https://dx.doi.org/10.22161/ijaers.78.36 ISSN: 2349-6495(P) | 2456-1908(O)

Environmental-economic assessment of lignocellulosic residual from the Legal Amazon for conversion in biochars and bioproducts for biorefineries

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Abstract**—** *Biochars are emerging ecological products that show excellent properties in areas such as carbon sequestration, soil improvement, bioremediation, activated carbon and bioenergy. These interesting materials can be synthesized from a wide variety of sources derived from waste, including lignocellulosic biomass waste. In this work, biochars were produced from residues from the Brazilian Amazon, such as green coconut, babassu and Brazil nuts. The synthesis of biochars was performed under pyrolysis conditions with a fixed time of 3 h and temperature variation of 250 ºC (T_1) and 400 ºC (T_2). Yields of biochar production >85%, carbon contents >56%, and oxygen contents >20% and calorific values >23 MJ.Kg^{-1}, demonstrate that biochars produced from residual biomass can be used as activated carbon and also as fertilizers in soils, thus adding value to such residues. Besides, the biomasses used were characterized and the achieved remarkable yields of fermentable sugars, reaching up to 70% in cellulose hydrolysis, which can be useful in the production of bioproducts. In addition, the efficient use of these biomasses will positively impact the productive chains involved, benefiting society, generating employment, income, Besides as mitigating an environmental liability.*

Keywords**— activated carbon, fermentable sugars, hydrolysis, Pyrolysis.**

I. INTRODUCTION

Biomass is an abundant and renewable resource, since, it comes as residual from economic conversion processes. Has been widely used, as raw material for the chemicals production and excellent energy supply, as a biofuel [1,2,3].

The main process involving biomass are hydrolysis and pyrolysis. For hydrolysis, the use of acid-catalyzed (diluted and/or concentrated), in mild conditions (<200 °C), is favorable to hydrolysis the hemicellulose, or in drastic conditions (high temperature), the chemical bonds, from cellulose fraction, glycosidic bonds β-(1→4), are break. Consequently, this process can be optimized according to the time, temperature and type of catalyst, in order to increase the yield of the desired final product [4,5,6]. Meanwhile, pyrolysis is performed according to the desired results. Slow pyrolysis, for example, is preferred to increase the yield of biochar; fast pyrolysis is to increase the yield of bio-oil [7]. Both are thermochemical processes carried out at a temperature of around 500 ° C, in an oxygen-free environment [8].

Biochar is a solid by-product of pyrolysis and has been attracting attention. Due to a large surface area and special characteristics, like the functional oxygen groups, mineral fractions and aromatic carbon, playing a fundamental role in chemical adsorption. The adsorption property of the biochar makes it is a promising candidate for immobilizing

https://dx.doi.org/10.22161/ijaers.78.36 ISSN: 2349-6495(P) | 2456-1908(O)

many types of contaminants, including heavy metals [9,10].

In addition, lignocellulosic biomass can be converted into fermentable sugars, mainly glucose and xylose, via the hydrolysis process [11], which can be used as a carbon source to produce, for example, bioethanol [12], levulinic acid (LA), formic acid (FA), 5-hydroxymethylfurfural (HMF) and furfural (FF) [13, 14]. The extraction of lignin occurs as a residue of hydrolysis, which can be used to generate heat, bio-oil and activated carbon [15,16,17].

In this context, the aim of this study was to determine the use of lignocellulosic residues (biomass) deposited from Amazon forest as an alternative energy source and its bioproducts, through the evaluation of biochar production and fermentable sugars from a green coconut, babassu and Brazil nut shell.

II. MATERIALS AND METHODS

2.1 Raw Material

Four raw materials were used to produce biochar: green coconut mesocarp (MC), babassu mesocarp (MB), Brazil nut shell pericarp (PC) and Brazil nut shell endocarp (EC). All samples were obtained in the Northern region of Brazil.

The green coconut residue *(Cocos nucifera)* was obtained from the commercial disposal of the raw material, after the withdrawn of liquid albumen (coconut water). The Brazil nut shell *(Bertholletia excelsa)* residues, were supplied by EMBRAPA Amazônia Oriental, and babassu (*Orbignya phalerata*) supplied by Tobasa Bioindustrial.

The collected samples were dried at room temperature, then in an oven at 50 ºC, crushed in a knife mill (Wiley type TE-650/1), sieved at 0.354 mm (45 mesh), and then stored in flasks for further analysis. All tests were performed in duplicate.

2.2 Biomass characterization

2.2.1 Chemical analysis

The samples were characterized according to the standard procedures of the American Society for Tests and Materials (ASTM).

2.2.1.1 Moisture content

The moisture content was determined (ASTM D3173 / D3173M-17) for 1 g of the ground and sieved sample, heated to 105 ± 5 ° C in an oven (Solid Steel SSD 110L) with air circulation for 12 h [18]. Then, it was placed in a desiccator for 20 min to be cooled and the moisture content was according to Equation (1):

$$Moisture\ (\%) = \frac{Mi - Mv}{Mi}\ x\ 100 \quad (1)$$

Where, *Mi* is the initial mass in grams of the sample; *Mv* is the mass of the sample in grams after heating.

2.2.1.2 Ash content

The ash content was determined in accordance with ASTM D3174-12, in which 1g of the ground and sieved sample will be left in a muffle at a temperature of 600 ± 50°C for approximately 4 h [19]. The difference between the initial and final weights provide the ash content, which can be determined according to Equation (2):

$$CZ\ (\%) = \frac{Mi - Mv}{Mi}\ x\ 100 \quad (2)$$

Where, *Mi* is the initial mass in grams of the sample; *Mv* is the mass of the sample in grams after heating.

2.2.1.3 Volatile matter content (VM)

The volatile matter content (VM) was determined according to ASTM D3175-20. The analysis consists of using 1 g of the previously dried sample and placing it in a muffle at 800 ± 10°C for 8 minutes [20]. After this time, the sample is placed in a desiccator to be cooled, for 60 min, then weighed. VM content according to Equation (3):

$$VM\ (\%) = \frac{Mi - Mf}{Mi}\ x\ 100 \quad (3)$$

Where, M_i is the initial mass in grams of the sample; M_f is the mass of the sample in grams after muffle oxidation.

2.2.1.4 Fixed carbon content (FC)

The fixed carbon content is an indirect measure and was determined according to Cai et al. [21], Equation (4):

$$FC\ (\%) = 100 - (\text{Moisture} + Ash + VM) \quad (4)$$

Where, Moisture is the moisture content; *Ash* is the ash content; *VM* is the volatile matter content.

2.2.2 Extractives

The extracts were extracted using the Soxhlet apparatus. Approximately 3g of each sample was used. The reaction time was 8 hours, with 190 mL of 95% ethanol (v/v). The extractive content was determined according to the protocol of the National Renewable Energy Laboratory [22]. Afterwards, the samples were placed in petri dishes for 48 h to dry. Extraction mass and the initial mass (raw sample) were weighed and applying the Equation (5) to determine the extractives:

$$Extractives\ (\%) = \frac{extraction\ mass}{mass\ of\ raw\ sample}\ x100 \quad (5)$$

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2.2.3 Acid Hydrolysis

The determination of carbohydrates and lignin were carried out using the standardized procedures of the NREL [23]. Thus, the acid hydrolysis of the sample was with 72% sulfuric acid and placed in a thermostatic bath at 30°C for 1 h.

Then, 84 mL of water was added and placed in the autoclave (Phoenix) at 120°C for 1 h. The samples were vacuum filtered (LT 65, Limatec, coupled), separating the liquid fraction for analysis of structural carbohydrates and acid-soluble lignin (ASL) and the solid to obtain the content of acid-insoluble lignin, also called Klason lignin (LK).

2.2.3.1 Lignin content

For analysis of ASL the method used was UV-Vis spectroscopy (HACH/Germany, DR5000) with a wavelength of 294 nm in 4% H_2SO_4 (m/v) white solution. For KL, the solids retained in filter crucibles were taken to an oven at 105 ºC for analysis of acid insoluble residues (AIR) and then subjected to a temperature of 575 ºC to measure acid insoluble ash (AIA). By difference of AIR and AIA, the insoluble lignin KL was obtained. From the sum of KL + ASL, Total Lignin (TL) was determined [23].

2.2.4 Determination of polysaccharides: Cellulose and Hemicellulose

In order to measure the fibrous component of biomass (Hemicellulose and cellulose), the determination of neutral detergent fiber (NDF) and acid detergent fiber (FDA) was performed. For the FDA fiber content, approximately 0.6 g of the dry and defatted sample were weighed, placed in a non-woven fabric bag, which was digested with H_2SO_4 at 1.25%, using the fiber digester model Marconi® MA-444/CI at 90ºC. In the NDF, approximately 0.6 g of the dry and defatted sample (after extraction) was weighed, placed in a tissue bag of non-woven fabric, which were digested in 1.25% NaOH using the fiber digester model Marconi® MA-444/CI at 90 º C. After digestion, the samples were dried in an oven at 105°C until reaching the constant weight [24]. The moisture-free content of hemicellulose was estimated by the difference between NDF and FDA.

2.2.5 Analysis of fermentable sugars: monomeric sugars

The fermentable sugars, glucose, xylose and arabinose, in the liquid fractions of acid hydrolysis were determined using a PerkinElmer Series 200 chromatography equipment, equipped with the Phenomenex Rezex ROA-Organic acid H^+ column (8%), and refractive index detector model RID-10A brand Shimadzu. The volume of the injected sample was 20 µL in constant temperature at 60 ºC. The mobile phase used was H_2SO_4 acid (5mM) with a flow of 0.6 mL min^{-1}. The concentrations of glucose, xylose and arabinose produced in the reactions were identified using the retention times of the D-glucose (Sigma-Aldrich, PA), xylose (Sigma-Aldrich, ≥ 99% purity) and arabinose (Sigma-Aldrich, ≥ 98% purity), calculated from the 6-point calibration curves ($R^2 > 0.99$).

The monomeric sugars concentrations, glucose, xylose and arabinose were determined as described by Lu et al. [25], using Equation (6). For the calculation, the correction factor of 0.88 (or 132/150) was used for C-5 sugars and 0.90 (or 162/180) for C-6 sugars according to the NREL methods [23].

$$\text{Sugar content (\%)} = \frac{\text{monomeric sugar} \times v \times F}{m} \times 100 \quad (6)$$

Where, *monomeric sugar* is the concentration in (g/L) of hexose or pentose; *m* is the mass of the biomass used (g); *v* is the final net volume of the acid hydrolysis process (*L*); *F* is the correction factor.

2.3. Bioproduct content

The maximum yields of levulinic acid (LA), formic acid (FA) and furfural (FF) were estimated from the fermentable sugars obtained during the hydrolysis process, using Equations (7), (8) and (9), as Rambo et al. [26].

$$LA\ (\%) = 0{,}5 \times \text{hexoses}\ \% \quad (7)$$

$$FF\ (\%) = 0{,}5 \times \text{pentoses}\ \% \quad (8)$$

$$FA\ (\%) = 0{,}2 \times \text{hexoses}\ \% \quad (9)$$

2.4. Biochar production

2.4.1. Pyrolysis procedure

The pyrolysis of the samples was carried out in a muffle furnace (Digimec FHMP) at different temperatures: 250 ºC and 400 ºC, with an increase of 5 ºC min^{-1}. Upon reaching the desired temperature, the samples stay in the muffle for 3 h, then cooled in the desiccator and weighed to calculate the biochar production. To carry out the treatment's porcelain crucibles (Chiarotti M-26) were used, these were filled with biomass and sealed in order to decrease O_2 during thermal degradation [27].

2.4.2. Pyrolyzed product

The yield of pyrolyzed product (PY) was calculated from the ratio between produced biochar (mPB) and initial dry biomass (mIB), according to Bueno [28], Equation (10).

$$PY(\%) = \frac{mPB}{mIB}\ x\ 100 \quad (10)$$

https://dx.doi.org/10.22161/ijaers.78.36 ISSN: 2349-6495(P) | 2456-1908(O)

The pyrolyzed product (PP) was calculated by average of two pyrolysis in the same temperature (n=2). The experimental error was smaller than 0.5% by weight.

2.5. Biochar characterization

The basic guidelines for standard methods and properties of the biochar were followed the International Biochar Initiative - IBI (version 2.1) [29].

2.5.1. Elementary analysis and Calorific value

The determination of the contents of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) was using the elementary analysis (Vario Macro CUBE – Elementar), and the oxygen (O) content was estimated according to ASTM D3176-15 [30].

The higher calorific value (HCV) was determined according to NREL/TP- 433-7965 [31], Equation (11), where A is ash.

$$HCV\,(MJ.Kg^{-1}) = 0.3491 \times C + 1.1783 \times H + 0.1005 \times S - 0.1034 \times O - 0.0151 \times N - 0.0211 \times A \quad (11)$$

2.5.2. pH

The pH of the biochars was determined in water, with the digital pH meter (AKSO, AK90). The method was to add distilled water (ratio of 1:20 m/v), mixed to form a homogeneous suspension over the sample and after 1.5 h measure the pH [32].

2.5.3. Functional groups

The technique Fourier-transform infrared spectroscopy (FTIR - Agilent Cary 630) was used to identify the functional groups on the biochar surface. The samples were scanned in two replicate runs. Spectral data were measured as absorbance (A) according to the equation: A=log10 (1/R), where R is the reflectance applied in the wavenumber from 4000 to 650 cm^{-1} (mid-infrared region) with 4 cm^{-1} resolution and 32 scans. The final spectrum was obtained by averaging the two replicate spectra per sample.

2.6. Activation of biochar

Activated carbon was produced from the biochar obtained from pyrolysis. The biochar was immersed in a solution of zinc chloride - $ZnCl_2$, at a concentration of 10% (m/v) in the ratio of 1:5, covered with a plastic film and rest for 24 h. Following the protocol, after that time, the samples were washed with distilled water and dried in an oven at 110 °C. The washed material was placed in a crucible, sealed and pyrolyzed in a muffle furnace (Digimec FHMP) at 600 °C for 2 h. After pyrolysis the activated carbon was washed with a solution of hydrochloric acid - HCl (2 moles.L^{-1}), to remove of $ZnCl_2$ and unclog the pores. Finally, the sample was dried in an oven at 110 °C for 24 h [33].

2.7. Economic analysis

The economic analysis was estimated in order to assess the viability of the production process, on a commercial scale, for the activated biochar, levulinic acid, formic acid and furfural. Considering only the investments and gross income, excluding the industrial reality. The calculation is based on the cash flow of inputs and outputs (Input-output) assuming the current market value [34]. The current market value was used for the bioproducts obtained and the reagents used. In contrast, zero cost for used waste was considered [35].

2.8. Statistical analysis

To statistically compare the positive and negative relationship between the calorific value and the chemical composition of the biomasses, Pearson's correlation coefficients (r) were observed . The r value can vary from -1 to +1, where values close to +1 indicate a significant positive relationship, values close to -1 translate into high negative correlations and 0 means that there is no interaction. Generally, values above ± 0.6 mean that there is a considerable correlation between the variables [36]. The figures and statistics were created in the Origin 8.0 program (*OriginLab Corporation*, *USA*, 2012).

III. RESULTS AND DISCUSSION

3.1 Physical-chemical characterization of raw biomass

The results of moisture, ash, volatile matter and fixed carbon of the raw samples are shown in Table 1, as well as the majority chemical composition of the lignocellulosic biomasses (cellulose, hemicellulose and lignin).

It is worth mentioning that the composition of these constituents varies from one species of biomass to another and even within a single species of plant, age, climatic conditions, soil characteristics, mode and storage location. In addition, different methodologies can be used in the chemical characterization of biomass, which can result in divergent values [4,37].

According to Chouhan Singh and Sarma [38], the volatile matter content implies an increase in the amount of bio-oil production via pyrolysis. Low moisture content (<14%) and ash (<7%) mean a higher yield in the production of bioproducts, increasing the efficiency of the process and preventing secondary reactions during hydrolysis. In addition, excess moisture in the biomass can

https://dx.doi.org/10.22161/ijaers.78.36 *ISSN: 2349-6495(P) | 2456-1908(O)*

reduce the calorific value [39].The low levels of extracts favor the formation of gas and coal [40].

The majority chemical composition of the studied biomasses is similar to those reported in the literature. When characterizing the green coconut residue, Mariano et al. [41] obtained contents of 35.45% cellulose, 43.90% hemicellulose and 18.16% lignin. Castro et al. [42] quantified for babassu residue 16.07% (w/w) of hemicellulose, 6.94% (w/w) of cellulose and 26.58%

Table 1: Chemical characterization of the raw biomass

Analysis (%)	*Raw sample*			
	MC	*MB*	*PC*	*EC*
Moisture	5.22 ± 0.02	7.25 ± 0.07	13.90 ± 0.00	11.35 ± 0.70
Ashes	2.82 ± 0.04	1.70 ± 0.14	6.75 ± 0.49	0.90 ± 0.28
VM	90.78 ± 0.28	86.70 ± 0.14	75.02 ± 0.71	77.45 ± 0.35
FC	1.18 ± 0.01	4.40 ±0.01	4.15 ± 0.01	10.40 ±0.01
Cellulose	30.50	33.55	2.35	23.33
Hemicellulose	30.61	34.11	50.82	23.12
Lignin	26.64	29.97	42.70	50.25
Extractives	12.16	2.37	4.13	3.33

Caption: MC: mesocarp of green coconut; MB: babassu mesocarp; PC: Brazil nut shell pericarp; EC: Brazil nut shell endocarp; VM: Volatile Materials; FC: Fixed Carbon.

(w/w) of lignin. For biomass of Brazil nut shells, Bonelli et al. [43] found holocellulose contents of 48.5%, 59.4% of lignin and 3.4% of extractives.

The results confirm that the studied biomasses are a source of valuable carbohydrates and the extraction in quantities of these compounds may be commercially viable. Fig. 1 shows the content of glucose, xylose and arabinose obtained from the liquid fraction of acid hydrolysis. Glucose values range from 13.5–22.5% (0.518–0.86 g L^{-1}), xylose from 3.7–28.3% (0.14–1.1 g L^{-1}) and arabinose from 0.62–25.75% (0.02–1.0 gL^{-1}).

Mariano et al. [41] obtained in the liquid hydrolyzate of the coconut residue mainly C5 and C6 sugars such as fructose (27.93%), glucose (20.38%), xylose (12.91%) and arabinose (8.53%), after 60 minutes of hydrothermal pretreatment followed by acid hydrolysis with 3% H_2SO_4. Using Brazil nut shells, Morales et al. [44], obtained 8.6% glucose, 7.9% xylose and 3.1% arabinose, under the same acid hydrolysis condition used in this work, with 72% sulfuric acid. For the hydrolysis of mesocarp babassu, López et al. [45] obtained high levels of glucose (up to 44 gL^{-1}) and xylose (up to 19 gL^{-1}).

3.2 Bioproducts

The estimated potential of lignocellulosic raw materials for the production of high value-added bioproducts from fermentable sugars obtained in hydrolysis are shown in Fig. 2. Glucose was found in greater quantity in the husk of green coconut, resulting in the estimate of LA and FA in quantities of 11.22% and 4.50%, respectively. In relation to pentoses, the highest percentage was found in the babassu mesocarp (xylose content of 28%), favoring furfural yield (27%). The lowest yields of LA, FF and FA were in the pericarp of the Brazil nut shell pericarp (PC).

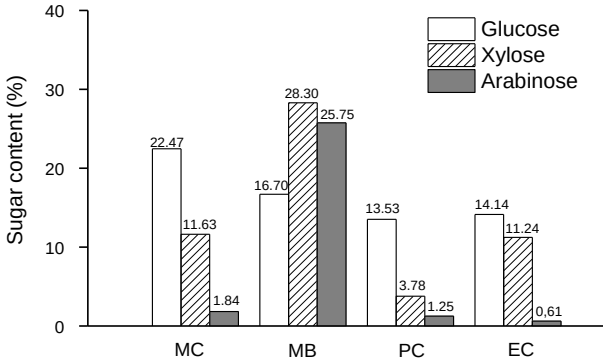


Fig. 1: Glucose, xylose and arabinose content obtained from the acid hydrolysis of the green coconut mesocarp (MC), babassu mesocarp (MB), Brazil nut pericarp (PC) and Brazil nut endocarp (EC).

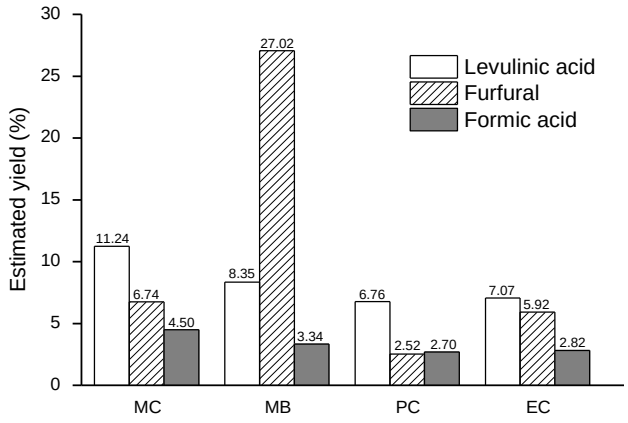


Fig. 2: Estimated yield of levulinic acid (LA), furfural (FF) and formic acid (FA) for the green coconut mesocarp (MC), babassu mesocarp (MB), Brazil nut shell pericarp (PC) Brazil nut shell endocarp (EC).

The literature for the yields of LA, FF and FA are demonstrated in Table 2. The estimated income of LA was higher than predicted by Sweygers et al. [4] for bamboo

https://dx.doi.org/10.22161/ijaers.78.36 *ISSN: 2349-6495(P) | 2456-1908(O)*

biomass, in a reaction catalyzed with 0.37 M HCl, for 3 h, at 160 ºC. For coconut biomass, the estimated FF value was close to that presented by Rambo et al. [26]. The PA content was lower than those mentioned in table 2.

Table 2: Literature results for experimental yields (%) of levulinic acid (LA), Furfural (FF) and formic acid (FA).

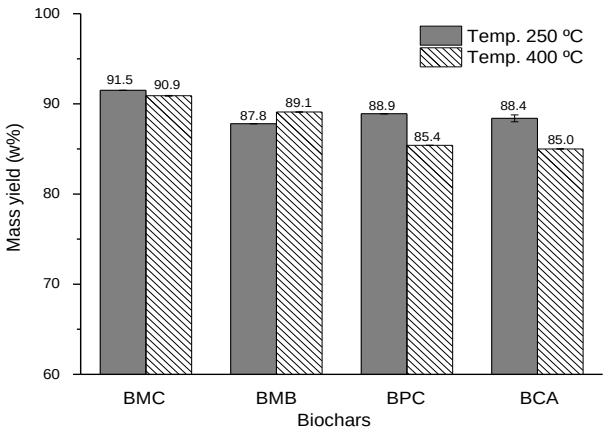
Biomass	Yield (%)			Literature
	LA	FF	FA	
Coconut husk	17.5	7.0	8.5	[26]
Pequi	23.7	65	–	[46]
Coffee beans	47.0	–	29	[47]
Corn cob	–	–	42.5	[48]
Bamboo	10.13	2.75	–	[04]

Although studies on the bioproducts in question for Brazil nut shell and babassu biomass have not been found, Cinelli et al. [49] presents results for the production of ethanol from babassu starch (glucose), 83% efficiency in converting starch to ethanol. In addition to ethanol, xylose can also be used for the production of xylitol, using specialized yeasts (DASGUPTA et al., 2017) and 5-hydroxymethylfurfural (HMF) [14], for example. The use of waste generated after the hydrolysis process also reveals the potential for producing activated carbon with a high surface area (542.0 $m^2.g^{-1}$) [17].

3.3 Pyrolysis yield

Biochar is a valuable input in the most diverse industries and stands out among the main products obtained after the pyrolysis process. In this study, the biochar produced had yields greater than 80% (Fig. 3).

The values obtained were higher than those reported by Gonzaga et al. [50] and Siengchum et al. [51] who found an average yield of 45% and 25.4 - 38.3% for the coconut husk biochar, in pyrolysis of 500 °C and 400–650 °C, respectively. However, the results were similar to that reported by Tsai et al. [52] of 75% for pyrolysis of coconut biomass at 400 ºC, Ghosh et al. [53] obtained a 17% biochar yield from the babassu mesocarp in pyrolysis at 750 ºC. Regarding chestnut shell, Jiang et al. [54] obtained a yield of 44.31% by weight when pyrolysed at 750 °C.



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ig. 3: Mass yield of the biochar of the green coconut mesocarp (BMC), the babassu mesocarp (BMB), the Brazil nut shell pericarp (BPC) and the Brazil nut shell endocarp (BEC) produced at different pyrolysis temperatures from raw biomass.

The yield of the residual solid from pyrolysis, according to Tsai et al. [52] show a decreasing trend as the pyrolysis temperature and the waiting time increase, where the formation of liquid and gaseous products occurs. According to Ortiz et al. [55] degradation reactions in pyrolysis with temperatures around 300 ºC produce higher yields of biochar. Novak et al. [56] attributed the decrease in biochar yield to the dehydration of hydroxyl groups and thermal degradation of cellulose and lignin structures. Abe et al. [57] report that cellulose and hemicellulose are decomposed at around 180-250 ºC, producing organic acids and phenolic substances.

3.4 Biochar characterization

The basic results needed to assess the utility of the biochar for use in the soil, as well as, elemental chemical composition, atomic proportions (H / C and [(O + N)/C]), ash content and higher calorific value (*HCV*), improved yield of biochar (BMC, BPC and BEC BMB 250 °C and 400 °C) are shown in Table 3. In this study, biochars were not compared to each other.

Biochar produced from green coconut and Brazil nut shell are classified as *Class 2* and babassu *Class 1*, with organic carbon content (C_{org}) between ≥ 30% and <60% and ≥ 60%, respectively [29]. According to Lima et al. [58] the percentage of carbon present in the BMB-400 ºC justifies, by itself, the use of this residue as a carbon source, similar to commercial activated carbons (75-85%).

https://dx.doi.org/10.22161/ijaers.78.36 *ISSN: 2349-6495(P) | 2456-1908(O)*

Table 3: Physical and chemical characteristics of the biochar obtained from the fractions of green coconut, babassu and Brazil nut shell.

Biochars	Elementary composition (%)					Ash (%)	Atomic relationship			pH	HCV MJ.Kg^{-1}
	C	H	N	O	S		H/C	O/C	C/N		
BMC-250 ºC	59.36	5.56	0.81	29.38	0.31	4.58	1.12	0.37	62.86	6.9	24.15
BMB-400 ºC	73.27	3.77	0.73	20.13	0.15	1.96	0.62	0.20	86.03	6.8	27.90
BPC-250 ºC	56.48	6.01	0.55	34.55	0.17	2.24	1.27	0.46	88.02	7.3	23.19
BEC-250 ºC	57.98	5.88	0.57	33.33	0.18	2.07	1.21	0.43	87.18	7.1	23.69

Caption: BMC: Biochar mesocarp of green coconut; BMB: babassu mesocarp biochar; BPC: Brazil nut pericarp biochar; BEC: Brazil nut endocarp biochar. C: Carbon or C_{org}; H: Hydrogen; N: Nitrogen; O: Oxygen; S: Sulfur; pH: Hydrogenionic potential; HCV: Higher Calorific Value.

The values of the elemental chemical composition of the biochar BPC-250ºC and BEC-250ºC are similar to those found by Bonelli et al. [43] for the Brazil nut residues. For the coconut mesocarp biochar (BMC-250 ºC) the results were inferior to those presented by Bispo et al. [59] for coconut pyrolysis at 700 ºC. The values for the babassu biochar (BMB-400 ºC) were similar to those reported by Lopes et al. [60] for a sample of the babassu coconut endocarp.

The atomic ratio H/C indicates the degree of aromaticity of the biochar [61]. Thermochemically processed materials that have an H/C value greater than 0.7 (BMC-250 ºC, BPC-250 ºC and BEC-250 ºC) can be thermochemically "altered", but are not considered thermochemically "converted" [29], preserving part of its original organic residues, such as CH_2 and fatty acids, lignin (aromatic nucleus) and cellulose (polar fractions) [62]. This property shows good biochar stability and its potential as a carbon sequestration agent in the soil [63]. In addition, Wei et al. [61] demonstrated that the H/C value can be a potential indicator for the mechanism of adsorption of organic contaminants. The BMB-400 ºC biochar is the only one within the required standards (<0.7).

The O/C ratios show that BMB-400 ºC (0.2) is theoretically the most stable biochar, followed by BMC-250 ºC (0.37), BEC-250 ºC (0.43) and BPC-250 ºC (0.46). According to Spokas [64], biochar with an O/C molar ratio of less than 0.2 are typically the most stable, with an estimated half-life of more than 1000 years; molar ratio O/C of 0.2-0.6 has an intermediate half-life (100-1000 years); and, the biochar with an O/C ratio greater than 0.6 has a half-life in the order of 100 years.

The C/N ratio for the biochar produced are between 50-100. This ratio (C/N) is an important parameter, as it strongly influences the response of the availability of phosphorus (P) and nitrogen (N) in the soil. Gao et al. [65] report that the application of biochar increased the available P by 45% and microbial biomass of P by 48%. In addition, applications of biochar in combination with organic fertilizer have shown significant potential to improve the availability of inorganic N in the soil. However, these effects of biochar on soil are inconsistent, as each combination of biochar/soil type requires additional characterization to better predict nutrient retention and release [50]. The pH values found demonstrate that the biochar obtained are neutral in nature (6.8-7.3) and therefore indicated for use in the soil [29] and for the purpose of raising the pH [63].

The HCV results obtained were in the range of 23.2 - 27.9 MJ.Kg^{-1}, revealing the energy potential of these residues as solid fuels, since the calorific capacity of these biochar is similar to that of bituminous coal (27- 33 MJ.Kg^{-1}) [66]. The results found for the higher calorific value are consistent with those reported in the literature Jiang et al. [54] when the nut shells were pyrolyzed at 250 ºC and 750 ºC, they obtained calorific value of the biochar of 18.88 MJ.kg^{-1} and 35.48 MJ.kg^{-1}, respectively. The calorific value of the coconut biochar was 23.68 MJ.kg^{-1} at a pyrolysis temperature of 600 ºC [67]. For babassu, Ranucci et al. [68] report calorific values between 36-45 MJ.kg-^{1}.

Fig. 4 shows the Pearson's correlation r between the calorific value of biochar and the biomass physical-chemical composition.The results revealed that, for the parameters of the next analyzes (moisture, volatile matter-VM, fixed carbon and ash content), only the VM can affect the calorific value. Lu et al. [69] points out that calorific value results mainly from combustion of organic

https://dx.doi.org/10.22161/ijaers.78.36 *ISSN: 2349-6495(P) | 2456-1908(O)*

compounds such as CF and VM. Therefore, the low content of CF obtained confirms this negative relationship. Brand [70] states that the calorific value decreases with high ash content, since mineral materials (ash) do not participate in the combustion process. In addition, low fixed carbon content and high ash yield are associated with low fuel quality [71]. The calorific value also decreased when the moisture content is high [72].

Evaluating the contents C, H, N, S and O, a positive correlation was found between the HCV and the content of C and N, the others showed a negative correlation. According to Protásio et al. [73] there is a tendency for HCV to be associated with higher percentage values of H and C. On the other hand, Ozyuguran et al. [74] demonstrate that H and S contents do not improve the performance of biomass calorific values. Protásio et al. [73] establish an inverse relationship between the O content, as the results in the present work. Huang et al. [75] state that high oxygen values decrease the calorific value. Ozyuguran et al. [74] concluded that only two parameters, including carbon and an extra element, nitrogen or oxygen, are ideal for predicting HCV.

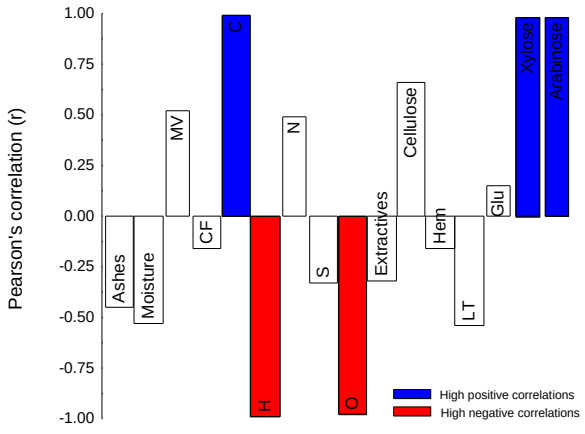

Fig. 4: Pearson's correlation between the physical-chemical composition and the calorific value the green coconut (BMC), babassu (BMB) and Brazil nut shell (BPC and BEC) biochars. VM: Volatile Materials; CF: Fixed Carbon; C: Carbon; H: Hydrogen; N: Nitrogen; S: Sulfur; O: Oxygen; Hem: Hemicellulose; LT: Total Liganin; Glu: Glucose.

Correlations based on structural chemical composition (cellulose, hemicellulose, lignin and extractives) are not viable due to the variation in the properties of the components [73]. However, the content of cellulose, hemicelluloses and lignin release energy in burning [76]. Only cellulose showed a positive relationship with HCV, probably due to its decomposition rate that occurs mainly in the range of 200 - 340 °C, while lignin decomposition occurs almost throughout the pyrolysis (340 - 900 °C) [54]. According to Guo et al. [77] the extracted biomass decomposes at 250 - 400 ° C and has greater activation energy. The sugar content had a positive relationship with the HCV, corroborating with Rambo et al. [26].

3.5 Functional groups

The results of the FT-IR analysis of the biochar produced are shown in Fig. 5. The biocharunder analysis have characteristics bands in the region between 3800 - 2700 cm^{-1}, which are attributed to the stretching vibration of the hydroxyl groups (OH) and CH. The BMC-400 °C sample showed a wide peak in this region with increasing temperature, as did the BPC-400 ºC sample which a sharp peaks at 3829 cm^{-1}, 3739 cm^{-1} and 3620 cm^{-1}. Jiang et al. [54] suggests the increase in temperature a large number of hydroxyls were reacted. Isitan et al. [78] attributes the peaks to the release of H_2O due to the breakdown of hydroxyl groups of the aliphatic groups.

The 2800-3000 cm^{-1} region is associated with asymmetric and symmetrical elongations in the methyl (-CH_3) and methylene (-CH_2) groups [79]. The 1704 -1612 cm^{-1} bands represented the stretching vibration of the carboxyl groups (C=O) between hemicelluloses and lignin [80,81]. Bands between 1605 - 1510 cm^{-1} (stretching vibration C=C) are associated with the position of the lignin band [82]. BPC showed sharp peaks in this region with an increase in temperature to 400 ºC. According to Brito et al. [79] these bands indicate an increase in aromaticity, due to the thermal decomposition of lignin.

The 1025 cm^{-1} and 890 cm^{-1} bands are attributed to the CH_2 scissor stretching and COC stretching into cellulose, respectively, these bands being sensitive to the amount of crystalline and amorphous cellulose [81]. In the literature have reported that functional groups containing oxygen, nitrogen and sulfur, in general, are prevalent in processes that involve adsorption of different types of compounds, including heavy metals [79,83]. Functional groups with these absorption bands are observed in the BPC and BEC at 400 ºC, in the region of 2400-1800 cm^{-1}.

3.6 Approximate economic analysis

The average yield for obtaining Biochars (BCV, BMB, BPC and BEC) was 91%, 88% 87% and 86% respectively, which corresponds on average to 880 kg of biochar produced, for each ton of biomass (Table 4). The market value considered for the gross biochar was US$ 0.23 per Kg for charcoal of industrial use, according to Secretariat of Finance, Ordinance No. 611/2015 from the State of Pará-Brazil [84].

https://dx.doi.org/10.22161/ijaers.78.36 *ISSN: 2349-6495(P) | 2456-1908(O)*

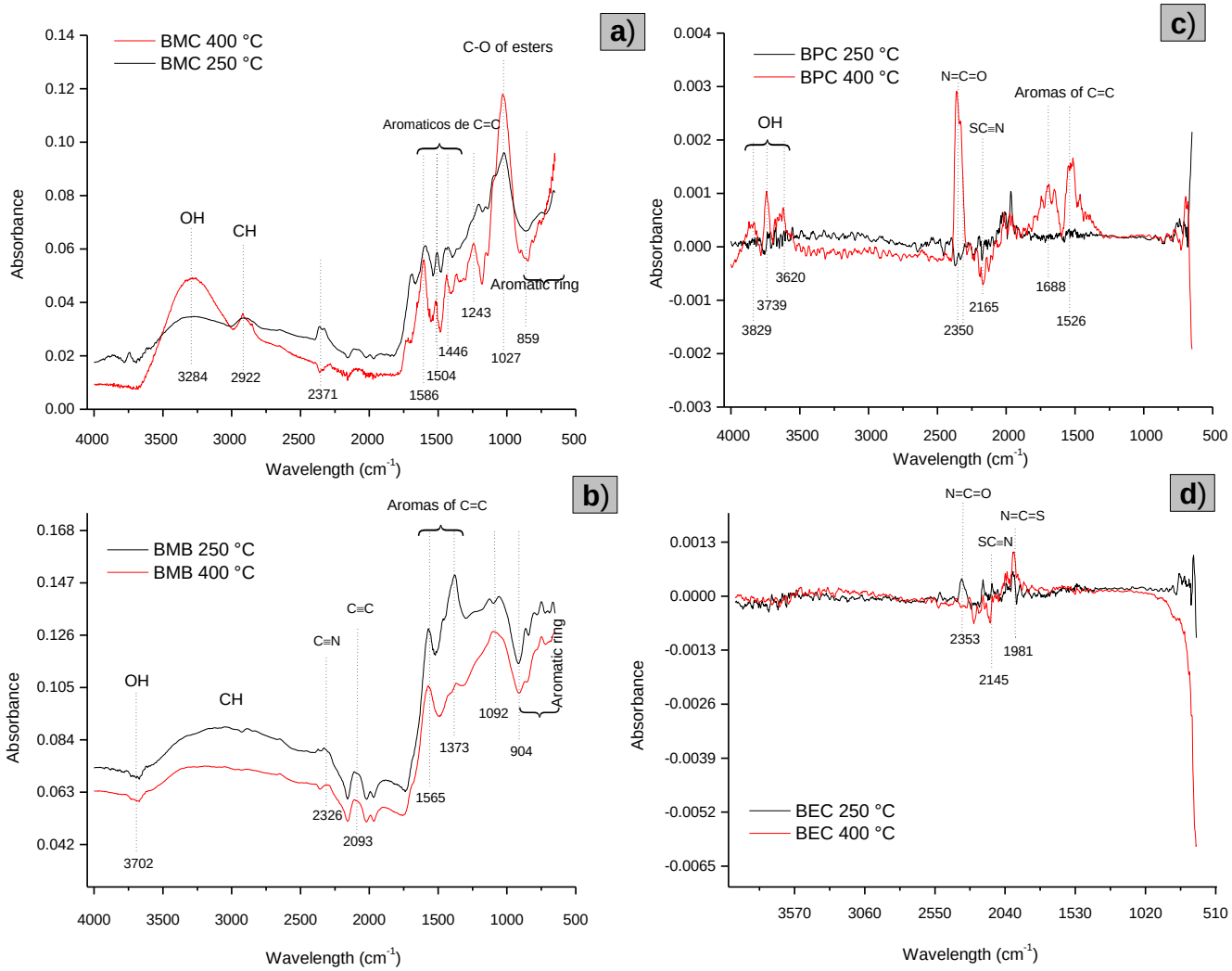

Fig. 5: Biochar spectra: Identification of functional groups by FTIR.

The activated biochar, from 10 g of biochar immersed in a solution of zinc chloride - $ZnCl_2$, at a concentration of 10%, a maximum yield of biochar was obtained after activation of 82%, 84%, 86% and 88%, for BCV, BMB, BPC and BEC biochar respectively, which corresponds to 850 kg of activated carbon. The price of high purity industrial activated carbon according to the catalog of a major supplier (Activated Charcoal Norit ®- Sigma Aldrich) is US$ 93.10 /kg. For the present study, a low to intermediate purity coal is considered, with a cost of US$ 20.00 /kg.

Table 4: Approximate economic balance of biochar and activated carbon.

BIOMASS	OUTPUT			INPUT			
	Conc. (1)	Quantities processed	Values (US$)	Biochar	Values (US$)	Activated biochar	Values (US$)
MC	-	1 t	-	910 Kg	209.30	746 Kg	14,920.00
MB	-	1 t	-	880 Kg	202.40	739 Kg	14,780.00
PC	-	1 t	-	870 Kg	200.10	748 Kg	14,960.00
EC	-	1 t	-	860 Kg	197.80	757 Kg	15,140.00

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$ZnCl_2$	10%	3,000 L	400.35	-	-	-	-
TOTAL			400.35		809.60		59.800,00
TOTAL BALANCE **(Output-Input)** for Biochar = US$ 809.60							
TOTAL BALANCE **(Output-Input)** for Activated biochar = US$ 59,399.65							

(1) concentration.

According the expenses with inputs, the consumption of electric energy, and considering that the biomass used does not have a market price, a total income of up to US$ 59,399.65 can be obtained from the biochar produced. The economic benefits can also be obtained from the sale of bioproducts. In relation to LA, FF and FA, the theoretical yield possible to obtain is 11.24%, 27.02% and 4.5% respectively, which can reach considerable commercial values according to Table 5.

The use of these residues (coconut mesocarp, babassu mesocarp, Brazil nut shell pericarp and Brazil nut shell endocarp) also brings social benefits, how to income generation, social and labor inclusion for low-income people involved in the production chain of these bioproducts, in addition to the economic recovery of this residue [85,86].

Table 5: Marketable bioproducts estimated from biomass hydrolysis.

BIOPRODUCTS	**BIOMASS**				**VALUE*** **(US$)**
	Estimated yield (%) and estimated mass yield (g)				
	MC	MB	PC	EC	
Levulinic acid	11.24 | (0.97)	8.35 | (0.72)	6.76 | (0.58)	7.07 | (0.61)	70.00 Kg
Furfural	6.74 | (0.58)	27.02 | (2.35)	2.52 | (0.21)	5.92 | (0.51)	117.00 Kg
Formic acid	4.50 | (0.39)	3.34 | (2.29)	2.70 | (0.23)	2.82 | (0.24)	131.00 L

*Commercial value obtained at Sigma-Aldrich.

Successful initiatives to transform lignocellulosic waste into business opportunities can be found in different segments of the Brazilian agrobusiness [86]. The Tobasa Bioindustrial, for example, develops projects for the full use of babassu in the Amazon forest. The Biorefinery has 150 employees and 1,500 extractivists as partners in the process of industrializing various products derived from babassu, including activated carbon [87].

IV. CONCLUSION

The results found revealed the potential of the residues of green coconut, babassu and Brazil nut shell in biorefineries. The processes employed made the use of these biomasses more efficient and competitive, with the production of a greater variety of bioproducts.

The acid hydrolysis process enables the subsequent bioconversion of fermentable sugars (glucose, xylose and arabinose) and added-value bioproducts, levulinic acid (LA), furfural (FF) and formic acid (FA), which are valuable chemical inputs in several sectors industry.

The thermochemical conversion of the biomass of green coconut, babassu and Brazil nut shell with the objective of producing biochar is an alternative, viable process, for the full use of these raw materials, with the generation of inputs of economic interest, and can be used as solid fuel, soil conditioner and bioremediation. In addition, the process contributes to the mitigation of the environmental problem of final disposal of this waste.

Therefore, the efficient use of these biomasses (green coconut, babassu and Brazil nut shell), points to the enormous social, economic and environmental potential. Added to this, product diversification, will for a fact have positive impacts on the various productive chains involved, benefiting society, generating employment and income, in addition to reducing environmental impacts. However, it is necessary to reflect on public policies that encourage the development of technologies and systems

https://dx.doi.org/10.22161/ijaers.78.36 *ISSN: 2349-6495(P) | 2456-1908(O)*

that contribute to the management and energy use of these residues in biorefineries, in order to stimulate the participatory and social inclusion aspects.

ACKNOWLEDGEMENTS

We are grateful to the National Council for Scientific and Technological Development (CNPq) for the scholarship, the Federal University of Tocantins (UFT) and the Federal Institute of Tocantins (IFTO).

REFERENCES

[1] Siqueira J. G. W., Rodrigues C., Vandenberghe L. P. de S., Woiciechowski A. L., Carlos Ricardo Soccol. (2020). Current advances in on-site cellulase production and application on lignocellulosic biomass conversion to biofuels: A review. Biomass and Bioenergy, 132, (2020), 105419. Doi: https://doi.org/10.1016/j.biombioe.2019.105419.

[2] Tan X., Liu Y., Gu Y., Xu Y., Zeng G., Hu X., Liu S., Wang X., Liu S., Li J. (2016). Biochar-based nano-composites for the decontamination of wastewater: A review. Bioresource Technology, 212, 318–333. Doi: 10.1016/j.biortech.2016.04.093.

[3] Reguyal F., Sarmah A. K., Gao, W. (2017). Synthesis of magnetic biochar from pine sawdust via oxidative hydrolysis of $FeCl_2$ for the removal sulfamethoxazole from aqueous solution. Journal of Hazardous Materials, 321, 868–878. Doi: 10.1016/j.jhazmat. 2016.10.006.

[4] Sweygers N., Somers M. H., Appels, L. (2018). Optimization of hydrothermal conversion of bamboo (*Phyllostachys aureosulcata*) to levulinic acid via response surface methodology. Journal of Environmental Management, 219, 95–102. Doi:10.1016/j.jenvman.2018.04.105.

[5] Chen X., Liu Y., Wu, J. (2019). Sustainable production of formic acid from biomass and carbon dioxide. Molecular Catalysis, 110716. Doi: 10.1016 /j.mcat.2019.110716.

[6] Tiong Y. W., Yap C. L., Gan S., Yap, W. S. P. (2019). Optimisation studies on the conversion of oil palm biomass to levulinic acid and ethyl levulinate via indium trichloride-ionic liquids: A response surface methodology approach. Industrial Crops and Products, 128, 221–234. Doi: 10.1016/j.indcrop.2018 .10.087.

[7] Carrier M., Hardie A. G., Uras Ü., Görgens J., Knoetze J. (Hansie). (2012). Production of char from vacuum pyrolysis of South-African sugar cane bagasse and its characterization as activated carbon and biochar. Journal of Analytical and Applied Pyrolysis, 96, 24–32. Doi: 10.1016/j.jaap.2012.02. 016.

[8] Mohan D., Pittman C. U., Steele, P. H. (2006). Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. Energy & Fuels, 20(3), 848–889. Doi: 10.1021/ef0502397.

[9] Klasson K. T., Uchimiya M., Lima, I. M. (2014). Uncovering surface area and micropores in almond shell biochars by rainwater wash. Chemosphere, 111, 129–134. Doi: 10.1016/j.chemos phere.2014.03.065.

[10] Li J., Li Y., Wu Y., Zheng, M. (2014). A comparison of biochars from lignin, cellulose and wood as the sorbent to an aromatic pollutant. Journal of Hazardous Materials, 280, 450–457. Doi: 10.1016/j. jhazmat.2014.08.033.

[11] Muharja M., Junianti F., Ranggina D., Nurtono T., Widjaja A. (2018). An integrated green process: Subcritical water, enzymatic hydrolysis, and fermentation, for biohydrogen production from coconut husk. Bioresource Technology, 249, 268–275. Doi: 10.1016/j.biortech.2017.10.024.

[12] Mishra A., Ghosh, S. (2019). Bioethanol production from various lignocellulosic feedstocks by a novel "fractional hydrolysis" technique with different inorganic acids and co-culture fermentation. Fuel, 236, 544–553. Doi: 10.1016/j.fuel.2018.09.024.

[13] Bizzi C. A., Santos D., Sieben T. C., Motta G. V., Mello P. A., Flores E. M. M. (2018). Furfural Production from Lignocellulosic Biomass by Ultrasound-assisted Acid Hydrolysis. Ultrasonics Sonochemistry. Doi: 10.1016/j.ultsonch.2018.09.011.

[14] Li, X., Xu, R., Yang, J., Nie, S., Liu, D., Liu, Y., & Si, C. (2019). Production of 5-hydroxymethylfurfural and levulinic acid from lignocellulosic biomass and catalytic upgradation. Industrial Crops and Products, 130, 184–197. Doi: 10.1016/j.indcrop.2018.12.082.

[15] Liu G., Bao J. (2017). Evaluation of electricity generation from lignin residue and biogas in cellulosic ethanol production. Bioresource Technology, 243, 1232–1236. Doi: 10.1016/j.bior tech.2017.07.022.

[16] Kang S., Fu J., Zhang G. (2018). From lignocellulosic biomass to levulinic acid: A review on acid-catalyzed hydrolysis. Renewable and Sustainable Energy Reviews, 94, 340–362. Doi: 10.1016/j.rser.2018.06.016.

[17] Rambo M. K. D., Nemet Y. K. S., Santana Junior C. C., Pedroza M. M., Rambo M. C. D. (2020). Comparative study of the products from the pyrolysis of raw and hydrolyzed baru wastes. Biomass Conversion and Biorefinery. Doi: https://doi.org/10. 1007/s13399-019-00585-0.

[18] ASTM D3173 / D3173M-17, Standard Test Method for Moisture in the Analysis Sample of Coal and Coke, ASTM International, West Conshohocken, PA, 2017.

[19] ASTM D3174-12, Standard Test Method for Ash in the Analysis Sample of Coal and Coke from Coal, ASTM International, West Conshohocken, PA, 2018.

[20] ASTM D3175-20, Standard Test Method for Volatile Matter in the Analysis Sample of Coal and Coke, ASTM International, West Conshohocken, PA, 2020.

[21] Cai J., He Y., Yu X., Banks S. W., Yang Y., Zhang X., Bridgwater A. V. (2017). Review of physicochemical properties and analytical characterization of lignocellulosic biomass. Renewable and Sustainable Energy Reviews, 76, 309–322. Doi: 10.1016/j.rser.2017.03.072.

[22] National Renewable Energy Laboratory - NREL. (2008). NREL/TP-510-42619: determination of extractives in biomass. Golden, Colorado 80401-3393.

[23] National Renewable Energy Laboratory - NREL. (2012) NREL/TP-510-42618: determination of structural carbohydrates and lignin in biomass. Golden, Colorado 80401.

[24] A.O.A.C. Association of Official Analytical Chemists. Methods of analysis of the Association of official Analytical Chemists.12 ed., Washington. 1995. 1994.1094 p.

[25] Lu J., Li X., Zhao J., Qu Y. (2012). Enzymatic Saccharification and Ethanol Fermentation of Reed Pretreated with Liquid Hot Water. Journal of Biomedicine and Biotechnology, 2012, 1–9. Doi:10.1155/2012/276278.

[26] Rambo M. K. D., Schmidt F. L., Ferreira, M. M. C. (2015). Analysis of the lignocellulosic components of biomass residues for biorefinery opportunities. Talanta, 144, 696–703. Doi: 10.1016/j.talanta.2015. 06.045.

[27] Pires I. C. de S. A. Produção e caracterização de biochar de palha de cana-de-açúcar (Saccharum sp.). Dissertação (mestrado) – Universidade Federal de São Carlos, Sorocaba, 2017.

[28] Bueno C. C. Biochar: caracterização estrutural e interações com nutrientes e microorganismos pedológicos. Tese (Doutorado) – Universidade Estadual Paulista "Júlio de Mesquita Filho". Instituto de Ciência e Tecnologia, Sorocaba, 2017.

[29] International Biochar Initiative (IBI). Standardized Product Definition and Product Testing Guidelines for Biochar that is used in Soil. IBI Biochar Standards, version 2.1, 2015.

[30] ASTM D3176-15. Standard Practice for Ultimate Analysis of Coal and Coke, ASTM International, West Conshohocken, PA, 2015.

[31] NREL/TP-433-7965*:* An atlas of thermal data for biomass and other fuels. National Renewable Energy Laboratory, 1995.

[32] Bardalai M., Mahanta D. K. (2018). Characterisation of Biochar Produced by Pyrolysis from Areca Catechu Dust. Materials Today: Proceedings, 5(1), 2089–2097. Doi:10.1016/j.matpr.2017.09.205.

[33] De Costa P. D., Furmanski L. M., Dominguini L. (2015). Produção, Caracterização e Aplicação de Carvão Ativado de Casca de Nozes para Adsorção de Azul de Metileno. Rev. Virtual Quim. (v) 7 (4), p. 1272-1285.

[34] Bevilaqua D. B. (2010). Acids production by means of acid hydrolysis of rice husk. Master Dissertation, Post-Graduation Program in Chemistry Federal University of Santa Maria, RS, Brazil.

[35] Gaudereto H. S., Cabral L. G., Rodrigues, F.A. (2017). Produção de ácido levulínico a partir do bagaço de cana: estudo cinético, simulação e viabilidade econômica. Engevista, v. 19, n.1, p. 236-255.

[36] Chelgani S. C. Exploring relationships of gross calorific value and valuable elements with conventional coal properties for North Korean coals. International Journal of Mining Science and Technology, v. 29, p. 867-871. Doi: https://doi.org/10.1016/j.ijmst.2019.09.005.

[37] Pratto B. (2015) Hidrólise enzimática da palha de cana-de-açúcar: estudo cinético e modelagem matemática semi-mecanística. Dissertação de Mestrado. PósGraduação em Engenharia Química. Universidade Federal de São Carlos. São Carlos-SP.

[38] Chouhan Singh A. P., Sarma A. K. (2013). Critical analysis of process parameters for bio-oil production via pyrolysis of biomass: a review. Recent Pat Eng 2013; 7:98–114.

[39] Charlton A., Elias R., Fish S., Fowler P., Gallagher J. (2009). The biorefining opportunities in Wales: Understanding the scope for building a sustainable, biorenewable economy using plant biomass. Chemical Engineering Research and Design, 87(9), 1147–1161. doi: 10.1016/j. cherd.2009.06.013

[40] Wang Y., Wu L., Wang C., Yu J., Yang Z. (2011). Investigating the influence of extractives on the oil yield and alkane production obtained from three kinds of biomass via deoxy-liquefaction. Bioresource Technology, 102(14), 7190–7195. Doi: 10.1016/j.biortech.2011.04.060.

[41] Mariano A. P. B., Unpaprom Y., Ramaraj R. (2020). Hydrothermal Pretreatment and Acid Hydrolysis of Coconut Pulp Residue for Fermentable Sugar Production. Food and Bioproducts Processing. Doi: 10.1016/j.fbp.2020.04.003.

[42] Castro A. M. de, Castilho L. dos R., Freire D. M. G. (2016). Characterization of babassu, canola, castor seed and sunflower residual cakes for use as raw materials for fermentation processes. Industrial Crops and Products, 83, 140–148. Doi: 10.1016/j.indcrop. 2015.12.050.

[43] Bonelli P., Della Rocca P.A, Cerrella E.G., Cukierman A.L. (2001). Effect of pyrolysis temperature on composition, surface properties and thermal degradation rates of Brazil Nut shells. Bioresource Technology, 76(1), 15–22. Doi: 10.1016/s0960-8524(00)00085-7.

[44] Morales A., Gullón B., Dávila I., Eibes G., Labidi J., Gullón, P. (2018). Optimization of alkaline pretreatment for the co-production of biopolymer lignin and bioethanol from chestnut shells following a biorefinery approach. Industrial Crops and Products, 124, 582–592. Doi: 10.1016/j.indcrop. 2018.08.032.

[45] López J. A., Lázaro C. da C., Castilho L. dos R., Freire, D. M. G., Castro, A. M. de. (2013). Characterization of multienzyme solutions produced by solid-state fermentation of babassu cake, for use in cold hydrolysis of raw biomass. Biochemical Engineering Journal, 77, 231–239. Doi: 10.1016/j.bej.2013.06.006.

[46] Scapin E., Rambo M. K. D., Viana G. C. C., Borges M. B., Rambo M. C. D., Santana Junior, C. C. (2020). Production of Furanic Compounds and Organic Acids from Brazilian Pequi (Caryocar brasiliensis Camb.) Residues Using Green Chemistry. J. Braz. Chem. Soc., Vol. 00, No. 00, 1-9, 2020.

[47] Kim B., Yang J., Kim M., Lee, J. W. (2020). One-pot selective production of levulinic acid and formic acid from spent coffee grounds in a catalyst-free biphasic system. Bioresource Technology, 122898. Doi: 10.1016/j.biortech.2020.122898.

[48] Lu T., Hou Y., Wu W., Niu M., Wang Y. (2018). Formic acid and acetic acid production from corn cob by catalytic

oxidation using O_2. Fuel Processing Technology, 171, 133–139. Doi: 10.1016/j.fuproc.2017.11.010.

[49] Cinelli B. A., López J. A., Castilho L. R., Freire D. M. G., Castro, A. M. (2014). Granular starch hydrolysis of babassu agroindustrial residue: A bioprocess within the context of biorefinery. Fuel, 124, 41–48. Doi: 10.1016/j.fuel.2014.01.076.

[50] Gonzaga M. I. S., Mackowiak C., de Almeida A. Q., de Carvalho Junior J. I. T., Andrade, K. R. (2018). Positive and negative effects of biochar from coconut husks, orange bagasse and pine wood chips on maize (*Zea mays* L.) growth and nutrition. CATENA, 162, 414–420. Doi: 10.1016/j.catena.2017.10.018.

[51] Siengchum T., Isenberg M., Chuang S. S. C. (2013). Fast pyrolysis of coconut biomass – An FTIR study. Fuel, 105, 559–565. Doi: 10.1016/j.fuel.2012. 09.039.

[52] Tsai W. T., Lee M. K., Chang Y. M. (2006). Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell in an induction-heating reactor. Journal of Analytical and Applied Pyrolysis, 76(1-2), 230–237. Doi: 10.1016/j.jaap.2005.11.007.

[53] Ghosh A., da Silva Santos A. M., Cunha J. R., Dasgupta A., Fujisawa K., Ferreira O. P., Lobo A.O., Terrones M., Terrones H., Viana B. C. (2018). CO_2 Sensing by in-situ Raman spectroscopy using activated carbon generated from mesocarp of babassu coconut. Vibrational Spectroscopy, 98, 111–118. Doi: 10.1016/j.vibspec.2018.07.014.

[54] Jiang K., Cheng C., Ran M., Lu Y., Wu, Q. (2018). Preparation of a biochar with a high calorific value from chestnut shells. New Carbon Materials, 33(2), 183–187. Doi: 10.1016/s1872-5805(18)60333-6.

[55] Ortiz L. R., Torres E., Zalazar D., Zhang H., Rodriguez R., Mazza, G. (2020). Influence of pyrolysis temperature and bio-waste composition on biochar characteristics. Renewable Energy. Doi: 10.1016/j.renene.2020.03.181.

[56] Novak J. M., Busscher W. J., Laird D. L., Ahmedna M., Watts D. W., Niandou M. A. S. (2009). Impact of Biochar Amendment on Fertility of a Southeastern Coastal Plain Soil. Soil Science, 174(2), 105–112. Doi: 10.1097/ss.0b013e3181981d9a.

[57] Abe, F. The thermochemical study of forest biomass. Forest Prod. Chem. 45, p. 91-95, 1988.

[58] Lima D. R., Hosseini-Bandegharaei A., Thue P. S., Lima E. C., de Albuquerque Y. R. T., dos Reis G. S., Umpierresd C.S., Diasad S. L. P., Tran H. N. (2019). Efficient acetaminophen removal from water and hospital effluents treatment by activated carbons derived from Brazil nutshells. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 123966. Doi: N10.1016/j.colsurfa.2019.123966.

[59] Bispo M. D., Schneider J. K., da Silva Oliveira D., Tomasini D., da Silva Maciel G. P., Schena T., Onorevoli B., Bjerk T. R., Jacques R. A., Krause, L. C., Caramão, E. B. (2018). Production of activated biochar from coconut fiber for the removal of organic compounds from phenolic. Journal of Environmental Chemical Engineering, 6(2), 2743–2750. Doi: 10.1016/j.jece.2018.04.029.

[60] Lopes T. R., Cipriano D. F., Gonçalves G. R., Honorato H. A., Schettino M. A., Cunha A. G., Emmerich F. G. Freitas, J. C. C. (2017). Multinuclear magnetic resonance study on the occurrence of phosphorus in activated carbons prepared by chemical activation of lignocellulosic residues from the babassu production. Journal of Environmental Chemical Engineering, 5(6), 6016–6029. Doi: 10.1016/j.jece.2017.11.028.

[61] Wei L., Huang Y., Huang L., Li Y., Huang Q., Xu G., Müller K., Wang H., Ok Y. S., Liu, Z. (2020). The ratio of H/C is a useful parameter to predict adsorption of the herbicide metolachlor to biochars. Environmental Research, 109324. Doi: 10.1016/j.envres.2020.109324.

[62] Chen B., Zhou D., Zhu L. (2008). Transitional Adsorption and Partition of Nonpolar and Polar Aromatic Contaminants by Biochars of Pine Needles with Different Pyrolytic Temperatures. Environmental Science & Technology, 42(14), 5137–5143. Doi: 10.1021/es8002684.

[63] Stylianou M., Christou A., Dalias P., Polycarpou P., Michael C., Agapiou A., Papanastasiou P., Fatta-Kassinos, D. (2020). Physicochemical and structural characterization of biochar derived from the pyrolysis of biosolids, cattle manure and spent coffee grounds. Journal of the Energy Institute. Doi: 10.1016/j.joei.2020.05.002.

[64] Spokas K. A. (2010). Review of the stability of biochar in soils: predictability of O:C molar ratios. Carbon Management, 1(2), p. 289-303.

[65] Gao S., De Luca T. H., Cleveland C. C. (2018). Biochar additions alter phosphorus and nitrogen availability in agricultural ecosystems: A meta-analysis. Science of The Total Environment. Doi: 10.1016/j.scitotenv.2018.11.124.

[66] Vazzoler, A. (2017) Introdução ao estudo das viabilidades técnica e econômica de processos químicos: Estimativas de custos para projetos conceituais e anteprojetos. ISBN 978-85-592-28330-8, Campinas, SP, 2017.

[67] Rout T.; Pradhan D.; Singh R. K.; Kumari N. (2016). Exhaustive study of products obtained from coconut shell pyrolysis. Journal of Environmental Chemical Engineering, 4(3), p. 3696–3705. Doi: 10.1016/j.jece. 2016.02.024.

[68] Ranucci C. R., Alves H. J., Monteiro M. R., Kugelmeier C. L., Bariccatti R. A., Rodrigues de Oliveira, C., Antônio da Silva, E. (2018). Potential alternative aviation fuel from jatropha (*Jatropha curcas* L.), babassu (*Orbignya phalerata*) and palm kernel (*Elaeis guineensis*) as blends with Jet-A1 kerosene. Journal of Cleaner Production, 185, 860–869. Doi: 10.1016/j.jclepro.2018.03.084.

[69] Lu Z., Mo J., Yao S., Zhao J., Lu J. (2017). Rapid Determination of the Gross Calorific Value of Coal Using Laser-Induced Breakdown Spectroscopy Coupled with Artificial Neural Networks and Genetic Algorithm. Energy & Fuels, 31(4), p. 3849–3855. Doi: 10.1021/acs.energyfuels.7b00025.

[70] Brand M. A. (2010). Energia de biomassa florestal. Rio de Janeiro: Interciência, 131 p.

[71] Özyuğuran A., Yaman S. (2017). Prediction of Calorific Value of Biomass from Proximate Analysis. Energy

Procedia, 107, p. 130–136. Doi: 10.1016/j.egypro.2016.12.149.

[72] Brand M. A., Stähelin T. S. F., Ferreira, J.C., Neves, M. D. (2014). Produção de biomassa para geração de energia em povoamentos de *Pinus taeda* L. com diferentes idades. Revista Árvore, 38(2), p. 353-360. Doi: https://doi.org/10.1590/S0100-67622014000200 016.

[73] Protásio T. de P., Bufalino L., Tonoli G. H. D., Couto A. M., Trugilho P. F., Guimarães Júnior M. (2011). Relação entre o poder calorífico superior e os componentes elementares e minerais da biomassa vegetal. Pesquisa Florestal Brasileira, 31(66), 113–122. Doi: 10.4336/2011.pfb.31.66.113.

[74] Ozyuguran A., Akturk A., Yaman, S. (2018). Optimal use of condensed parameters of ultimate analysis to predict the calorific value of biomass. Fuel, 214, p. 640–646. Doi: 10.1016/j.fuel.2017.10. 082.

[75] Huang C., Han L., Yang Z., Liu X. (2009). Ultimate analysis and heating value prediction of straw by near infrared spectroscopy. Waste Management, 29(6), p. 1793–1797. Doi: 10.1016/j.wasman.2008. 11.027.

[76] Patil R. A., Deshannavar U. B. (2018). To Study the Effect of Mechanical Comminution on Lignin Percentage and Calorific Value of Dry Sugar Cane Leaves. Materials Today: Proceedings, 5(9), 18135–18141. Doi: 10.1016/j.matpr.2018.06.149.

[77] Guo X., Wang S., Wang K., Liu Q., Luo Z. (2010). Influence of extractives on mechanism of biomass pyrolysis. Journal of Fuel Chemistry and Technology, 38(1), p. 42–46. Doi: 10.1016/s1872-5813(10)60019-9.

[78] Işıtan S., Ceylan S., Topcu Y., Hintz C., Tefft J., Chellappa T., Guo J., Goldfarb, J. L. (2016). Product quality optimization in an integrated biorefinery: Conversion of pistachio nutshell biomass to biofuels and activated biochars via pyrolysis. Energy Conversion and Management, 127, 576–588. Doi: 10.1016/j.enconman.2016.09.031

[79] Brito G. M., Cipriano D. F., Schettino M. Â., Cunha A. G., Coelho E. R. C., Freitas J. C. C. (2019). One-step methodology for preparing physically activated biocarbons from agricultural biomass waste. Journal of Environmental Chemical Engineering, 103113. Doi: 10.1016/j.jece.2019.103113.

[80] Okenwa Ufodike C., Obiozo Eze V., Faisal Ahmed M., Oluwalowo A., Gyu Park J., Liang Z., Wang H. (2019). Investigation of molecular and Supramolecular Assemblies of Cellulose and Lignin of Lignocellulosic Materials by Spectroscopy and Thermal Analysis. International Journal of Biological Macromolecules. Doi: 10.1016/j.ijbiomac.2019.09.21 4.

[81] Khan A. S., Man Z., Bustam M. A., Nasrullah A., Ullah Z., Sarwono A., Shah F. U., Muhammad N. (2018). Efficient conversion of lignocellulosic biomass to levulinic acid using acidic ionic liquids. Carbohydrate Polymers, 181, 208–214. Doi: 10.1016/j.carbpol.2017.10.064.

[82] Wu Q. Q., Ma Y. L., Chang X., Sun, Y. G. (2015). Optimization and kinetic analysis on the sulfuric acid – Catalyzed depolymerization of wheat straw. Carbohydrate Polymers, 129, 79–86. Doi: 10.1016/j.carbpol.2015.04.053.

[83] Yang, X., Wan, Y., Zheng, Y., He, F., Yu, Z., Huang, J., Wang H., Okj Y. S., Jianga Y., Gao, B. (2019). Surface functional groups of carbon-based adsorbents and their roles in the removal of heavy metals from aqueous solutions: A critical review. Chemical Engineering Journal. Doi: 10.1016/j.cej. 2019.02.119.

[84] Secretariat of Finance (Secretaria de Estado da Fazenda). Portaria SEFA Nº 611/2015. Altera o Boletim de Preços Mínimos de Mercado, constante da Portaria nº 354, de 14 de dezembro de 2005, os produtos conforme especifica. Publicado no DOE – PA, 2015. In: https://www.legisweb.com.br. Access: May 2020.

[85] Eleutério G. A., Lorenzon R. Z., COUTO M. C. L. (2017). Estimativa do custo de implantação de uma unidade de beneficiamento da casca do coco verde consumido *in natura*. In: Congresso da Associação Brasileira de Engenharia Sanitária e Ambiental**,** III-352.

[86] Makishi F. (2012) Criação de valor compartilhado na cadeia de reciclagem: processamento dos resíduos da comercialização do coco verde. Dissertação (Mestrado), Departamento de Engenharia de Alimentos – Universidade de São Paulo, Pirassununga.

[87] Brito, V. (2019). Caso de sucesso - Tobasa Bioindustrial. Notícias SEBRAI - Serviço Brasileiro de Apoio às Micro e Pequenas Empresas, Centro Sebrae de sustentabilidade. In: http://sustentabilidade.sebrae.com.br Acess: June 2020.