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WOOD QUALITY OF 10 CLONAL PROGENIES OF RUBBER TREE AS RAW MATERIAL FOR BIOENERGY

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ABSTRACT

The use of wood as a bioenergetic source requires knowledge of its technical properties. The rubber tree *Hevea brasiliensis* has an economic life cycle of 25 to 30 years in Brazil. It is used for extracting rubber and generating residual wood for fuel. Our goal was to characterize the wood quality of 10 clonal progenies as a source of raw material for bioenergy. Ten clonal progenies of 12-year-old *Hevea brasiliensis* from an experimental planting in Selvíria municipality were evaluated. Three trees per clone were evaluated for individual properties of Higher Heating Value, immediate chemical analysis, chemical composition, fiber dimensions, thermogravimetric analysis of wood under nitrogen atmosphere and Fourier Transform Infrared Spectrosocopy analysis. We highlight clone IAC 311 for fuel because it presents elevated Higher Heating Value and fixed carbon and less volatile material. However, the other genetic materials studied also meet the specifications for energy use and can be highly viable given their physical, chemical, energy, and thermal properties.

Keywords: Bioenergetic source, chemical composition, *Hevea brasiliensis*, thermogravimetric biomass, wood density.

INTRODUCTION

The reduction of fossil fuels, especially oil, natural gas and coal, was discussed by Gonçalves *et al*. (2015), while their substitution by renewable energy sources was suggested by Mehmood *et al*. (2017). The generation of energy through wood can be a good alternative to replace the energy generated by fossil fuels, since it emits less greenhouse gases in the combustion process, considering that the use of fossil fuels leads to numerous problems to the environment, which is caused by excess CO_2 in the atmosphere, including: acid rain, caused by the reaction between pollutants and water vapor in the atmosphere; gradual decrease of the ozone layer and water contamination (Skeva *et al*. 2014). Vegetal biomass can be used to obtain the most varied forms of energy, whether by direct or indirect conversion. The advantages of using this material as a substitute for fossil fuels include less atmospheric pollution and the stability of the carbon cycle. Compared to other types of renewable energy, vegetable biomass stands out for its high energy density and the ease of storage, conversion, and transport of this material (Saccol *et al.* 2020).

The internal supply of energy in Brazil consists of 43,5 % of renewable sources, of which biomass corresponds to 9,8 % Energy Research Company (2022). According to data from Brazilian tree industry (2023), areas with forests planted for industrial purposes in Brazil totaled 9,9 million in 2022 and contributed 91 % of all wood produced for industrial purposes.

Species and clones of *Eucalyptus* and *Corymbia* are widely used as sources of biomass in Brazil (Tenorio and Moya 2013). However, knowledge of other forest species and clonal progenies, such as *Hevea brasiliensis*, can be an alternative to increase the use of forest biomass and reduce dependence on fossil fuels in the energy matrix, thus contributing to the country's economic development.

Hevea brasiliensis is an important forest species because its main output is latex, which is responsible for the fabrication of several synthetic products for industrial use. However, when rubber trees no longer reach acceptable levels of latex production, which varies between 25 and 30 years of age (Lima *et al*. 2020), their exploitation becomes economically unfeasible. Consequently, these trees are felled for reformulation of planting, and, in general, the wood does not have an adequate destination, other than use as firewood in small rural locations. No thought has been given to its energetic characteristics for industrial use (Ramos *et al*. 2016).

Since 1995, the Brazilian State of São Paulo has established itself as the main rubber producer, representing half of the country's production (Gonçalves *et al*. 2001). The planted area in Brazil has been increasing significantly, from 159,500 ha to 218,307 ha in 2022 alone (Indústria Brasileira de Árvore 2023). This increase in the cultivable areas of the species in Brazil, was due to the potential of the rubber tree species in capturing CO_2 and other gases harmful to the environment and the use of the species in agroforestry systems (Satakhun *et al*. 2019). Thus, the species has potential for latex extraction, helps to balance the environment, and is a source of renewable biomass for clean energy production.

According to Ratnasingam *et al.* (2009), aside from latex, *H. brasiliensis* produces a large amount of biomass, an estimated 2,1 m^3 from each tree at 25 years old with a tree diameter of 40 cm and 20 m in height. Therefore, it is well past time to consider identifying alternative uses of this biomass, as well as study of this waste to produce energy, which would help reduce dependence on fossil fuels with implications for the environment (Brun *et al*. 2017).

Wood quality evaluation for energy purposes aims to measure and classify the superior characteristics of clonal progenies because such evaluation is essential to decision-

90 making in the implementation of reforestation projects aimed at the use of biomass as an
91 energy source. Wood characteristics provide a way to differentiate among different clone
92 types (Lima *et al*. 2011). According to Protásio *et al*. (2019), the main wood properties
93 for the selection of energy species are basic density, higher heating value, lignin content,
94 ash contents, fiber wood anatomy and thermal behavior.

95 Among wood properties, basic density is considered one of the most important
96 parameters among physical wood properties, as it affects most other properties. Its effects,
97 however, are interactive and difficult to assess in isolation, requiring knowledge of other
98 quality wood properties for the selection of superior clonal genotypes (Pereira *et al*.
99 2016). According to Purba *et al.* (2021), forest biomass quality for energy production
100 varies among genetic materials between and within wood, thus it is important to evaluate
101 wood quality to validate its suitability for use. Scriba *et al.* (2021), cite that the study of
102 wood properties among clones with potential employment in the forestry market is
103 important for the selection and recombination of superior genetic material from the best
104 individuals with the best quality of the desired technological properties for the
105 establishment of better-quality plantations for the desired use.

106 Chemical and anatomical composition of wood is also relevant for energy use.
107 Specifically, when wood is thermally degraded, it undergoes a transformation process
108 whereby all its primary components, including cellulose, hemicellulose, and lignin, are
109 drastically altered, in turn affecting its energetic properties (Yu *et al*. 2017).

110 The immediate chemical analysis of an energy source provides a profile of volatile
111 material contents, fixed carbon, and ash (residual material), all of which influence the
112 properties of burning fuel because volatile constituents burn quickly, and fixed carbon
113 burns slowly (Fernandes *et al*. 2013). The content of volatile materials and fixed carbon
114 is causally related to calorific value, increasing the burning time of the energy source.

The content of volatile materials and fixed carbon in wood are interdependent properties since the percentage of ash thereof is generally low (Silva *et al*. 2020).

Thermal stability is an essential consideration when selecting biomass with energy potential. Techniques, such as thermogravimetric analysis (TGA), make it possible to understand biomass decomposition as a function of heating in thermochemical conversion processes. Thermogravimetric analysis consists of analyzing variation of sample mass using a system with controlled temperature and atmosphere. In addition to obtaining information on composition and thermal stability, this analysis provides an assessment of temperature ranges at which decomposition is most pronounced (Yeo *et al*. 2019). The evaluation of energy properties and efficiency of material allows the selection of more competitive materials compared to other energy sources.

In this context, our objective was to characterize the quality of the wood from 10 clones of *Hevea brasiliensis,* as a source of raw material for bioenergy through the characterization of the anatomical properties of fiber length and width, physical property basic density of the wood: energy properties through the characterization of the higher heating value, immediate analysis through the contents of extractives, lignin and holocellulose. We also evaluated the chemical characterization of the main chemical groups of wood through FTIR- Fourier Transform Infrared Spectroscopy, and biomass characterization through thermal degradation by thermogravimetric (TGA) analysis.

MATERIALS AND METHODS

Selection of species and planting

Wood samples were collected from 30 with 12-year-old rubber *Hevea brasiliensis* (Willd. ex Juss.) Muell. Arg. trees (Table 1), three of each clonal progeny, in the municipality of Selvíria, Mato Grosso do Sul State (20°20′S, 51°24′W, elevation 350 m).

The trial plantation was established in 2006 at a spacing of 3 m × 3 m from seeds of 10 free-pollinated clones (IAC 40ill., IAC 41ill., IAC 326ill., IAC 311ill., IAC 301ill., IAN 873ill., GT1ill, PB 330ill., Fx 2261ill., and RRIM 725ill.). Soil in the experimental area was classified as Red Latosol with clayey texture (Santos *et al*. 2006). In 2018, three selected trees of clonal progenies were felled, and discs 10 cm in thickness from each tree at breast height (1,30 m from the ground) were cut from each tree. From each disc, samples close to the bark were used to determine HHV, chemical constituents, wood density, fiber dimensions, thermogravimetric parameters, and properties under Fourier-Transform Infrared Spectroscopy- FTIR.

Table 1: Improved population (PM) consisting of 10 open-pollination progenies located in Selvíria, MS.

Clonal progenies	Parental
IAC 40ill.	RRIM 608 x AVROS 1279.
IAC 41ill.	RRIM 608 (AVROS 33 x Tjir 1) x AVROS 1279 (AVROS 256 x AVROS 374)
IAC 326ill.	RRIM 623 (PB 49 x Pil B 84) x Fx 25 (F351 X AVROS 49)
IAC 311ill.	AVROS 509 (Pil A 44 x Lun N) x Fx 2 5 (F351 x AVROS 49)
IAC 301ill.	RRIM 605 x AVROS 1518.
IAN 873ill.	PB 86 x FB 1717.
GT1ill.	Primary clone
PB 330ill.	PB 5/51 x PB 32/36
Fx 2261ill.	F 1619 x AVROS 183.
RRIM 725ill.	Fx25 (F351 x AVROS 49)ill.
Ill.= illegitimate (progenies obtained from a free-pollination clone).	

Determination of chemical and energy properties

Wood was ground in a Wiley knife mill, of metallic steel type, manufactured by the Marconi-materials company, with the company located in the municipality of Piracicaba,

in the state of São Paulo, Brazil, transformed into sawdust, and then sieved with 40-60 mesh to later characterize its chemical and energetic properties.

Higher Heating Value

Samples were fragmented into smaller pieces with a hammer and chisel and milled in a micro mill. The samples, before the determination of the Higher Heating Value (HHV), were dried in greenhouses to determine the moisture content. To perform the analysis, the isoperibolic method was used with an IKA C200, calorimeter of the type coated plastic from the company Biovera-Laboratory Equipment and Technical Assistance, with its company based in Rio de Janeiro, in the state of Rio de Janeiro, Brazil. the methodology adopted for the determination of the HHV, according to ASTM D5865-98 (2004).

Proximate analysis

Prior to these analyses, the biomasses (all treatments) were dried in an oven at 100 °C for 10 minutes to get the moisture to 0 %. The determination of ash content was performed according to the standard ASTM D1102-84 (2013), and the volatile content was determined according to ASTM E872 (1982). Both tests were done in triplicate. Both standards were adopted, as all material was used for the calculation. The fixed carbon content was calculated according to equation 1.

$$FCC = 100 - (AC + VC) \quad (1)$$

Where: FCC= Fixed Carbon Content (%); AC= Ash Content (%); VC= Volatile Content (%).

Chemical Assays

To determine extractives (EX) and lignin (LI) contents, TAPPI standards T204 (2004a) and T222 (2004b) were used, respectively. The samples were fragmented into smaller pieces with a hammer and chisel and milled in a micro mill. The resulting powder was

sieved through 40 mesh and 60 mesh screens, and the material retained on the last sieve was used for analysis. The analyses were sequential such that the extractives were first removed, then lignin by acid treatment, with holocellulose (HO) content finally calculated. For extractive contents, extractions were performed in solutions of toluene:alcohol (2:1v:v) and alcohol, at times exceeding 12 h in a Soxhlet extractor. For lignin, extractive-free powder was prepared in several stages with 72 % sulfuric acid to obtain insoluble and soluble lignin (Cary 100 UV–visible spectrophotometer). Finally, the two lignin values were added. The content of insoluble lignin (IL) was determined according to equation 2.

$$IL = \left(\frac{DWlig}{DW}\right) x\ 100 \qquad (2)$$

Where: DW=dry sawdust weight, and DWlig=dry weight of insoluble lignin. Soluble lignin (SL) filtrates and the blank were read at two wavelengths (215 nm and 280 nm), respectively, using quartz cuvettes.

The soluble lignin (SL) content was determined according to equation 3.

$$SL = \frac{(\{4{,}53 * (L.215 - blank) - L.280 - blank\})}{(300 * DW)} x100 \qquad (3)$$

Where: DW=dry sawdust weight. Ex and Li were expressed as a percentage (%) of oven-dried weight of unextracted wood.

After determining the levels of extractives, soluble and insoluble lignin, the holocellulose (HO) content was calculated according to equation 4.

$$HO = [100 - (Ex + Li)]$$

Where: Ex=Extractives and Li=Lignin.

To determine each variable, a triplicate was used for each clone of *Hevea brasiliensis.*

204 **Wood density**
205

206 Wood density was determined by the ratio between dry mass and saturated volume,
207 according to Brazilian standard NBR:11941 procedures (ABNT 2003).

208 **Fiber analysis**
209

210 Small pieces were cut from the side of samples, and macerations were prepared
211 according to the modified Franklin method (Berlyn and Miksche 1976). Modifications
212 resulted from the differences caused by the higher concentration of hydrogen peroxide
213 used in our study. Macerations were stained with alcoholic safranin and mounted in a
214 solution of water and glycerin (1:1). Fiber measurements were performed on an Olympus
215 CX 31 microscope equipped with a camera (Olympus Evolt E330) and a computer with
216 image analyzer software (Image-Pro 6.3). Terminology followed the IAWA list (IAWA
217 1989). Fiber length (FL) and fiber wall thickness (FWT) were evaluated.

218 **Thermogravimetric analysis (TGA)**
219 Sieved samples consisted of remnants retained in the 30-mesh sieve. Approximately
220 20 mg of clonal material from each progeny was heated from 0 ºC to 700 ºC at 20 ºC/min^{-1}
221 under nitrogen atmosphere, using TGA 55 equipment. The degradation analysis was
222 performed for each thermogravimetric event of rubber tree clones.

223 From TG curves, mass loss calculations were performed in the following temperature
224 ranges: 50 ºC - 100 °C, 100 ºC - 250 °C, 250 ºC - 400 °C, 400 ºC - 600 °C and 600 ºC -
225 700 °C. The residual mass at 700 °C was also calculated for each clonal progeny of *Hevea*
226 *brasiliensis*.

227 **Fourier Transform Infrared Spectroscopy (FTIR)**

228 Sieved samples consisted of remnants retained in the 30-mesh sieve. Approximately
229 10 mg of the material were used to read the absorbance spectra using a Perkin Elmer

model Spectrum 65 spectrometer in the region from 500 cm^{-1} to 4000 cm^{-1}, spectral resolution of 4 cm^{-1} and 32 scans.

Data analysis

Tests of homogeneity and analysis of variance (ANOVA) were performed, and when significant difference was detected between treatments, the Tukey test was used, at 1 % significance. The data were analyzed with the statistical software SigmaPlot version 12.

RESULTS AND DISCUSSION

Chemical and energetic properties, basic density and fiber analysis

Table 2 shows the values for the energetic properties for each of 10 rubber clonal progenies. The values of HHV ranged from18357 $kJ \cdot kg^{-1}$ (IAC-301ill.) to 19070 $kJ \cdot kg^{-1}$ (IAC-311ill.), fixed carbon from 15,16 % (IAC-40ill.) to 15,72 % (IAC-311ill.), volatile material from 82,79 % (IAC-311ill.) to 83,92 % (IAC-301ill.), and ash content from 0,42 % (IAC-311ill.) to 1,49 % (IAC-301ill.). The values oscillated among the different rubber tree clonal progenies, presenting different values in their energetic and chemical properties.

The values of energy and chemical characteristics, wood density and wood fiber of rubber tree clonal progenies showed different behaviors. Progenies IAC 311ill., PB 330ill., IAC 41ill., IAC 301ill., and IAN 873ill. presented higher lignin and fixed carbon levels that contributed to HHV (Table 2), thus presenting superior energy performance compared to other clones. According to Trugilho and Silva (2001), these differences in energy properties can be associated with chemical composition that can affect the energy characteristics of biomass.

However, Muzel *et al*. (2014) reported Brazilian forest species that presented higher HHV and were, therefore, widely used for energy generation, as noted by the author above. Studying the wood of clones of *Eucalyptus grandis* and *H. brasiliensis,* Telmo and

255 Lousada (2011) reported HHV of 17895 kJ·kg^{-1} and 17897 kJ·kg^{-1}. Such similarity
256 between these species highlights the wide use of *Eucalyptus* in Brazil for the generation
257 of energy.

258 **Table 2:** Comparison among 10 12-year-old rubber tree clonal progenies, according to
259 energetic properties, chemicals, wood density and fiber analysis, from clonal progenies
260 trial in Selviria, MS, Brazil.

Clonal progenies/ Properties	IAC 40ill.	IAC 41ill.	IAC 326ill.	IAC 311ill.	IAC 301ill.	IAN 873ill.	GT1ill.	PB 330ill.	Fx 2261ill.	RRIM 725ill.
HHV (kJ·kg^{-1})	18895 ab	18827 ab	18770abc	19070a	18357c	18729abc	18791abc	18895ab	18524bc	18867abc
CC (%)	15,16c	15,70 a	15,42bc	15,72a	15,66ab	15,25c	15,39bc	15,61ab	15,27c	15,56ab
VMC (%)	83,75ab	83,44cd	83,39d	82,79e	83,92a	83,67b	83,23d	83,55d	83,65bc	83,69b
AC (%)	1,08b	0,87cd	0,86cd	1,49e	0,42a	1,08b	1,38e	1,03bc	0,74d	0,75d
EC (%)	8,0a	5,9bc	4,8c	7,1ab	6,6b	6,6b	6,8b	7,1ab	6,3b	6,9ab
LC (%)	23,4 abcd	24,0 ab	23,1 abcd	24,5 a	23,9 abc	23,8 abc	22,5 cd	24,1 ab	21,9 d	22,9 bcd
HC (%)	68,6 bc	70,1 abc	72,1 a	68,4 c	69,56bc	69,6 bc	70,7 ab	68,8 c	71,8 abc	70,3 bc
ρ bas (g·cm^{-3})	0,423bc	0,440b	0,495a	0,429bc	0,404c	0,422bc	0,447b	0,448b	0,452b	0,452b
FL (µm)	1025 bc	992 c	1024 c	1077 abc	981 c	1165 a	1139 a	1115 ab	1051 abc	1069 abc
FWT (µm)	3,0 bcd	3,5 abc	3,0 cd	3,7 abc	2,7 d	4,3 a	3,7 abc	3,2 bcd	3,2 bcd	3,8 ab

Ill. = illegitimate (progenies obtained from a free-pollination clone); HHV= Higher heating value; CC = carbon content; VMC = volatile matter content; AC = ash content; EC = extractives content; LC = lignin content; HC = holocellulose content; ρbas = Wood density; FL= fiber length; FWT = fiber wall thickness. Distinct letters in rows differ statistically (P<0,001) by Tukey's test.

261 For decades, HHV of wood for power generation was considered 18830 kJ·kg^{-1}. HHV
262 differences between clones observed in this study can be explained by the ecological
263 group of the wood (Tan, 1989). Among hardwoods, rubber tree clones have expected
264 HHV of 19089 kJ·kg^{-1}. This value was observed in the present study, which reported
265 values ranging from 18357 kJ·kg^{-1} (IAC 301ill.) to 19070 kJ·kg^{-1} (IAC 311ill.). The work
266 of Tan (1989b) also reports an HHV for rubber tree of 19700 Kj·kg^{-1}, and Werther *et al*.

(2000) report an HHV for rubber tree residues of 18410 kJ·kg^{-1}. In Brazil, values between 16500 kJ·kg^{-1} and 18000 kJ·kg^{-1} are approved for commercial energy uses.

Clones with higher volatile and ash contents had lower HHV, including IAC 301ill. (83,92 %), IAC 40ill. (83,75 %), RRIM 725ill. (83,69 %), IAN 873ill. (83,67 %), Fx 2261ill. (83,65 %), PB 330ill. (83,55 %), GT1ill. (83,23 %), IAC 41ill. (83,44 %), and IAC 311ill. (82,79 %), consequently reducing the energy potential of the fuel. However, fixed carbon content is directly related to calorific power, meaning that a higher fixed carbon content implies greater resistance to thermal degradation of biomass within the burning apparatus for power generation (Chaves *et al*. 2013).

The highest contents of fixed carbon were found for clonal progenies IAC 311ill. (15,72 %) and IAC 41ill. (15,70 %). It is said that the percentage of fixed carbon refers to the fraction of coal that burns in the solid state. Therefore, fuels with high levels of fixed carbon in both clonal progenies are preferable for steel use, owing to thermal stability and high energy power (Neves *et al*. 2011).

Ash content should be in the range of 1 % - 3 % for good energy performance (Schoninger and Zinelli 2012). Thus, the values for this energetic characteristic are within the expected pattern for good energy yield since ash values ranged from 0,42 % (IAC 301ill.) to 1,49 % (IAC 311ill.).

In Brazil, species of *Eucalyptus* are widely used for energy production because of their rapid growth and energetic properties (Jesus *et al*. 2017). However, recent studies show similarity in energetic properties between rubber tree clones. Bersh and Brum (2018) characterized *Eucalyptus* and reported HHV values between 13970 kJ·kg^{-1} and 14250 kJ·kg^{-1}, volatile materials of 83,17 % - 86,16 %, ash content of 0,57 % - 0,60 %, and 13,27 % - 14,25 % of fixed carbon content. These values show that rubber tree clones

share similar and superior energetic properties, highlighting their use for bioenergy production when compared to *Eucalyptus* wood.

According to Paula (2003), wood from clones has higher fiber wall thickness and length, as well as higher lignin and extractive content. Consequently, this wood is increasingly recommended for energy production for its biomass production, resulting in a greater amount of mass per unit of volume and, consequently, greater energy release capacity. Wood with high lignin content contributes to high gravimetric yield and gives greater resistance to charcoal thermal degradation since this wood has more condensed structures that degrade at higher temperatures (Castro *et al*. 2013; Oliveira *et al*. 2010).

In this context, clones of higher basic densities present larger dimensions in their anatomical constitution. This characteristic is not true across the clonal spectrum as clone IAC 301ill. presented lower density and smaller fiber dimensions. The increase in wood density is followed by an increase of fiber wall thickness and length (Oliveira *et al*. 2010), but this was not observed in the present study. IAN 873ill. was taller and wider, but still had lower density than other clones.

As lignin and extractive content increase, density increases proportionally. Thus, we find an increase in the energy yield of fixed carbon content and HHV (Dias-Junior *et al*. 2015). This premise was not observed for rubber tree clones IAN 873ill. and IAC 40ill. in that they presented lower wood density, even while their HHV and fixed carbon content were higher than those values in other clones. The lower wood density and HHV value of IAC 301ill. may be related to the age of the tree and anatomical characteristics of the species itself (Protásio *et al*. 2014).

Basic density is an important property of wood and should be considered for energy use of a given biomass since that characteristic is causally related to energy production.

That is, the higher the density, the greater the amount of energy stocked per unit volume (Queiroz *et al*. 2004). It is recommended that wood used as an energy source should present values above 0,40 g·cm^{-3} of wood density (Alzate *et al*. 2005), which is confirmed for all clones listed in Table 2.

The differences found in energetic properties of wood among *H. brasiliensis* clones result from the chemical composition values, fiber dimensions and wood density of the biomass. Studies on other species report that HHV is mainly dependent on lignin and extractive content. High levels of lignin favor the energetic properties of fixed carbon and HHV, which can be attributed to carbon-carbon bonds between monomeric phenyl-propane units present in lignin, which hinder their decomposition, and to the higher content of carbon of this molecular component of biomass (Bufalino *et al*. 2012, Dietenberger and Hausburg 2016).

Holocellulose is considered the most abundant component of the cell wall. However, it is amorphous and offers no resistance to high temperatures of thermal degradation, hampering its use in energy production because of its negative interference in biomass energy, HHV and physics properties (Tan and Largervist 2011). Clones with higher holocellulose levels present lower HHV, specifically IAC 326ill., Fx 2261ill., IAC 41ill., and GT1ill.

Energy from biomass is usually obtained through thermochemical technologies, especially combustion. High ash content is disadvantageous because it decreases the transfer of heat in fuel and increases corrosion of the equipment used in the process. It also decreases the HHV of biomass (Protásio *et al*. 2014, Soares *et al*. 2014).

Only a few studies have reported on the characteristics of wood for energy purposes. For example, Menucelli *et al*. (2019) studied 10 clonal progenies of rubber tree and

reported characteristics superior to clones evaluated in the present study, such as fiber length between 1189 µm - 1097 µm, fiber wall thickness of 4,55 µm - 5,13 µm, extractive contents between 12,42 % - 16,34 %, lignin content between 27,51 % - 22,47 %, and wood density from 0,57 $g \cdot cm^{-3}$to 0,66 $g \cdot cm^{-3}$. These wood characteristics promoted higher HHV content between 18592 $kJ \cdot kg^{-1}$ and 19757 $kJ \cdot kg^{-1}$, values that could be attributed to differences in genetic material (Soares *et al*. 2014).

Fourier Transform Infrared Spectroscopy (FTIR)

Table 3 summarizes the main chemical and functional groups found in the wood of *H. brasiliensis* clones according to Tyutkova *et al*. (2019), being identified by the number of waves of the carboxylic groups: = C-H (902 cm^{-1}), C-O-O (1114 cm^{-1}), - C-H (1464 cm^{-1}), C = O (1743 cm^{-1}), C-H (2924 cm^{-1}) and O-H (3370 cm^{-1}).

Table 3: Characteristic bands of infrared spectra (FTIR) for *Hevea brasiliensis* clones and their respective functional groups.

Wavenumber (cm^{-1})	Functional group	Chemical group
902	=C-H	Bond oscillation cellulose
1114	C-O-C	Bond oscillation cellulose
1464	C-H	Bond oscillation in lignin
1743	C=O	Unconjugated Keto group xylan
2924	C-H	Bond symmetric oscillation in aromatic methoxyl, and methylene groups of side chains
3370	O-H	Valence oscillation in bond water

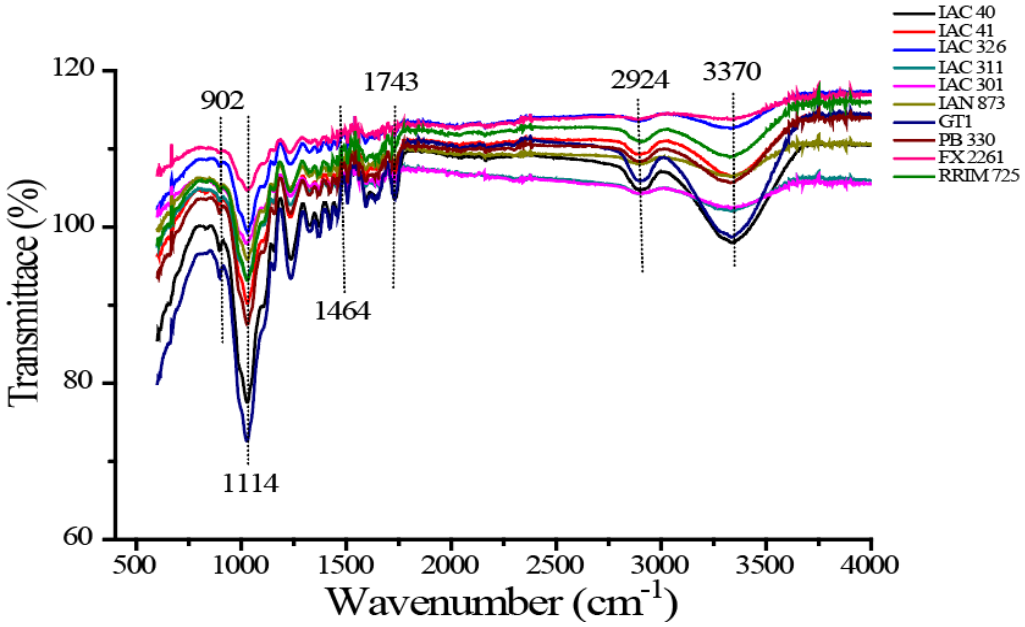
One can observe that all clones have a strong absorption band at 1114 cm^{-1} where the lignin present in wood is located (Schuerch 1989). However, clones IAC 40, GT1, PB 330, IAC 41, RRIM 725, and IAN 873 had higher wavelengths in this spectrum. This could be explained by the chemical structure of wood because these clones have higher

358 levels of lignin (Table 2) and, hence, higher resistance to thermal degradation of the
359 material, as characterized by the stretch mode of the O-H combination.

360 According to Figure 1, the group found at 1743 cm^{-1} can be attributed to C=O,
361 indicating the presence of an acetyl or carboxylic acid group derived from lignin. The
362 high proportion of these chemical groups indicates an increase in HHV (Table 1). The
363 same behavior was reported by Schuerch (1989).

364 It was possible to notice a strong striation between bands 1743 cm^{-1} and 2924 cm^{-1},
365 larger than the other spectral bands reported. The bands are characterized by strong
366 bonding between hemicellulose and lignin, which is characterized mainly by C-H, N-H
367 and O-H that are desirable for energy production (Popescu *et al*. 2011).

368 At band 3370 cm^{-1}, the phenolic groups bonded to hydrogen formed O-H chemical
369 groups (Pandey and Pitman 2003). This group is responsible for high degradation
370 resistance of the wood, which is dependent on lignin content, as was possible to observe
371 in this study. Clones with higher lignin levels present higher absorption spectra, namely
372 IAC 40 and GT1, in the present study (Figure 1).



373 **Figure 1:** Main spectra obtained for *Hevea brasiliensis* wood clone.

374 **Thermogravimetric analysis (TGA)**

375 Table 4 shows averages of mass loss of different clonal progenies of *Hevea*
376 *brasiliensis*, as a function of temperature ranges from 50 ºC to 700 ºC.

377 **Table 4:** Mean values of mass loss (%) of different clonal progenies of *Hevea*
378 *brasiliensis* as a function of temperature ranges.

Clonal progenies	**50-100 (ºC)**	**100-250 (ºC)**	**250-400 (ºC)**	**400-600 (ºC)**	**600-700 (ºC)**	**Residual mass ***
IAC 40ill.	1,55	3,02	64,22	5,90	1,35	23,96
IAC 41ill.	1,16	2,86	71,39	4,95	1,19	18,45
IAC 326ill.	1,55	2,57	64,56	5,68	1,15	24,49
IAC 311ill.	1,71	2,68	66,13	5,62	1,12	22,74
IAC 301ill.	1,80	3,45	62,12	6,27	1,37	24,99
IAN 873ill.	1,44	2,65	66,42	5,87	1,67	21,95
GT1ill.	1,91	2,83	64,29	5,96	1,46	23,55
PB 330ill.	2,37	3,19	63,60	6,66	1,84	22,34
Fx 2261ill.	1,61	2,81	65,30	6,28	1,91	22,09
RRIM 725ill.	1,66	3,93	63,14	6,12	1,63	23,52
Mean	1,68	3,00	65,11	5,94	1,47	22,80

* Residual mass, considering the mass of wood absolutely dry (s).

379 The first two temperature ranges, 50 ºC - 100 ºC and 100 ºC - 250 ºC, correspond to
380 drying of wood (Vieira 2019), making an average total of 4,68 % of initial average total
381 loss for clonal progenies of *Hevea brasiliensis*.

382 Between 250 ºC and 400 ºC, an average loss in biomass of 65,11 % was verified. It
383 can be inferred that most of this lost mass results from degradation of hemicellulose,
384 cellulose, and volatile emissions, as well as the start of partial lignin decomposition

(Lopéz-González *et al*. 2013). The maximum rate observed among clonal progenies of *Hevea brasiliensis* in this range of degradation refers to the maximum degradation of cellulose, as this constituent corresponds to 40 % - 45 % of the wood (Pereira *et al*. 2013). According to figure 2, it is possible to observe the mass losses of *Hevea brasiliensis* clones at different temperatures.

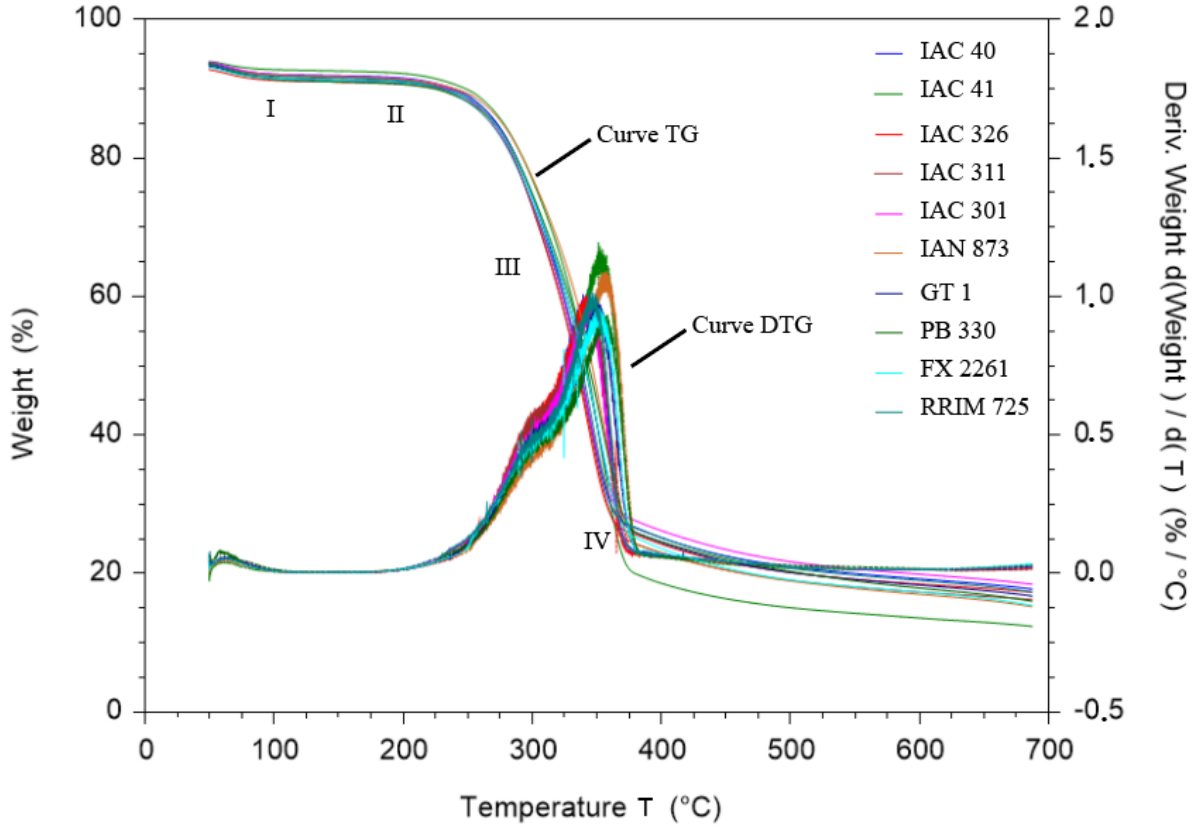


Figure 2: TG and DTG curves of mass losses for *Hevea brasiliensis* clones.

Between 400 and 600 ºC, the average mass loss was 5,94 %. According to Shen *et al*. (2010) for this temperature range, wood thermal degradation of 5 % to 10 % can be expected, as was observed in *Hevea brasiliensis*.

The general average mass loss observed in the 600 ºC to 700 ºC range was 1,47 %, showing that hemicelluloses and celluloses were totally degraded and that the observed mass loss refers to lignin in small proportion since it is a more thermally stable wood component. The absence of a peak of degradation related to lignin likely results from the fact that its thermal decomposition occurs over a wide temperature range, emphasizing

399 that only a fraction decomposes at temperatures below 450 ºC, as mentioned by Huang *et*
400 *al*. (2009).

401 The residual mass refers to total wood that is converted into charcoal at the end of the
402 carbonization process. Lower residual masses were observed for clones IAC 41ill. (18,45
403 %) and IAN 873ill. (21,95 %), but higher residual masses for IAC 326ill. (24,99 %) and
404 IAC 301ill. (24,49 %). The values for other clonal progenies were close. These
405 differences between residual masses can be explained by the clonal effect of the species
406 (Vieira 2019).

407 In Brazil, *Eucalyptus* clones are widely cultivated for energy production (Ferreira *et*
408 *al*. 2017). However, it was found that clonal progenies of *Hevea brasiliensis* are more
409 thermally resistant than 12 *Eucalyptus* clones studied by Vieira (2019), which obtained
410 an average residual mass of 22,03 %. On the other hand, they are less thermally resistant
411 to *Eucalyptus* clones studied by Pereira *et al*. (2013), who report residual masses at 7,5
412 years with values of 25,11 %, these differences being attributed to wood chemical
413 constitution.

414 **CONCLUSIONS**

415 The results found in this work corroborate those of *Eucalyptus* species used in the
416 generation of energy. However, clonal progeny IAC 311iil. presented superior
417 characteristics with higher values of calorific value, fixed carbon and lower content of
418 volatile material.

419 Through the analysis of wood quality, we identified which programs cloned with lower
420 densities presented smaller HHV and smaller fiber components, as specifically observed
421 in clonal progeny IAC 301.

422 FTIR showed functional groups characteristic of wood, including =C-H, C-O-O, -C-
423 H, C=O and O-H. They are part of the chemical composition of wood and are suitable for
424 energy production.

425 Wood thermogravimetric analyses did not show significant variations between clonal
426 progenies since we were able to distinguish the stages of thermal degradation, especially
427 those associated with hemicelluloses and cellulose in the range of 250 ºC - 400 ºC. We
428 observed satisfactory residual mass values for the conversion of wood to charcoal.

429 In general, the ten genetic materials of *Hevea brasiliensis* have biomass suitable for
430 commercial energetic use and are highly viable owing to their physical, chemical, energy
431 and thermal characteristics.

432 **AUTHORSHIP CONTRIBUTIONS**

433 E. P. A.: Conceptualization, Resources, Data Curation, Funding aquisition, Investigation,
434 Methodology, Validation, Writing- review & editing; E. L. L.: Conceptualization,
435 Validation, Writing-Original draft, Data Curation, Software; M. L. M. F.s:
436 Conceptualization, Resources; F. M. Y.i: Conceptualization, Resources; F. G. D. S. J.:
437 Conceptualization, Resources; M. A. D. M.: Conceptualization; J. C.: Conceptualization;
438 M. L. T. D. M.: Conceptualization; P. D. S. G.: Conceptualization.

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