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Utilization of pequi Residual Biomass from the Brazilian cerrado for obtaining raw and activated biochars and bio-oil

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Abstract*— *The pequi (Caryocar brasiliense Camb) is a fruit native to the Cerrado, with a production of 765 tons per year. However, their peels (76% of the fruit) are generally discarded. In this study, the physical-chemical characterization of the biomass of the pequi was carried out and physical activation processes were developed through slow pyrolysis and physical chemical activation with zinc chloride ($ZnCl_2$) to produce bio-based products, including bio-oil (30.5%) and biochar (34%). Analytical techniques, such as mid-infrared spectroscopy, gas chromatography coupled with mass spectrometry, surface area, pore size, approximate and elementary analysis, helped to elucidate, identify and quantify such compounds. The biochars produced showed a low surface area of 30,30 m^2/g (BET) and 39.11 m^2/g (Langmuir), however the superior calorific power of activated carbon (29.59 $kJ.g^{-1}$) and raw coal (26,92 $kJ.g^{-1}$) highlight the potential of biochar for use as a solid fuel. Bio-oil, on the other hand, presented valuable chemicals in its fraction, such as vaccenic acid (21.23%), palmitic acid (19.73%) and furfural acid (7.04%).

***Keywords*— Bioproducts, Peel of pequi, pyrolysis, residue.**

I. INTRODUCTION

The cerrado is the second largest biome in Brazil, concentrated mainly in the central-west region and occupies two million square kilometers, corresponding to 24% of the country's territorial extension. It stands out as a global hotspot, with a wide ecological diversity, about 11,627 species, and its hydrological function highlights the importance that the biome plays in the environment and society [1,2].

The pequi (*Caryocar brasiliense* Camb) is a fruit native to the Cerrado. Fruit production in Brazil in 2018 was 765 tons (core), of which 441 tons were in the northern region alone[3]. Despite all production, in general, only pyrenes (21.6%) are used, making the rest of the fruit (76% of peel) waste from the process[4]. That said, it is important to understand the use of these residues and their alternative use for the production of biochar and bio-oil [5].

Pyrolysis is a physical-chemical process, which can be performed slowly or quickly, to produce such compounds. Slow pyrolysis enhances the yield of biochar, while rapid pyrolysis benefits the yield of bio-oil [6]. The composition of bio-oil consists of a complex mixture of different substances such as: ketones, phenols, aldehydes and hydrocarbons, which provide the production of chemicals and applications in biofuels [7]. Among the applications of bio-oil we can highlight: heating furnaces, boilers, diesel engines and turbines. It can be incorporated into other chemicals to produce adhesives and resins. Due to the diversity of chemical compounds, they can be characterized and used in the pharmaceutical and chemical industries [8-9].

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The biochar, considered an organic residue, basically composed of carbon and ash, has chemical and physical characteristics that contribute to: removal of pollutants in the soil, improvement of photosynthesis, increase of carbon sequestration, decrease of Greenhouse Gases - GHG, and containment of soil erosion [10-13]. The biochar can be activated chemically or physically and serve as a powerful adsorbent for the removal of pollutants, drugs, and purification processes [14].

In this context, the objective of this research was to perform the slow pyrolysis of the residues of the raw pequi (peel), in order to verify the potentials of bio-oils, biochars and activated biochars, as alternative sources of bioproducts.

II. MATERIALS AND METHODS

2.1 Sample preparation

The pequi mesocarp (*Caryocar brasiliense* Camb) was collected in the indigenous village of the Xerente tribe, in the city of Tocantínia, in the state of Tocantins, which is part of the Legal Amazon of Brazil. The collected material was processed at the Chemistry Laboratory of the Federal University of Tocantins, where the fractions were separated manually, the shells were dried in an oven at 60ºC for 24 hours, ground in a Willye knife mill (model Star FT 50, Fortenox) and deposited in hermetically sealed glass bottles. All analyzes were performed in duplicates.

2.2 Pyrolysis Process

The raw samples were inserted into the Pyrex tubular fixed bed reactor to be subjected to the pyrolysis process. Thus, 30g of biomass at 500 °C was used for 30 min [15] For the transfer of vapors and aerosols from pyrolysis, chloroform was used in the helium flow (20 mL min^{-1}) and two chloroform traps (50 mL) kept in ice/salt baths. After the pyrolysis process, the liquid residue (bio-oil) and the solid residue (biochar) were stored for further analysis. The solids separator was used to recover all the solid material resulting from pyrolysis. The biochar yield (%) was calculated according to equation 1, and the bio-oil yield was calculated according to equation 2.

$$Biochar\ yield\ (\%) = mfc/mic\ X100 \quad (1)$$

Where: *mfC*: Final mass of Charcoal; *miC*: Initial mass of Charcoal.

$$Bio-oil\ yield\ (\%) = mfb/mibX100 \quad (2)$$

Where: *mfB*: Final mass of Bio-oil; *miB*: Initial mass of Bio-oil.

2.3 Activation of coal

The activation of the coal was carried out with a solution of zinc chloride - $ZnCl_2$ (Merck) with a concentration of 10% m/v in the proportion of 1: 5 (coal: solution, mass: volume) was added to the biomass sample. Then, the sample container was covered with film paper for 24 hours. Subsequently, the sample was washed with distilled water and kiln-dried at 110 ± 5 °C [16].

The washed biomass was placed in a cordierite crucible, closed with rock wool and cordierite plate, and once again it was pyrolyzed in a vertical oven (Jung 815), at 600 ± 5 °C, for 2 hours. A 2 mol solution of hydrochloric acid - HCl (Merck). L^{-1} was used to wash the activated carbon, removing and unclogging the pores. The process was concluded with drying the charcoal in an oven at 110 ± 5 °C for 24 h, resulting in the pequi peel activated carbon.

2.4 Biochar analysis

2.4.1 Approximate chemical analysis

The approximate chemical analysis was carried out following the procedures of the American Society for Tests and Materials (ASTM). The biomass was taken to the greenhouse, remaining for 12h at 105 °C to determine the humidity [17]. Then, this material was kept for 3 hours at a temperature of 600 °C to determine the ash content [18]. The volatile matter was measured with the aid of the muffle at 800 ± 10 ºC for 7 min, based on a dry sample of 1.0 g [19]. Through the difference between the ash content and volatile matter, the percentage of FC was determined.

2.4.2 Elementary analysis

The elementary analyzer (vario macro Cube - Hanau, Germany) was used to determine the elementary compositions (C, H, N and O). The Oxygen (O) content was obtained according to ASTM-D3176-15 [20].

2.4.3 Superior Heat Power (HHV)

To estimate the HHV content, the content of carbon (C), nitrogen (N), hydrogen (H), sulfur (E), oxygen (O) and ash (A) was previously measured. The determination of HHV values followed the standard of ASTM-D3176-15 [20] according to equation 3.

$$HHV\ \left(\frac{kj}{g}\right) = 0.3491 * C + 1.1783 * H + 0.1005 * S - 0.1034 * O - 0.0151 * N - 0.0211 * A \quad (3)$$

2.4.4 Surface Area Brunauer, Emmett and Teller - BET

The biochar samples (0.5 g) were taken to the Surface Area System and Porosimetry equipment (ASAP 2010 micro-merit model) to establish the N_2-BET surface

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area and the pore size arrangement. The diameter range used as standard was 0.35 to 300 nm for the pores and 0.01 to 3,000 m²/g in the surface area range, the treatment temperature was 30 to 350 °C.

2.4.5 Infrared Spectroscopy (FTIR)

Changes in functional groups were identified through FTIR analysis. Using a single beam Agilent Technologies spectrometer (Cary 630 FTIR), the samples were analyzed using a range from 500 to 4000 cm^{-1} with 0.5 nm increments. The samples were made in triplicates and the medium spectrum was used.

2.4.6 Determination of pH

The pH of raw biomass and biochars was determined with a pH meter (TECNAL, model 3MP, according to the NREL/TP-433-7965 method) [21] 1:20 (w/w) distilled water was added to the samples in order to form a homogeneous suspension and after 1.5 h the pH was determined.

2.5 Bio-oil Analysis

2.5.1 Determination of Bio-Oil Density

The bio-oil density was analyzed using a 10 mL glass pycnometer in a thermostatic bath at 20 °C.

2.5.2 Determination of Bio-Oil pH

For pH determination, 10 mL of bio-oil was inserted into the digital pH meter (TECNAL, Model 3MP).

2.5.3 Analysis by Gas Chromatography Mass Spectrometry (GC-MS)

With the aid of GC-MS QP2010 Plus equipment equipped with a capillary column Rtx-5MS WCOT (30 m × 0.25 mm x 0.25 µm), the organic and aqueous bio-oil fraction were separated. For the chromatographic separation, the planning for the use of temperatures was followed: for 1 min (isothermal), raised to 7 ºC min^{-1} at 100 ºC and then at 4 ºC min^{-1} at 320 ºC followed by 10 min at 320 ºC. The carrier gas used was helium at 1.90 mL/min. To obtain the mass spectra, the IEI mode (with ionization energy of 70 eV) was used.

III. RESULTS AND DISCUSSION

3.1 Physico – chemical characterization of pequi biomass

A previous study by the authors shows the results of the chemical analysis (Table 1) of the pequi (Caryocar brasiliensis Camb.) [22] residues, and were used as the basis for this work.

Table 1. Chemical analysis of the raw dry biomass

Component	Concentration ± SD/ (%)
AIL	20.44 ± 0.30
ASL	5.48 ± 0.40
TL	25.71 ± 0.75
Humidity	7.00 ± 0.20
Ashes	2.82 ± 0.20
CF	25.27 ± 0.80
Cellulose	36.3 ± 0.08
Hemicellulose	5.35 ± 0.06
Extractives	34.47 ± 0.08

SD: standard deviation; AIL: acid insoluble lignin; ASL: acid soluble lignin; TL: total lignin; CF: fixed carbon. Source: Scapin et al [22].

When charcoal is to be produced, the ratio of lignin, extracts and hemicellulose is inversely proportional. Lignin and Extractives are important in the conversion of biomass to coal, as high levels of these substances affect thermal stability and a higher value of energy released in the combustion process, thus contributing to better quality of coal [23]. The results of the total value of lignin (25.71%) and extractives (34.475) in this study are satisfactory. High rates of hemicellulose are undesirable to produce charcoal, as it causes greater thermal instability [24]. In this study, a low hemicellulose value of 5.35% was obtained.

3.2 Phrolysis

The yield of the pyrolysis process ranges from 30 to 70% for bio-oil and 15 to 50% for solid coal and depends on the type of reactor, the raw material and the operating conditions. Under the conditions of this study (30 minutes at 500 °C) the bio-oil yield is 20 to 40% and the biochar from 25 to 50% [25].

In this study, the pyrolysis process presented a yield of 30.5% bio-oil, of 34% biochar (Figure 1). The yield of bio-oil and biochar resulting from pyrolysis are related to fraction size, temperature and time [26]. When characterizing the seed pyrolysis products of pequi Miranda et al., [27], they obtained 40% charcoal and 43% bio-oil. The authors point out that the good results of bioproducts come from the degradation of lignin and extracts and emphasize that biomass is promising for the generation of heat and energy in the industry.

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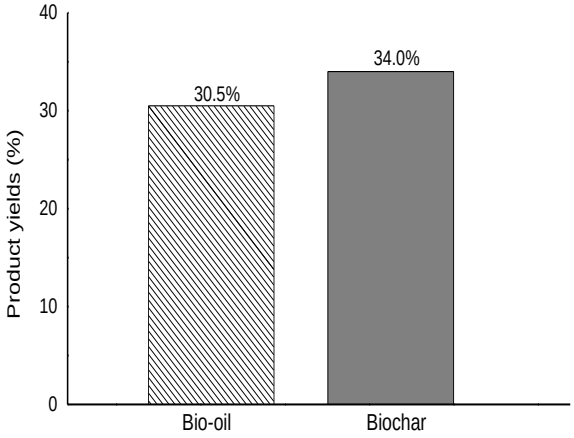

Fig 1: Yields of pyrolysis products

In the work developed by Bridgwater et al., [28] highlighted that the average biochar yield of slow pyrolysis residues varies from 30 to 35% in relation to the initial biomass, values close to those found in this study. The bio-oil yields presented in our research are compatible with the study by Lazzari et al.,[7] for coconut fiber (33%) and rice husk (30%). Silva [23] using pequi peel obtained a yield of 32.61% for biochar, Borba et al., [29] when studying the use of pequi peel biochar for glyphosate removal, identified a yield of 33.1%.

Maximizing the yields of biomass pyrolysis coal can be achieved with appropriate technology and operating conditions. Charcoal, with carbon content in the range of 80 to 90% and yields as high as 35%, can be obtained in a retort reactor. Even higher yields can be achieved by increasing the pressure of the carbonization process [30].

In their kinetic study Foong et al.,[25] highlighted in their study that, based on the calculation of the compound annual growth rate (CAGR) of 13.3% (2016-2024), the authors projected that the global demand for activated biochar by 2024, will be 5.1 million ton.

3.3 Biochar

The characteristics of the biochars (crude and activated) from the peel of the pequi are shown in Table 2. In this study, the potential use of biochars for use in agriculture and their properties were analyzed based on the revisions of the standards of the International Biochar Initiative - *IBI* (version 2.1) and European Biochar Certificate (EBC).

Table 2. Approximate analysis, elemental, pH, and caloric value of the biochar

Analyze (%)	Activated Biochar	Raw Biochar
Humidity	6.24 ± 0.001	5.4 ± 0.001
Ashes	9.01 ± 0.001	1.27 ± 0.001
MV	46.66 ± 1.34	59.07 ± 0.430
FC	38.09 ± 0.001	34.26 ± 0.001
pH	4.7 ± 0.001	9.5 ± 0.001
C	78.74 ± 0.226	71.57 ± 0.053
H	2.63 ± 0.1284	3.6 ± 0.009
N	1.66 ± 0.0298	1.49 ± 0.002
O	7.72 ± 0.0194	22.03 ±0.054
S	0.25 ± 0.668	0.18 ± 0.010
HHV (kJ. g^{-1})	29.59 ± 0.045	26.92 ± 0.033

VM: Volatile materials; FC: Fixed carbon; pH: Hydrogenionic potential; C: Carbon; H: Hydrogen; N: Nitrogen; O: Oxygen; S: Sulfur; HHV: Calorific Power.

According to *IBI* standards, the gross biochar produced is class 1, with organic carbon contents (C_{org}) > 60% falling into category "A". The carbon content may gradually increase due to the release of organic substances rich in hydrogen and oxygen during the pyrolysis and activation stages, but Costa et al., [16] found the opposite, after the process of activating the nut shell biochar with $ZnCl_2$, the carbon content decreases from 79.6% (biochar) to 78.4% in activated carbon. The activation of the pequi peel coal increased the carbon content, from 71.57% (raw coal) to 78.74% (activated carbon).

High carbon content contributes to better efficiency in energy conversion and gasification, due to the greater release of heat per unit mass of biomass [27]. Agbor et al. [30], in their review of biomass burning, highlight that biomass fuels have less carbon and nitrogen and more hydrogen and oxygen compared to fossil fuels. This relationship shows that biomass is less dense than fossil derivatives, however the results of the present study highlight the opposite, as the values of C (78.74%) and N (1.66%) are higher than H (2, 66%) and O (7.72%), demonstrating the potential of using the pequi peel biochar as an energy source.

After the activation process, it was observed that the ash and moisture contents also increased, in comparison to the raw biochar (Table 2). Regarding raw biomass (Table 1) reported by Scapin et al., [22] these

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levels are close, except for the ash content of activated carbon, which reached 9%.

The moisture content of the biochar must be low (3 to 10%) in order not to affect the potential for adsorption of activated carbon and to enable its commercial use, in addition high humidity values compromise the costs of transportation, drying, storage and handling of biomass [31-32]. Both moisture content in raw coal (5.4%) and activated carbon (6.24%) are within this range.

As well as humidity, the ash content cannot be high either, since high ash contents interfere with the yield of pyrolysis products, decreasing the liquid organic fractions and increasing the gas fractions. In his report on the raw biochar of the pequi Silva [23], found 5.19% for ash content, while Khuenkaeo & Tippayawong [34] found different values of ash for the raw coals, 1.66% for the coconut husk biochar and 7.22% for bamboo residue.

The pH values changed after the activation process. The raw biochar has a basic nature (9.5) and the activated biochar has a slightly acidic nature (4.7). Abreu et al., [35] obtained similar pH values for activated charcoal from sugarcane bagasse (4.62). Coals of an acidic nature have the potential to adsorb protons. This characteristic is relevant for use in the soil, as it increases the capacity of retaining nutrients and water in the soil due to the high capacity of cation exchange and surface area.

In short, Silva [23] highlights in his research that the pequi peel biochar has characteristics that promote beneficial changes in soil acidity, raising the pH, and reducing exchangeable aluminum, making it possible to use it as a soil corrector.

The calorific value of the biochar increased after activation, (>29 $kJ.g^{-1}$) demonstrating the potential of using pequi activated carbon as solid fuels. The calorific power of biochars (raw and activated) is greater than that of biomass in natura (Table 1), this is due to the presence of recalcitrant aromatic compounds that store more energy, due to the pyrolysis process [23-27]. In their research with the pequi core Miranda et al.,[27] obtained calorific value close to 25 $kJ.g^{-1}$. The low moisture content of the pequi peel contributes to the calorific value of the coals, favoring their energy use [38].

According to data from IBGE [3], 21,495t of pequi fruit were produced, 70% of the fruit corresponds to the skin, thus generating 15t of waste. With the biochar calorific value (29.59 $kJ.g^{-1}$), we obtain a potential of 443.85 $t/kJ.g^{-1}$ annually. Thus, the biochar of the pequi peel has great potential for energy production, in addition to the correct destination of the waste, it prevents the spread of diseases, odor and soil contamination due to improper destination [23].

The biochar of the pequi sample did not show satisfactory values of surface area (BET and Langmuir) and micropore size (Table 3) when compared with activated carbon from other biomasses. According to the guidelines for the certification of the biochar (European Biochar Certificate version 4.8), the minimum specific surface area required is >150 m^2/g [39]. In the present study, the minimum value required by the standard was not reached. Therefore, the activating agent $ZnCl_2$, was not efficient to increase the values of surface area and microporous size.

Table 3. BET, Surface area Langmuir and micropores the size of activated carbon from the peel of the pequi.

	BET area Surface (m^2/g)	Surface area Langmuir (m^2 / g)	Micropores of size (cm^3 / g)	Authors
Activated Biochar	30.3002 ± 0.3038	39.1146 ± 0.3639	0.023127	Authors, 2020.
Activated Biochar Comercial	597.33	-	0.22	Linhares et al., 2016.

After chemical activation of the pequi core biochar with potassium carbonate, Dias [41] found values of 54.03 (m^2/g) for BET surface area and 0.045 cm^3/g for pore volume and, just as the results found in this research, these values were also low.

3.4 FT – spectroscopy

FT-IR analysis (Figure 2) shows the spectrum of pequi biomass and biochars; indicating possible chemical transformations of the structure after pyrolysis and activation of the biochar.

Intense bands for the biochars produced were identified in regions between 3800 - 2700 cm^{-1} are related

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to the OH stretching vibration, possibly pointing to the existence of alcohols, phenols and organic acids [55].

Aldehyde and aliphatic compounds are identified in the raw biomass due to the elongation of CH, CH_2 and CH_3 in the bands between 3000 and 2800 cm^{-1} [41].

The presence of C=O (esters, organic acids and aldehydes) were attributed to the peaks of 1710 and 1720 cm^{-1} and the heteroaromatic compounds (CO) are in the bands between 1100 to 1200 cm^{-1} [41].

The bands close to 940 cm^{-1}, are attributed to the COC stretching in cellulose, these bands are sensitive to the amount of crystalline and amorphous cellulose [42]. The presence of phenolic peaks (RCH=CH_2 and aromatic rings) was mainly attributed to lignin and undegraded cellulose during pyrolysis, clearly demonstrating the phenolic nature of charcoal for all spectra, showing that their structures resisted and remain after the processes [55].

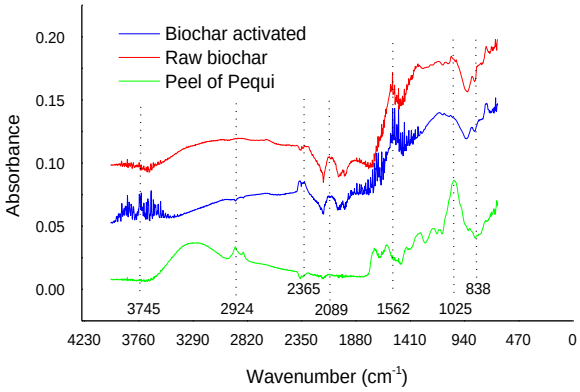

Fig.2: FTIR analysis of pequi biomass and biochars.

3.5 Bio-oil

Bio-oil consists of numerous compounds, among which acids, furans, phenols, alcohols, hydrocarbons, ketones, aldehydes and esters are highlighted. The recovery and use of bio-oil demonstrate the efficiency of the energy conversion of pequi peels [15].

In their survey on the chemical and physical characteristics of pequi, Oliveira et al., [43] reported that factors such as soil, water availability, fruit size and distance between trees interfere with the quality and quantity extracted from bio-oil, as well as its structural and operational variables.

The main compounds identified in the bio-oil (>1%) are described in Table 4. Among the main components of the bio-oils found in the pequi biomass are acids, aldehydes, phenols and hydrocarbons as shown in Figure 3. These compounds were also the main products observed in other studies [41-45].

The vaccenic acid (21.23%), found in a percentage higher than the others recovered bio-oil, a fatty acid is used in fast food industries [44]. Another compound found in large quantities was palmitic acid or hexadecanoic acid (19.73%), very common as a dietary supplement and fortifying agent in dairy products [45].

Phenolic and aldehyde compounds from bio-oil can be used as meat browning and flavoring agents [47]. Within the bio-oil components of the pequi peel, we obtained 13.4% aldehydes and 12.7% phenols.

Tsai et al., [48] studied the coconut oil fiber bio-oil, the compounds found mostly were: 1,2-benzenediol (8.6%), phenol (7.8%), acetic acid (3.6 %), 2,6-dimethoxyphenol (2.8%) and 3-methyl-1,2 benzenediol (2.7%).

When researching the production of bio-oil from rice husk and straw, bamboo, cane bagasse and neem husks, Gautam and Chaurasia [49], highlighted that the presence of CH, C=C, alcohols and phenolic compounds in the bio-oil obtained from all biomass species leads to the possibility of being used as fuel.

The composition of bio-oil is influenced by the raw material and temperature. According to Lyu et al., [51] high temperatures lead to the formation of aldehydes and acids, decreasing phenols. As shown in Figure 3, we can observe this behavior, higher values were obtained for acid (50.7%) and aldehyde (13.74%) and less for phenol (12.7%), hydrocarbon (7.44%) and alkane (1.51%).

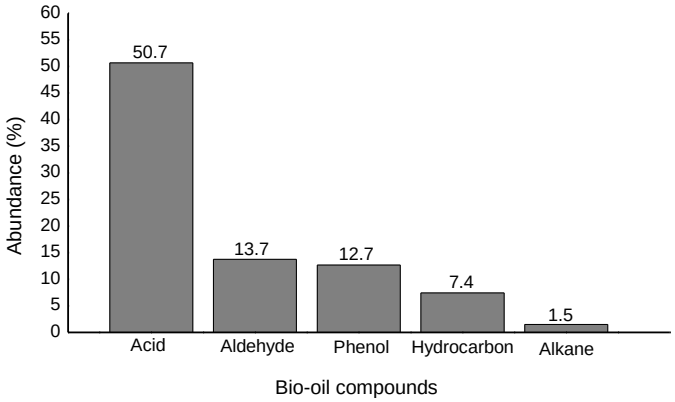

Fig.3: Chemical composition of bio-oils from pequi peel.

Bio-oils were also evaluated for their acid/alkaline nature. The recorded pH value is considered acid. The pH of the bio-oil obtained from the lignocellulosic biomass generally varies between 2 and 3 (acid), usually due to the presence of carboxylic acids.[41] The density of the bio-oil obtained was 1.09 g/cm^3, and is related to the water content

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present in the liquid. Mohan et al.,[51] when reviewing biomass pyrolysis, highlight the density value of woody biomass bio-oil (1.2 g/cm³), whereas Santos et al., [56] obtained 1.05 g/cm³ of density for sugar cane straw. The density of fossil oil is 0.75-1.0 g/cm^3, so the average density value of bio-oil becomes potential to replace fossil oils, employing some processes to bring the density even closer so that can be used on a commercial scale [52].

IV. CONCLUSION

The yields of biochar (34%) and bio-oil (30.5%) are satisfactory and were obtained through pyrolysis, making it a good method for treating the pequi's raw waste. Biochars (Raw and Activated) can potentially be used as solid fuel in industries due to their high calorific value and carbohydrate content, associated with low moisture and ash content. Activated biochar, on the other hand, showed potential to be used in agriculture as a fertilizer, due to low pH values associated with significant amounts of nitrogen.

The chemical compounds of high added value present in bio-oil can be used in several areas of the industry, including vaccenic acid, palmitic acid and furfural acid, highlighting the value of the biomass that would be discarded.

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