



## *Pachira aquatica* fruits shells valorization: renewables phenolics through analytical pyrolysis study (Py-GC/MS)

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**ABSTRACT:** *This research valorized *Pachira aquatica* Aubl.'s fruit shells (PAS) through its energetic characterization and flash pyrolysis for biofuels or chemicals production. The characterization was performed through proximate and ultimate analysis, bulk density, higher heating value (HHV), hemicellulose, cellulose and lignin content, thermogravimetric analysis and absorption spectra in the infrared region obtained by Fourier-transform infrared spectroscopy technique (FTIR). The analytical flash pyrolysis was performed at 500°C in a Py-5200 HP-R coupled to a gas chromatograph (Py-GC/MS). The PAS biomass presents potential for thermochemical energy conversion processes due to its low moisture and ash content, 76.90% of volatile matter, bulk density of 252.6 kg/m<sup>3</sup> and HHV of 16.24 MJ/kg. Flash pyrolysis products are mostly phenols or light organic acids derived from the decomposition of polysaccharides. Results confirmed the potential of PAS to produce bio-phenolics, such as 4-methoxyphenol which is an important active ingredient for skin depigmentation used in drugs and cosmetics, and as phenolic extract that can be used as a precursor to resins, applications that convert this forest waste into bio products for industry into a green circular economy.*

**Key words:** *munguba, energy characterization, lignocellulosic biomass, forest wastes, analytical flash pyrolysis.*

### Valorização das cascas dos frutos da *Pachira aquática*: fenólicos renováveis através de estudo analítico de pirólise (Py-GC/MS)

**RESUMO:** *Este trabalho teve como objetivo a valorização das cascas dos frutos da *Pachira aquatica* Aubl. (PAC) através da sua caracterização energética e pirólise flash para produção de biocombustíveis ou produtos químicos. A caracterização foi realizada através de análises imediata e final, densidade aparente, poder calorífico superior (PCS), conteúdos de hemicelulose, celulose e lignina, análise termogravimétrica e espectros de absorção na região do infravermelho obtidos pela técnica de espectroscopia no infravermelho com transformada de Fourier (FTIR). A pirólise flash analítica foi realizada a 500 °C em equipamento Py-5200 HP-R acoplado a um cromatógrafo à gás (Py-GC/MS). A biomassa das PAC apresenta potencial para processos de conversão termoquímica de energia devido ao seu baixo teor de umidade e cinzas, além de 76,90% de materiais voláteis, densidade aparente de 252,6 kg/m<sup>3</sup> e PCS igual a 16,24 MJ / kg. Os produtos da pirólise rápida são principalmente fenóis ou ácidos orgânicos leves derivados da decomposição de polissacarídeos. Os resultados confirmam o potencial das PAC para produzir bio-fenólicos, como o 4-metoxifenol que é um importante ingrediente ativo para despigmentação da pele usado em medicamentos e cosméticos, e como extrato fenólico que pode ser usado como precursor de resinas. Estas aplicações convertem esses resíduos florestais em produtos biológicos para a indústria em uma economia circular verde.*

**Palavras-chave:** *munguba, caracterização energética, biomassa lignocelulósica, resíduos florestais, pirólise rápida analítica.*

## INTRODUCTION

The use of lignocellulosic biomass as energy source has aroused worldwide interest due to its economic potential and environmental concerns of reducing the dependence on fossil fuels and emissions of polluting gases (ODETOYE et al., 2019). Biomass can be defined as any resource of organic origin, renewable

and possible to be applied in energy generation processes (MENDONÇA JUNIOR et al., 2020). In addition, it can also be exploited to generate other products with added value (CARVALHO et al., 2020).

Different biomasses, such as wood (VARMA et al., 2019), agricultural wastes (HAWASH et al., 2017) and microalgae (LI et al., 2019), have been studied in the literature with the goal of obtaining

bio products or biofuel through different processes of energy conversion.

Among the different biomass processing technologies for energy purposes, pyrolysis is noteworthy, which is characterized by the thermal decomposition of organic materials in the absence of oxygen producing a solid fraction (biochar), non-condensable gases and condensable liquids (bio-oil), which are precursor to chemicals, fertilizers, liquid fuels and hydrogen (VALLE et al., 2019; CAMPUZANO et al., 2019; TAHIR et al., 2019; HUANG et al., 2019; ARAVIND et al., 2020).

Bio-oil, the main product of fast pyrolysis, is a complex organic mixture of water, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, furans, alkenes, nitrogen and oxygen compounds, that present high chemical instability, viscosity and low energy potential needing upgrading to improve its energetic use (HU & GHOLIZADEH, 2019). Several alternatives for bio-oil valorization include physical treatments, such as fractional condensation and thermal treatment; catalytic pyrolysis of biomass; the ex-situ catalytic cracking of volatile compounds resulting from biomass pyrolysis, aiming the production of olefins and aromatics; hydrodeoxygenation (HDO) of pyrolysis products to produce fuels; the cracking of crude bio-oil in projected units, aiming specific selection of compounds; and processing in fluidized catalytic cracking units (FCC) (VALLE et al., 2019; CAMPUZANO et al., 2019).

Among different sources of biomass, lignocellulosic waste should be highlighted since its use as energy source in addition to add value to biomass still reduces the environmental liability of its inappropriate disposal. In this way *Pachira aquatica* Aubl. (PA), popularly known as Munguba, Castanheira-do-Maranhão or Cacau-Selvagem deserves attention due to high waste production after seeds processing.

Native from the Amazon forest, PA can be reported from southern Mexico to the north of Brazil and is mostly used in urban landscaping, restoration of wetlands, and degraded soils and forests (JORGE & LUZIA, 2012; RAISER et al., 2020). The PA tree produces seeds rich in lipids with high productivity which present potential for exploration for foods, pharmaceuticals, medicine, cosmetics and biofuels industries (JORGE & LUZIA, 2012; SILVA et al., 2015; RAISER et al., 2018; OLIVEIRA et al., 2019; RODRIGUES et al., 2019; SILVA et al., 2020; RAISER et al., 2020).

Although, there is a high potential use of the oil from *Pachira aquatica* seeds, the fruit shells

are still wastes with few defined applications. There are no reports of their shell's utilization or research on its energy potential. Thermochemical processes, such as pyrolysis, can promote a sustainable application of this biomass, allowing the generation of renewable energy and chemical products, adding value to the production chain of this species.

High energy density, low ash and moisture content, and high energy recovery in dry basis are among the most important characteristics for biomass application in thermochemical processes. It is possible to obtain a bio-oil yield up to 75%, 15 to 25% of solids (coal), and 10 to 20% of gases based on the initial dry mass of the feedstock, through flash pyrolysis using suitable parameters and reactors (MADHU et al., 2018; PIMENTA et al., 2018).

This study investigated the potential for sustainable use of *Pachira aquatica* residues from Brazil to produce bio-oil via flash pyrolysis. The present study carried out an extensive physical-chemical characterization of *Pachira aquatica* fruits shells and identified flash pyrolysis products for evaluate the potential for biofuels or bioproducts recovery.

## MATERIALS AND METHODS

### *Biomass preparation*

The *Pachira aquatica*'s fruits (Figure 1) were collected from six trees present in Natal city, Rio Grande do Norte, Brazil. After being collected, the fruits were sun-dried to lose excessive moisture, and the shells were separated from the seeds and grinded in a knife mill.

The granulometric distribution of the biomass was performed through the screening test according to standard NBR NM 248/2003. The selected granulometry, between 0.250 e 0.149 mm, was analyzed in a laser granulometer CILAS ANALYZE 1090 in triplicate. The samples were dispersed in liquid medium using Extran soap and Ultrasonic bath in order to prevent the agglomeration of the particles.

The *Pachira aquatica* fruits shells (PAS) collected in different trees have been analyzed individually to evaluate the difference between its bulk density, moisture, volatile, ash, fixed carbon content and estimated Higher heating value (HHV). A mixture of all PAS analyzed has been also considered as sample to evaluate its energetic potential to pyrolysis application.

### *Biomass characterization*

The bulk density was performed in triplicate according to standard ASTM E873-

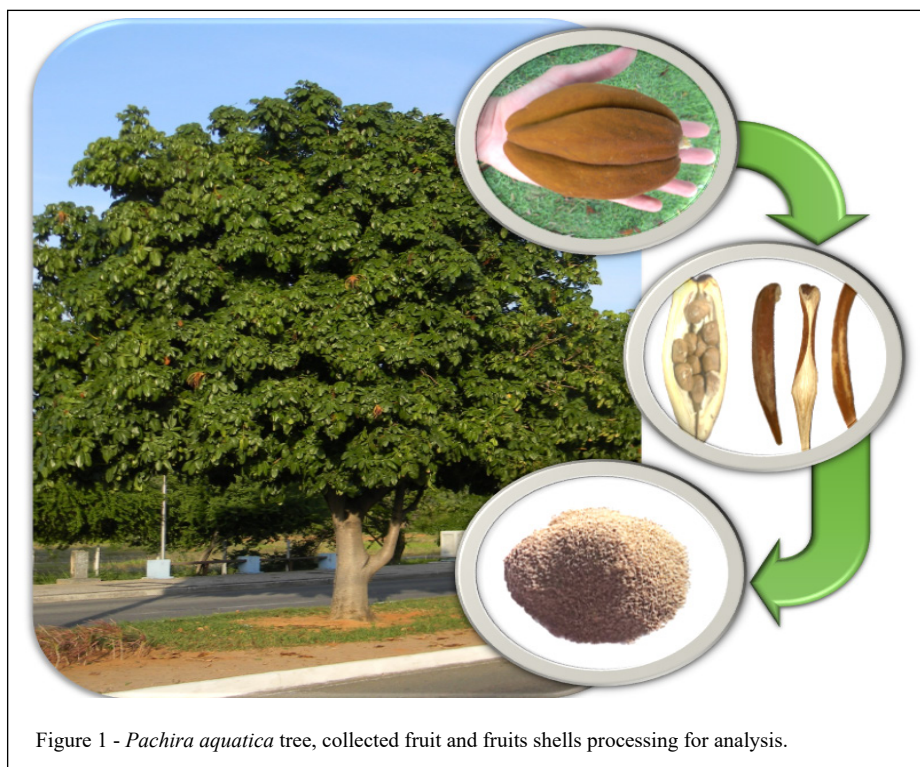


Figure 1 - *Pachira aquatica* tree, collected fruit and fruits shells processing for analysis.

82 (2006) measuring the mass of the sample (g) and dividing it by the volume (cm<sup>3</sup>) occupied in a graduated test tube. The proximate analysis was developed according to standards ASTM E871-82 (2006), ASTM E872-85 (2006) and ASTM E1755-01 (2007) to determine the moisture, volatile matter and ash content, respectively. The fixed carbon content was quantified by equation 1.

$$\% \text{ Fixed Carbon} = 100 - (\% \text{ Moisture} + \% \text{ Volatile} + \% \text{ Ash}) \quad (1)$$

The ultimate analysis of biomass was determined from correlations with the proximate analysis according to the model proposed by PARIKH et al. (2007), following the Equations 2, 3 and 4.

$$C (\%) = 0.637(\text{Fixed Carbon}) + 0.455(\text{Volatiles}) \quad (2)$$

$$H (\%) = 0.052(\text{Fixed Carbon}) + 0.062(\text{Volatiles}) \quad (3)$$

$$O (\%) = 0.304(\text{Fixed Carbon}) + 0.476(\text{Volatiles}) \quad (4)$$

Where C is the percentage of Carbon, O is the percentage of oxygen and H is the percentage of hydrogen.

The cellulose and hemicellulose content were determined through acid detergent fiber (ADF) and neutral detergent fiber (NDF) tests following the methodology proposed by SOEST & WINE (1967). In order to determine the lignin content, Klason method (SOEST & WINE, 1967) was applied directly.

Thermal analysis of the biomass was performed using a thermogravimetric balance Q600 SDT from TA Instruments® at 30 to 900 °C, heating rate of 5 °C.min<sup>-1</sup>, synthetic air and N<sub>2</sub> flow of 100 mL.min<sup>-1</sup>, using 10 mg of biomass. The absorption spectra at the infrared region was obtained by Fourier Transform Infrared Spectroscopy (FTIR) in a spectrophotometer Shimadzu IRPrestige-21®, using potassium bromide (KBr) as dispersing agent for preparation of pellets with a concentration of 1% in relation to the sample mass. The spectrum was obtained in the region 4000-400 cm<sup>-1</sup> using the transmittance mode.

The Higher heating value (HHV) for the biomass mixture sample analyzed was determined using a calorimeter bomb according to standard ASTM E711-87 (1987). The HHV of the samples of the different trees was estimated based on the correlation equation with the proximate analysis proposed by PARIKH et al. (2005), according to equation 5:

$$\text{HHV} = 0.3536 (\text{Fixed Carbon}) + 0.159 (\text{Volatiles}) - 0.0078 (\text{Ash}) \quad (5)$$

#### Pyrolysis

The pyrolysis was performed at 500 °C, 10 °C/ms, in a Py-5200 HP-R pyrolyzer from CDS Analytical

coupled to a gas chromatograph, using 1 mg of biomass placed between the top and bottom of quartz wool in a quartz tube (25.38 mm x 1.75 mm ID). The pyrolysis vapors were carried at 50 mL.min<sup>-1</sup> of N<sub>2</sub> (99.999%) to a Tenax trap for desorption at 300 °C, transferred through a transfer line heated at 300 °C and injected at split mode of 1:30 in a GC-MS/MS 3900 VARIAN. The products were separated by a VF-5ms column (30 m × 0.25 mm x 0.25 µm) using 1 mL.min<sup>-1</sup> of He (99.999%) as the carrier gas. The column oven temperature program was as follows: constant temperature of 40 °C for 4 min, 40–280 °C at 10 °C min<sup>-1</sup>, 280 °C constant for 14.5 min. The identification of the chromatographic peaks was performed by spectral similarity greater than 85%, after a detailed analysis of each spectrum using the NIST commercial library.

## RESULTS AND DISCUSSIONS

The *Pachira aquatica* fruits shells (PAS) presented 90% of the particles with a diameter of 112.9 µm according to the laser granulometric analysis. The particle size distribution plays an important role in energy conversion processes, since the smaller the size of the biomass particles the greater is the heat transfer and devolatilization, altering the kinetic of decomposition reaction (EKINCI et al., 2020). The bulk density of PAS is between 226.9 and 291.0 kg.m<sup>-3</sup>, as shown in table 1. This variable is related to the energy density of biomasses, influencing their thermal behavior (EVARISTO et al., 2016).

The characterization results of dry basis biomass (Table 1) indicated suitable values for thermochemical conversion processes: low moisture and ash content, high volatiles content, and a moderate bulk density. The moisture reduces the HHV and

inhibit ignition because an amount of energy is used to dry the biomass (SAMADI et al., 2020; NUNES et al., 2020). In addition, high moisture content can damage the storage, causing fungal proliferation and material degradation, as well as increasing transport costs.

The PAS presented between 75.35 and 77.95% of volatile matter, values close to those observed for others lignocellulosic biomass (BARBOSA et al., 2019; SILVA et al., 2019; NUNES et al., 2020). The high volatiles content is an important characteristic for biomass application in pyrolysis processes, because it indicated that a large fraction of biomass is converted into steam and gas when heated, which leads to the possibility of high yield of bio-oil (SILVA et al., 2019).

The ash content around 5% observed is considered a moderate value for thermochemical conversion application. High ash content (above 10%) is undesired for thermochemical process because can cause problems, such as reduced burn rate, increased fouling, slag formation and corrosion in pyrolysis reactors (VARMA & MONDAL, 2017). The fixed carbon content reported in PAS has between 15.6 and 16.1% is equivalent to observed for the macaúba epicarp (16.1%) (EVARISTO et al., 2016); however, higher than sugarcane bagasse (7.6%), corn stover (3.3%), pineapple crown leaves (7.1%) and cotton stalk (13.3%) (SILVA et al., 2019).

No significant difference has been observed on characterization results of PAS samples from distinct location and the mixture of them shown at table 2. According to ultimate analysis its molecular formula is CH<sub>1.55</sub>O<sub>1.04</sub>N<sub>0.01</sub> with high O content, which is related to their lignocellulosic structure of 18.6% of hemicellulose, 45.2% cellulose and 10.8% lignin (Table 2).

Table 1 - Energetic characterization of *P. aquatica* fruits shells harvest in different location.

Matrices	-Physical Characterization-	-Immediate Analysis-				-Higher Heating-
	Bulk Density (kg/m <sup>3</sup> )	Moisture (%)	Volatile Matter (%)	Ash (%)	Fixed Carbon* (%)	Higher Heating Value** (MJ/kg)
1	226.9±0.003	6.50±0.24	77.36±1.47	5.99±0.05	10.14	15.60
2	237.2±0.002	6.80±0.33	77.95±0.30	4.08±0.08	11.16	16.07
4	254.2±0.004	6.55±0.78	75.83±0.25	5.35±0.09	12.28	16.12
11	291.0±0.007	6.67±0.29	75.64±0.49	5.22±0.14	12.46	16.16
12	260.9±0.004	6.43±0.19	75.35±0.13	5.67±0.14	11.89	16.14
13	259.2±0.001	6.15±0.95	76.25±0.61	6.09±0.18	11.51	15.91

\*Fixed carbon calculated by difference.

\*\*Estimated according to PARIKH et al. (2005).

Table 2 - Characterization of *Pachira aquatica* fruit shells biomass analyzing the mixture homogeneous.

Characterization	Content
Immediate Analysis (%)	
Moisture	6.58 ± 0.19
Volatiles	76.90 ± 0.39
Ash	5.57 ± 0.08
Fixed carbon*	11.43
Bulk density (kg/m <sup>3</sup> )	252.6 ± 0.003
Higher heating value (MJ/kg)	16.24
Hemicellulose (%)	18.62
Cellulose (%)	45.23
Lignin (%)	10.80
Elemental analysis (%)**	
C	42.05
H	5.33
O	39.85

\*Percentage of fixed carbon calculated by difference.

\*\*Estimated according to the model proposed by PARIKH et al. 2007.

The low lignin content confirmed the low fixed carbon value showed in table 1, and the high O content (39.85%) is probably because of the C-O bonds found in higher concentrations in the polysaccharides. The PAS presented HHV (16.2 MJ/kg) higher than other observed lignocellulosic biomasses applied in combustion for energy generation, such as cashew nuts

(14.3 MJ/kg), rice husk (15.9 MJ/kg), bean shells (15.1 MJ/kg) and elephant grass (15.6 MJ/kg) (BRAGA et al., 2014; OLIVEIRA et al., 2019). The HHV value also confirmed the potential of this biomass for combustion.

The FTIR spectrum of PAS shown in figure 2 present an axial deformation of -OH bond in the range of 3400 cm<sup>-1</sup> related to -OH groups of phenols, cellulose and hemicellulose (VARMA & MONDAL, 2017; SILVA et al., 2018). The axial deformation of the methylene group has been observed at 2924 cm<sup>-1</sup> and axial vibrations of the C<sub>sp</sub><sup>2</sup>-H bonds of the aromatic rings and the C=C, usually associated with lignin, has been observed at 1612 cm<sup>-1</sup> (VARMA & MONDAL, 2017; SILVA et al., 2018). The oxygen presence has been also observed at C-O bonds, mostly from cellulose and hemicellulose, reported at 1000 to 1200 cm<sup>-1</sup> (VARMA & MONDAL, 2017; SILVA et al., 2018).

The thermal behavior of biomass of PAS was evaluated using thermogravimetric analysis. The TG curve represents the changes in mass related to the increase in temperature, while the DTG curve represents the loss of mass that occurs as a function of temperature (REIS et al., 2019). Figure 3A showed a combustion process, presenting the occurrence of four main mass loss events. The first one occurs in the range of 30 to 130 °C and corresponds to approximately 6.5% of mass loss associated to moisture release (VARMA & MONDAL, 2017; REIS et al, 2019). The second event is evidenced by a more expressive mass loss of 62%, showed

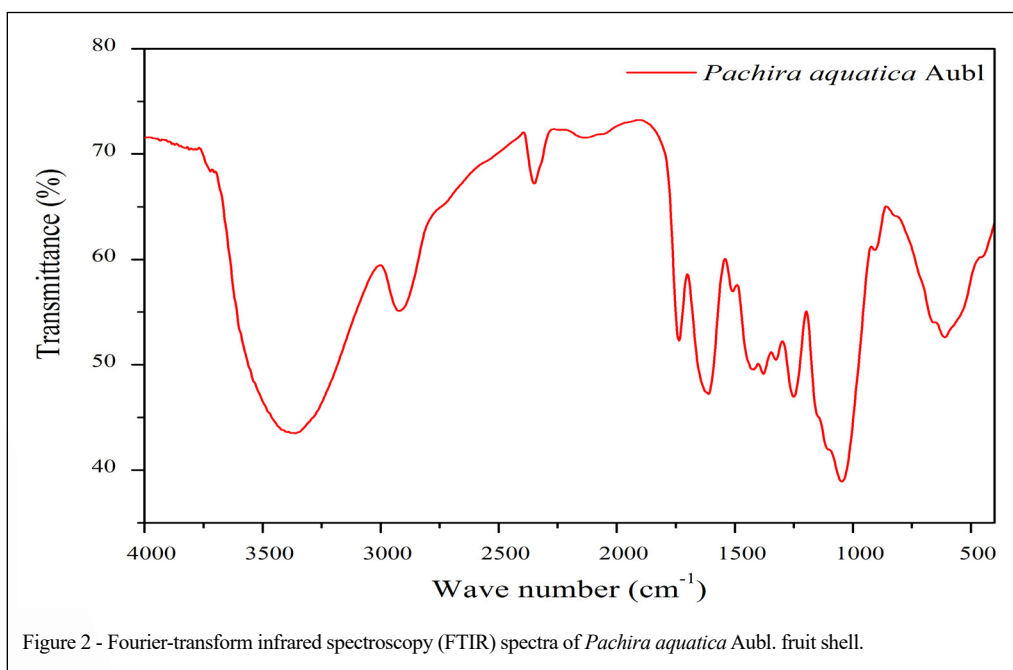


Figure 2 - Fourier-transform infrared spectroscopy (FTIR) spectra of *Pachira aquatica* Aubl. fruit shell.

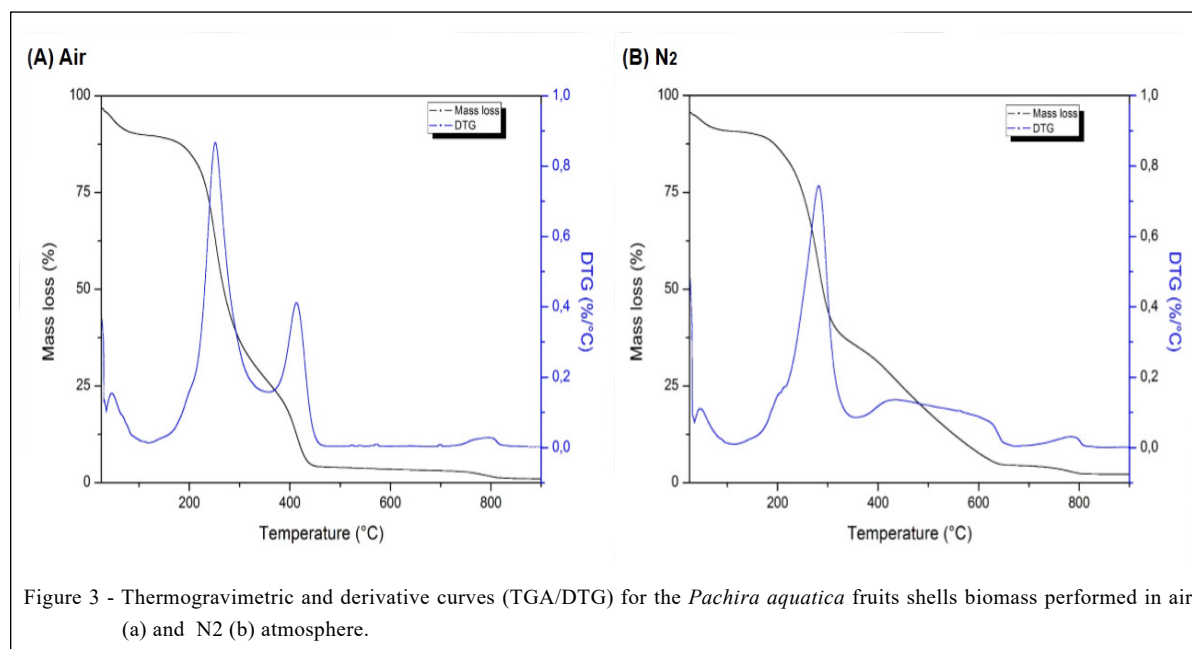
by DTG between 130 to 350 °C, associated to the degradation of hemicellulose, part of cellulose and lignin. Hemicellulose is a compound that presents low thermal stability when compared to cellulose and lignin, and commonly decomposes under temperatures in the range of 220 to 315 °C (VARMA & MONDAL, 2017; REIS et al., 2019; CALIXTO et al., 2021). The third occurs between 350 and 450 °C, associated to the thermal degradation of cellulose with 23% of mass loss. The cellulose presents a complete degradation in the range of 280 to 360 °C, and it is more stable than the hemicellulose due to the presence of hydrogen bonds, which promote a strong interaction between the cellulose chain (VARMA & MONDAL, 2017; SILVA et al., 2018; REIS et al., 2019). The last event is defined by the decomposition of lignin, which occurs slowly, overlapping the other events due to the polyaromatic characteristic of this component. Lignin presents a complex molecular structure, formed by phenylpropane units, which justifies its higher thermal resistance (SILVA et al., 2018; REIS et al., 2019). It was observed that after 450 °C there was a decrease of the degradation process of the biomass, which remained stable until 750 °C, confirming the low ash content (~3%) of PAS.

Figure 3B shows the pyrolysis process, in which 4 main mass loss events can be observed. The first between 30 and 120 °C, evidenced by a mass loss of 6.5%, associated to moisture. The second, from 120 and 360 °C, associated to degradation of hemicellulose

and cellulose, representing 55% of mass loss. The third event has been observed between 360 and 670 °C is due to the decomposition of residual cellulose, but also continuous lignin degradation (VARMA & MONDAL, 2017; SILVA et al., 2018). The last one is related to a small mass loss occurring between 670 and 840 °C, associated to the fixed carbon decomposition.

The flash pyrolysis result of PAS is presented in the chromatogram shown in figure 4, as well as the main peaks identified listed in table 3. Approximately 49 oxygenated compounds were identified (Table 3) in the chromatogram of flash analytical pyrolysis of PAS, including phenols, ketones, alcohols, short-chain oxygenated compounds (C<sub>1</sub>-C<sub>4</sub>), such as acetic acid, and few nitrogenated compounds. The C<sub>1</sub>-C<sub>4</sub> is the major class (49%) between identified compounds, which are resulted by degradation reactions responsible for desmetilation, decarbonilation, that result in organic acid, such as acetic acid, formic acid, methyl acetate. The identified ketones, furans and alcohols may be associated with the decomposition of cellulose and hemicellulose as primary pyrolysis products, while the high phenolic compounds yield can be associated to secondary pyrolysis products and depolymerization of lignin and protein.

In figure 5, the identified compounds were separated by class. Among the PAS identified pyrolysis products volatiles, 25% are phenolic compounds, being 21% of methoxy kind. The mequinol that are an important active ingredient in



drugs used for skin depigmentation represents 6.2% of products. Others compounds such as acetate-4-methoxy-phenol, eugenol, 2,6-dimethoxyphenol, 2-methoxy-4-(1-propenyl)-phenol and phenol, have been identified.

Investigating fifteen different types of biomass, Lazzari et al. (2018) observed that a large amount of phenolic compounds was identified in all the analyzed samples. It was observed that the predominantly phenolic composition in the bio-oils obtained from coconut fiber (CF), rice husks (RH), peach cores (PC), peanut husks (PS), Eucalyptus sawdust (ES), bagasse from sugar cane (SCB) and pineapple leaves (PL) are due to the lignin content present in these biomasses (LAZZARI et al., 2018).

The characterization of the bio-oil obtained from the biomass pyrolysis of sugar cane found that phenols were the main class of compounds identified, suggesting its application as a raw material for the chemical industry (BARROS et al., 2018).

The high content of phenolic compounds in the bio-oil makes this product potential for the synthesis of phenol-formaldehyde (PF) resins (VALLE et al., 2019), suggesting that it can be applied in substitution to petroleum derivatives being an alternative to valuation of *Pachira aquatica*'s shells valuation.

Phenol is an important building block with relevant commercial applications; its derivatives

can be used in textile and automotive industry, synthetic polymers, adhesives, pesticides, herbicides, insecticide and fungicide (LAZZARI et al., 2016; VARMA & MONDAL, 2017). The current main route for phenol production is the oxidation of cumene and benzene, non-renewable petroleum-based chemicals that causes environmental pollution and climate change emissions. The flash pyrolysis of the *Pachira aquatica* fruits shells can be a greener alternative for phenolics production and partial substitution of phenols derived from petroleum.

Although, the extraction of compounds of interest from the bio-oil is possible, there is a representative fraction that remains not taken advantage of and recent literature suggested that the improvement of the bio-oil obtained from the biomass pyrolysis is fundamental for the consolidation and industrial implantation of this product and its derivatives (VALLE et al., 2019). Among the main valuation methods for upgrading bio-oil, catalytic cracking and hydrodeoxygenation stand out (ALVAREZ et al., 2019; VALLE et al., 2019; BARBOSA et al., 2019).

Therefore, it is suggested to carry out new studies to improve and make it technically and economically feasible the extraction and application of bio-oil from *Pachira aquatica* Aubl.'s fruit shells pyrolysis.

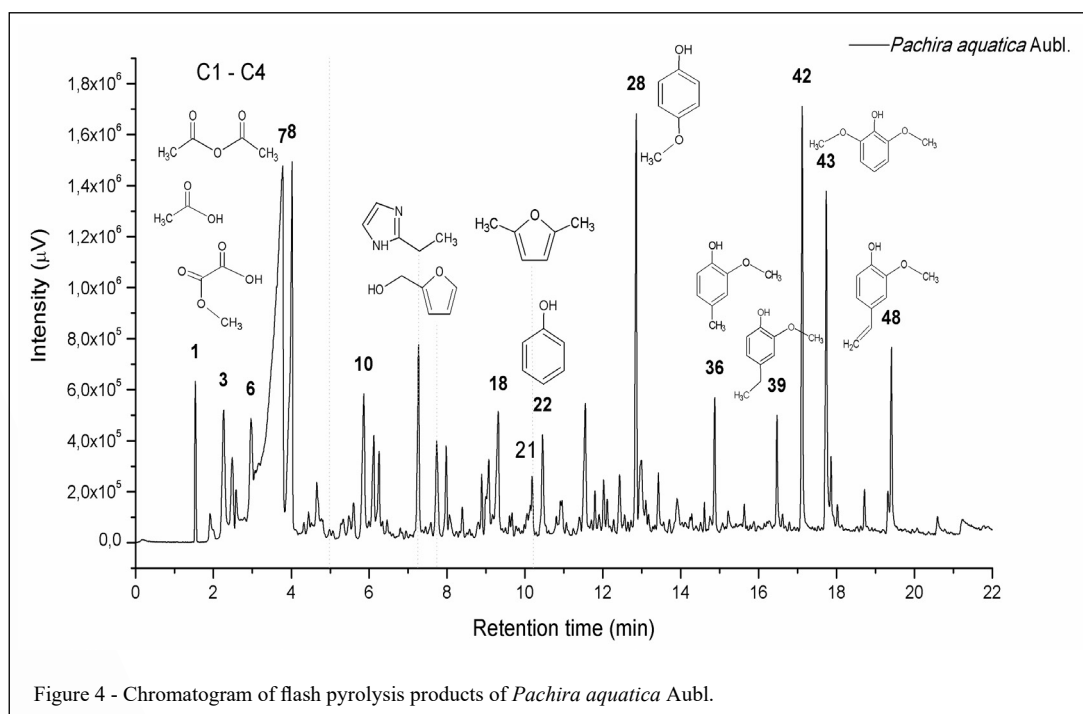
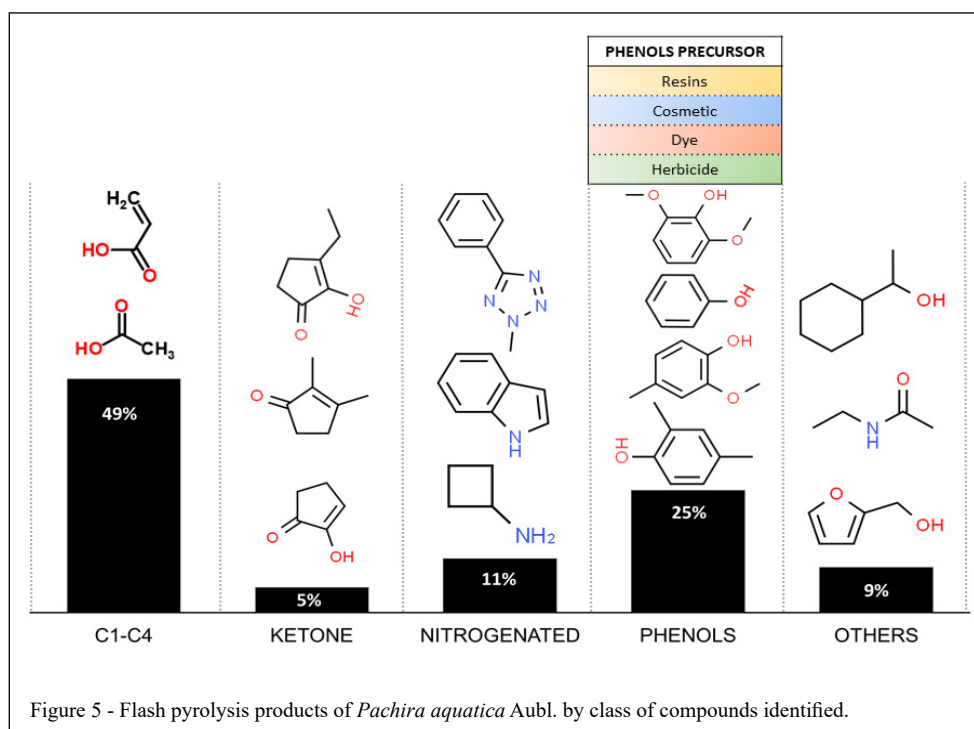


Table 3 – List of flash pyrolysis products of *Pachira aquatica* Aubl.

Peaks	Retention Time (min)	-----Compound Identified-----	-Molecular Formula-	Area/mg (10 <sup>5</sup> )	-----Class-----
1	1.53	C <sub>1</sub> -C <sub>4</sub>		11.81	Oxygenated
2	1.92	C <sub>1</sub> -C <sub>4</sub>		5.11	Oxygenated
3	2.26	C <sub>1</sub> -C <sub>4</sub>		21.37	Oxygenated
4	2.48	C <sub>1</sub> -C <sub>4</sub>		10.67	Oxygenated
5	2.58	C <sub>1</sub> -C <sub>4</sub>		4.14	Oxygenated
6	2.97	C <sub>1</sub> -C <sub>4</sub>		11.93	Oxygenated
7	3.78	C <sub>1</sub> -C <sub>4</sub>		195.8	Oxygenated
8	4.02	C <sub>1</sub> -C <sub>4</sub>		61.91	Oxygenated
9	5.6	3-Propylcyclopentene	C <sub>8</sub> H <sub>14</sub> (110)	3.94	Hydrocarbon
10	5.86	Cyclobutylamine	C <sub>4</sub> H <sub>9</sub> N (71)	22.70	Nitrogenous
11	6.12	N-ethylacetamide	C <sub>4</sub> H <sub>9</sub> NO (87)	11.37	Acetic Acid
12	6.25	Cyclobutylamine	C <sub>4</sub> H <sub>9</sub> N (71)	7.67	Nitrogenous
13	7.74	2-Furanmethanol	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub> (98)	14.50	Furan
14	7.98	Acetic anhydride	C <sub>4</sub> H <sub>6</sub> O <sub>3</sub> (102)	8.94	Anhydride
15	8.4	2-cyclopentene-1,4-dione	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub> (96)	2.38	Ketone
16	8.89	Cyclopentene	C <sub>5</sub> H <sub>8</sub> (68)	4.94	Hydrocarbon
17	9.07	2-Propanoic acid, methyl ester	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> (86)	12.36	Carboxylic Acid
18	9.31	2-Hydroxy-2-cyclopenten-1-one	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub> (98)	17.82	Ketone
19	9.6	1-Cyclohexylethanol	C <sub>8</sub> H <sub>16</sub> O (128)	1.01	Alcohol
20	9.67	2-Cyclohexen-1-one	C <sub>6</sub> H <sub>8</sub> O (96)	1.60	Ketone
21	10.18	2,4-Dimethylfuran	C <sub>6</sub> H <sub>8</sub> O (96)	3.34	Furan
22	10.46	Phenol	C <sub>6</sub> H <sub>6</sub> O (94)	14.03	Phenols
23	11.8	2,3-Dimethyl-2-cyclopenten-1-one	C <sub>7</sub> H <sub>10</sub> O (110)	3.14	Ketone
24	12.02	2-Methylphenol	C <sub>7</sub> H <sub>8</sub> O (108)	4.54	Phenols
25	12.12	2-Hydroxy-3,4-dimethyl-2-cyclopenten-1-one	C <sub>7</sub> H <sub>10</sub> O <sub>2</sub> (126)	2.38	Ketone
26	12.43	4-Methylphenol	C <sub>7</sub> H <sub>8</sub> O (108)	7.09	Phenols
27	12.56	3-Ethyl-2-cyclopenten-1-one	C <sub>7</sub> H <sub>10</sub> O (110)	0.94	Ketone
28	12.87	4-Methoxyphenyl acetate	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub> (166)	41.87	Phenols
29	13.1	4,5-Dimethyl-2-cyclohexen-1-one	C <sub>8</sub> H <sub>12</sub> O (124)	1.53	Ketone
30	13.43	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	C <sub>7</sub> H <sub>10</sub> O <sub>2</sub> (126)	5.33	Ketone
31	13.9	2,4-Dimethylphenol	C <sub>8</sub> H <sub>10</sub> O (122)	5.81	Phenols
32	14.28	2,3-Dimethylphenol	C <sub>8</sub> H <sub>10</sub> O (122)	2.14	Phenols
33	14.51	2,4-Dimethylphenol	C <sub>8</sub> H <sub>10</sub> O (122)	0.94	Phenols
34	14.61	4-Methoxy-3-methylphenol	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub> (138)	2.27	Phenols
35	14.75	2-Methoxy-4-methylphenol	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub> (138)	1.22	Phenols
36	14.87	2-Methoxy-4-methylphenol	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub> (138)	11.83	Phenols
37	15.22	1,2-Benzenedimethanol	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub> (138)	2.30	Phenols
38	15.64	2-Ethyl-6-methylphenol	C <sub>9</sub> H <sub>12</sub> O <sub>2</sub> (152)	2.23	Phenols
39	16.47	4-Ethyl-2-methoxyphenol	C <sub>9</sub> H <sub>12</sub> O <sub>2</sub> (152)	10.43	Phenols
40	16.62	2-Methyl-5-phenyltetrazole	C <sub>8</sub> H <sub>7</sub> N <sub>4</sub> (160)	1.10	Nitrogenous
41	16.79	Indole	C <sub>8</sub> H <sub>7</sub> N (117)	0.74	Nitrogenous
42	17.12	N-4,5-Trimethylphenyl-1,2-diamine	C <sub>9</sub> H <sub>14</sub> N <sub>2</sub> (150)	42.30	Nitrogenous
43	17.74	2,6-Dimethoxyphenol	C <sub>8</sub> H <sub>10</sub> O <sub>3</sub> (154)	35.27	Phenols
44	17.86	Eugenol	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub> (164)	4.00	Phenols
45	18.03	2-Methoxy-4-propylphenol	C <sub>10</sub> H <sub>14</sub> O <sub>2</sub> (166)	1.72	Phenols
46	18.72	2-Methoxy-4-(1-propenyl)-phenol	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub> (164)	3.26	Phenols
47	19.32	4-Hydroxy-3-methoxy benzoic acid	C <sub>8</sub> H <sub>8</sub> O <sub>4</sub> (168)	2.66	Carboxylic acid





## CONCLUSION

The *Pachira aquatica* Aubl. fruits shells presented as lignocellulosic biomass with potential for application in thermochemical processes of energy conversion due low moisture and ash content, moderate of volatile matter (76.9%), bulk density of 252.6 kg/m<sup>3</sup> and 16.24 MJ/kg of HHV. The flash pyrolysis products are mostly oxygenated compounds, such as phenols and small molecular weight derived from decomposition reaction, suggesting its potential for the synthesis of several bio-phenolics products after bio-oil pretreatment. The PAS can be valorized through flash pyrolysis route to obtain renewable phenolic from biomass waste ensuring the circular economy of the species.

## ACKNOWLEDGEMENTS

The authors would like to acknowledge the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, Brasil (CAPES/FAPERJ) for the financial support, the Laboratório de Tecnologia Ambiental (LABTAM/UFRN), the Instituto de Química (IQ/UFRN) and the Escola Agrícola de Jundiá of Universidade Federal do Rio Grande do Norte (EAJ/UFRN) for facilities. Special thanks to CAPES for supporting a Master scholarship to Luiz Augusto da Silva Correia and Guilherme Quintela Calixto and for financing this research in part. This study was financed in part by the CAPES - Finance Codes 88882.375742/2019-1 and 1751776, and by Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq (Project codes: 307433/2020-0 and 140525/2020-3).

## DECLARATION OF CONFLICT OF INTEREST

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

## AUTHORS' CONTRIBUTIONS

All authors contributed equally for the conception and writing of the manuscript. All authors critically revised the manuscript and approved of the final version.

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