

Original Research

Carnauba Straw as Feedstock for Solid Biofuel Production

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Abstract

Carnauba straw (*Copernicia prunifera*), residual biomass derived from wax extraction, was evaluated as a potential feedstock for bioenergy production. The characterization was carried out using elemental analysis, proximate analysis, Higher Heating Value (HHV), FTIR spectroscopy, SEM, and FRX. The carbonization, using a Muffle Furnace, was applied as a thermal conversion technique to improve the fixed carbon content, and preliminary densification was done to assess the potential for future production of briquettes. The C, H, N, O, and S percentages were 44.43%, 5.34%, 2.25%, 46.17%, and 1.81%, respectively. The percentage of fixed carbon (14.17%) increased to 31.10% (250°C) and 35.68% (300°C) after carbonization. At 400°C, the HHV presented a decrease of 9.62%, and ash content increased by 177.66%. FTIR spectra showed bands characteristic of hemicellulose, cellulose, and lignin at 3414 - 3393 cm^{-1} (O-H) and decrease of absorbance of 74.01% to 81.37% after carbonization; 1738 - 1603 cm^{-1} (C=O), with reduction in the order of 73.94% to 78.31%, and 48.97% to 73.76%, when compared to the absorbances of the biomass in nature. The SEM of the carnauba straw in nature presented the main structural components (cellulose, lignin, and hemicellulose). After carbonization, evidence of degradation and coal formation was observed, which corroborates with the decrease in the HHV and increase of ash. The FRX was inserted in the SEM images, and the elements detected were Ca, K, and S. The quantities and order of abundance in biomass natural and carbonized were compatible with other biomasses used as biofuel. The carnauba straw in natural and carbonized was densified to understand the characteristics of the compacted material. The sample carbonized at 300°C presented a solid with the potential for future production of briquettes. All results follow other reported biomasses and could lead to further investigation of the carnauba straw as feedstock for solid fuel production without or in a mixture with other agricultural residues.

Keywords

Copernicia prunifera; biofuel; carbonization; elemental analysis; proximate analysis; HHV; biowaste

1. Introduction

Faced with the climate changes caused by the exacerbated consumption of fossil fuels, renewable energies are becoming more prominent, and new feedstocks have been used due to their energy potential [1-4]. In this scenario, vegetable biomass gains a principal role as one of the most abundant and exploited sources [5, 6].

Brazil is dominant for having a significant quantity of biomasses, both cultivated and from agroindustrial, forestry, and wood processes. However, the use of residues requires a change in the way of disposal to prevent them from being directed to landfills and dumps [7].

The use of residual biomasses can have both economic and environmental positive impacts. However, logistics still brings the problem of transport, storage, and handling, which can represent high costs due to low density and the large volume occupied by biomasses. A possibility to mitigate this problem is the compaction of these biowastes producing briquettes [7, 8].

To assess the energetic potential of biomasses is necessary to determine physicochemical properties, and among them are granulometry and bulk density [9]; immediate analysis, which is composed of moisture, volatiles, ash, and fixed carbon contents [5]; elemental analysis, which quantifies chemical elements such as carbon, hydrogen, oxygen, sulfur, nitrogen, and other [10, 11]; obtaining the lignin, cellulose, and hemicellulose contents [12]; and the Higher and Lower Heating Value (HHV and LHV) that determine energy release during complete combustion [9, 13].

However, a disadvantage of natural biomass is its considerable moisture content, which reduces the HHV and LHV [3]. A method to mitigate this problem is partial carbonization, which increases calorific value and minimizes interference factors [5, 14]. The incomplete combustion at elevated temperatures removes moisture and volatile compounds and partially degrades some biological structures that interfere with the burning process. There is a decrease in the amount of oxygen and hydrogen in the sample, and consequently, the carbon content increases. In addition, it causes the cracking of complex structures, favoring energy release during the burning process [15, 16].

Nevertheless, it is necessary to identify the ideal carbonization temperature for each biomass to obtain the best result because biomass begins to degrade in thermal processes above a specific temperature [17], decreasing the calorific value and increasing the ash content [5]. Thus, it is essential to determine the optimum temperature for the carbonization process.

Among biomasses available in Brazil, an abundant biowaste in the north and northeast is the carnauba straw obtained from the wax extraction process [18]. Carnauba wax is a material well studied in the literature and with applications in several areas such as pharmaceutical, food, cosmetics, anticorrosive for electronic components, and lubricant [19]. In general, also it is exported in the yellow-brown flakes form for application as a paper coating [20]. After removing the wax, the straws, considered biowaste, are discarded or burned [20]. A few related uses for straw are roofing houses and handicrafts [6, 21], but there are also applications as fibers for polymer reinforcement [19, 20]. As carnauba straw is a lignocellulosic biomass that probably possesses a potential for bioenergy generation, its evaluation using essential indicators such as elemental analysis, proximate analysis, Higher Heating Value, spectroscopy, and other experiments for energy applications is crucial for the sustainable development of the society and advancing of the frontier of knowledge of the field.

As the possibility of enabling efficient use of the carnauba straw, this work shows its characterization through immediate and elemental analysis and determination of the Higher Heating Value (HHV). In addition, biomass carbonization experiments were carried out at 250, 300, 350, and 400°C to identify the ideal temperature that maximizes the energy potential. Finally, the feasibility of producing briquettes from natural and carbonized biomasses was evaluated by the compaction process and analysis of their behavior. The novelty of the work was the evaluation of the waste generated in the carnauba wax industry – straw –, in natural and carbonized, for the study of the characteristics aiming for the potential application as biofuel. The influence of carbonization on energy properties was also studied.

2. Materials and Methods

2.1 *Carnauba Straw Sample*

10 kg of the carnauba straw, obtained from the wax extraction process, was collected in Morrinhos-Ceará-Brazil, geographical coordinates - Latitude: 3°14'20" S and Longitude: 40°7'0" W, in January 2019. The biomass was stored in a plastic bag (Figure 1), at room temperature, until the execution of the experiments.



Figure 1 Carnauba straw.

The biomass was grounded to standardize the particle size, sieved (60 mesh), dried in an oven at a temperature of 105°C (± 10), and stored in plastic bags until the execution of the experiments.

2.2 *Carnauba Straw Carbonization*

The carbonization was carried out following the methodology proposed by Kipngetich 2022 [22] and Silva et al. 2023 [5], with some modifications, using the temperatures of 250, 300, 350, and 400°C ($\pm 10^\circ\text{C}$), and a muffle furnace Quimis®, model 0318M24 (SP, Brazil). After reaching the programmed temperature, the sample remained for 15 minutes in heating, maintaining the temperature. Finished the experiments, the crucibles were stored in a desiccator. Figure 2 shows the steps and details of the carnauba straw carbonization.

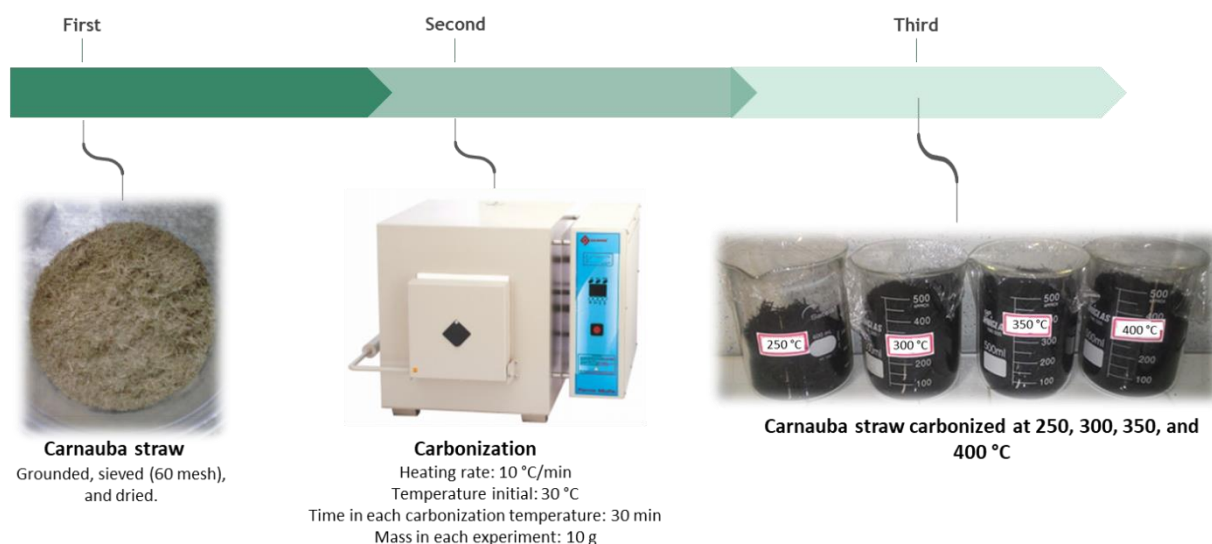


Figure 2 Steps and details of the carnauba straw carbonization.

2.3 Characterization

The elemental analysis was carried out using an Elemental Analyzer PerkinElmer® 2400 Series II CHNS/O, Higher Heating Value (HHV) (ASTM D5865-19 [23]) using a Bomb Calorimeter IKA® 2400 model C-200, and Proximate analysis which consists of moisture (ASTM D3173/D3173M-17a), volatile matter (ASTM D3175-18), ash (ASTM D3174 - 12(2018)e1), Fixed carbon (ASTM D3172-13 [24]) were performed using a Laboratory oven, De Leo model 1980W, and a Muffle furnace, Quimis model 0318M24. All experiments were performed in quadruplicate.

The infrared spectra were obtained using a Spectrum One FT-IR Spectrometer, range of 4000 – 100 cm⁻¹ and KBr pellets. Scanning electron microscopy (SEM) and X-Ray fluorescence spectroscopy (FRX) analyses were performed to evaluate the chemical composition and morphology of the samples. SEM was performed on the VEGA3 TESCAN electron microscope using SEM MAG of 5.00 kx. The samples were first metalized in a vacuum Sputter Coater metallizer with a thin gold film. The FRX was carried out in the SHIMADZU model EDX-7000 equipment equipped with a rhodium tube, applying a power of 4 kV to the macerated samples.

The results were evaluated by statistical analysis, including a verification of the normality of the groups by the Shapiro–Wilk test. The normal data are shown by mean ± sample standard deviation and non-normal data by median (first quartile; third quartile). The difference between groups was verified by the ANOVA test followed by the Tukey test as a post-doc for parametric data, and by the Kruskal-Wallis test followed by the Dunn's Test as a post-doc for non-parametric data. The correlation and linear regression for the HHV and proximate analysis data *versus* temperature were verified. Pearson's correlation was used for parametric data and Spearman's for non-parametric data. For variables that correlation was confirmed, the model was adjusted. The tests adopted a significance level of 5% ($\alpha = 0.05$). The significant level refers to the chance of a different result if the test was repeated using the same population, representing the null hypothesis. The default used in the literature is 0.05 [25]. Thus, if the possibility of a null hypothesis is less than 5%, the obtained result is considered statistically significant. The statistical analyses used Jamovi 2.3.24 and JASP 0.17.1.0 [26].

2.4 Solid Biofuel Production (Briquettes)

Solid biofuels were produced from carnauba straw in natural and carbonized using 6.5 g in each experiment (Figure 3: AISI 304 stainless steel mold, the internal diameter of 50 mm). For compaction procedure was applied 7.5 ton, resulting in 38.2 MPa, maintained for 5 minutes under pressure and 5 minutes without pressure. Details of the stainless steel mold and compression procedure were described in the previous work of Nunes et al., 2022 [5, 8]. Figure 4 shows the steps and details of the mechanical densification process of the carnauba straw carbonized at 300°C.



Figure 3 AISI 304 stainless steel mold used in solid biofuel production.

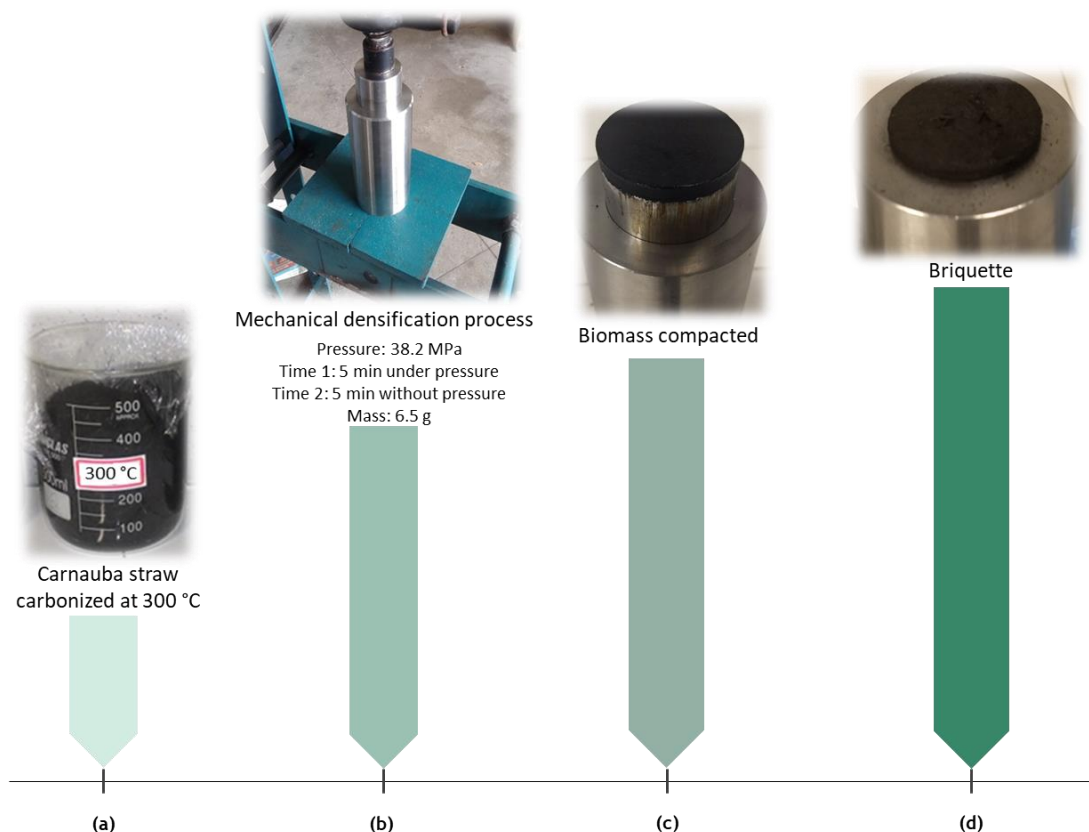


Figure 4 Steps and details of the mechanical densification process of the carnauba straw carbonized at 300°C.

The consistency and quality of the solid biofuels were evaluated to verify the viability of future briquette production.

3. Results and Discussion

3.1 Elemental Analysis

Table 1 shows the results of the elemental analysis of the carnauba straw in percentages of carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O).

Table 1 Elemental analysis of the carnauba straw.

Sample	C (%)	H (%)	N (%)	S (%)	O (%)
Carnauba straw	44.43	5.34	2.25	1.81	46.17

The results follow Tavares and Santos 2013 [27]. A desired characteristic for a potential fuel is a low concentration of sulfur which reduces the release of SO₂, a toxic gas that causes corrosion in the furnaces. Low nitrogen levels are also preferred due to the formation of nitrogen oxides (NO_x), which can increase respiratory problems and contribute to photochemical smog and acid rain formations [28].

The nitrogen content was higher than wood fuel and charcoal. Pereira et al., 2013 [12] tested firewood obtained from six varieties of *Eucalyptus spp* and obtained nitrogen between 0.09 and

0.12% and sulfur contents between 0 and 0.01%. In the same work, charcoal was produced using a carbonization process in a Muffle at 450°C for 4.5 h, obtaining an average nitrogen content of 1.05% and showing no detectable sulfur content due to volatilization during pyrolysis.

Silva et al., 2019 [11] compared the elemental composition of wood and leaves of trees found in southern Brazil, including *Eucalyptus grandis*, one of the varieties evaluated in the work of Pereira et al., 2013 [12]. Wood generally presents a nitrogen content between 0.49 and 1.35%, and the leaves between 2.54 and 3.81%, much closer to carnauba straw.

3.2 Fourier Transform Infrared (FTIR) Spectroscopy

Figure 5 shows the FTIR absorbance spectra of carnauba straw in natural and carbonized at 250, 300, 350, and 400°C (a), the spectra expansion of carnauba straw carbonized at 250 and 300°C (b), and carnauba straw carbonized at 350 and 400°C (c). The assignment of the absorption bands is presented in Table 2. The results were compared to other biomasses [6, 29, 30].

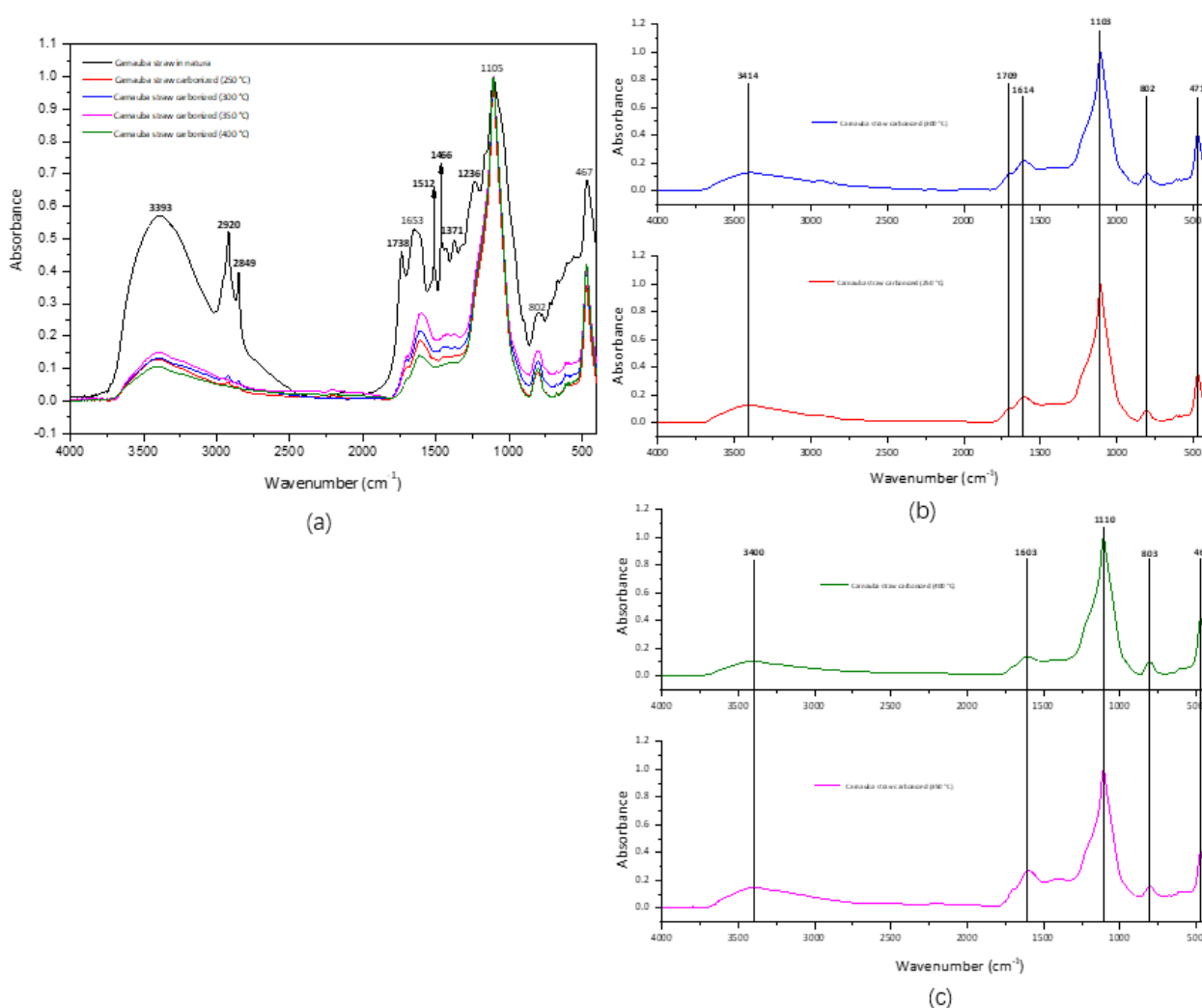


Figure 5 FTIR absorbance spectra of carnauba straw in natura and carbonized at 250, 300, 350, and 400°C (a); the spectra expansion of carnauba straw carbonized at 250 and 300°C (b), and carnauba straw carbonized at 350 and 400°C (c).

Table 2 FTIR absorption bands in spectra obtained from carnauba straw in natura and carbonized at 250, 300, 350, and 400°C, and their assignments.

Sample	Wavenumber (cm ⁻¹) Absorbance Band assignment	
Carnauba straw	3393	0.572
Carnauba straw	3414	0.129
Carnauba straw carbonized at 250°C	3414	0.130
Carnauba straw carbonized at 300°C	3400	0.149
Carnauba straw carbonized at 350°C	3400	0.106
Carnauba straw carbonized at 400°C	2920	0.524
Carnauba straw	2849	0.398
Carnauba straw carbonized at 250°C	nd	nd
Carnauba straw carbonized at 300°C	nd	nd
Carnauba straw carbonized at 350°C	nd	nd
Carnauba straw carbonized at 400°C	nd	nd
Carnauba straw	1738	0.460
Carnauba straw	1653	0.530
Carnauba straw carbonized at 250°C	1709	0.100
Carnauba straw carbonized at 300°C	1614	0.186
Carnauba straw carbonized at 350°C	1709	0.119
Carnauba straw carbonized at 400°C	1614	0.215
Carnauba straw	nd	nd
Carnauba straw carbonized at 350°C	1603	0.270
Carnauba straw carbonized at 400°C	nd	nd
Carnauba straw	1512	0.411
Carnauba straw	1466	0.490
Carnauba straw	1371	0.496
Carnauba straw carbonized at 250°C	nd	nd
Carnauba straw carbonized at 300°C	nd	nd
Carnauba straw carbonized at 350°C	nd	nd
Carnauba straw carbonized at 400°C	nd	nd

O-H stretching
Present in Lignin, cellulose and hemicellulose
References: [6, 30-33]

C-H symmetric methyl and methylene stretching
Present in Lignin, cellulose, and hemicellulose
References: [6, 30-32]

C-H asymmetric methyl and methylene stretching
Present in Lignin and hemicellulose
References: [6, 30-32]

C=O ketone, aldehyde, carbonyl, aliphatic groups stretch
Present in Hemicellulose
References: [6, 30, 32, 33]

C=O stretching (unconjugated)
Present in Lignin
References: [6, 30-33]

C=C aromatic skeletal vibrations
Present in Lignin
References: [6, 30, 31, 33, 34]

CH₂ deformation stretching
Present in Lignin and hemicellulose
References: [6, 30, 31, 34]

C-H bending
Present in Cellulose, hemicellulose, and lignin
References: [6, 30, 32-34]

Carnauba straw	1236	0.676	Acyl-oxygen CO–OR stretching vibration
	1105	1.000	Present in Hemicellulose
Carnauba straw	nd	nd	References: [6, 30]
carbonized at 250°C	1103	1.000	
Carnauba straw	nd	nd	C–O of guaiacyl unit stretching vibration
carbonized at 300°C	1103	1.000	Present in Lignin
Carnauba straw	nd	nd	References: [6, 30, 32]
carbonized at 350°C	1110	1.000	
			C–H deformation
			Present in Lignin
Carnauba straw	nd	nd	References: [35]
carbonized at 400°C	1110	1.000	
			C–O, C=C, C–C–O stretching
			Present in Cellulose, Hemicellulose, Lignin
			Reference: [33]
Carnauba straw	802	0.275	
Carnauba straw	802	0.088	C–H stretching out of plane of aromatic ring
carbonized at 250°C			
Carnauba straw	802	0.122	O–H bending
carbonized at 300°C			Glycosidic linkage
Carnauba straw	803	0.154	Present in cellulose
carbonized at 350°C			References: [35, 36]
Carnauba straw	803	0.100	
carbonized at 400°C			

nd = not detected

The FTIR spectrum and band assignments of carnauba straw naturally follow the literature of other lignocellulosic biomasses [6, 30–36]. The peaks assigned to the main components, cellulose, hemicellulose, and lignin, are present [33]. However, after biomass carbonization at temperatures of 250, 300, 350, and 400°C, the spectra profiles changed significantly (see Figure 3 (b), (c)). The absorbance of the band assignments at 3414/3400 cm⁻¹ reduced in the order of 74.01% to 81.37%, at 1709 cm⁻¹ in the order of 73.94% to 78.31%, and at 1614/1603 cm⁻¹ in the order of 48.97% to 73.76%, when compared the assignments of biomass in nature. The behavior after carbonization of the carnauba straw follows the results found by Volli et al. (2021) [37] in their study entitled comparative studies on thermochemical behavior and Kinetics of lignocellulosic biomass residues using TG-FTIR and Py-GC/MS. Commonly, the thermal degradation of biomass is composed of three main stages, such as elimination of surface moisture (<200°C) in the first; the average active pyrolysis range (devolatilization, 200 - 600°C) occurring a substantial mass loss (70% - 90%) in the second; and decomposition (>600°C) in the third [37]. According to Volli et al. (2021) [37], a narrow temperature range of 295 - 430°C was observed for cellulose. The volatilization of the unbranched and ordered structure of glycoside linkage (intra-intermolecular hydroxyl groups) by acetal and pyranose rings provides a unique narrow degradation range with higher thermal stability [37]. The decomposition of cross-linked phenol polymer (hydroxyl and methoxy) at around 350°C results in the formation of guaiacol, syringyl, aromatic hydrocarbons, and p-hydroxyphenyl compounds with

phenolic –OH groups [37], probably the reason why O-H stretching assignment ($3414/3400\text{ cm}^{-1}$) reduces but not disappear in the spectra of the carnauba straw carbonized.

The assignment C-H stretching ($2920/2849\text{ cm}^{-1}$) of lignin, cellulose, and hemicellulose were not detected in the spectra after carbonization of biomass (see Figure 3 (b) and (c)), and C=O ($1738\text{--}1709\text{ cm}^{-1}$) stretching of ketone/aldehyde/carbonyl/aliphatic groups reduced drastically in the spectra of the samples carbonized at 250 and 300°C, and disappeared in the biomass carbonized at 350 and 400°C. These profiles are compatible with the gaseous functional groups identified by FTIR spectra during the thermal degradation of cellulose and lignin due to the breakage of the methylene ($-\text{CH}_2-$), methyl ($-\text{CH}_3$), and methoxyl ($-\text{OCH}_3$) groups [6, 37]. The assignments C-O, C=C, C-C-O stretching, and C-H deformation ($1110/1103\text{ cm}^{-1}$) of lignin practically did not reduce the absorbance, and this corroborates with the higher thermal stability of the lignin [6, 37].

3.3 Scanning Electron Microscopy (SEM) and X-ray Fluorescence Spectroscopy (FRX)

Figure 6 shows the results of Scanning Electron Microscopy (SEM) and X-ray fluorescence spectroscopy (FRX) (insert) of the carnauba straw in natural and carbonized at 250, 300, 350, and 400°C. It can observe by SEM that the standard structure of the carnauba straw in nature presents the main structural components (cellulose, lignin, and hemicellulose) [6]. Figure 6 (a) shows the structure of the carnauba straw in natura with epidermis, cuticle, and stomata [38]. Figure 6 (b) presents the structure of the carnauba straw carbonized at 250°C. At this temperature, gases such as carbon monoxide, carbon dioxide, and hydrocarbons are released, probably due to the beginning of the cellulose degradation process [6, 37]. Also can be observed the disappearance of the epidermis, the appearance more evident of the stomata, and better visualization of the palisade parenchyma and the spongy parenchyma [39]. The structure of biomass carbonized at 300°C is presented in Figure 6 (c), which is observed fiber rupture, and the parenchyma layers already appear disorganized, probably due to the decrease of the mechanical resistance with the increase in temperature [40]. At 300°C, a significative accumulation of ash and carbonized materials was not observed, which could explain the low moisture content and Higher Heating Value maintenance. Figures 6 (d) and (e) show biomass carbonized at 350 and 400°C, respectively. At these temperatures, it observed an evolution in the degradation of the material. Figure 6 (d) presents a morphology similar to the biomass carbonized at 300°C, and Figure 6 (e) shows a more carbonized material with evidence of degradation and coal formation, which corroborates with the decrease in the HHV and increase of ash [39, 41].

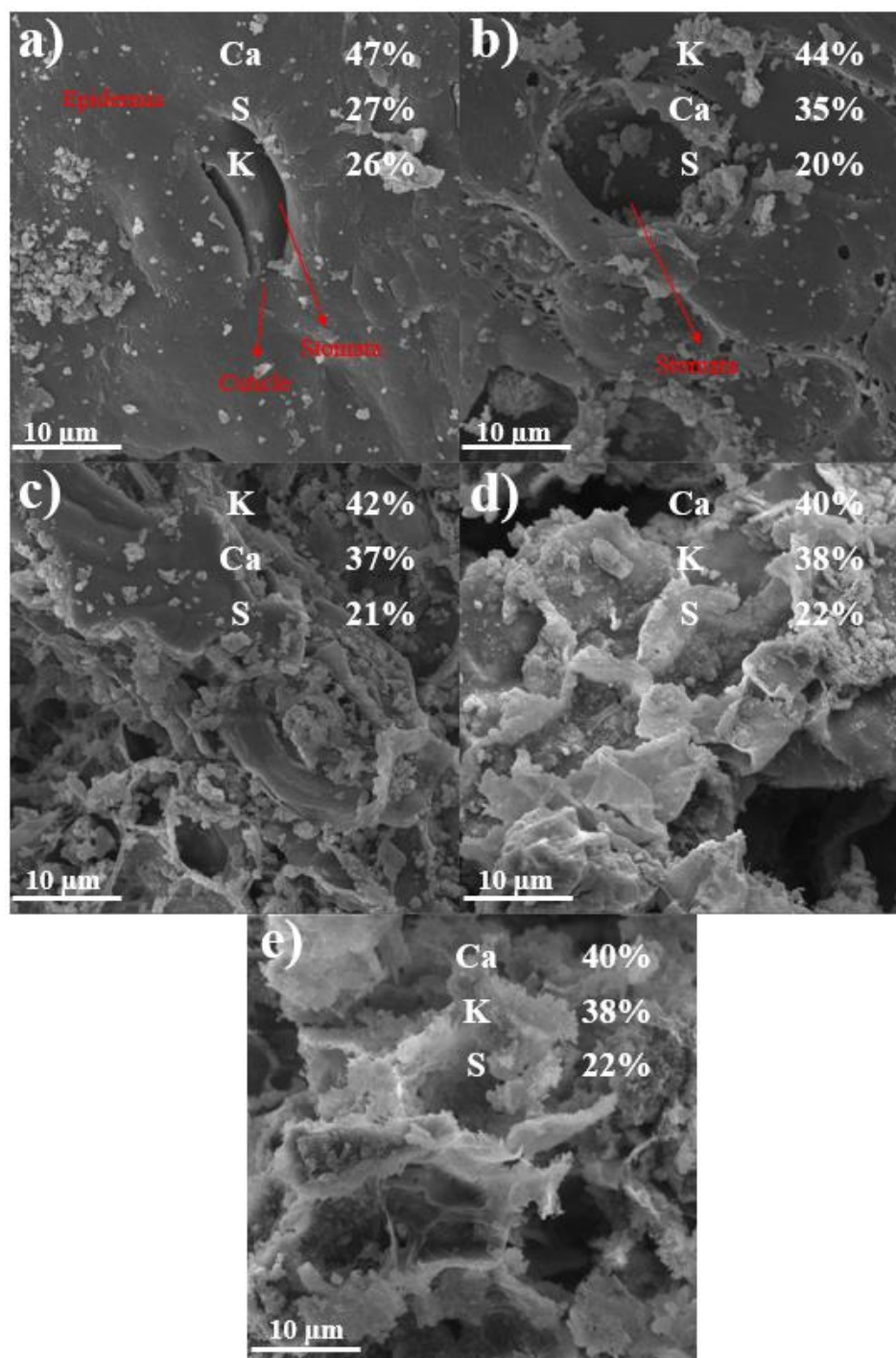


Figure 6 Scanning Electron Microscopy and X-ray fluorescence spectroscopy (insert) of the carnauba straw in natura (a), carnauba straw carbonized at 250°C (b), carnauba straw carbonized at 300°C (c), carnauba straw carbonized at 350°C (d), and carnauba straw carbonized at 400°C (e).

The FRX is inserted in the SEM images (normalized for the main atoms). The presence of calcium, sulfur, and potassium and the variation in their percentages with the increased temperature was observed. There was no evidence of a decrease in any mineral, which is probably due to the place of analysis. Given the increase in the utilization and trade of biomass, the quantitative elemental analysis by XRF is essential information. The elements detected were Ca, K, and S, and the quantities

and order of abundance in biomass in natural and carbonized are compatible with other biomasses used as biofuel [5, 42].

3.4 Higher Heating Value (HHV) and Proximate Analysis

Table 3 shows the HHV and Proximate Analysis results for carnauba straw in natural and carbonized (250, 300, 350, and 400°C), and Figure 7 shows the box plot distribution for the HHV and Proximate Analysis for carnauba straw in natural and carbonized.

Table 3 Results of HHV and Proximate Analysis for carnauba straw in natura and carbonized.

Sample	HHV (MJ/kg)	Volatile matter (%)	Moisture (%)	Ash (%)	Fixed Carbon (%)
In natura	17.26 ± 0.03 ^a	64.97 ± 1.04 ^a	11.11 ± 0.96 ^a	9.23 (9.2;9.79) ^a	14.17
250°C	18.74 ± 0.07 ^b	47.04 ± 2.70 ^b	2.38 ± 0.39 ^b	17.27 ± 1.40 ^{ba}	33.32
300°C	20.69 ± 0.11 ^c	44.05 ± 0.64 ^b	4.54 ± 0.47 ^c	15.73 ± 1.12 ^{ba}	35.68
350°C	17.62 ± 0.17 ^d	37.69 ± 0.68 ^c	7.75 ± 0.43 ^d	19.85 ± 1.35 ^{bc}	34.72
400°C	15.59 ± 0.10 ^e	33.01 ± 1.64 ^d	6.77 ± 0.94 ^d	27.09 ± 0.65 ^c	33.14

* Different letters in the same column indicate a statistically significant difference ($p < 0.05$).

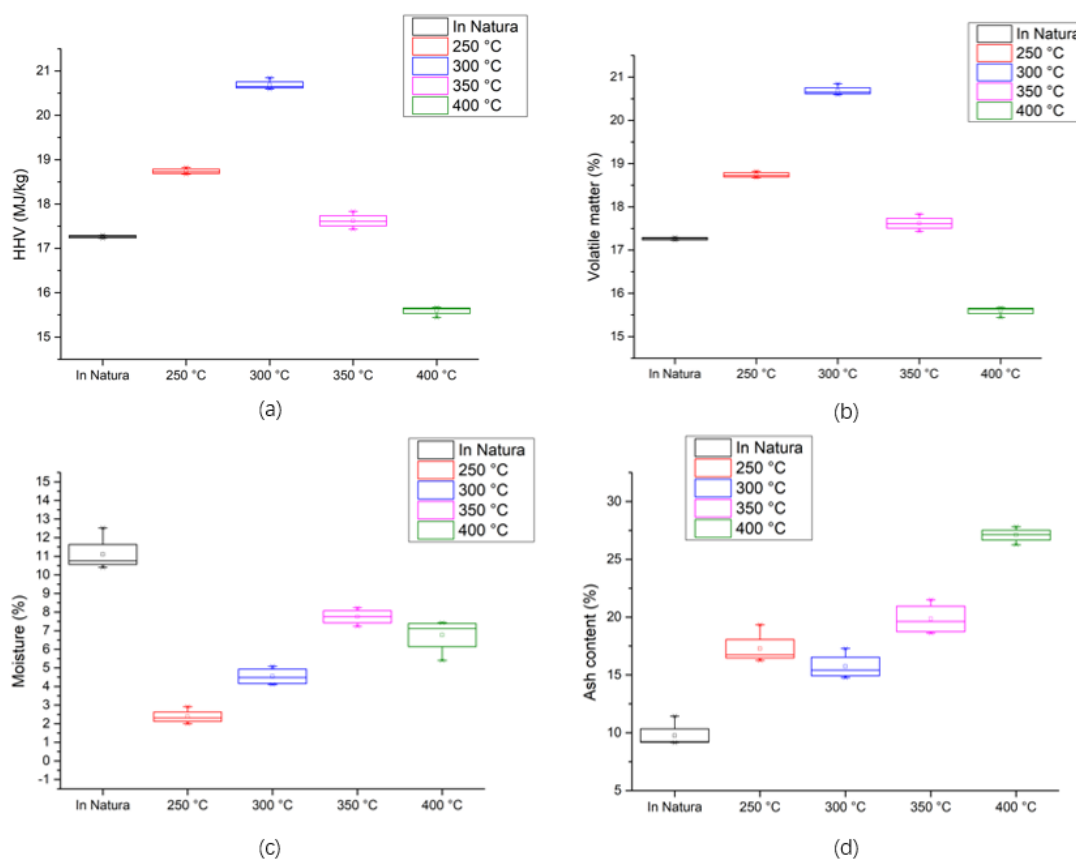


Figure 7 Box plot distribution for the HHV (a) and Proximate Analysis (Volatile Matter (b), Moisture (c), and Ash Content (d)) for carnauba straw in natura and carbonized.

Fixed carbon (FC) was calculated from the averages of moisture, volatile matter, and ash, and it is possible to observe that after carbonizations, the FC increased significantly (see Table 3), following the trend presented by other authors [4, 12]. According to the statistical analysis, all data groups showed normal distribution, except ash for carnauba straw. Thus, the HHV, moisture, and volatile matter were evaluated by parametric tests and the ash data by non-parametric tests.

For Higher Heating Values, all groups were significantly different ($p < 0.05$). The biomass carbonized at 300°C obtained the highest average value (20.69 MJ/kg), while the carbonized at 400°C the lowest (15.59 MJ/kg). Thus, the temperature of 400°C would not be indicated for the carbonization of carnauba straw, as it reduces the energy quality of this biomass. The highest HHV values are close to the values for Eucalyptus and Pine firewood (18 - 22 MJ/kg) and follow the values reported in the literature for carnauba straw (17.8 MJ/kg and 17.51 MJ/kg) [43].

For Volatile Matter (VM), the groups 250 and 300°C were statistically equal (see Figure 7). The observed trend is that the VM decreases with increasing carbonization temperature. The moisture at temperatures 350 and 400°C are also statistically equal, and at 250 and 300°C showed a slight increase. However, all post-carbonization moistures were lowest than 10%, a favorable characteristic for biofuels [44]. There are woods with a moisture content of 6.96% [45] and charcoal of 8.7% [3]. As previously reported, ash data were evaluated by non-parametric tests. The groups of carnauba straw in natural and carbonized at 400°C were the only ones that showed a significant difference.

3.5 Linear Regression and Correlation

The correlation between HHV and Proximate Analysis results for carbonized carnauba straw at temperatures 250, 300, 350, and 400°C was verified. Pearson's correlation analyzed the HHV, Moisture, Volatile Matter, and the ash by Spearman's correlation, see Table 4.

Table 4 Correlation results between HHV and Proximate Analysis for carbonized carnauba straw at temperatures 250, 300, 350, and 400°C.

Variable	Correlation	Result
HHV (MJ/kg)	Pearson's R	-0.757
	p-value	<0.001
Volatile Matter (%)	Pearson's R	-0.959
	p-value	<0.001
Moisture (%)	Pearson's R	0.855
	p-value	<0.001
Ash (%)	Spearman's rho	0.764
	p-value	<0.001

All results showed significant correlations. HHV, Moisture, and Ash showed a high correlation, and the Volatile Matter (VM) showed a very high correlation [46, 47]. The HHV and VM presented negative correlations, while Moisture and Ash were positive. This result confirms a direct or inverse trend of variation of the parameters with the carbonization temperature. In addition, the assumption for linear regression of each variable was verified, considering the carbonization temperature as a predictor variable, see Table 5.

Table 5 Linear regression results of HHV and Proximate Analysis for carbonized carnauba straw at temperatures 250, 300, 350, and 400°C.

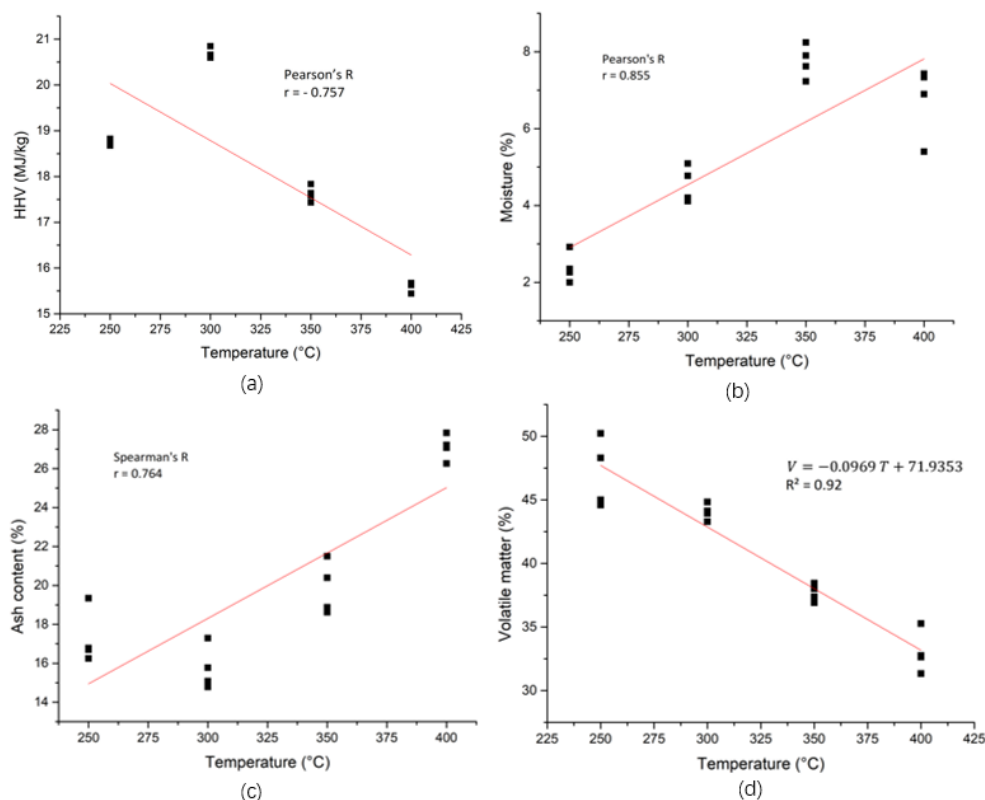
Dependent variable versus carbonization temperature	Normality of residuals - Shapiro Wilk	Heteroskedasticity - Harrison McCabe	Autocorrelation - Durbin-Watson
HHV	0.015	0.997	<0.01*
Volatile Matter (VM)	0.81	0.94	0.268
Moisture (M)	0.419	0.002*	<0.01*
Ash (A)	0.178	0.792	0.034*

* Significant results infringe on the assumption of linear regression.

The only variable admitted by the three assumptions was the VM. Linear regression for Volatile Matter, considering the carbonization temperature as a predictor variable, showed a significant result of less than 1%, which means that the chance of obtaining a different equation with another sample from the same population is 1% (see Table 6). Figure 8 presents the correlations for HHV, Moisture, and Ash and the linear regression for VM.

Table 6 Linear regression statistic for Volatile Matter (VM).

Predictor	Estimate	Standard Error	t	P value
Intercept	71.9353	2.51021	28.7	<0.001
Slope	-0.0969	0.00761	-12.7	<0.001

**Figure 8** Correlations for HHV (a), Moisture (b), and Ash (c) and the linear regression for Volatile Matter (d).

The coefficient of determination (R^2) was 0.92, and the linear correlation (Volatile Matter *versus* Temperature) can be verified by Equation 1.

$$VM(\%) = -0.0969 \cdot T(^{\circ}C) + 71.9353 \quad (1)$$

where: VM = Volatile Matter (%) and T = Temperature ($^{\circ}C$).

3.6 Solid Biofuels Production

Compactions of carnauba straw in natural and carbonized were performed. The carbonized biomass at $300^{\circ}C$ was chosen since the best results of HHV and Proximate Analysis occurred at this temperature. Figure 9 shows the solid biofuel produced from carnauba straw in nature.



Figure 9 Solid biofuel produced from carnauba straw in natura.

The solid biofuel produced from carnauba straw carbonized ($300^{\circ}C$) are shown in Figure 10.



Figure 10 Solid biofuel produced from carnauba straw carbonized ($300^{\circ}C$).

As can be seen, it was possible to compact carbonized carnauba straw ($300^{\circ}C$), showing potential for future production of briquettes. However, the compacted solid shows a fragile consistency in the mold removal step. This behavior may be due to lignin degradation during carbonization, which is responsible for acting as a binder during the compaction process. The heating that occurs due to biomass friction inside the mold decreases the plasticity of the lignin. This characteristic is observed in the consistency of the solid biofuel from carnauba straw in nature (Figure 10). Generally,

carbonized biomass briquettes present difficulty in compaction when compared to natural biomass [48]. However, this can be solved by adding a binder or another biomass with a higher lignin content [48], as evaluated by Silva et al. 2023 [5] in the production of the briquettes using the mixture carnauba straw and babassu cake (50%), and carnauba straw, carnauba stalk, and babassu cake (30% + 30% + 40%). Several authors report the inefficient agglomeration for carbonized biomass briquettes and the use of combustible binders such as cassava starch and water [3], pyrolytic oil or tar [49], resin [2], and non-combustible binders as inorganic clay materials [50].

4. Conclusion

Carnauba straws in natural and carbonized were compacted to understand the characteristics of the solids, and according to the results, they showed potential for future briquettes production. However, carbonized samples presented an advantage regarding energetic performance. Among carbonization temperatures, 300°C showed the best results evaluating Higher Heating Value (HHV), lower ash content, and intermediate Volatile Matter and Moisture contents. HHV and Proximate Analysis presented a strong correlation with carbonization temperature (r above ± 0.7), and it was possible to establish a linear regression for VM ($R^2 = 0.92$). FTIR spectra showed bands characteristic of hemicellulose, cellulose, and lignin, and absorbances showed differences between samples in natural and carbonized. The SEM of the carnauba straw in nature presented the main structural components (cellulose, lignin, and hemicellulose). After carbonization, evidence of degradation and coal formation was observed, which corroborates with the decrease in the HHV and increase of ash. The FRX was inserted in the SEM images, and the elements detected were Ca, K, and S. The quantities and order of abundance in biomass in natural and carbonized were compatible with other biomasses used as biofuel. The carnauba straw in natural and carbonized was densified to understand the characteristics of the compacted material. The sample carbonized at 300°C presented a solid with the potential for future production of briquettes. All results follow other reported biomasses and could lead to further investigation of the carnauba straw as feedstock for solid fuel production without or in a mixture with other agricultural residues.

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Author Contributions

The authors contributed equally to this work.

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Competing Interests

The authors have declared that no competing interests exist.

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