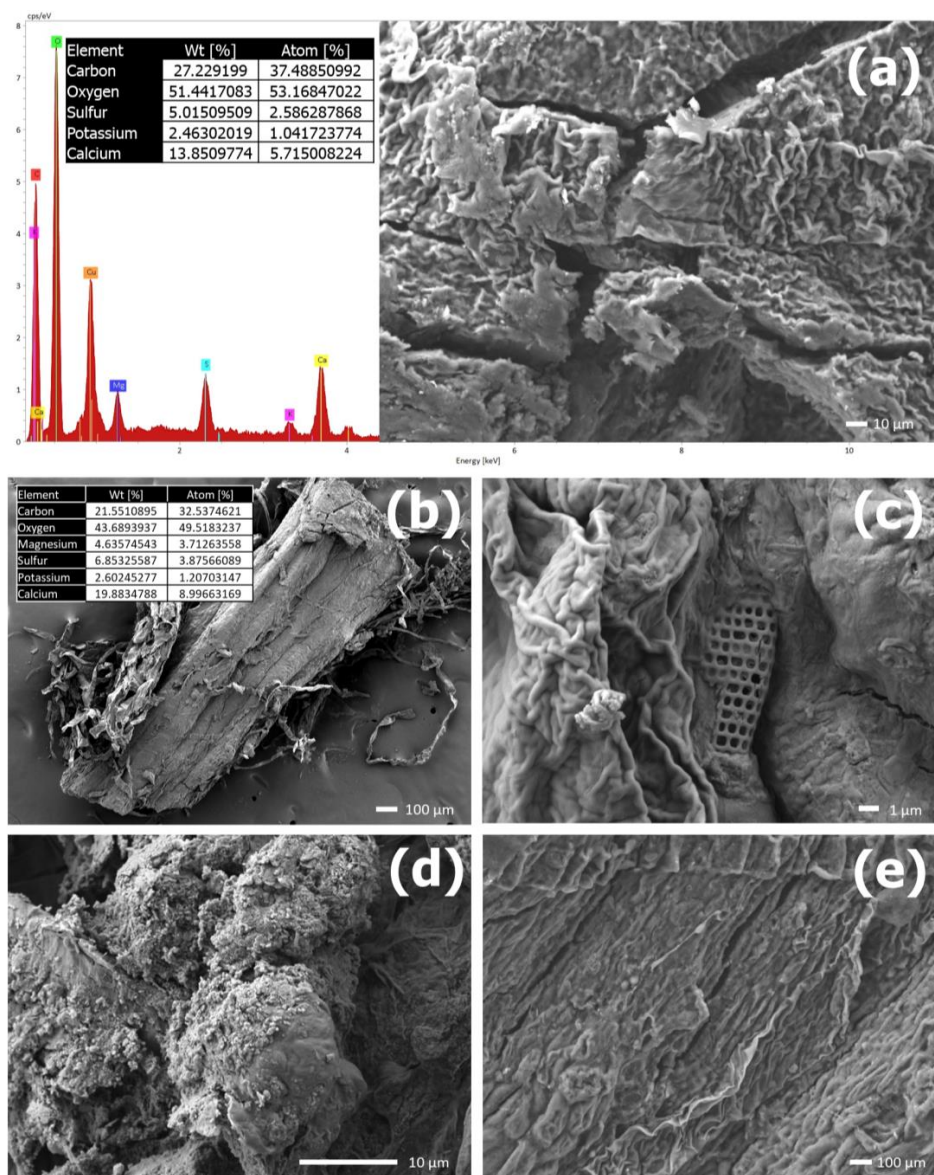**Figure 5.** X-ray diffraction (DRX) analysis of *Sargassum* spp.

Figure 6. SEM analysis: (**a**) energy-dispervise X-ray spectroscopy (EDS) of the stem; (**b**) EDS of the leaves; (**c**) macroporous morphology; (**d**) vesicles; (**e**) leaves.

SEM analysis (Figure 6) revealed the morphology of *Sargassum* spp., showing that the results of the elemental chemical composition determined by *energy*-dispersive *X-ray spectroscopy (EDS)* (Figure 6a,b) correspond to the phases of the compounds identified by DRX (Figure 6). Another observation is the presence of macroporous structures (Figure 6c–e) that are characteristic of seagrasses that contain calcite and dolomite [56]. The chemical composition revealed by SEM and DRX was consistent with the results of infrared spectroscopy (Figure 7).
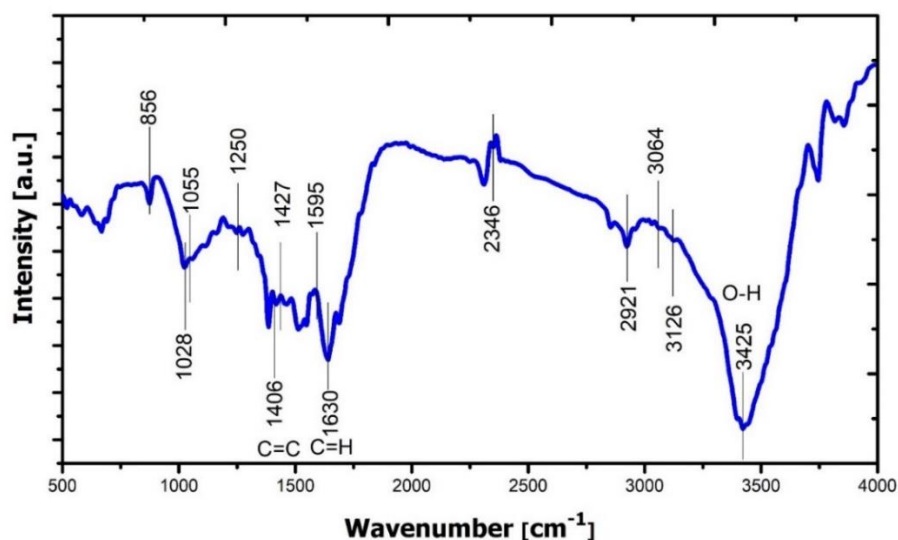

Figure 7. FTIR characterization of *Sargassum* spp.

The infrared spectroscopy analysis (FTIR), shows a strong and broad absorption band at 3406 cm^{-1} and the medium peak at 1408 cm^{-1} (Figure 7) which correspond to O-H stretching vibrations that characterize the presence of hydroxyl groups in compounds like cellulose, hemicellulose, and lignin [60–63]. The intensities of the high bands between 1630 and 1406 cm^{-1} represent C=C stretching and suggest the presence of lignin and aromatic compounds, while the weak peak at 1250 cm^{-1} can be attributed to S=O stretching in sulfate esters and CO stretching in phenols. The band affiliated at 1055 cm^{-1} is indicative of COC stretching in the xylan of the hemicellulose. These bands are characteristics of different types of *Sargassum* spp., including those reported on Mexico's Caribbean coasts [60–63].

The characterization by FTIR and SEM is consistent with the chemical composition of the principle polymeric components –cellulose, hemicellulose, and lignin– detected by fiber analysis in the *Sargassum* spp. These results are presented in Table 1 as values in ranges determined for each compound, with reference to the samples collected from the Mexican Caribbean coast.

Table 1. Chemical composition of the principle polymeric components of *Sargassum* spp.

Species	Hemicellulose (%)	Cellulose (%)	Lignin (%)	Additional Extractives (%)
Sargassum spp.	7.7–8.7	9.2–13.1	8.7–10.5	67.7–74.4
Standard deviation	0.6	2.1	1.0	2.8

3.3. Potential for Energy Exploitation

One advantage of many solid biofuels is their ease of use. Firewood, for example, is a widely-used fuel in rural areas of Mexico [11] that is extracted from forests and used, almost immediately, to satisfy the needs of both residential and industrial sectors. Something similar occurs with densified materials derived from wood waste or residues such as sawdust. These compacted materials are generally used for immediate combustion [16]. We foresee a similar scenario regarding *Sargassum* spp. The calorific

value of these algae measured 13.5–13.8 MJ/kg, a figure that, in the worst case scenario, would provide approximately 203.74 MJ/m^3 of dry material, considering a low level of exploitation of 11.1% of the total weight of the algae collected; this estimation assumes that the other 88.9% are not exploitable due to moisture loss and the content of sand and other algae with lower energy content (though this may be overestimated because the sand content is low). This estimate may change in the months of greatest influx, when all that is extracted is mainly *Sargassum* spp., and the scenario of energy use would be greater [40]. Based on this first approximation of the extraction and processing of *Sargassum* spp. with simple mechanical grinding (agate mortar), the potential for generating exploitable energy seems promising.

As a first example, considering only the *Sargassum* spp. removed from a few municipalities along the coast of the Mexican Caribbean in the month of August 2015 (reported by the Secretary of Environment of Quintana Roo see Rodríguez-Martínez et al. [19]), the amount of exploitable energy indicated by the calorific value calculated herein could provide 3.9 terajoules (TJ; Figure 8a), as shown in Figure 8. In terms of energy content, this is equivalent to approximately 205.26 tons of primary use *Pinus* spp. wood (per unit equivalent mass) [64], or 81.25 tons of the liquid gas distributed in Mexico [11]. This is a significant volume of exploitable energy. It is important to note that Wang et al. (2018) [65] observed a huge belt of *Sargassum* spp. in the area of the Atlantic Ocean between West Africa and the Gulf of Mexico that contained >20 million tons of biomass in the month of June 2018. Even in the most unfavorable scenario, the potential exploitable bioenergy contained in that volume of *Sargassum* spp. that arrive on the Mexican Caribbean coast in 2018 would be >30 petajoules (PJ), an astounding figure that represents a little over 15% of total energy consumption in Mexico generated by burning firewood in that same year (249.08 PJ) [11].
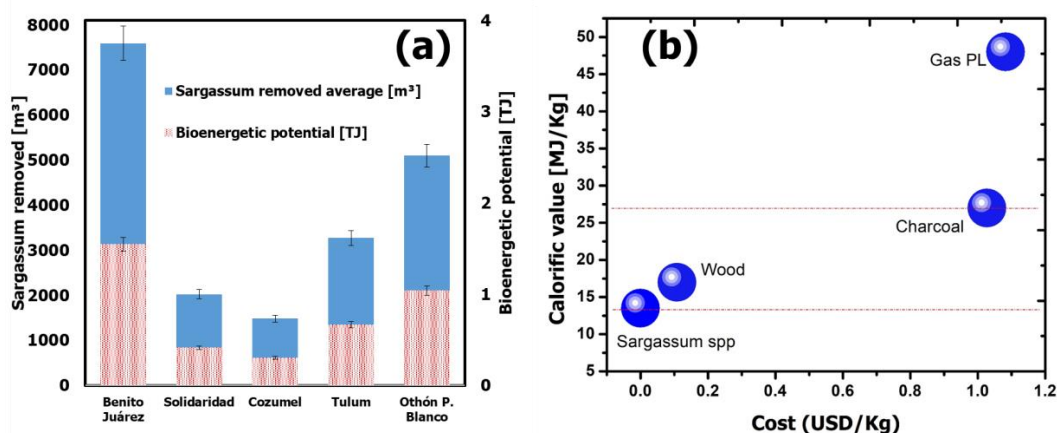

Figure 8. (**a**) Potential for exploitable bioenergy from coastal municipalities of Quintana Roo with reference to the *Sargassum* spp. removed in August 2015 (Rodríguez-Martínez et al. [19]); (**b**) economic-energy analysis of diverse fuels.

Flows of *Sargassum* spp. onto the coasts of the Mexican Caribbean coast have been frequent. Reports indicate that in September 2015 the volume averaged 2360 m^3/km [19]. Figures were lower for 2016 and 2017, but increased again in 2018. In May of that year, the average influx was 8793 m^3/km [66]. The scenarios of 2015 and 2018 represent an energetic potential in the form of solid biofuel of 480.82 GJ/km and 1791 GJ/km, respectively. A comparison of the exploitable energy derived from *Sargassum* spp. to other solid biofuels and liquid gas in the state of Quintana Roo presents the interesting results [67] as shown in Figure 8b. Although this material cannot compete with liquid gas in terms of calorific value, it is comparable to such fuels as firewood and pellets made of densified materials [16], and its behavior is similar. At present, the cost of the extraction of this material is being assumed by hotels and the Mexican government and it is being disposed of as garbage. Moreover, it is essential to remove the *Sargassum* spp. from the beaches of the Mexican Caribbean because the economic effects

and socioenvironmental damage it causes are increasing steadily. This means that added value can be generated for *Sargassum* spp., first, as a solid biofuel with promising properties that would contribute to the production of sustainable fuels.

In 2018, the volume of *Sargassum* spp. (mixed with sand, seagrasses, and, sometimes, other algae) removed from beaches by nine hotels between Cancun and Playa del Carmen, with a total beachfront of 8.01 km, was 290,626 m^3. The volume removed from those same sites in 2019 was 224,721 m^3. Averaged across sites, the monthly volume of *Sargassum* spp. collected for removal by those hotels in 2018 was 3.2×10^3 m^3 km^{-1} (95% CI: 2.3–4.1; range: 1.0–5.4×10^3 m^3 km^{-1}), while the figures for 2019 were 1.7×10^3 m^3 km^{-1} (95% CI: 1.2–2.3; range: 0.01–5.7×10^3 m^3 km^{-1}) (Rodríguez-Martínez et al., in prep.) (see Figure 9a,b). In both years, the peak month was May and high spatial variability in the *Sargassum* spp. depositions occurred among beaches throughout the year. The bioenergetic potential of *Sargassum* spp. can be appreciated in Figure 9c. In 2018, the bioenergy potential was 0.61 TJ/km/month, while in 2019 it was 0.47 TJ/km/month. An extrapolation of this analysis can reveals that for an 80-km of coastline from Cancun to Playa de Carmen, 43.20 TJ/month could be used. On average (2018–2019) the bioenergetic potential was 0.651 TJ/km/month.
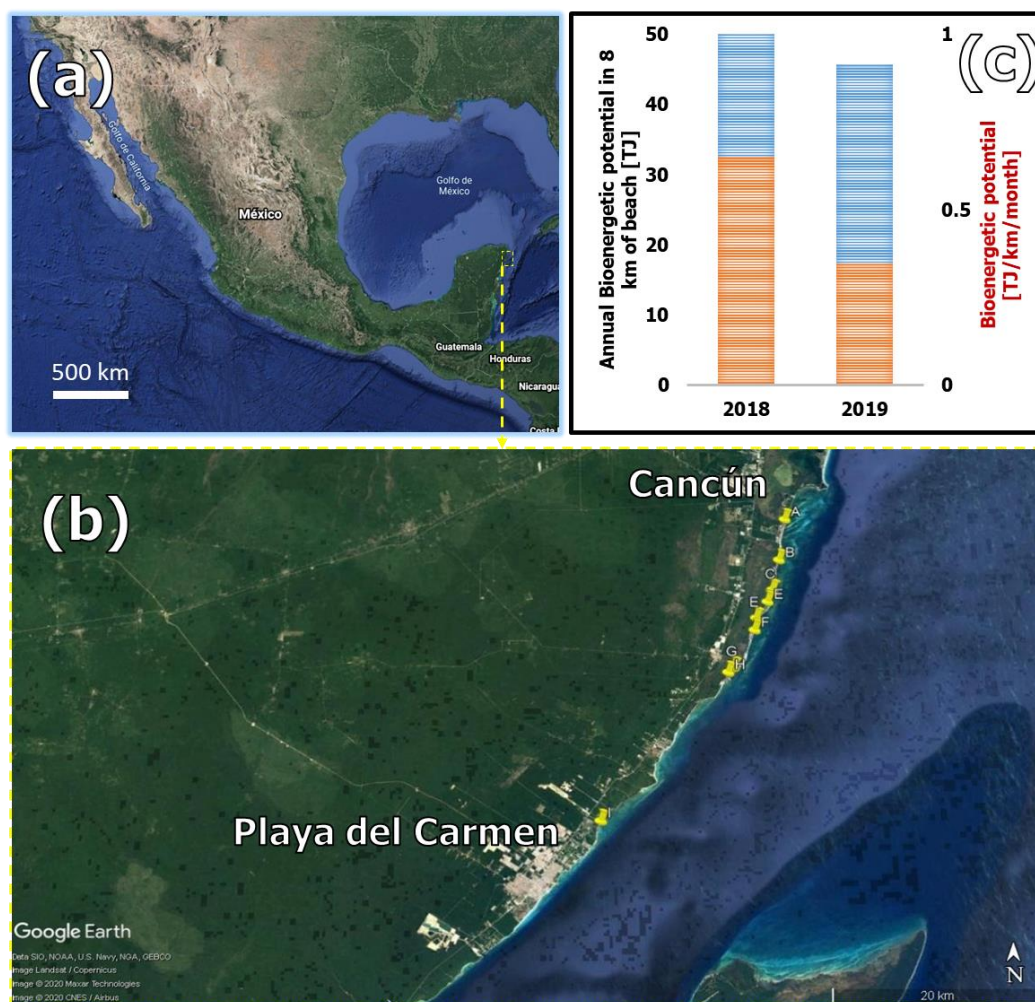

Figure 9. Analysis of exploitable energy of *Sargassum* spp. (**a**,**b**) spatial location of the hotels that provided data on the volume of beachcast material removed in 2018 and 2019; (**c**) potential exploitable bioenergy.

The data reported by hotels include *Sargassum* spp. mixed with sand, seagrasses, and sometimes other types of algae. The relative abundance of each component varied along the coast depending on

the extension of the seagrass beds, their condition, and the characteristics and use of the machinery and management protocols used by different hotels. Data on the volume of *Sargassum* spp. for the summer months might be underestimated as on some days the hotels lacked sufficient capacity to remove all the material that accumulated on their beaches. The volume:weight ratio can vary due to several factors: the condition of the alga (e.g., dry, fresh, decomposing); the amount of water retained (e.g., collected upon arrival or several hours later); and the amount of sand mixed in.

The prospective energy analysis shown in Figure 9c considers the same assumptions mentioned above; that is, an estimate of only 11.1% of exploitable energy content. However, even this scenario reveals a favorable panorama for the use of these algae as a solid biofuel. Moreover, derived from the thermogravimetric analysis, we identified its potential for exploitation as a secondary biofuel that can produce methane and hydrogen, two fuels with high added value in energy, economic, and ecological terms.

4. Conclusions

This study presents an approach to, and a bioenergy perspective on, *Sargassum* spp. collected from the coasts of the Mexican Caribbean, as a primary-use solid biofuel. Results of the characterization identified the presence of such polymeric compounds as cellulose, hemicellulose, and lignin, as well as materials like calcite and dolomite, which could have complementary uses in the construction and energy-storage sectors. We also analyzed the kinetics of the thermogravimetric process of *Sargassum* spp. using the Horowitz-Metzger method to determine non-isothermal heating in the range of 25–900 °C in N_2. Our TGA-DTG analysis highlighted three main degradation zones for *Sargassum* spp. with diverse peaks (DTG) at distinct formation temperatures that indicate diverse products of biomass degradation. Our study further ascertained key kinetic parameters: activation energy, reaction order, and the frequency factor with approximate values of 186 kJ/mol, 1, and 5.76×10^5 min^{-1}, respectively. Applying the Horowitz-Metzger method allowed us to obtain good linear adjustment, which was verified in almost the entire process of degradation of *Sargassum* spp. These results establish antecedents for future research and may open a path towards the production of biofuels (CH_4, H_2) with direct application in solid oxide fuel cells (SOFCs) that could generate electrical energy especially for remote areas of Mexico. The study also determined the potential for exploitable energy on the order of 0.203 GJ/m^3 from the *Sargassum* spp. collected, and conducted a prospective analysis of the exploitation of these algae from the northern sector of the Mexican Caribbean coast, which showed that the material collected from 8 km of beaches in 2018 and 2019 could generate over 40 TJ of energy in the form of solid biofuel. This suggests the potential advantages of exploiting *Sargassum* spp. from the coasts of Mexico, whether as a primary-use solid biofuel, or as a gaseous biofuel. This alternative would not only help mitigate the problems associated with removing these algae, but could also generate collateral benefits for the energy, economic, and environmental sectors. In conclusion, the *Sargassum* spp. hold considerable promise as a raw material for producing sustainable biofuels.

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