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TESE

CARACTERIZAÇÃO E MÚLTIPLOS USOS DE ESPÉCIES NATIVAS DA MATA ATLÂNTICA

Carlos Eduardo Silveira da Silva

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Caracterização e Múltiplos Usos de Espécies Nativas da Mata Atlântica

CARLOS EDUARDO SILVEIRA DA SILVA

Orientador
Dr. Alexandre Monteiro de Carvalho

e supervisão dos professores
Dr. Fernando José Borges Gomes
Dr. João Vicente de Figueiredo Latorraca

Tese apresentada como requisito parcial para obtenção do grau de **Doutor em Ciências**, no Programa de Pós-Graduação em Ciências Ambientais e Florestais, área de concentração Ciência e Tecnologia de Produtos Florestais.

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TESE APROVADA EM 25/08/2021

____
Dr. Alexandre Monteiro de Carvalho. Dr. UFRRJ
(Advisor)

____
Cristiane Pedrazzi. Drª. UFSM

____
Daniel Piotto. Dr. UFSB

____
Graziela Vidaurre Baptista. Drª.UFES

____
Roberto Carlos Costa Lelis. Dr. UFRRJ

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ALEXANDRE MONTEIRO DE CARVALHO
PROFESSOR DO MAGISTERIO SUPERIOR
PPGCAF (12.28.01.00.00.00.00.27)
Matrícula: 1486653

(Assinado digitalmente em 03/09/2021 12:39)
ROBERTO CARLOS COSTA LELIS
PROFESSOR DO MAGISTERIO SUPERIOR
IF (12.28.01.26)
Matrícula: 1219274

(Assinado digitalmente em 03/09/2021 11:57)
DANIEL PIOTTO
ASSINANTE EXTERNO
CPF: 171.129.138-29

(Assinado digitalmente em 03/09/2021 10:48)
CRISTIANE PEDRAZI
ASSINANTE EXTERNO
CPF: 810.821.690-72

(Assinado digitalmente em 03/09/2021 10:56)
GRAZIELA BAPTISTA VIDAURRE
ASSINANTE EXTERNO
CPF: 078.905.237-77

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RESUMO GERAL

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A pesquisa foi realizada com material oriundo da Reserva Natural Vale, localizada no município de Linhares, Espírito Santo e teve como objetivo estudar seis espécies nativas, sendo estas: *Joannesia princeps* Vell., *Spondias venulosa* (Engl.) Engl., *Copaifera lucens* Dwyer, *Astronium concinnum* Schott ex Spreng., *Handroanthus serratifolius* (Vahl) S. O. Grose, e *Libidibia ferrea* var. *parvifolia* (Mart. ex Tul.) L. P. Queiroz visando caracterizar as propriedades das madeiras nativas brasileiras e potencial uso das mesmas. De acordo com o inventário disponibilizado pela empresa foram selecionados 15 indivíduos por espécie, com idades variando entre 17 e 31 anos, e com o material obtido na área, 3 toras de 2.10 m por espécie, originando o material para realização das análises propostas. Os resultados comprovaram uma significativa correlação (R^2) com as espécies mais densas (*Handroanthus serratifolius* e *Libidibia ferrea* var. *parvifolia*). A avaliação dos resíduos de *Joannesia princeps* e *Astronium concinnum* no processo de briquetagem usando diferentes condições de pressão (900, 1200 e 1500 Pound-Force por Square Inch - PSI) e adição de lignina Kraft (2, 4 e 6% em relação ao peso total) afirmou que a adição de 6% KL com um valor de pressão de 1500 PSI promoveu melhores propriedades do briquete (densidade aparente, módulo de ruptura e valores de aquecimento) em *Joannesia princeps* Vell. A espécie *Astronium concinnum* (Engl.) Schott apresentou resultados distintos, sendo os melhores promovidos quando se utiliza 2% KL com 900 PSI, mas o aumento no% KL pode promover melhores propriedades de resistência. A análise da extração de lignina e conversão de carboidratos após a etapa de tratamento hidrotérmico (HTT) utilizando hidrólise enzimática (EH) e solventes em madeiras de *Joannesia princeps* e *Astronium concinnum* mostraram que a Rota 1 resultou em maior eficiência na remoção de lignina mais expressiva nas espécies *Joannesia princeps*. A inclusão da sequência EH após HTT, estudada na Rota 2, não resultou em maior eficiência de remoção de lignina para as duas biomassas estudadas, mas influenciou no rendimento de conversão de glucana. *Joannesia princeps* apresenta maior potencial de extração de lignina quando submetida a reações mais prolongadas a 195 ° C, fato relacionado à composição química, estrutura anatômica e propriedades físicas. Ressalta-se que esta pesquisa contribui, mas há necessidade de pesquisas com espécies nativas brasileiras, de diferentes biomas, para gerar dados florestais e propriedades tecnológicas visando seu uso potencial em diferentes segmentos industriais.

Palavras-chave: florestas nativas, propriedades tecnológicas da madeira, briquetes, lignina.

GENERAL ABSTRACT

SILVA, Carlos Eduardo Silveira da. **Characterization and Multiple Uses of Brazilian Atlantic Forest Species**. 2021. 112 p. Thesis (Doctor Science in Environmental and Forestry Sciences). Forest Institute, Federal Rural University of Rio de Janeiro, Seropédica, 2021.

The research was carried out in the Vale Natural Reserve, located in the city of Sooretama, Espírito Santo state and its objective was to evaluate the wood properties of six native species, *Joannesia princeps* Vell., *Spondias venulosa* (Engl.) Engl., *Copaifera lucens* Dwyer, *Astronium concinnum* Schott ex Spreng., *Handroanthus serratifolius* (Vahl) S. O. Grose, and *Libidibia ferrea* var. *parvifolia* (Mart. ex Tul.) L. P. Queiroz, aiming to characterize the properties of these woods and their potential use. According to the inventory available by the company, 15 individuals were selected per species, aged between 17 and 31 years, and with the material obtained in the area, 3 logs of 2.10 m per species originating the material for the analyzes proposed. The results proved a significant correlation (R^2) with resistographic analysis and the densest wood species (*Handroanthus serratifolius* and *Libidibia ferrea* var. *parvifolia*). The evaluation of *Joannesia princeps* and *Astronium concinnum* residues in briquetting using different pressure conditions (900, 1200 and 1500 Pound-Force per Square Inch - PSI) and addition of Kraft lignin (2, 4 and 6% in relation to the total weight) stated that the addition of 6% KL with a pressure value of 1500 PSI promoted better briquette properties (bulk density, modulus of rupture and heating values) in *Joannesia princeps* Vell. The *Astronium concinnum* (Engl.) Schott species presented distinct results, with the best ones being promoted when using 2% KL with 900 PSI, but the increase in % KL can promote better strength properties. The analysis of lignin extraction and carbohydrate conversion after the hydrothermal treatment (HTT) step using enzymatic hydrolysis (EH) and solvents in *Joannesia* princeps and *Astronium concinnum* woods showed that Route 1 resulted in greater efficiency in the removal of lignin more expressive in the species *Joannesia princeps*. The inclusion of the EH sequence after HTT, studied in Route 2, did not result in higher lignin removal efficiency for the two studied biomasses, but it did influence the glucan conversion yield. *Joannesia princeps* has greater lignin extraction potential when subjected to longer reactions at 195 °C, a fact related to chemical composition, anatomical structure and physical properties. It is noteworthy that this research contributes, but there is a need for research on Brazilian native species, from different biomes, to generate forestry data and technological properties aiming at their potential use in different industrial segments.

Keywords: native forests, technological properties of wood, briquettes, lignin.

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SUMMARY

1. GENERAL INTRODUCTION

The Atlantic forest is one of the richest biomes in Brazil and the world, in diversity of fauna and flora. One of the remnants of this biome, due to constant degradation, is in the Vale Natural Reserve, in Espírito Santo state, Brazil. This reserve includes a plantation of forest experimentation with more than 100 native species of the biome and with more than 30 years.

This wealth of species is unfortunately unknown and few studies on woods are found in literature, more specifically related to the technological properties of the biomass of these species and their possible applications.

According to Bertolini *et al.* (2015), the information on native species with wood potential is mostly limited to aspects of seedling production, and there is a great lack of systematized information, mainly regarding the implementation of commercial plantations, regardless of the type of forest product required. According to the same authors, this fact is due to the focus of study in the last decades on exotic species such as the genera *Eucalyptus* and *Pinus*, species that together cover 8.6 million hectares of the Brazilian territory in the year of 2019 (IBÁ 2020), with considerable knowledge about forestry, technological properties of wood, great incentives in the introduction and commercialization of these species.

In this sense, researches have sought greater knowledge on the forestry of native species that have rapid growth, combined with the high productivity of wood, aiming its use in the timber industry. For this, it is necessary that the forestry research institutions turn their interests to studies of the use of native biodiversity, including timber species of regional occurrence, being essential the greater encouragement to these surveys, through public policies of support, aiming not only to conservation, but also the production, reproduction, genetics of these. Thus, the evaluation of the plantations and their possible or potential uses that native species possess should be studied (BERTOLINI *et al.* 2015).

A major development of timber production occurred after the creation of Brazilian law 5.106 (1966) on fiscal incentives, where the government sponsored a large-scale reforestation policy. This allowed an increase of approximately 500 thousand hectares to about six million hectares of planted forests, where more than three million hectares corresponded to the planting of *Eucalyptus* spp. and more than two million to the planting of *Pinus* spp. This incentive policy ended in 1988, due to the excess of tax incentive concession and an exacerbated increase in deforestation in the Amazon region (JANUÁRIO 2008).

The law no. 11.428 (2006) and its regulation by decree 6.660 (2008), which provide for the use and protection of the Atlantic Forest, despite regulating the planting of native species, discourages producers from economically exploiting timber species in forest formations, since forbidding the management of primary vegetation in any condition, and restricting secondary to advanced and medium stages of regeneration for commercial purposes, which are the main exploitable sources of timber (BRASIL 2006).

The lignocellulosic biomass studies increased a lot on the last decades and its application has gained more and more space in the world, discovering, modifying and increasing the production of high value products allied to reduce the wastes and the compromise of a more sustainable world. The wood has natural characteristics that transform each object produced from this raw material, unique, unequaled, and the variety of species accentuate their exclusivity. The timber production chain can be segmented into two main strands, use as fuel and/or industrial applications (structural, sawnwood, pulp and paper, and others), considering the different end uses. To make timber even more present in construction, programs and incentives in the area tend to involve government, engineers, industry, and, most importantly, researchers working on climate, implications in forest areas, innovations in the area design and economic development.

In Brazil, there has been an increasing number of researches on the production of forest restoration as well as on homogenous plantations for the purpose of civil construction, improving management for the improvement of the final product expected. Contributing to this, it is important to mention that Brazil have a big participation on the studying and production of pulp and paper, and others chemicals as biofuels, in all the world aiming to substitute the fossil fuels. Biomass can replace fossil fuels, being a renewable source of energy (MUHAMMAD *et al.* 2018). This information relates to the biorefinery concept defined by the International Energy Agency (IEA) Bioenergy Task 42 that affirms that biorefining as the "sustainable and synergetic transformation of low-value biomass into marketable food and feed ingredients, products (chemicals, materials) and energy (fuels, power, heat)" (BELL *et al.* 2014; DESSBESSEL *et al.* 2017).

With the inventory of the Reserve, six forest species were chosen according to the criterion of basic density class (light, medium and heavy) and from this stage it was realized some experiments in 15 trees per species. After this step, 3 of these were harvested, totalizing 18 harvested trees, originating the material for the other analyzes proposed in the chapters of this research. The processed wood originated the boards and material for the analysis of physical properties, and the residues of two of these species were used as raw material for carrying out research.

2. MATERIALS AND METHODS

2.1. Study area

The study area is located in the Vale Nature Reserve (Figure 1), in an experimental planting area, focused on forestry, with some experiments implemented in the 1980s and others in the 1990s. The area is located in Sooretama, located in the state of Espírito Santo (ES) and the predominant vegetation in the Reserve is the Perennial Forest. It is located between the geographical coordinates 19° 06' and 19° 18' south latitude and 39° 45' to 40° 19' west longitude and the altitude oscillates between 28 and 65 meters (ROLIM *et al.* 2016).

According to the Köppen classification, the region has a hot and humid climate, corresponding to the Awi (Tropical humid) type. For the period from 1975 to 2004, the average annual temperature is 23.3°C, varying from 20 to 26°C (average annual minimum and maximum), average annual relative humidity of 85.8% and average annual rainfall of 1.227 mm, characterized by strong variability between years (ROLIM *et al.* 2016).

It is important to mention that the study was carried out in the year 2018, and that the species studied were of different ages, ranging from 17 to 31 years old, and all plantings were carried out in the 2x2 m spacing (1.667 trees per hectare), subject to periodic thinning over time to decrease competition.

With the information of the historic of the area based in growth data (height, volume and diameter increment), and with a list of 30 potential species to use in the native species forestry, were chosen six of these for the development of the present study using the density criteria to choose two species in different density classification (low, medium and high density) according with classification proposed by IPT (1985). The species were harvested, later measured through a rigorous survey and legally brought in accordance with the protocols authorized by Instituto Brasileiro do Meio Ambiente e dos Recursos Naturais Renováveis (IBAMA) with Documento de Origem Florestal (DOF) number 1799973503, 17935356 and Instituto de Defesa Agropecuária e Florestal do Espírito Santo (IDAF) 6250/2017.

The location of individuals and species is shown in Figure 1 and has 2.45 km of dispersion between them.

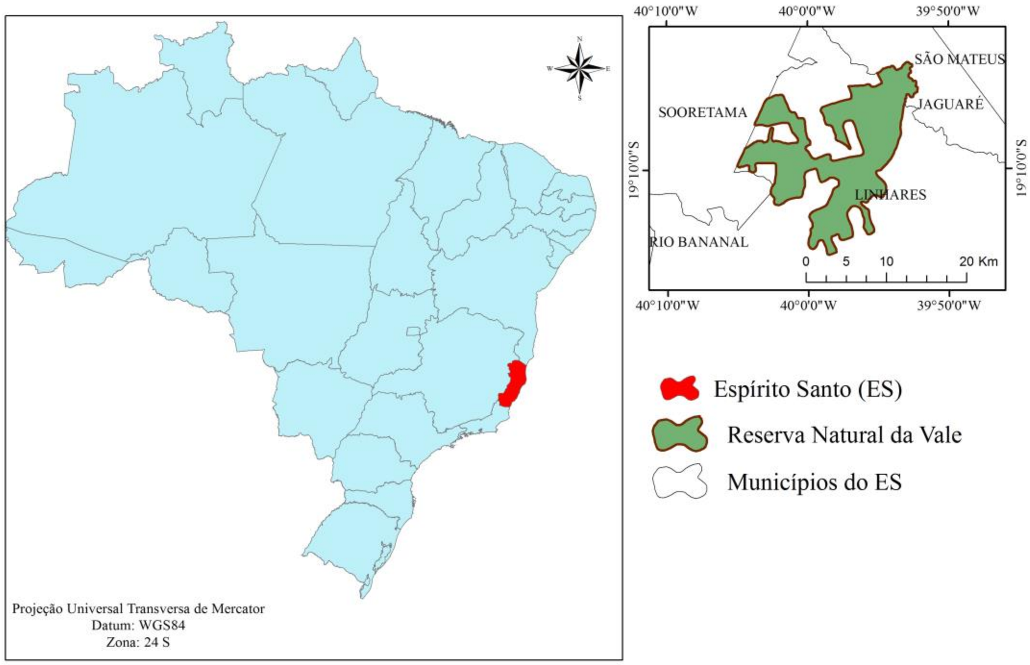

Figure 1. Location of Vale Natural Reserve, Espírito Santo state, Brazil. Source: Silva *et al.* (2021).

2.2. Species studied

2.2.1. *Spondias venulosa* (Engl.) Engl.

Also called *Spondias venulosa* Engl., commonly known as acajá, cajá-verde, manguinha do Espírito Santo, belongs to the Anacardiaceae family. According to Lorenzi (1998) it is a semi-deciduous tree, heliophyte, climax, being able to reach up to 23 m in height and up to 60 cm in diameter (Figure 2). It is pollinated by insects and its dispersion is zoocorical.

The species is found in the terrestrial substrate, is a Brazilian native tree, but it is not endemic in Brazil. The plantation of this species have 24 years old (ROLIM & PIOTTO 2018, 2019).

A B C

Figure 2. Individuals of *Spondias venulosa* (Engl.) Engl. of Vale Natural Reserve, being (A) species haste; (B) wood visual appearance; and (C) cross section 10x zoom. Source: Own authorship and adapted from ROLIM & PIOTTO (2018, 2019).

The *Spondias venulosa* wood has easy workability, of average natural durability, which makes it suitable for carpentry and carpentry, being used for linings and toy manufacturing (LORENZI 1998), and in the northern region for the construction of small vessels also being recommended for ecological reforestation.

According to Rolim & Piotto (2018, 2019) the species has no history in the timber market, but its tasty fruit has traditional local markets. The wood presents indistinct heartwood and sapwood, brownish-light beige, uncharacteristic odor, indistinct taste, coarse texture, straight grain, and little variance in luster. Anatomically the wood presents axial parenchyma visible only under magnification and paratracheal vasicentric; medium, numerous, and non-stratified rays; small to medium, numerous, diffuse-porous, and predominantly solitary and occasionally multiples vessels; and growth rings slightly delimited by fibrous tissue. The wood presents low density, resistance, hardness and can be indicated for use in packages, boxes, and utensils (ROLIM & PIOTTO 2018, 2019).

2.2.2. *Joannesia princeps* Vellozo

It is known as boleira, cutieira, belongs to the family Euphorbiaceae, being an endemic species from Brazil (Figure 3), tree found in terrestrial substrate distributed in the north, northeast and southeast, covering the rain forest region of the Atlantic Forest biome (SOUSA *et al.* 2007; AZEVEDO & SILVA 2006). The plantation of this species have 16 years old (ROLIM & PIOTTO 2018, 2019).

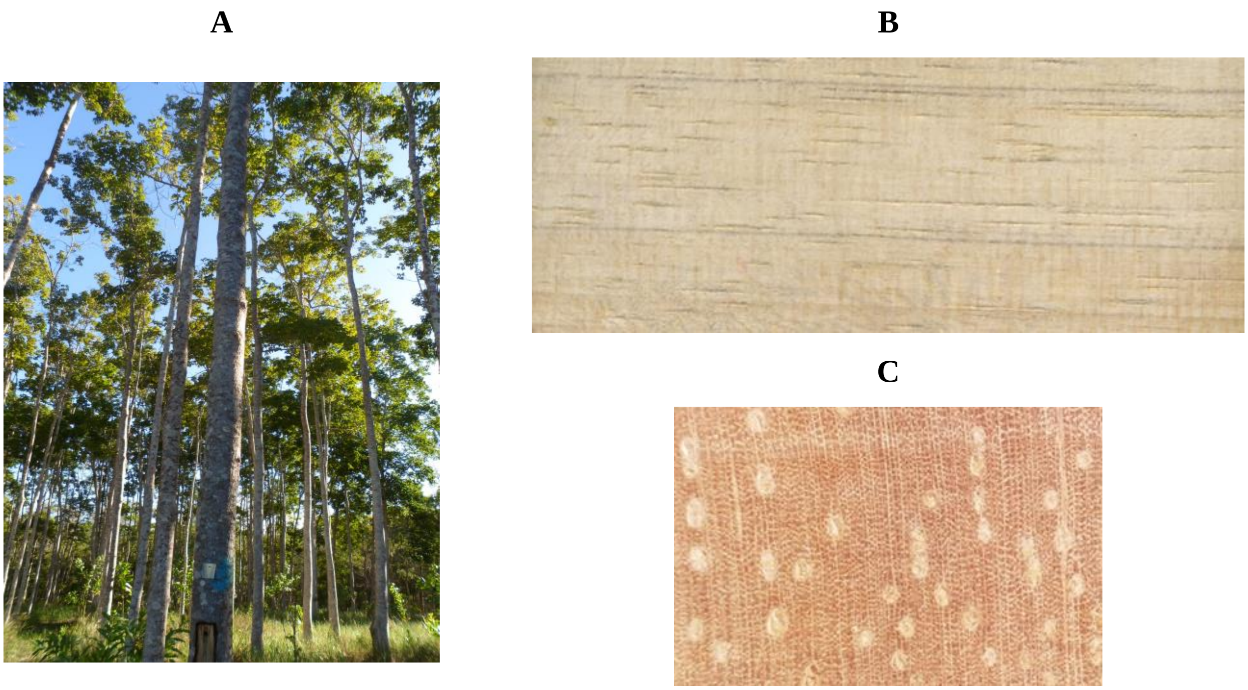

Figure 3. *Joannesia princeps* Vellozo in the Vale Nature Reserve, being (A) species haste; (B) wood visual appearance; and (C) cross section 10x zoom. Source: Own authorship and adapted from ROLIM & PIOTTO (2018, 2019).

The wood of this species is porous, of very round fibers, with light color sometimes and yellow spots. The wood is destined to the manufacture of phosphorous sticks, for cellulose, planked for linings, canoes and rafts, scalars and box-office. The seeds of *Joannesia* presents around 37% of oil, utilized for industrial and pharmaceutical applications (SILVA & LEMOS 2002). For the role it plays in feeding the fauna through its fruits, it is recommended in the composition of forests destined to the repopulation of degraded areas of permanent preservation in reason of its nutrient contribution (BOTERO *et al.* 2008).

According to Rolim & Piotto (2018, 2019) the species has no tradition of wood production, but is indicated for use in carpentry and structures, chemical applications as biodiesel additive and cellulose production, and the oil from the seeds presents antibacterial and laxative properties.

The wood presents indistinct whitish-beige heartwood and sapwood, uncharacteristic odor, indistinct taste, medium texture, straight grain, and little variance in luster. Anatomically the wood presents axial parenchyma visible only under magnification an apotracheal diffuse in clusters forming irregular lines; non-stratified numerous to very numerous rays; medium to large, few, diffuse-porous, predominantly solitary and radial multiples vessels; and growth rings slightly delimited by fibrous tissue. The wood presents low density, and can be indicated for use in non-structural processes, packaging segments, boxes, and cladding that does not require finishing with excellent texture (ROLIM & PIOTTO 2018, 2019).

2.2.3. *Copaifera lucens* Dwyer

Known as copaíba-vermelha, belonging to the family Fabaceae (Figure 4). It is a native tree, endemic to the northeast and southeast, covering the phytogeographical domains of the Atlantic Forest (COSTA 2017). The plantation of this species have 31 years old (ROLIM & PIOTTO 2018, 2019).

Figure 4. *Copaifera lucens* Dwyer of Vale Natural Reserve, being (A) species haste; (B) wood visual appearance; and (C) cross section 10x zoom. Source: Own authorship and adapted from ROLIM & PIOTTO (2018, 2019).

The wood of this species have a more restricted to the use of resin, mainly for the manufacture of drugs for wound healing (SOUZA 2015). According to Rolim & Piotto (2018, 2019) the species can present, not all trees, essential oil production, with high market value in North and Southeast Brazil. The same authors affirm that some *Copaifera lucens* Dwyer are planted with the aim of oil eventual wood production.

The wood presents distinct heartwood and sapwood, brown heartwood with darker rays and grayish beige sapwood, characteristic odor, slightly astringent taste, medium texture, straight to irregular grain, and variance in luster. Anatomically the wood presents axial parenchyma barely visible without magnification, paratracheal aliform losangular and in marginal bands; and non- thin, numerous, unstratified rays; very few to few, diffuse-porous, predominantly solitary and in multiples of two in radial arrangement vessels; and growth rings delimited by parenchyma in marginal bands. The wood presents medium density and hardness and can be indicated for use in light structures, furniture, frames, packages, boxes, and utensils (ROLIM & PIOTTO 2018, 2019).

2.2.4. *Astronium concinnum* Schott ex Spreng.

It belongs to the family of Anacardiaceae, is commonly known as gonçalo-alves, aroeira-rajada, guarubu-violeta and mucuri (Figure 5). This species occupies the terrestrial substrate, native and endemic to Brazil. The species is distributed widely by different biomes of the national territory covering the northeast and southeast. Its wood is more used in exteriors, buildings, floors and furniture (LORENZI 2002) and has high-quality wood with high market demand and has been extensively exploited in the Atlantic Forest (ROLIM & PIOTTO 2018, 2019). The plantation of this species have 22 years old (ROLIM & PIOTTO 2018, 2019).

A **B**

C

Figure 5. *Astronium concinnum* Schott ex Spreng. of Vale Natural Reserve, being (A) species haste; (B) wood visual appearance; and (C) cross section 10x zoom. Source: Own authorship and adapted from ROLIM & PIOTTO (2018, 2019).

The wood presents distinct heartwood and sapwood, reddish-brown heartwood and light yellow sapwood, uncharacteristic odor, indistinct taste; irregular slightly leaning grain; fine texture, no variance in luster. Anatomically the wood presents axial parenchyma only visible under magnification, paratracheal scarce; thin to medium, few to numerous, non-stratified rays; small to medium, numerous, semi-ring-porous, solitary and radial multiples, obstructed by tylosis vessels; and growth rings delimited by fibrous tissue and semi-ring-porous. The wood presents medium to high density and high hardness wood and can be indicated for structural use in construction, frames, furniture and floors (ROLIM & PIOTTO 2018, 2019).

2.2.5. *Libidibia ferrea* var. *parvifolia* (Mart. ex Tul.) L. P. Queiroz

This species has the synonyms *Caesalpinia ferrea* Mart. ex Tul. and *Caesalpinia ferrea var. parvifolia* Benth., belonging to the family Fabaceae-Caesalpinoideae (Figure 6), having common name of pau-ferro. It is a species of terrestrial substrate, native and endemic to Brazil, distributed in the northeast and southeast (QUEIROZ 2009). The plantation of this species have 24 years old (ROLIM & PIOTTO 2018, 2019).

A B

C

Figure 6. *Libidibia ferrea* var. *parvifolia* (Mart. ex Tul.) L. P. Queiroz of Vale Natural Reserve, being (A) species haste; (B) wood visual appearance; and (C) cross section 10x zoom. Source: Own authorship and adapted from ROLIM & PIOTTO (2018, 2019).

Analyzing the workability, it can be affirmed that the wood planning, turning, sanding and is difficult for drilling, but it can be considered a good quality wood, very durable, with high resistance to attack of fungi. Because it is moderately heavy and of medium mechanical properties, the wood of this species can be used in light internal construction and framing, in the manufacture of high quality furniture, domestic floors, boats, transports, laminates and plywood, tool handles and utensils, packaging and pallets, cooperage, musical instruments, decoration and decoration (IPT 1989). According to Rolim & Piotto (2018, 2019) the wood is little used as timber, likely because its wood is very hard and difficult to work.

The wood presents distinct heartwood and sapwood, dark gray heartwood and light yellow sapwood both with fibrous appearance, uncharacteristic odor, bitter taste, medium texture, straight grain, and variance in luster. Anatomically the wood presents axial parenchyma visible without magnification, losangular paratracheal aliform, aliform with linear extension, confluent, and in lines; thin, numerous, stratified rays; small, numerous, difuse-porous, and predominantly solitary and in multiples of two in tangential arrangement vessels; and growth rings delimited by fibrous tissue. The wood presents high density, good stability and can be indicated for construction and structural uses, frames, furniture and flooring (ROLIM & PIOTTO 2018, 2019).

2.2.6. ***Handroanthus serratifolius*** (Vahl) S. O. Grose

It has synonyms such as *Bignonia serratifolia* Vahl, heterotypic *Bignonia araliacea* Cham., *Bignonia conspicua* Rich. ex DC., *Bignonia flavescens* Vell., and others. It is commonly known as ipê ovo de macuco (Figure 7), belonging to the family Bignoniaceae (FERREIRA *et al.* 2004; CORADIN *et al.* 2010; CARRERO *et al.* 2014). This species is found in the terrestrial substrate, being a species native and not endemic to Brazil. It presents national destruction in the north, northeast, south, being present in the phytogeographical domains of another biomes (ANDRADE 2015). The plantation of this species have 28 years old (ROLIM & PIOTTO 2018, 2019).

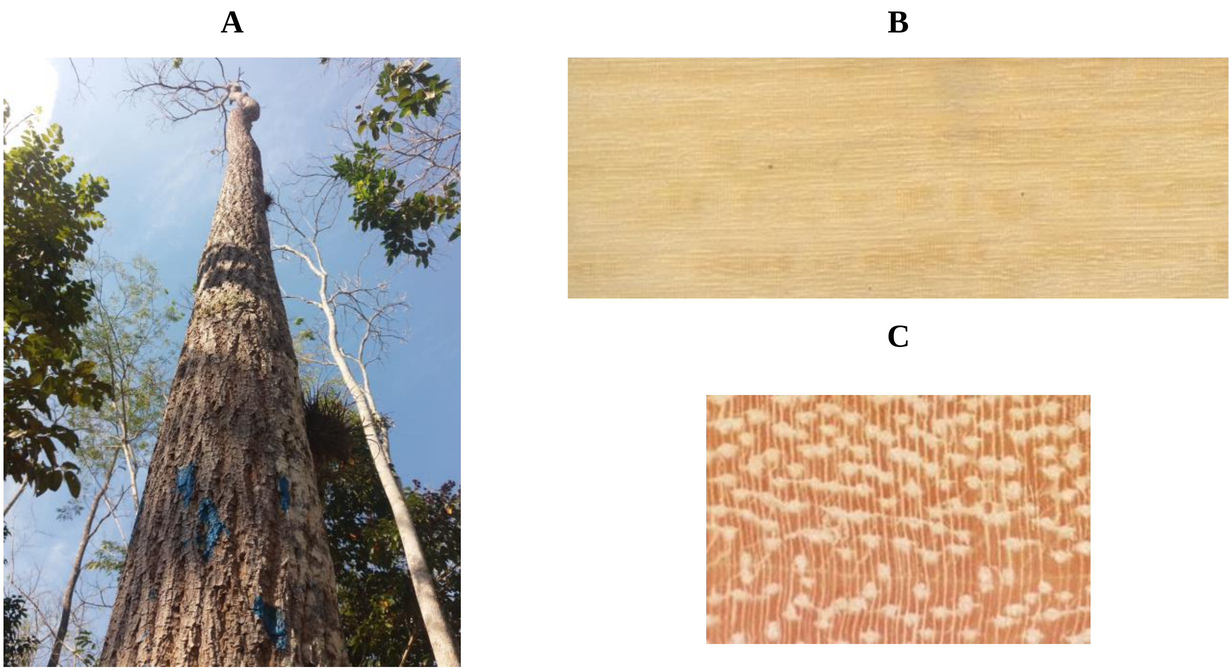

Figure 7. *Handroanthus serratifolius* (Vahl) S. O. Grose. Source, being (A) species haste; (B) wood visual appearance; and (C) cross section 10x zoom. Source: Own authorship and adapted from ROLIM & PIOTTO (2018, 2019).

The wood of this species is widely used as a raw material for furniture, civil and naval construction (FERREIRA *et al.* 2004; TREVISOR 2010; CARRERO *et al.* 2014), being one of the most valuable species in the current timber market, and is heavily logged in the Amazon (ROLIM & PIOTTO 2018, 2019). The species is also indicated for the afforestation of urban centers (LORENZI 2008). The species has been used in medicine by the fact of the wood presents a substance with bactericidal, fungicidal and antitumor activity (CHENNA *et al.* 2001; PORTILLO *et al.* 2001; NUÑEZ *et al.* 2004; PARK *et al.* 2005).

The wood presents indistinct yellowish-beige heartwood and sapwood, uncharacteristic odor, indistinct taste, medium texture, interlocked grain, and little variance in luster. Anatomically the wood presents axial parenchyma only visible under magnification, paratracheal vasicentric, aliform, confluent, forming small oblique arrangements occasionally in narrow marginal bands; thin, few, stratified rays; small, very numerous, difuse-porous, solitary and radial multiples vessels; and growth rings delimited by fibrous tissue and parenchyma rows in marginal bands. The wood presents high density and hardness being indicated for structures, construction, stakes and poles, floors, frames, cladding, tool handles, artisanal goods and utensils (ROLIM & PIOTTO 2018, 2019).

3. THESIS DIVISION

This research was divided into 4 (four) chapters, with:

- **Chapter I** is related to the correlation of non-destructive analyzes performed on living trees of the 6 species mentioned, using the technique of resistographic analysis with physical properties of basic and bulk density of species wood obtained after felling trees;
- **Chapters II and III** assess the potential use of Kraft lignin, a co-product of the pulp and paper industries, in the briquetting densification process using residues from mechanical processing of wood from the *Joannesia princeps* Vell. and *Astronium concinnum* (Engl.) Schott species. The choice of species was based on their different densities (medium and low) and potential industrial use of their woods. Both species have long trunks, usually > 8m, well formed and straight or with a slightly devious. *Joannesia princeps* Vell. is considered average to high growth rate in diameter at breast height - DBH (> 0.75 cm/year), and *Astronium concinnum* presents slow rate of growth in DBH (< 0.75 cm/year) (ROLIM & PIOTTO 2018, 2019);
- **Chapter IV** studies the same wood residues in chemical processes for lignin extraction and sugar conversion using hydrothermal treatment (autohydrolysis) and enzymatic hydrolysis. Figure 8 illustrates the division of chapters performed in this research.

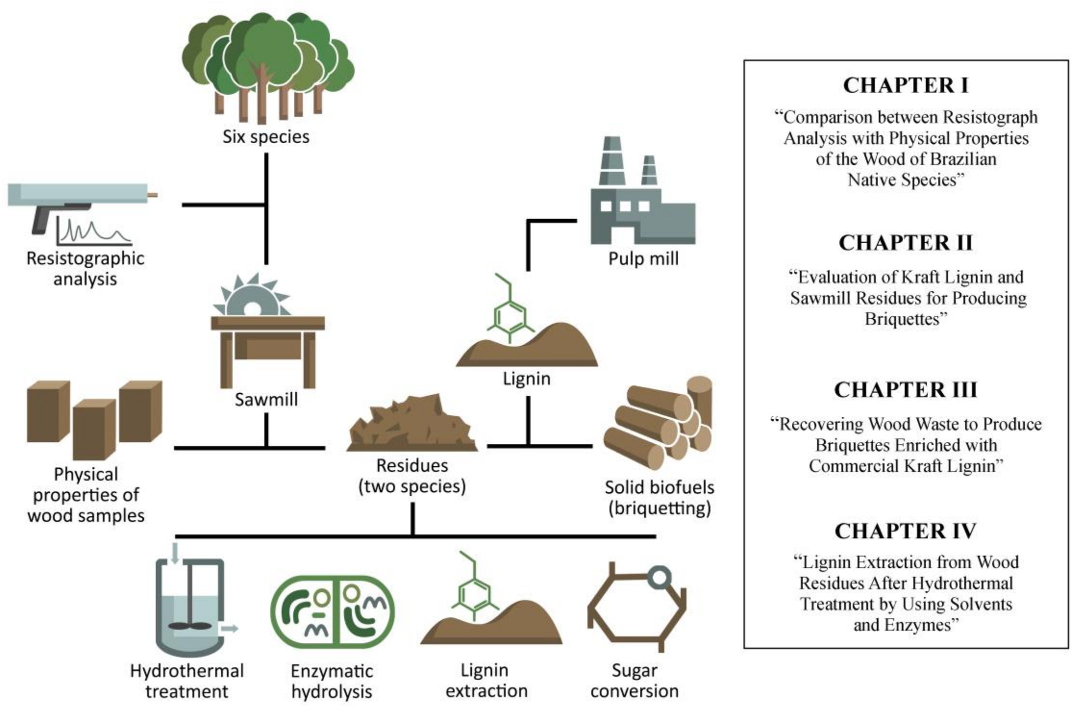

Figure 8. Graphic representation of the division of chapters approached in this research.

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CHAPTER I

COMPARISON BETWEEN RESISTOGRAPH ANALYSIS WITH PHYSICAL PROPERTIES OF THE WOOD OF BRAZILIAN NATIVE TREE SPECIES[1]

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ABSTRACT

There is just little information about the technological aspects of the wood of Brazilian native tree species, which limits their suitable use. The objective of this study was to evaluate the resistograph amplitudes of the wood from six native tree species in different wood density classes, and correlate them with their wood densities to demonstrate the efficiency of this nondestructive technique. The results of the resistograph analysis divided the species into three classes. Analyses of basic and bulk densities of their wood showed statistically significant differences among the evaluated samples that divided them into four classes. The comparison of resistograph method and observed densities showed only a slight difference among the density classes. Therefore, it was found in this study that resistograph analysis may be used for explaining wood properties as well as achieving satisfactory correlations with their actual values, especially the physical properties of species with high wood density.

Keywords: nondestructive method, density, Brazilian species.

1. INTRODUCTION

A significant challenge facing modern societies is the need to become sustainable, in other words, regarding the needs and rational use of natural resources. Many natural resources have been continuously explored and exploited by our society over the years, including forests. In South America, the Brazilian Atlantic Forest biome merits special attention, as its associated ecosystems covering approximately 12.4% of the Brazilian territory (ATLAS DOS REMANESCENTES FLORESTAIS DA MATA ATLÂNTICA 2021), which is "home" to a significant portion of the world's biological diversity.

To achieve the rational use of natural resources by society, in particular forestry resources, it is necessary to invest in science and technology for discovering new marketable species, as well as strategies for their sustainable exploitation. The first step in this process is to determine the technological behavior of the wood of different tree species, which can help one to plan their potential uses. However, there is little information on the link between of technological properties of the wood from Brazilian native tree species. Among these properties, the physical ones play a particularly important role because they determine the quality of the wood and its utilization in forestry activities.

Among wood parameters, density is an index of quality that is highly valued by researchers and forest improvers due to the proven heritability and easy of evaluation, which can help to determine the potential uses of woods (WU *et al.* 2010). To evaluate this characteristic, several nondestructive methods, without causing harm to it or its potential use, have been developed and applied.

The resistograph is an ideal device for describing the variation in the radial profile of wood by drilling into it, which is related to its hardness and density (KAHL *et al.* 2009; ACUÑA *et al.* 2011; CHEN & GUO 2016). Specifically, the resistance of the wood to be drilled depends on its density.

The analysis performed by the resistograph equipment evaluates the resistance posed by the wood against a small diameter rod that enters at a certain drilling speed. A graph of the distance traveled inside the trunk by the amplitude of the resistance imposed on the drill rod is then generated, with this amplitude then being correlated with the density of the wood (ECKARD *et al.* 2010; ACUÑA *et al*. 2011; RINN 2012; COUTO *et al*. 2013). This resistance can also detect local internal defects, cracks and decay (JASIÉNKO *et al.* 2013; TANNERT *et al.* 2014; ZHANG *et al.* 2015).

In recent years, few studies have been carried out on the use of resistograph analysis as a tool to be correlated with wood density values, with the aim of determining potential uses for native tree species in Brazil. Thus, the objective of this study was to demonstrate the effectiveness of this nondestructive methodology (i.e. using the resistograph device) to explain the relationship between the technological behaviors of wood and its physical properties (i.e. density).

2. MATERIALS AND METHODS

2.1. Description of the study area

The research materials for this study came from one homogeneous experimental plantation, established for the purpose of timber production, located inside the Vale Natural Reserve in Sooretama, Espírito Santo State, Brazil. The reserve contains homogeneous plantations of native tree species ranging from 17 to 31 years old and includes more than 100 native species of the Atlantic Forest, originating from seeds of the matrix reserve. After performing a census of the area, six species were chosen (Table 1) and these selected species have been expected to have distinct wood densities based on data classification found in the literature (IPT 1985), two species with wood of low density; two species with wood of medium density; and two species with wood of high density.

According to this classification, the woods with density lower than 0.50 g/cm³ are classified as low density, 0.50 to 0.72 g/cm³ as medium density and woods with density upper to 0.72 g/cm³ are classified as heavy density.

Table 1. Basic density of the species analyzed in this study.

Species	Basic density (g/cm^3)	Source
Joannesia princeps Vell.	0.40 - 0.55	LORENZI 1992; SILVA & LEMOS 2002
Spondias venulosa (Engl.) Engl.	0.36 - 0.56	LORENZI 1992; ROLIM & PIOTTO 2018
Copaifera lucens Dwyer	0.67	ROLIM & PIOTTO 2018

Astronium concinnum (Engl.) Schott	0.64 - 0.68	SANTOS *et al*. 2011
Handroanthus serratifolius (Vahl.) S. O. Grose	0.70 - 0.98	SHIMAMOTO *et al.* 2014
Libidibia ferrea var. *parvifolia* Benth	0.81	ROLIM & PIOTTO 2018

Ninety trees were selected for study, divided among these six species, with 15 trees used per species. Three trees were harvested per species, and the first 2.1-m long log was taken from each tree. Thus, it could be observed that 15 trees were selected for the nondestructive tests, and of these three trees were felled to produce material for destructive analysis.

2.2. Resistograph analysis

The resistograph analysis was carried out using 15 trees per species by following the instruction manual included in the apparatus. With the aid of a Global Positioning System (GPS), two drillings were carried out on each individual tree in the north-south and east-west directions. Hence, 30 resistograph analyses were performed per species, and 180 resistograph analyses in total.

The main variable examined in this study was the resistograph amplitude measurements (RA%), which could be defined as a number representing the difficulty for the drill rod to drill through the wood. The perforation was standardized at 10 cm for each individual, of which the bark was estimated to represent 10% in later analyses of the results. The software used for resistograph analysis was the program Decom version 2.34c.

2.3. Evaluation of physical properties

After the primary wood processing of each log into boards, the boards that had the best orientation of their anatomical elements were chosen. The samples to be used for the analysis of density were then prepared according to the NBR 7190 standards (ABNT 1997), and six samples were selected per board, resulting in 18 specimens per species.

The method chosen for using in the determination of basic density and bulk density (at 12% moisture) was the gravimetric method. All specimens were measured and weighed in the green, saturated and dry conditions. With these data, it was possible to calculate the values of the basic density (Equation 1) and bulk density (Equation 2) of the wood of each individual and species as follows:

$$\rho_b = \frac{m_s}{V_u} \qquad \text{(Equation 1)}$$

where ρ_b = basic density (g/cm^3); m_s = dry weight of the sample at 103 ± 2°C (g); and V_u = volume of the test sample in the saturated state (cm^3); and

$$\rho_{blk} = \frac{m_{12\%}}{V_{12\%}} \qquad \text{(Equation 2)}$$

where ρ_{blk} = bulk density at 12% moisture (g/cm^3); $m_{12\%}$ = weight of the sample at 12% moisture (g); e $V_{12\%}$ = volume of the test sample at 12% moisture (cm^3).

2.4. Comparison between results of nondestructive and destructive analyses

The data obtained met the requirements of normality and homogeneity for parametric tests. Therefore, analysis of variance (ANOVA) was performed to compare the differences of densities among the different species.

Based on the results of the above analysis, the coefficient of determination (R^2) of the relationship between the results of the nondestructive and destructive analyses of the resistograph amplitude with the physical properties of the individuals was calculated using a linear regression. This was performed to test the effectiveness of this nondestructive methodology in explaining the technological behaviors of the wood.

3. RESULTS AND DISCUSSION

3.1. Resistograph amplitude analysis

In Figure 9, the relation of the resistograph behavior to the drilling length can be seen. The resistograph amplitudes of the species analyzed and the results of the Tukey HSD test comparing the means among species are shown in Table 2. The results of the analysis of the resistograph amplitude allowed the species examined to be divided into three distinct classes. *Libidibia ferrea* var. *parvifolia* (Mart. ex Tul.) L. P. Queiroz showed a resistograph amplitude value that was much and significantly higher than that of the other species, and thus being in a higher density class when compared to them. *Handroanthus serratifolius* (Vahl) S. O. Grose, *Copaifera lucens* Dwyer and *Astronium concinnum* Schott ex Spreng. had the same density class. *Astronium concinnum* was placed in the lowest density class, along with *Spondias venulosa* (Engl.) Engl. and *Joannesia princeps* Vellozo.

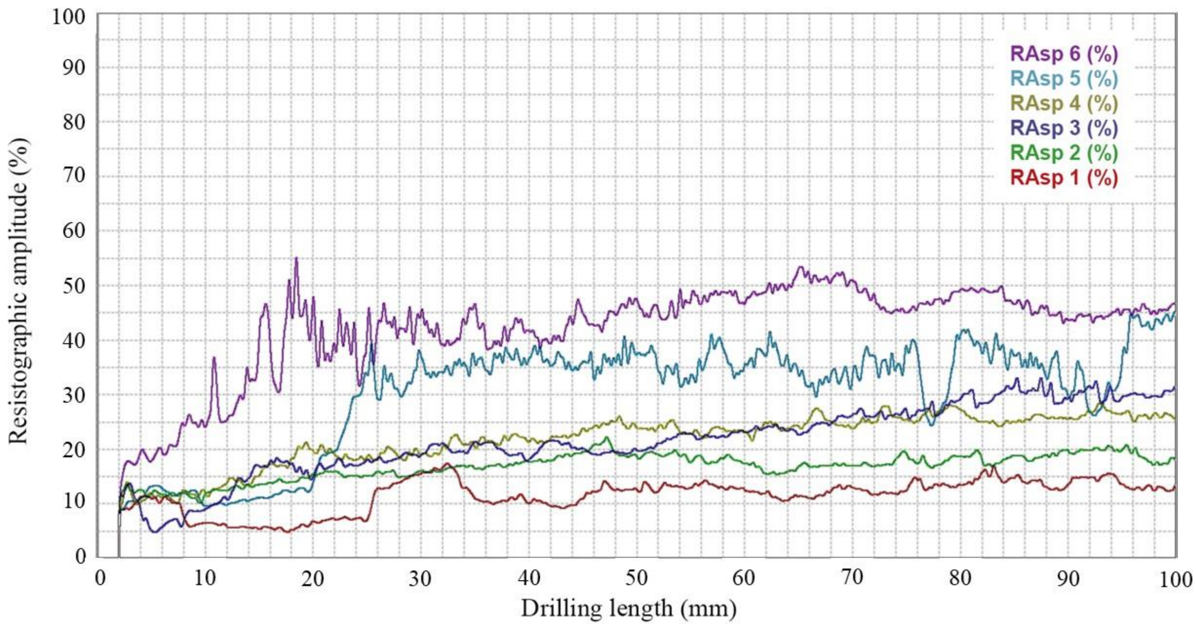

Figure 9. Graphic representation of the average technological characteristics of the woods of different species during resistograph drilling operation. RA = resistograph amplitude (%); sp. 1 = *Joannesia princeps* Vell.; sp. 2 = *Spondias venulosa* (Engl.) Engl.; sp. 3 = *Copaifera lucens* Dwyer; sp. 4 = *Astronium concinnum* (Engl.) Schott; sp. 5 = *Handroanthus serratifolius* (Vahl.) S. O. Grose; sp. 6 = *Libidibia ferrea* var. *parvifolia* Benth.

Table 2. Mean resistograph amplitude values of the analyzed species, listed in descending order.

Species	Resistograph amplitude (%)
Joannesia princeps Vell.	12.05 (± 1.8) c
Spondias venulosa (Engl.) Engl.	15.75 (± 2.9) c
Astronium concinnum (Engl.) Schott	17.87 (± 5.1) bc
Copaifera lucens Dwyer	21.33 (± 2.1) b
Handroanthus serratifolius (Vahl.) S. O. Grose	22.37 (± 1.2) b
Libidibia ferrea var. *parvifolia* Benth.	31.92 (± 1.9) a

Values in parentheses indicate the coefficient of variation for each mean; means with the same letter (a, b, c) were not significantly different statistically between species at a significance level of 5%.

The study concerning technological behaviors of wood using the resistograph device is relatively new, especially in Brazil, where only a few studies have been done over the last decade with wood from Brazilian trees (Table 3) to verify their potential use in various applications.

Table 3. Resistograph amplitude values of the wood of Brazilian trees found in the literature.

Species	Resistograph Amplitude (%)	Source
Clones of *Eucalyptus*	10.1 - 20.9	GOUVÊA *et al.* 2011
Cedrela fissilis Vell.	10.6	SILVA *et al.* 2017
Eucalyptus grandis	11.77	COUTO *et al.* 2013
Eucalyptus urophylla	12.99	COUTO *et al.* 2013
Hybrid clones of *Eucalyptus*	15.2	DIAS *et al.* 2017
Clones of *Eucalyptus*	23.9	OLIVEIRA *et al.* 2011

Comparing the results found in this study with those in the literature, it could be stated that the characteristic of the wood of Brazilian native trees matches its physical properties. Therefore, denser wood has higher resistograph amplitude, and in the same way, wood with lower density presents smaller resistograph amplitude.

3.2. Physical properties of wood

The results of the destructive evaluation of the physical properties (basic and bulk densities) of the wood of the six species studied are shown in Table 4. Normality tests were performed on the data, and significant differences among the means for different species were found using Tukey's test (Table 4).

Table 4. Values of the basic (ρ_b) and bulk (ρ_{blk}) densities (at 12% moisture) of the wood of the species studied, listed in descending order.

Species	ρ_b (g/cm^3)	ρ_{blk} (g/cm^3)
Joannesia princeps Vell.	0.32 ± 0.02 d	0.41 ± 0.03 d
Spondias venulosa (Engl.) Engl.	0.34 ± 0.03 d	0.44 ± 0.03 d
Copaifera lucens Dwyer	0.55 ± 0.03 c	0.67 ± 0.04 c
Astronium concinnum (Engl.) Schott	0.64 ± 0.006 b	0.84 ± 0.07 b
Handroanthus serratifolius (Vahl.) S. O. Grose	0.80 ± 0.02 a	1.03 ± 0.01 a
Libidibia ferrea var. *parvifolia* Benth.	0.81 ± 0.02 a	1.08 ± 0.07 a

Means followed by the same letter did not significantly differ statistically at a significant level of 5%.

The results obtained can be interpreted as implying the existence of four distinct density classes for both basic and bulk densities. The highest density class included the species *L. ferrea* and *H. serratifolius*. These values reaffirm that these species present basic and bulk densities that can be considered high (heavy), as they were previously listed in the classification of Instituto de Pesquisas Tecnológicas (1985).

The second class comprised the species *A. concinnum*, indicating that it had values of basic density considered medium, and bulk density considered high (heavy). The third class included *C. lucens*, which presented values of basic and bulk densities that characterize it as a species of medium wood density.

The fourth and last class included the species *S. venulosa* and *J. princeps*, which both presented values of basic and bulk densities that characterize them as having wood of low density.

3.3. Comparison of the resistograph amplitudes with the density values

Table 5 shows the observed correlations between the results of the resistograph analysis and the densities (basic and bulk) of each species. The resistograph amplitude and basic density of all species were significant correlated. The species with higher density values showed stronger correlations between their resistograph amplitudes and both basic and bulk densities, with particularly high R^2 values found between their resistograph amplitudes and basic densities. This fact was highlighted by the high R^2 values found for the species *L. ferrea* (0.98), *H. serratifolius* (0.98) and *A. concinnum* (0.97).

Table 5. Correlation of resistograph amplitude (RA) consisting of values of basic (ρ_b) and bulk densities (ρ_{blk}). Values in the table are the R^2 values of comparisons between RA and density.

Species	RA*ρ_b	RA*ρ_{blk}
Copaifera lucens Dwyer	0.55	0.70
Spondias venulosa (Engl.) Engl.	0.62	0.68
Joannesia princeps Vell.	0.62	0.62
Astronium concinnum (Engl.) Schott	0.97	0.80
Handroanthus serratifolius (Vahl.) S. O. Grose	0.98	0.71
Libidibia ferrea var. *parvifolia* Benth.	0.98	0.80

The species *J. princeps* (0.62) and *S. venulosa* (0.62) presented more satisfactory R^2 values when the resistograph amplitude was compared with the basic density variable than did *C. lucens* (0.55).

It is important to mention that the species with lower values of basic density (*S. venulosa* and *J. princeps*) presented moisture contents of approximately 20%, while medium density species (*C. lucens* and *A. concinnum*) had an average value of 18.3%, and the heavy density species (*H. serratifolius* and *L. ferrea*) 16.3%. According to the work of Logsdon & Calil Junior (2002), Krestchmann (2008) and Glass & Zelinka (2010), the physical and mechanical properties depend on the moisture content of the wood, being wood resistance tends to decrease when this content is high. However, the *C. lucens* wood was the only species that presented different characteristic according to this analysis, because even presenting a medium moisture content compared to the others, this species showed lower correlation with the basic density.

When analyzing the correlation between the resistograph amplitude and the bulk density (at 12% moisture), stronger correlations (higher R^2 values, explaining how well a regression line fits the data) were found for the species *L. ferrea* (0.80) and *A. concinnum* (0.80), followed by *H. serratifolius* (0.71), *C. lucens* (0.70), and *S. venulosa* (0.68), while *J. princeps* (0.62) had the weakest correlation between these variables.

Few previous studies have evaluated the correlation of the resistograph amplitude of wood with the actual wood density, and in the majority of cases such studies compared the RA% only with the basic density of the species, and were done on exotic species. Working with *Eucalyptus*, Gouvêa *et al.* (2011) found R^2 values ranging from 0.19 to 0.74. By researching native species, Carrasco (2013) found the R^2 value equal to 0.86 between the RA% and the bulk density, and Silva *et al*. (2017) found the R^2 value equal to 0.55 for *Cedrela fissilis* Vellozo when evaluating the relationship between its RA% and basic density. Through this study, it was verified that there are still few studies that have used the resistograph method to analyze the physical properties of wood, with most of them being applied to the *Eucalyptus* genus and in essence, finding weak correlations.

4. CONCLUSIONS

The results of this study indicated that a nondestructive methodology using resistograph analysis may be used to estimate the potential uses of wood based on its density, as it could explain the technological behaviors of wood by achieving strong correlations with the wood's physical properties, more precisely those in species with higher wood density. Although the use of resistograph technology is recommended to assess the wood characteristics of live trees, more studies are necessary to optimize the use of this nondestructive technique with the aim of predicting wood density and suggesting potential technological uses for it.

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CHAPTER II

EVALUATION OF KRAFT LIGNIN AND SAWMILL RESIDUES OF *Joannesia princeps* Vellozo FOR PRODUCING BRIQUETTES

ABSTRACT

The aim of becoming a society based on the rational utilization of the natural resources, has led to the consideration of many alternatives by academic and industrial sectors. Co-products of wood processing and cellulose mills can be used for bioenergy generation. The densification of biomass involves handling, transportation and storage issues, and furthermore, when industrial forest residues such as lignin are added to this biomass, the final energetic product may have some improved properties, adding value to the chain. The purpose of this study was to evaluate the usage of the woody industrial waste, the sawdust from *Joannesia princeps* Vellozo enriched with Kraft lignin as an additive, aiming to produce briquettes. One of the main findings from this work was the possibility to obtain a briquette with better properties (higher bulk density and higher resistance) when using 6% of Kraft lignin as an additive and a pressure of 1500 PSI (10.3 MPa).

Keywords: biorefinery; different sources; potential uses.

1. INTRODUCTION

The use of all the components from lignocellulosic biomasses is related to integrated biorefinery processes. This is a concept that has gained a lot of attention in the last decade and has resulted in the development of researches with the aim to advance and optimize the rational use of biomass for the generation of bioenergy, macromolecules and aromatics (LUO & ABU-OMAR 2017). Lignocellulosic biomass as a renewable source has the potential to decrease the dependence of the society on fossil fuels to generate bioenergy and mitigate the environmental problems, leading to a more sustainable society.

The main idea of the biorefineries based on lignocellulosic biomass includes the separation of the main components of the biomass, such as lignin, carbohydrates, among others. In this context, the studied materials on a large scale are cellulose and lignin, specially from hardwood. Currently, there are industrial facilities in the world designed to extract and offer lignin to the market (LUO & ABU-OMAR 2017) deal to the concept of bioeconomy and sustainability (MACFARLANE *et al.* 2014; NDIBEWU & TCHIETA 2018).

The Kraft lignin (KL) may have different applications, however its use is still a challenge for having heterogeneous chemical compositions, being it investigated for producing thermoset, thermoplastic and energy, for example (PNNL 2007; NIELSEN *et al.* 2009; AZADI *et al.* 2013; DUONG *et al*. 2014; SCOWN *et al.* 2014; UPTON & KASKO 2016) and on this research the focus is on the agglutinating and energy properties.

Considering the concerns on the rational utilization of the lignocellulosic biomass by our society, wood processed in the sawmills, which is a common activity in many countries, is another neglected raw material, which is a considerable source of funds and taxes. The wood is poorly used, with around 40-60% of waste generated from the log wood (OBERNBERGER & THEK 2004) which in general is burned in the sawmills to generate energy or discarded into landfills (ACKOM *et al*. 2010). The main problem of selling these wastes to produce energy is their low density, which makes transport not possible. However, there are many techniques for increasing the biomass density aiming to increase its usage to produce energy, e.g., pelleting, briquetting.

Pellet density and abrasion resistance are influenced by the physical and chemical properties of the raw material and the temperature and applied pressure during the pelleting process (CLAVIJO *et al.* 2020). Gilvari *et al.* (2019) affirms that the most important quality parameters of solid bio-materials are the compressive strength, abrasion resistance, impact resistance, moisture adsorption, and density. Richards (1990) studying briquettes affirms that resistance to crushing, durability, impact resistance, and water adsorption are four crucial factors to be taken into account in developing and evaluating the densification process and quality of densified materials.

According to Gilvari *et al.* (2019) there are some examples of international standards to measure the quality of densified materials (biofuels) as compressive strength (ISO17225-2; ÖNORM M 7135), bulk density (DIN 51705 2001; EN 15103 2010); and heating values generated in the biomaterial combustion (DIN EN 14918 2010).

The lignin content is an important parameter in sawdust particles bonding (SHYAMALEE *et al.* 2015). Natural lignin in biomass cell wall composition allows the binding and softening in higher temperatures developing a compact unit (KERS *et al.* 2010; LUMADUE *et al.* 2012; NGUSALE *et al.* 2014). Therefore, the addition of technical lignin as a binder in the briquetting process can promote better bonding, size reduction, stability, durability and combustion efficiency properties (WAMUKONYA & JENKINS 1995; BHATTACHARYA *et al.* 2002; KERS *et al.* 2010; BOSCHETTI *et al.* 2019b; OLUGBADE *et al.* 2019).

The elemental composition of the biomass, bulk density, tensile strength and heating values are important parameters to characterize and study briquetting processes (KARUNANITHY *et al.* 2012; MAIA *et al.* 2014; JITTABUT 2015; SETTE JUNIOR *et al.* 2017; ONUKAK *et al.* 2017; DESHANNAVAR *et al.* 2018; BOSCHETTI *et al.* 2019a,b). In this context, the use a utilization of compacted biomass (i.e. briquettes) enriched with Kraft lignin may be an alternative rational strategy for using these forestry residues as renewable energy sources. There are a few studies which have reported the use of compacted biomass rich in lignin to produce energy (LURII 2008; PEREIRA *et al.* 2016; GOUVÊA *et al.* 2017). Lignosulphonate and kraft lignin, derived from lignin, which is the strengthening agent in plants and trees, have also been investigated for their binding properties (BOUDET 2000; EKEBERG *et al.* 2006; LEOKAOKE *et al.* 2018).

Lignin can function as a fuel source as well as a thermally fusing binder that conveys strength to the bricks in the high temperature pyrolytic heat area of the cupola. Although lignin has the potential for fuel generation, firstly by uncoupling lignin polymer from other cell wall polymers and secondly by exploiting the properties of lignin polymer for biofuel or for the production of other commercially useful compounds (VAVILALA *et al.* 2019). The use of lignin for other non-fuel applications appears to be the more promising, higher value and energy-conserving option (AYYACHAMY *et al.* 2013).

The aforementioned studies are related to the most common raw materials found, such as *Pinus* and *Eucalyptus* woods. There are many other sources that require further investigations. For example, the species *Joannesia princeps* Vellozo, which is a pioneer species with a long lifespan, from the Brazilian Atlantic Forest, and is studied for reforestation purposes (ROLIM & PIOTTO 2019). According to the same authors this species presents long trunks, usually higher than 8 meters, formed and straight with a slight devious and grows more than 0.75 cm/year at the diameter at breast height. These characteristics highlight the use of wood from this species as a rich source of raw material for forestry and use in different wood segments.

This wood feedstock has been used in sawmills, and the resulting residues can provide an opportunity to improve and enrich a green product that is economically viable and does not harm the environment. The production of densified materials that uses residues from wood processing industry and used wood as feedstock characterizes a densified material of class B (EUROPEAN STANDARD 2009). The objective of this research was to evaluate the application of the woody waste as feedstock, the sawdust of *Joannesia princeps* Vell. enriched with Kraft lignin as an additive in different proportions/concentrations, aiming to produce and evaluate briquettes parameters for bioenergy generation.

2. MATERIALS AND METHODS

2.1. Raw Materials

In this work residues from the preparation of wood timber were used. The specie of wood, *Joannesia princeps* Vell., is considered a potential wood species and is commonly found in the seasonal and ombrophilous Atlantic forest of some Brazilian states (FLORA DO BRASIL 2020).

Three trees samples were collected, through random drawing and resorting in case trees located on the edge of the plantation were draw, from an experimental station in the Vale Natural Reserve, located in Sooretama, Espírito Santo state, Brazil. The residues were obtained from a machining process commonly found on a sawmill. The residues (sawdust) without bark, were collected and stored. The Kraft lignin used as an additive in the briquetting process was obtained from a Brazilian Kraft pulp mill company that processes *Eucalyptus* spp. as feedstock and was used without any modification.

2.2. Raw Materials Characterization

The chemical composition of wood was carried out by grounding 1 kg of wood residue in a Wiley type mill to produce sawdust of variable sizes. The obtained sawdust was screened according to the Tappi Standard T 257-cm02 (TAPPI 2012). The sawdust fraction that passed through the 40 mesh, and was retained in the 60 mesh screen was air dried and conditioned in a room with a controlled humidity and temperature (20 ± 1˚C, 50 ± 2% RH) until an equilibrium moisture was achieved (~10%). This sawdust (raw sawdust) was used for chemical analyses. The analysis of ash was carried out directly on the raw sawdust, according to the Tappi Standard T 15 os-58 (1991) combined with T 211 (TAPPI 2002). The extractive contents of the biomass were assessed by extractions using ethanol/toluene (1:2); ethanol and hot water solvent, according to the Tappi Standard T264 cm-97 (1997). The syringyl: guaiacyl ratio was determined following the alkaline nitrobenzene oxidation proposed by Lin & Dence (1992). This method describes the degradation of the constitutive lignin building units - p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) moieties into aldehydes.

The contents of uronic acids, acetyl groups and sugars (glucan, mannan, galactan, xylan and arabinan) in the extractive free biomass were determined (SOLAR *et al.* 1987; SCOTT 1979; WALLIS *et al.* 1996; SCAN 2009). The uronic acid was measured by colorimetric determination, acetyl groups were determined by the liberated acetic acid by high performance liquid chromatography (HPLC), and the sugar content was determined in an acid hydrolyzate by ion chromatography (IC). The acid insoluble lignin, and acid soluble lignin were determined according to TAPPI T222 om-97 (1998) standard procedure and TAPPI UM 250 (1991), respectively.

The Deutsches Institut Für Normung method (DIN) EN 14918 (2010) was used to determine the low and high heating values (LHV and HHV, respectively) using an IKA300® adiabatic calorimeter pump. The LHV and HHV were determined by equations available in Annex E in the DIN EN 14918. The elementary analysis of the wood biomass followed the DIN EN 15104 (2011) procedures. This method consists in the combustion of a known mass of the sample in oxygen converted into ash and gaseous products, and the carbon dioxide, water vapour and nitrogen mass fractions of the gas stream are determined quantitatively by instrumental gas analysis procedures. The obtained data was compared with compared to *Eucalyptus* spp. wood data, most commonly planted and researched hardwood species in Brazil.

2.3. Briquetting

The briquetting process was conducted using a laboratory briquette machine with a piston press (LB-32, Lippel, Brazil). The briquetting conditions were determined experimentally through preliminary tests of pressure application and the time required for pressing and cooling. The temperature chosen (120 °C) was determined as a function of the lignin plasticization, which is a compound responsible for the bond between the wood particles during the application of pressure. Three compression pressure conditions were used: 900 PSI (6.2 MPa); 1200 PSI (8.27 MPa); and 1500 PSI (10.3 MPa) with pressing and cooling times of 6 minutes, totalizing 12 minutes of process.

To determine the briquetting conditions, preliminary tests relating to compaction time, cooling time and temperature were carried out. The conditions chosen were those where briquettes were obtained without cracks and with less deformation.

The proportion of Kraft lignin mixed with the wood fines was 0, 2, 4, and 6%, and the mass of each briquette was fixed to 20 g, amounting 12 treatments, with 6 repetitions of each one. When an excess of the Kraft lignin is used, it loses its efficiency as a binding agent and it negatively affects the briquette density (BOSCHETTI *et al.* 2019a). Preliminary tests were performed and no more than 6% of lignin was used to avoid problems occurring with the equipment, due to the lignin plasticization.

In order to evaluate the quality of the briquettes and the briquetting process, visual analyses were first carried out to observe the presence of cracks and deformations on their sides, as well as analysis of the variations of the briquettes (height and diameter) and loss of mass in the briquetting. These visual observations were performed after the cooling time during measurements of height and diameter of briquettes.

2.4. Evaluation of briquettes performance

These studied variables include moisture content, heating value, abrasion resistance, particle density, ash content, and ash melting point. The bulk density analysis was performed according to the Vital (1984) method. The modulus of rupture value, conducted by the compressive strength test, was calculated as a function of the area and the resistance strength of the briquette to the rupture stress.

The modulus of rupture result was determined using a software coupled with the universal test equipment called “Contenco-Pavitest”. The analysis procedure was in accordance with the Brazilian standard NBR ISO 11093-9 (2009) with adaptations. The equipment applies a perpendicular force on the upper side of the briquette through a piston until it ruptures. The force was determined by a preliminary test speed (3.5 mm.min-1). The briquette was tested in the vertical position, and the forces were applied parallelly, according to methodology adapted from the norm ABNT NBR ISO 11093-9 (2009). The briquettes high heating values also were determined by following the (DIN) EN 14918 (2010) standard.

The Shapiro & Wilk test (1965) was used to test the normality of the briquettes data. The data were also submitted to analysis of variance using the Cochran test (1950) to evaluate differences between treatments. The Tukey's t-test was applied at a 95 % significance level when significant differences between the results were found.

3. RESULTS

3.1. Characterization of the raw material

The results on the composition of the species are described in the Table 6, taking into account the importance of the chemical composition of the materials related to the bulk density and briquette rupture modulus. There is a lack of literature regarding the chemical composition of Brazilian native hardwood species, therefore the comparison of the data from this study were compared to *Eucalyptus* spp. (Table 7) (GOMIDE *et al.* 2005; MOKFIENSKI *et al.* 2008; NEVES *et al.* 2011; ZANUNCIO & COLODETTE 2011; TRUGILHO *et al.* 2012; MARTINO *et al*. 2013; PEREIRA *et al.* 2013; ZANUNCIO *et al*. 2013; CARVALHO *et al.* 2015, EICHLER *et al.* 2017; MORAIS *et al.* 2017), which is the most abundant hardwood species used in Brazil for energy application.

Table 6. Chemical composition of the evaluated residues from *Joannesia princeps* Vellozo.

Species	Lignin (%)			Carbohydrates (%)							Total Extr. (%)	Ash (%)	S/G	Sum (%)
	AIL	ASL	Total	Acetyl Groups	Uronic Acids	Glc	Xyl	Man	Ara	Gal				
Joannesia princeps	18.9	2.6	21.5	2.2	2.8	44.4	12.1	1.8	0.6	0.7	11.2	2.5	1.52	97.3
Eucalyptus spp.	21.0 - 30.2	2.9 - 5.1	24.1 - 33.1	1.6 - 3.6	3.2 - 5.9	38.0 - 51.0	9.9 - 14.7	0.3 -1.1	0.1 - 1.6	0.5 - 1.4	0.9 - 10.0	0.15 - 0.83	2.0 - 3.8	-

Where AIL: acid insoluble lignin; ASL: acid soluble lignin; Glc: Glucan; Xyl: Xylan; Man: Mannan; Ara: Arabinan; Gal: Galactan; Total Extr.: Total extractives; S/G: syringyl: guaiacyl ratio.

Table 7. Elemental analysis and high heating value (HHV) and low heating value (LHV) of the wood biomass.

Species	Elemental Analysis (%)						HHV (KJ/kg)	LHV (KJ/kg)
	C	H	N	S	O	Sum		
Joannesia princeps	48.0	5.72	0.11	0.08	43.6	97.5	18.5	17.3
Eucalyptus spp.	46.5 - 54.6	5.6 - 7.4	0.2 - 2.4	0.01-0.09	39.8 - 47.0	-	16.7 - 22.1	18.8 - 19.2

Elemental analysis and biomass properties are intrinsically related to heating values (HHV and LHV), since hydrogen is the element that releases the highest amount of energy during combustion, followed by carbon (TURNS 2013; BOSCHETTI *et al.* 2019a). In Table 8, the composition of the Kraft lignin is presented.

Table 8. Compositional data and heating values of the Kraft lignin.

Carbohydrates (%)					Ashes (%)	HHV (KJ/kg)	LHV (KJ/kg)
Glucan	Xylan	Mannan	Arabinan	Galactan			
0.13	0.09	0.36	0.03	0.05	14.2	21.7	20.8

3.2. Briquetting process

The temperature in briquetting process has significant impact on the briquette quality and strength. (KERS *et al*. 2010). The lignin softening temperature is correlated to the moisture content of the feedstock, being around 130°C in 10% (wet basis) moisture (SHYAMALEE *et al.* 2015). The glass transition temperature (Tg) is an important factor to produce durable and stable bonding briquettes (KALIYAN & MOREY 2010). However, the lignin origin interferes in its properties, being hardwood lignin Tg (124-174°C) and softening temperature lower when compared with softwoods lignin, due to the fewer presence of phenolic hydroxyl groups (GLASSER 1999; KUBO & KADLA 2004; STETLE *et al.* 2011; KUN & PUKÁNSZKY 2017). Therefore, the applied compaction temperature (120 °C) was higher than the glass transition temperature of the lignin (KALIYAN & MOREY 2010; STELTE *et al.* 2012; BOSCHETTI *et al.* 2019a). The glass transition conditions may also have reduced the viscosity and thus increased the mobility of the binding components when using a lignosulphonate (FINNEY *et al.* 2009; LEOKAOKE *et al.* 2018).

The working humidity was 8%, which was within the ideal range proposed by KALIYAN & MOREY (2009). The use of humidity higher than 8% would cause the briquettes to rupture. When the raw material moisture content is very low or above the indicated humidity, it can impair the packaging of the material or produce an unstable briquette, which can disintegrate when stored or transported (QUIRINO 1991), resulting in lower durability and therefore becomes higher susceptibility to damage (MORENO *et al.* 2016).

The amount of lignin per kg of dry matter is very important in briquetting (MANKOWSKI & KOLODZIEJ 2008; KERS *et al.* 2010; ALARU *et al.* 2011). According to Boschetti *et al*. (2019a) studying higher concentrations of kraft lignin can promote significant modifications in briquettes, and lower concentrations can also contribute to resistance and calorific variables. Therefore, it can be inferred that, depending on the proportion of biomass in the briquettes, there is an optimum lignin content, which gives the briquette maximum resistance, and that a high content of this component can reduce its mechanical resistance and that conditions changes in different biomasses, equipment and conditions of study. Berghel *et al.* (2013) studied sawdust compactation with kraft lignin to develop pellets and concluded that from 1% of added KL there are modifications in mechanical durability. Another important factor is the purity of the lignins used in the densification processes, since despite having similar properties, the technical lignins commonly have different elemental compositions related to the manufacturing process.

Table 9 shows results relating to the briquetting processes on the bulk density, modulus of rupture (MOR) and heating values. These results are considered important parameters for the quality of the briquettes highlighting that no significant variations were observed in the sizes (height and diameter) of the studied briquettes. The Kraft lignin should be added to the briquettes to increase the resistance when using lignocellulosic materials at compaction temperatures below the ideal levels for plasticization, contributing to the increment in the heating value (GOUVÊA *et al.* 2017).

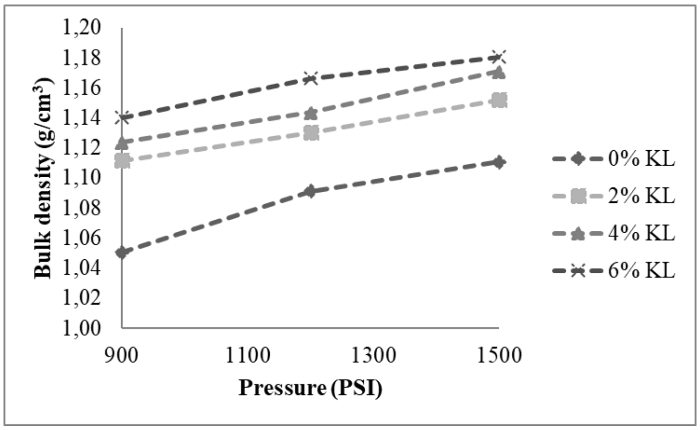
It is important to mention that according to the European Standards (2009) that approaches the pellets specifications, there is a limit of additive that can be incorporated in the densified material. This limit is of 2% of the pressing mass of the material, and this percentage is related to the market price of the final densified briquette.

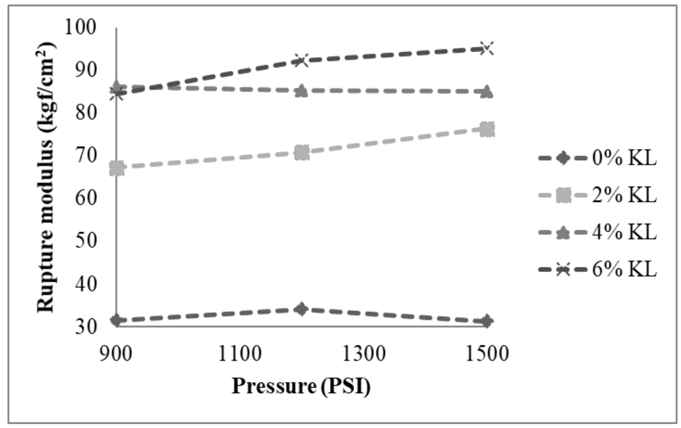
Table 9. Mean values of bulk density (ρ_{ap}), modulus of rupture (MOR), and briquettes heating values per treatment.

Treatments	Pressure (PSI)	Kraft lignin (%)	$\bar{\rho}_{ap}$ (g/cm^3)	MOR (kgf/cm^2)	LHV (KJ/kg)	HHV (KJ/kg)
T1	900	0	1.05 ± 0.01 ^{f}	31.49 ± 1.47 ^{de}	17.6 ± 0.1 ^{ab}	19.4 ± 0.10 ^{abc}
T2	1200	0	1.09 ± 0.02 ^{de}	34.07 ± 2.33 ^{d}	17.4 ± 0.1 ^{cd}	19.2 ± 0.10 ^{cd}
T3	1500	0	1.11 ± 0.01 ^{d}	26.14 ± 6.15 ^{de}	17.5± 0.0 ^{c}	19.3 ± 0.00 ^{c}
A1	900	2	1.11 ± 0.03 ^{d}	63.02 ± 10.9 ^{c}	17.7 ± 0.0 ^{a}	19.5 ± 0.00 ^{a}
A2	1200	2	1.13 ± 0.02 ^{cd}	66.98 ± 12.33 ^{c}	17.7 ± 0.1 ^{a}	19.5 ± 0.05 ^{ab}
A3	1500	2	1.15 ± 0.01 ^{bd}	73.90 ± 6.33 ^{c}	17.6 ± 0.0 ^{b}	19.4 ± 0.00 ^{ab}
B1	900	4	1.12 ± 0.03 ^{cd}	86.21 ± 12.4 ^{a}	17.6 ± 0.0 b	19.4 ± 0.05 ^{ab}
B2	1200	4	1.14 ± 0.02 ^{bcd}	85.32 ± 2.59 ^{b}	17.3 ± 0.1 ^{d}	19.1 ± 0.05 ^{de}
B3	1500	4	1.17 ± 0.01 ^{a}	85.12 ± 6.85 ^{b}	17.2 ± 0.0 ^{e}	19.0 ± 0.00 ^{e}
C1	900	6	1.14 ± 0.01 ^{cd}	84.46 ± 6.26 ^{b}	17.5 ± 0.0 ^{c}	19.3 ± 0.00 ^{c}
C2	1200	6	1.17 ± 0.01 ^{a}	92.30 ± 5.81 ^{a}	17.6 ± 0.0 ^{b}	19.4 ± 0.00 ^{ab}
C3	1500	6	1.18 ± 0.01 ^{a}	95.17 ± 7.45 ^{a}	17.7 ± 0.1 ^{a}	19.5 ± 0.10 ^{ab}

Equal letters in the same column indicate equality between the values of the averages at a significance level of 95%.

The incorporation of 2% of KL promotes a significant increase in the mechanical characteristics doubling the tensile properties of the material, but did not have significant implications in the bulk density and the heating values. In general, the inclusion of 6% of KL contributed to the increase in the bulk density and increase the rupture modulus of the briquettes. The bulk density variables presented greater differences when the pressure of 900 PSI was applied. Whereas, the rupture modulus presented greater differences at a pressure of 1500 PSI (Figure 10).





(A) **(B)**

Figure 10. Properties of the briquettes, being: (A) bulk density; (B) rupture modulus, where KL: Kraft lignin.

Concerning the briquettes heating values (LHV and HHV), it was possible to observe that the briquette made with 6% KL and 1500 PSI presented the highest heating value, but these values were not statistically different among studied treatments. Based on the observed data, the lignin addition did not impair the briquettes heating value.

4. DISCUSSION

4.1. Characterization of the raw material

Regarding the lignin content (Table 6), the evaluated biomass presented a lower content when compared to the other wood species, such as *Eucalyptus* spp. studied previously (GOMIDE *et al.* 2005; NEVES *et al.* 2011; TRUGILHO *et al*. 2012; ZANUNCIO *et al.* 2013; PEREIRA *et al.* 2013; EICHLER *et al.* 2017), which are also used for producing briquettes (BOSCHETTI *et al.* 2019a,b).

Lignin content is related to the energy efficiency (MARSK 2008; MENDU *et al.* 2012) of the lignocellulosic biomass, which is essential for the adhesive properties of the material. Lignin can improve adhesion between particles, resulting in better bonding and stability (LI *et al.* 2018). This is possible because of the condensation reactions of the lignin during the pressing process contributing to the bonding mechanism (OKUDA *et al.* 2006).

The syringyl:guaiacyl ratio of *Joannesia princeps* Vell. was lower when compared to the eucalyptus ratio, values ranges from 2.0 to 3.8 (GOMIDE *et al.* 2005; MOKFIENSKI *et al.* 2008; PEREIRA *et al.* 2013; MARTINO *et al*. 2013; MORAIS *et al.* 2017). The heating value of wood can also be influenced by the S/G ratio (PROTÁSIO *et al.* 2017). This information is important to verify that the biomass lignin is more reactive due to the factor of higher content of coniferyl groups compared to eucalyptus. The guaiacyl unit has a higher C/O ratio compared to the syringyl unit and this increases the heating values (SOARES *et al.* 2014, PROTÁSIO *et al.* 2017).

Regarding the carbohydrate content, as expected for hardwoods, the main sugars were the glucan (44.4%) and xylan (12.1%), similar to the results found in the study of Gomide *et al.* (2005), Mokfienski *et al.* (2008), Neves *et al.* (2011), and Morais *et al.* (2017) using *Eucalyptus* sp. in Brazil.

The amount of acetyl groups and uronic acids, both hemicelluloses components (MORAIS *et al.* 2017) can determine the potential use of the wood. The acetyl groups reported in this study is lower than the values found in hardwood species such as *Eucalyptus* sp. (GOMIDE *et al.* 2005; MORAIS *et al*. 2017). The presence of acetyl groups can influence the digestibility of the biomasses being a limit factor for conversion processes (PAN *et al*. 2006; MELATI *et al.* 2019).

The content of uronic acid was lower than the data found by Gomide *et al.* (2005), Zanuncio & Colodette (2011), Carvalho *et al.* (2015), Morais *et al.* (2017). Therefore, with the information of these acids content, the wood of this species can have different uses, *Joannesia princeps* Vell. wood may have application for the bleached pulp production, and reinforce the medicinal use of the species (DONATO-TRANCOSO *et al.* 2014), as it has potential in the development of chemicals for pharmaceutical, medicinal and materials industries (TOMASZEWSKA *et al.* 2018).

According to research by Gomes *et al.* (2015) hardwood species (i.e. *Eucalyptus* clones) present extractives up to 10%. The presence of high levels of substances such as extractives favours generation and release of high levels of energy (ZANUNCIO *et al.* 2013).

Another important parameter of the biomass for energy application is the ash content. A high ash content is disadvantageous because it decreases the heat transfer in the fuel and the biomass heating value (BRAND 2010; PAULA *et al.* 2011a,b; PROTÁSIO *et al.* 2011a,b), as well as increases the corrosion of the equipment used in the process (TAN & LAGERLVIST 2011). The ash contents between several species, and also *Eucalyptus* species varied between 0.10 % and 0.83 % in the studies carried out by Ferreira *et al.* (1997), Neves *et al.* (2011), Protásio *et al.* (2011), Pereira *et al.* (2013), Trugilho *et al.* (2015), Eichler *et al.* (2017), Morais *et al.* (2017), and Simetti *et al.* (2018), while for *Pinus* species values between 0.15 and 0.25 % were reported (MENDES *et al.* 2002).

Analysis such as the elemental composition and the heating values of the wood biomass of *Joannesia princeps* Vell. are presented in Table 7. The elemental composition of the evaluated raw material was similar to those for *Eucalyptus* wood (TRUGILHO *et al.* 2012; PEREIRA *et al.* 2013; EICHLER *et al.* 2017; SILVA *et al.* 2019), except for nitrogen, which presented a much lower level than that found for *Eucalyptus* clones (EICHLER *et al.* 2017). The sulphur content was significant higher than the *Eucalyptus* wood content, however it has been studied that the briquetting process can reduce sulphur and nitrogen release during combustion (HAN *et al*. 2019; QI *et al.* 2021).

The LHV and HHV of the *Joannesia princeps* wood were quite similar to those the values found in the literature (TURNS 2013; EICHLER *et al.* 2017; PEREIRA *et al.* 2016; BOSCHETTI *et al.* 2019a) for *Eucalyptus* and *Pinus* biomasses.

Regarding the carbohydrate content in Table 8, it was possible to observe the composition of the Kraft lignin used in the process, when compared to data in literature (ONUKAK *et al.* 2017). On the other hand, the ash content observed was 14.2%, which was much higher than the values reported in the literature (TOMANI 2010), but similar to found by Pereira *et al.* (2016). Based on the ash content, the results of the heat values were lower than the ones reported in the literature (TOMANI 2010; TEIXEIRA *et al*. 2018; BOSCHETTI *et al*. 2019b).

4.2. Briquetting Process

As expected, the bulk density increased, due to the agglutination and plasticization of lignin. The briquettes incorporated with 6% of Kraft lignin showed a greater difference when compared to the ones produced by the main standard procedures, which presented the best results. The greatest difference was found in the control treatment at 900 PSI compared to the treatment that incorporated 6% of KL to 900 PSI, presenting a difference of 0.09 g/cm^3 of difference. The studies of Boschetti *et al.* (2019a) also showed that the incorporation of 6% of Kraft lignin gives the best results for bulk density. This is important, because high-quality fuels should present high density and strength, with higher energy content (ONUKAK *et al.* 2017) to burn for a longer time (OBERNBERGER & THEK 2004).

The heating values of the *Joannesia princeps* sawdust briquettes did not showed difference between the studied treatments and presented lower values when compared to literature data. Boschetti *et al.* (2019a,b) using the same process temperature and similar pressure conditions for *Eucalyptus* and *Pinus* biomasses achieved higher values of LHV, ranging from 18.5 to 18.8 KJ/kg. This fact can be resulted of the distinct chemical composition of the studied biomass and the Kraft lignin. The use of other technical lignins and lignocellulosic biomasses is recommended for a better understanding of agglutination process interference in different raw material sources densification.

The rupture modulus increased after a rise in pressure (1500 PSI) and a larger amount of lignin was incorporated (6% KL). The maximum rupture significantly interferes with the quality of briquettes, since it is related to its transport and storage and to a certain extent to its durability (GOUVÊA *et al.* 2017). The higher the density, the higher the compressive strength modulus (ONUKAK *et al.* 2017).

Boschetti *et al*. (2019a) studying *Hymenolobium petraeum* Ducke, *Eucalyptus* sp., and *Pinus* sp. briquettes also found similar results, proving that 6% of impregnated Kraft lignin gives better bulk density and rupture modulus properties. Pereira *et al.* (2016) results upon studying pellets confirms that the use of at least 2% of Kraft lignin can change properties of hardwood compressed materials.

5. CONCLUSIONS

The addition of kraft lignin to *Joannesia princeps* sawdust briquettes contributes to the improvement of physical and mechanical properties, with regard to density, mechanical durability, and strength. The addition of kraft lignin for densified biomaterials production is feasible, as long as purer lignins are used. It was possible to obtain a briquette with better properties (higher bulk density, higher tensile strength to compression and high heating values) when using 6% of Kraft lignin as an additive and a pressure of 1500 PSI (10.3 MPa). However, the studied treatments did not imply in the heating values modifications. Considering the market aspects of the briquettes, an inclusion of 2% KL can promote significant modifications in the mechanical properties allowing the production of more resistant and durable biomaterials. In line with the sustainable uses of the available biomasses, the use of a briquette produced under these conditions provides the potential use of the lignocellulosic residues generated by a sawmill as raw material/feedstock for sustainable energy generation. In addition, using a common residue from the pulp mills, adds technological value to the final product, enabling the generation of energy and the maximization of the profit generated in this process.

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CHAPTER III

RECOVERING WOOD WASTE OF *Astronium concinnum* (Engl.) Schott TO PRODUCE BRIQUETTES ENRICHED WITH COMMERCIAL KRAFT LIGNIN[1]

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ABSTRACT

Aiming to use lignocellulosic biomass as energy source, one of the process that may aggregate values is the densification process, which allows the production of bioenergy using solid fuels, mainly for reducing transportation costs. In this research, solid fuel from co-briquetting of wood residues from sawmill using commercial kraft lignin as binder was investigated. The effects of compression pressure (900, 1200 and 1500 PSI) and briquette formulation (varying wood and kraft lignin proportion) on the quality and characteristics of briquettes were evaluated. The main findings were that briquetting of wood residues with kraft lignin resulted in an improvement of bulk density, strength rupture modulus, low heating value (LHV) and high heating value (HHV). The briquettes using 4 and 6% of kraft lignin, and submitted to 1200 to 1500 PSI, presented higher bulk density and strength resistance, respectively. On the other hand, the heating values showed highest results with the addition of 2% lignin at 900 PSI, being this the legal range for additives in briquettes for many countries such as in European Union.

Keywords: hardwood biomass densification, heating values, solid fuel.

1. INTRODUCTION

Lignocellulosic biomass is considered a renewable and alternative material as a potential energy source for the society (LUTTERBACHER *et al.* 2015; CHEN *et al.* 2016; WELFLE 2017; JI *et al.* 2018; WELFLE *et al.* 2020). The renewable supplies rank fourth in the world total energy demand after oil, coal, and natural gas (HUANG *et al.* 2020; GUO *et al.* 2020), being biomass the most significantly type of renewable supply and due to its advantages of being widely sourced, sustainable, and environmentally friendly, it has attracted more and more interest of academic and industrial sectors (GLOBAL BIONERGY STATISTICS 2019). Considering the concerns on the rational utilization of the lignocellulosic biomass by our society, wood processed in the sawmills, which is a common activity in many countries, is another neglected raw material, since it is available in a large volume. In these activities, the wood is poorly used, with around 40-60% of waste being generated from the log wood processing (OBERNBERGER & THEK 2004), which in general is burned in the sawmills to generate energy or discarded into landfills (ACKOM *et al.* 2010).

A challenge for using waste lignocellulosic biomass is that it must be transported from where they are generated, often in milling sites and open fields, to the storage facilities, which may affect the energy balance and costs (MIAO *et al.* 2011; KARAGIANNIDIS 2012; KENNEY *et al.* 2013; KUMAR *et al.* 2015; STREZOV & ANAWAR 2019). One effective strategy to address these concerns is through mechanical densification of the biomass. Mechanical densification is the compaction of biomass to definite sizes, which improves the bulk densities and minimizes the irregularities in shape of biomass, facilitating the transportation (KALIYAN & MOREY 2009). In lignocellulosic biomass processing for the production of solid fuel, pelletizers and briquette press are the most commonly used equipment for mechanical densification. These solid fuels are frequently used as substitute fuels in boilers to produce steam that may be used for electricity production, for example.

Kaliyan & Morey (2009) and Ajiboye *et al.* (2016) support that as a result of the shape and size, among other variables, can determine the compressibility and the products of the densification. Briquettes with higher density values, produced from agriculture and forest residue, may substitute or compliment solid fuels such as charcoal, firewood and coal. The briquettes are high energy density materials, require lower transportation and storage costs, present uniform quality such as constant humidity content, and high mass fluency (SAMUELSSON *et al.* 2009; NILSSON *et al.* 2011).

Several studies have experimentally investigated the characteristics of alternative biomass briquettes, as wood residues, under different conditions of pressure. The results show that the sawdust, most abundant waste or residue in wood-based industries (EMERHI 2011), may generate briquette with better characteristics than other materials (CHIN & SIDDIQUI 2000).

Aiming to improve the mechanical and physico-chemical properties of the solid fuel, many organic and inorganic binders may be used for the densification process (AHN *et al.* 2014; RAJASEEVAN *et al.* 2016) such as starch, protein, fiber, fat/oil, and other additives. The addition of binders in the densified solid fuel production using lignocellulosic biomass as raw materials might have a positive outcome on the strength, in a similar way to the resins used in the production of wood boards (ZHANG *et al.* 2018; LUBWAMA *et al.* 2020).

Considering the available materials from the based forest industry that could be used for bindering purpose, the kraft lignin appears as a promissory material, since it is a hydrophobic compound and it also presents a higher heating value when compared to the whole lignocellulosic biomasses (BOUDET 2000; EKEBERG *et al.* 2006; GOUVÊA *et al*. 2018; BOSCHETTI *et al.* 2019a,b). The worldwide lignin production is approximately 50 million tons (DEMUNER *et al.* 2019) and this by-product have distinct adhesive characteristics and may be used as a densification binder (BOSCHETTI *et al.* 2019b). The use of lignin as binder is relatively new and studies of this application as a binder have been done recently (STELTE *et al.* 2012; AGRAWAL *et al.* 2014; SHYAMALEE *et al.* 2015; PEREIRA *et al.* 2015; MOUSA *et al.* 2017; AAMIRI *et al.* 2019; HÁZ *et al.* 2019; BOSCHETTI *et al.* 2019a,b). The resulting briquettes would cost less to transport, easier to handle and storage (TUMULURU *et al.* 2011).

Regarding the available lignocellulosic biomasses for being used as raw materials, the residual material of the industrial processes seems to be an alternative for improving the rational utilization of the natural resources. Concerning the specie of wood, *Astronium concinnum* (Engl.) Schott, a hardwood species, belongs to the family of Anacardiaceae, commonly known as gonçalo-alves, aroeira-rajada, guarubu-violeta and mucuri, which is a raw material widely used commercially due to its wood quality and availability (ROLIM & PIOTTO 2019). Its wood is more used in exteriors, buildings, floors and furniture (LORENZI 2002a,b, 2014) and its basic density value is around 0.64 g/cm^3 (SILVA *et al.* 2020).

The main goal of this research was to evaluate the application of common woody industrial waste from sawmills (sawdust of *Astronium concinnum* (Engl.) Schott) enriched with eucalypt kraft lignin as an additive, aiming to produce briquettes.

2. MATERIALS AND METHODS

2.1. Raw Materials

In this work residues from the wood sawmill processing *Astronium concinnum* (Engl.) Schott were used. The wood samples evaluated were 22 years old. Three trees samples were collected from an experimental station in the Vale Natural Reserve, which is inside the Atlantic Forest biome, located in Sooretama, Espírito Santo State, Brazil. The residues were obtained from a machining process commonly used on a sawmill. The residues (sawdust) were collected and air dried to a moisture content of about 15% and stored in plastic bags. The commercial kraft lignin used as an additive in the briquetting process was obtained from a Brazilian kraft pulp mill, Suzano Pulp and Paper, which uses *Eucalyptus* spp. as feedstock.

2.2. Methods

The wood biomass, commercial kraft lignin and briquettes were characterized according to the methods described in Table 10.

Table 10. Methods used to characterize wood biomass, kraft lignin and briquettes.

Analysis	Standard
Sawdust fractionation	TAPPI T257-cm02 (2012)
Extractives	TAPPI T264 cm-97 (1997)
Ash	TAPPI T15 os-58 (1991); T211 (2002)
Carbohydrates	WALLIS *et al.* (1996); SCAN-CM 71:09 (2009)
Soluble lignin	TAPPI UM 250 (1991)
Insoluble lignin	TAPPI T222 om-97 (1998)
Acetyl groups	SOLAR *et al.* (1987)
Uronic acids	SCOTT (1979)
Elemental analysis (CHNSO)	DIN EN 15104 (2011) which was measured by using a TruSpec Micro - Leco Instruments 628 Series C/H/N elemental analyzer with oxygen and sulfur module
Low and High Heating Values	DIN EN 14918 (2010)
Briquettes bulk density	VITAL (1984)
Rupture Modulus of Briquettes	NBR ISO 11093-9 (2009)

The briquetting process was conducted using a laboratory briquette machine with a piston press (LB-32, Lippel, Brazil). The briquetting conditions were determined experimentally through preliminary tests of pressure application and the time required for pressing and cooling. The temperature chosen (120 °C) was determined as a function of the lignin plasticization, which is a compound responsible for the bond among the wood particles during the application of pressure (FILIPPETTO 2008). Three compression pressure conditions were used: 6.20 MPa (900 PSI); 8.27 MPa (1200 PSI); and 10.30 MPa (1500 PSI), with pressing and cooling times of 6 minutes.

To determine the briquetting conditions, preliminary tests relating to compaction time, cooling time and temperature were carried out. The conditions chosen were those where briquettes were obtained without cracks and with less deformation. The working moisture was 8%, obtained by using a laboratory greenhouse, which was within the ideal range proposed by Kaliyan & Morey

(2009). The use of moisture higher than 8% would cause the briquettes to rupture. When the raw material moisture content is very dry or above the indicated value, it can impair the packaging of the material or produce an unstable briquette, which may disintegrate when stored or transported (QUIRINO 2004), resulting in lower durability and therefore becomes more susceptible to damage (MORENO *et al.* 2016).

The proportion of Kraft lignin mixed with the wood fines was 0, 2, 4, and 6%, and the mass of each briquette was fixed to 20 g, amounting 12 treatments, with 6 repetitions of each one. When an excess of the kraft lignin is used, it loses its efficiency as a binding agent and it negatively affects the briquette density (HÁZ *et al.* 2019). Preliminary tests were performed and no more than 6% of lignin was used to avoid problems occurring with the equipment, relating to the lignin plasticization, and considering that just 2% of additives may be used in briquettes in many countries, for instance in European Union, the values above this range were used just for evaluating the potential performance delivered by the additive. In order to evaluate the quality of the briquettes and the briquetting process, visual analyzes were first carried out to observe the presence of cracks and deformations on their sides, as well as analyzes of the variations of the dimensions (height and diameter) and loss of mass in the briquetting. These visual observations were performed after the cooling time during measurements of height and diameter of briquettes.

The modulus of rupture result was determined using software coupled with the universal test equipment called “Contenco-Pavitest”. The analysis procedure was in accordance with the Brazilian standard NBR ISO 11093-9 (ABNT 2009) with adaptations. The equipment applies a perpendicular force on the upper side of the briquette through a piston until it ruptures. The force was determined by a preliminary test speed (3.5 $mm.min^{-1}$). The briquette was tested in the vertical position, and the forces were applied parallelly, according to methodology adapted from the ABNT NBR ISO 11093-9 standard (ABNT 2009).

Unfortunately, there was not found literature data which report on the raw material investigated in this study. Therefore, several hardwood species were used as a reference for comparing the results from this work. This also indicates that this work collaborates for disseminating some unpublished scientific information on the raw material used.

Aiming to analyze results obtained in this work, the Shapiro & Wilk test was used to verify the normality of the briquettes data (SHAPIRO & WILK 1965). The data were also submitted to analyses of variance using the Cochran test (COCHRAN 1950) to evaluate differences among treatments. The Tukey's t-test was applied at a 95% significance level, when significant differences among the results were found.

3. RESULTS

The results on the wood residues and eucalypt kraft lignin composition are described in Table 11, taking into account the chemical composition importance of the materials for energy conversion. As also previously described, there was not found literature data which report on the raw material investigated in this study, being the findings on the wood composition an important piece of information for many other works.

Table 11. Chemical characterization of the evaluated biomass and kraft lignin.

	Analysis	***Astronium concinnum* biomass**	**Kraft lignin**
Elemental analysis, %	C	48.40	56.00
	N	0.17	0.14
	H	6.30	4.70
	O	44.50	20.70
	S	0.03	4.20
Soluble extractives, %		6.2	-
Soluble lignin, %		3.8	4.5
Insoluble lignin, %		19.8	80.9
Total lignin, %		23.6	85.4
Carbohydrates, %	Glucan	47.0	0.1
	Xylan	11.1	0.1
	Mannan	1.7	0.4
	Arabinan	0.2	0.1
	Galactan	0.7	0.1
Ash, %		0.7	14.2
High heating value, KJ/kg		19.0	21.7

Low heating value, KJ/kg	17.7	20.8

3.1 Briquetting process

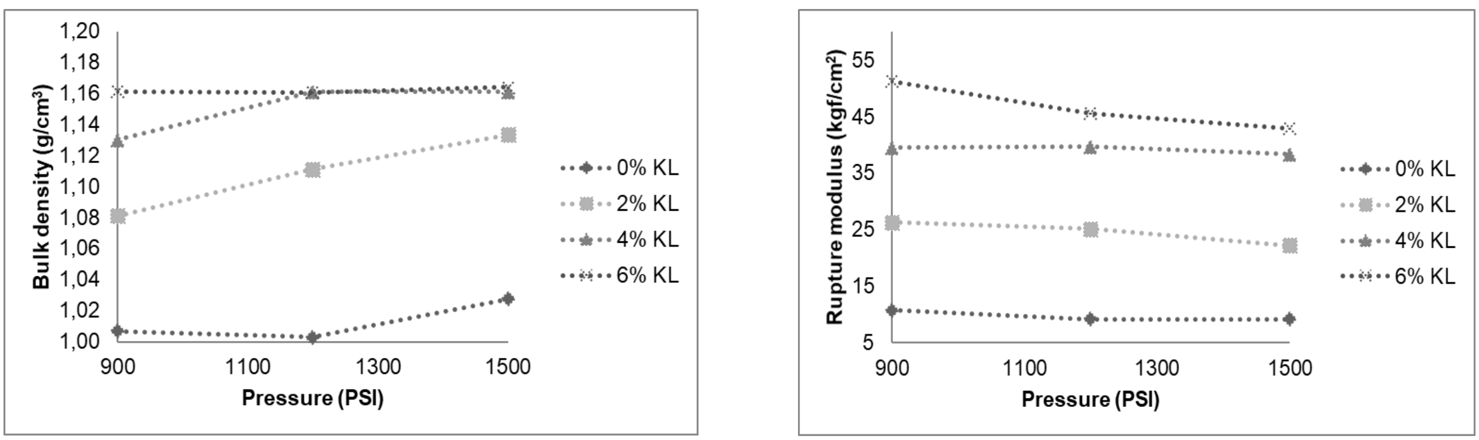
Table 12 shows results relating to the briquetting processes on the bulk density, modulus of rupture (MOR) and heating values (LHV and HHV) of the studied briquettes. These results are considered important parameters for the quality of the briquettes.

Table 12. Mean values of briquettes bulk density (ρ_ap), modulus of rupture (MOR) and heating values (LHV and HHV) per treatment.

Treatments	$\bar{\rho}_{ap}$ **(g/cm³)**	**MOR (kgf/cm²)**	**LHV (KJ/kg)**	**HHV (KJ/kg)**
T1	1.01 ± 0.01 ^{f}	10.7 ± 13.6 ^{cd}	16.3 ± 0.00 ^{e}	18.2 ± 0.00 ^{e}
T2	1.00 ± 0.04 ^{fg}	9.2 ± 14 ^{cd}	16.3 ± 0.00 ^{e}	18.2 ± 0.00 ^{e}
T3	1.03 ± 0.03 ^{e}	9.1 ± 12.7 ^{cd}	16.2 ± 0.00 ^{f}	18.1 ± 0.00 ^{f}
A1	1.08 ± 0.01 ^{d}	26.3 ± 10.3 ^{c}	16.9 ± 0.00 ^{a}	18.8 ± 0.00 ^{a}
A2	1.11 ± 0.01 ^{c}	25.1 ± 10.3 ^{c}	16.6 ± 0.01 ^{cd}	18.4 ± 0.05 ^{d}
A3	1.13 ± 0.01 ^{b}	22.2 ± 9.9 ^{cd}	16.7 ± 0.00 ^{c}	18.5 ± 0.05 ^{bc}
B1	1.13 ± 0.03 ^{ab}	30.6 ± 7.9 ^{c}	16.8 ± 0.00 ^{b}	18.7 ± 0.00 ^{b}
B2	1.16 ± 0.02 ^{a}	39.7 ± 5.7 ^{b}	16.7 ± 0.00 ^{c}	18.6 ± 0.00 ^{cd}
B3	1.16 ± 0.01 ^{a}	37.3 ± 5.8 ^{b}	16.7 ± 0.00 ^{c}	18.6 ± 0.00 ^{cd}
C1	1.16 ± 0.01 ^{a}	51.4 ± 4.6 ^{a}	16.9 ± 0.01 ^{ab}	18.7 ± 0.05 ^{ab}
C2	1.16 ± 0.02 ^{a}	45.6 ± 3.5 ^{ab}	16.3 ± 0.01 ^{ef}	18.5 ± 0.05 ^{c}
C3	1.16 ± 0.01 a	43.0 ± 1.4 ^{b}	16.3 ± 0.00 ^{e}	18.1 ± 0.05 ^{ef}

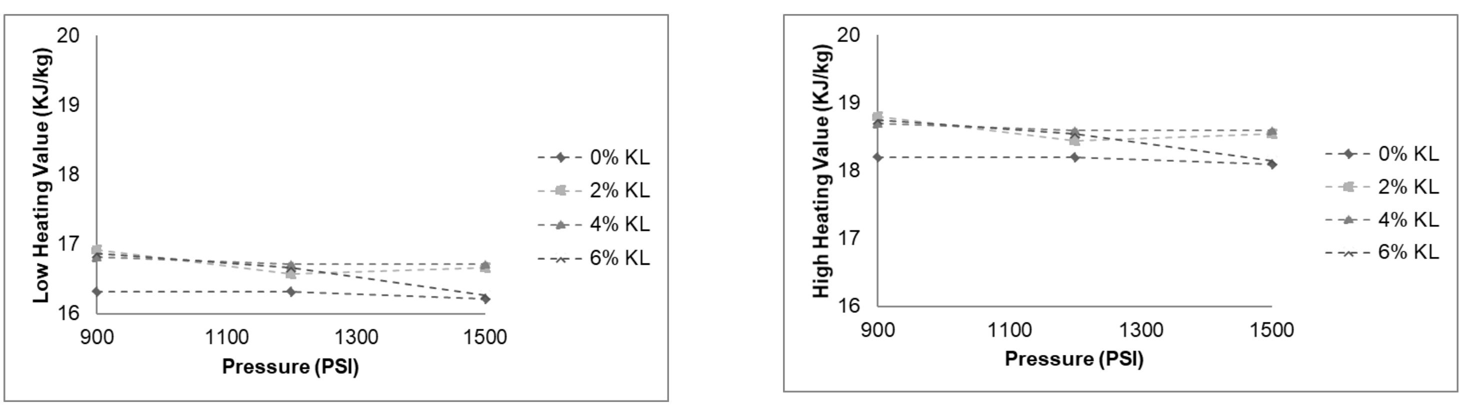
Note: (T1) pressure 900 PSI; (T2) pressure 1200 PSI; (T3) pressure 1500 PSI; (A1) 2% Kraft lignin sample with 900 PSI; (A2) 2% Kraft lignin sample with 1200 PSI; (A3) 2% Kraft lignin sample with 1500 PSI; (B1) 4% Kraft lignin sample with 900 PSI; (B2) 4% Kraft lignin sample with 1200 PSI; (B3) 4% Kraft lignin sample with 1500 PSI; (C1) 6% Kraft lignin sample with 900 PSI; (C2) 6% Kraft lignin sample with 1200 PSI; (C3) 6% Kraft lignin sample with 1500 PSI. Equal letters in the same column indicate equality between the values of the averages at a significance level of 95%.

As expected, the bulk density increased, due to the agglutination and plasticization of lignin. The produced briquettes with 4 and 6%, respectively treatments B and C, of incorporated kraft lignin did not show difference related to the bulk density. However, these treatments showed difference in treatments T (0% KL) and A (2% KL). In general, the use of additives in briquettes are limited to two percent, but this study showed that the inclusion of 4 and 6% of KL contributed to the increase in the bulk density, also 4% and 6% (at 900 PSI) presented significant increase in the rupture modulus of the briquettes (Figure 11). On the other hand, the decrease of the rupture modulus in treatments C2 and C3 was observed, and it can be explained by cohesion strength among the particles with higher pressure due to the chemical composition of *wood* biomass and the kraft lignin used, which possess lower content of lignin and a significant percentage of ashes on its composition, which may affect the binder process.



(A) (B)

Figure 11. Properties of the briquettes, being: (A) bulk density; (B) modulus of rupture.



(A) (B)

Figure 12. *Astronium concinnum* briquettes heating values using different concentrations of kraft lignin (KL) as additive, being (A) low heating value; (B) high heating value.

Analyzing the values shown in Table 12 and Figure 12 is possible to affirm that the briquettes produced in 900 PSI showed higher heating values. The lowest heating value (LHV) was obtained when using 0% KL at higher pressure values (1500 PSI). The briquettes produced with 2% KL presented the highest HHV, followed by the 4% KL and 6% KL, respectively.

4. DISCUSSION

The elemental analysis is a factor that depends on comparison age due to anatomical and structural changes that happen inside the biomass. It was possible to observe that wood biomass evaluated (*Astronium concinnum)* in this research presented similar percentage of carbon (46.0 - 49.95%), hydrogen (4.8 - 6.2%), nitrogen (0,1 - 2.4%), oxygen (43.1 - 46.7 %), and sulfur (0.01 - 0.05 %) when compared to the other commercial woods such as *Eucalyptus* spp. (SANTANA *et al.* 2012; TRUGILHO *et al.* 2012; PEREIRA *et al.* 2013; BORGES *et al.* 2016; MORGAN *et al.* 2016; VEIGA *et al.* 2017; SILVEIRA 2018; SILVA *et al.* 2019). In this study the elemental analysis was completely measured, as previously explained, being the sum of CHNSO almost 100%. In general, the oxygen is calculated by difference, which always generates values of 100% for the sum of these elements (SANTANA *et al.* 2012; TRUGILHO *et al.* 2012; PEREIRA *et al.* 2013; BORGES *et al.* 2016; MORGAN *et al.* 2016; VEIGA *et al.* 2017; SILVEIRA 2018; SILVA *et al.* 2019).

For the biomass, the observed extractives value was higher than that reported in the literature for *Eucalyptus* spp. According to research by Gomide *et al.* (2005), Gomes *et al.* (2015), Boschetti *et al*. (2019a,b) hardwood species (i.e. *Eucalyptus* clones) present extractives up to 5%. Extractives are correlated to the volatile compounds, which collaborate with the heating value (DEMIRBAS 2002).

Regarding the total lignin content, the evaluated wood presents 23.6%, a lower value when compared to eucalypt (26.7- 31.7%) (BOSCHETTI *et al.* 2019a; BORGES *et al.* 2016; VEIGA *et al.* 2017; GOMIDE *et al.* 2005). The carbohydrates content (60.7%) is also lower when compared to eucalypt carbohydrates content (64.5 - 70.2%) analyzed by Gomide *et al.* (2005). The lignin content is correlated with the fixed carbon collaborating to the biomass heating value (DEMIRBAS 2002, 2003a,b, 2007; FAHMI *et al.* 2007; TANGER *et al.* 2013), being high values of this parameter desired for energy conversion.

The ash content, another important parameter to heating values, was similar to eucalypt wood (0.1 - 0.4%) according to Pereira *et al.* (2016), Borges *et al.* (2016), Morgan *et al*. (2016), Veiga *et al.* (2017) and Silveira (2018). The ash content is not desirable for energy application collaborating for decreasing heating value (DEMIRBAS 2002; TANGER *et al.* 2013; ARASCHI *et al.* 2019). The ash content is also undesirable for the operation of boilers, where the biomass can be burned for converting it into energy (SOMMERSACHER *et al.* 2011; CHERNEY *et al.* 2013; KUMAR *et al.* 2015), since ash is responsible for generating incrustations, corrosion, unscheduled stops for maintenance, for example.

The high heating and low heating values of the evaluated wood biomass were quite similar to those values described in the literature (BEZZON 1994; EICHLER *et al.* 2017; BOSCHETTI *et al.* 2019b) for lignocellulosic biomasses.

Regarding to the kraft lignin composition, it is possible to verify that the studied lignin in this research has similar percentage of carbon (49.8 - 61.8%), hydrogen (5.0 - 6.5%), nitrogen (0.1 - 1.3%), but lower oxygen content (29.2 - 37.9%) and significantly higher content of sulfur (0.8 - 2.5%) (DUARTE *et al.* 2001; ZHOU & LU 2014; GORDOBIL *et al.* 2016; BOSCHETTI *et al.* 2019a). This information and the higher ash content directly influence in the lignin purity and energy generation. A higher ash content is disadvantageous because it decreases the heat transfer in the fuel and the biomass heating value (PAULA *et al.* 2011a,b; PROTÁSIO *et al.* 2011a,b; BRAND 2011), as well as increasing the corrosion of the equipment used in the process (TAN & LAGERLVIST 2011).

The purity is also related to the acid insoluble (Klason lignin) and soluble lignin presented in the binder material. Compared to Zhou & Lu (2014) and Boschetti *et al.* (2019a) the studied kraft lignin used in this research is more impure, presenting lower contents of total lignin on its composition. However, the carbohydrates content presented is lower than other studies (DUARTE *et al.* 2001; ZHOU & LU 2014; GORDOBIL *et al.* 2016).

4.1. Briquetting process

This study pointed that when using more than 2 % of additives, for instance, the use of6% of kraft lignin showed the highest and the same values of bulk density not depending on the pressure used in the briquetting process. The studies of Boschetti *et al.* (2019a,b) also showed that the incorporation of 6% of Kraft lignin has the best results for bulk density. This is important, because high-quality fuels should present high density and strength, with higher energy content (ONUKAK *et al.* 2017) to burn for a longer time (GUO *et al.* 2020).

The rupture modulus increased after a rise in pressure and a larger amount of lignin was incorporated (6% KL). When the lowest pressure value was used (900 PSI), it was observed the optimum point of the briquetting, regarding the durability and maximum rupture.

Boschetti *et al.* (2019a) studying *Hymenolobium petraeum* Ducke, *Eucalyptus* spp., and *Pinus* spp. briquettes also found similar results, proving that 6% of impregnated Kraft lignin gives better bulk density and rupture modulus properties. Pereira *et al.* (2016) studying pellets confirms that the use of at least 2% of Kraft lignin can change properties of hardwood compressed materials.

The heating values indicate that the best cohesion strength of the sawdust and lignin occurred in the lower value of pressure aiming to deliver heating value. It is important to observe that the heating value is directly related to the fixed carbon content and is also associated with volatile and ash content (DEMIRBAS 2002). Besides the studied lignin presents a high carbon content, which is desirable, it is also presented a high ash content, which reduces the heating value of the briquettes, mainly when the proportion of lignin addition in the briquette increases. This result indicates that the commercial kraft lignin needs to be designed for being applied to the energy application, since in the literature it is possible to observe the commercial eucalypt kraft lignin with 0.01-1.4% of ash (TOMANI *et al.* 2011), 13% less than the commercial kraft lignin used in this study, which may collaborate for improving also the briquette heating value beside other strength properties.

5. CONCLUSIONS

In order to produce briquettes with higher heating values, it was concluded that evaluated biomass added with lower concentrations of Kraft lignin at 900 PSI generate the best results. The addition of 2% of lignin showed the best performance, however using 4 and 6% of Kraft lignin combined with higher pressure values better briquettes properties (bulk density and rupture modulus) can be obtained. The use of higher concentrations may enter in disaccordance with most standards for using additives in briquettes.

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CHAPTER IV

LIGNIN EXTRACTION FROM WOOD RESIDUES AFTER HYDROTHERMAL TREATMENT BY USING SOLVENTS AND ENZYMES

ABSTRACT

This study aimed to analyze the lignin extraction from sawmill wood residues through hydrothermal treatments followed by solvent extraction step. Two Brazilian hardwood species (*Joannesia princeps* Vellozo and *Astronium concinnum* (Engl.) Schott, called B1 and B2, respectively) sawdust were used as raw material. The Route 1 performed the lignin extraction after the hydrothermal treatment (HTT) step using acetone as solvent (acetone extracted lignin - AEL), and Route 2 included an enzymatic hydrolysis (EH) step prior to the solvent extraction (enzymatic acetone extracted lignin - EAEL). Both routes were evaluated with two distinct hydrothermal treatment severities reaction (P-factor 800 and 2000). Studies on the composition of biomasses generated in the processes were carried out, and yields of lignin extraction and glucan conversion were done based on feedstock composition data. The Route 1 promoted higher lignin efficiency removal in both biomasses at P-factor 2000, B1 and B2 presented 76.5% and 43% AEL, respectively and glucan conversion equals to 76.9 and 56.9%. The EH sequence adopted in route 2 did not significantly impair the lignin extraction, but affected the glucan conversion, B1 presented 79.2% and B2 72.5%. Comparing the biomasses, B1 species presented better results in both extraction routes, but in Route 1 the greater efficiency in lignin removal (AEL) was more effective in higher severities (P- factor 2000), which may be explained by the biomass composition. The inclusion of EH sequence after HTT, studied in Route 2, did not result in higher removal efficiency of lignin (EAEL) for the two biomasses studied, but increases the glucan conversion efficiency.

Keywords: autohydrolysis, biorefinery concept, lignin extraction.

1. INTRODUCTION

The use of residues from the forest-based industries and the study of new applications for them is one of the premises related to the concept of the lignocellulosic biorefineries, aiming to contribute to the generation of multiple products and mitigate the generation of industrial wastes. In lignocellulosic biorefineries the current efforts are applied on the optimization of hemicelluloses removal from biomass. Among the most common processes stands out the hydrothermal treatment (HTT), also known as autohydrolysis or liquid hot water extraction. This process simply requires water as solvent and is commonly used as wood pretreatment for dissolving pulp production and for conversion of hemicelluloses in biofuels and biobased chemicals. Biomass pre-treatments such as HTT, when used as pre-treatment in a pulp mill, bring several advantages, such as obtaining pulp with higher carbohydrate contents as well as favoring its bleaching steps (GELLERSTEDT 2007).

The HTT has a defined modeling, based on the P-Factor to assess the severity in the process, a variable that takes into account the time and temperature (SIXTA 2006). Another common process adopted after lignocellulosic pre-treatment, targeting the fully separation of biomass components, is the enzymatic hydrolysis (EH). This process aims to release cellulose molecules from the lignin chain through the selective action of enzymes, such as cellulases (SOCCOL *et al*. 2011; YANG *et al*. 2011). According to Kumar & Murthy (2006) and Walker & Wilson (1991) the enzymatic hydrolysis is composed by complex mechanisms that break the amorphous part of the cellulose structure. Kumar & Murphy (2006) relates that many cellulolytic organisms can effectively degrade cellulose (PERCIVAL ZHANG *et al*. 2006). Wang *et al.* (2016) affirmed that lignin present in hydrothermally pretreated biomass can negatively influence the carbohydrates conversion. Lignin presence creates a physical barrier that impedes the enzymes to achieve the carbohydrates structure affecting its hydrolysis (MOSIER *et al.* 2005; WANG *et al.* 2016).

Besides sugar-based biorefineries, the biorefinery concept has been strongly considered in pulp and paper industries, in which all side-streams of the process are recovered aiming higher value-added applications. In this context, other wood-based processes such as a sawmill could benefit if biorefinery concept is also applied. This sector generates large volumes of sawdust residues, which are currently burned to supply energy or end-up in landfills (EUROPEAN COMMISSION 2017; TRIPATHI *et al.* 2019). The efforts on the use of sawdust residues as feedstock for other applications includes energy industry, manufacturing industries and agricultural industries approaching, per example, densification processes aiming to generate energy generation and/or raw material for materials. Such examples elucidate the lack of studies with other biomasses and approaches that could in fact leverage high value added products from sawdust residues.

Paone *et al.* (2020) affirms that lignin and its native phenolic constituents have a particular interest for a lignocellulosic biorefinery aimed to produce sustainable production of green aromatic compounds. However, the variation of the physiochemical properties and structure can impact the valorization of lignin (CAO *et al.* 2019).

Lora & Wayman (1978) and Sixta (2006) mentioned that HTT contributes to the hydrolysis of the biomass, allowing that organic acids formed by the acetyl groups catalyze the hydrolysis of the low molecular weight carbohydrates and induce the solubility of lignin in certain solvents, thus facilitating the extraction of lignin from the wood. In addition, according to Ruiz *et al.* (2013), Vallejos *et al*. (2015a,b), and Jesús Rangel *et al.* (2016), hardwoods and grasses are more suitable than softwoods for hydrothermal treatments, which may be explained due to their higher acetyl groups content, providing an increase in catalyst concentration in the reaction medium. Our group has shown in a preliminary study the possibility of extracting lignin from hydrothermal treated solids only by applying aqueous acetone at room temperature after optimizing the HTT conditions targeting lignin as main stream (LOURENÇON *et al.* 2019). The wood feedstocks, *Joannesia princeps* Vellozo and *Astronium concinnum* (Engl.) Schott evaluated in this study, although not popular species, have been used in Brazilian sawmills; therefore, efforts on the valorization of this residual biomass is paramount. Herein, the objective of this work was to apply hardwood residues from sawmill as feedstock for HTT, to extract lignin (by green organic solvent) and glucose (by EH) and to investigate the influence of lignin on EH and the influence of EH on lignin extraction.

2. MATERIALS AND METHODS

2.1 Raw material

The residues (sawdust) of two native Brazilian wood species from three trees wood processing, *Joannesia princeps* Vellozo (Biomass 1, B1) with 17 years old, and *Astronium concinnum* (Engl.) Schott (Biomass 2, B2) with 22 years old, were used in this study. Three trees of each specie were harvested from an experimental station in the Vale Natural Reserve, located in

Sooretama, Espírito Santo state, Brazil. The biomasses were sawed and the residues were collected, ground and screened (60 mesh) according to Tappi Standard T 257 cm-02 (2012) procedure.

2.2 Chemical analysis of the biomasses

The extractive contents were quantified after ethanol:toluene followed by hot water extraction, according to Tappi Standard T264 cm-97 (1997). The acid insoluble lignin, acid soluble lignin and carbohydrates were determined according to the National Renewable Energy Laboratory (NREL/TP-510-42618) (SLUITER *et al.* 2008). The lignin syringyl/guaiacyl (S/G) ratio was determined following the Lin & Dence (1992) procedure. The carbohydrates content was determined following Wallis *et al.* (1996); SCAN-CM 71:09 (2009) procedures, and the acetyl groups were measured following Solar *et al.* (1996) procedure.

2.3 Hydrothermal Treatment (HTT)

Sixta (2006) affirms that the severity of the HTT process can be as represented in Equation 1, where *t* is reaction time in hours, *T* is temperature in Kelvin, *k* is the reaction rate constant at temperature *T*. The activation energy used in Equation 1 is 125.6 kJ/mol (or 30 kcal/mol) from the hemicelluloses reaction.

$$P - factor = \int_0^t \frac{k\,(T)}{k_{100°C}}\,dt = \int_0^t e^{40.48 - \frac{15106}{T}}\,dt \qquad \text{Eq (1)}$$

About 4.5 grams of wood sawdust (0,55 - 0,125 mm particle size) with extractives was placed in a 50mL batch reactor (Parr reactor 4841 with temperature controller, pressure gauge and mechanical stirrer) with 18 mL of deionized water, reaching a liquid-to-wood (L/S) ratio of 4:1 (g/g). The temperature of 195°C was fixed and distinct severities were obtained at fixed P-factor value (800 and 2000), by assuming an Arrhenius-type equation with an activation energy of 125.6 kJ/mol (SIXTA 2006). These parameters were selected based on preliminary investigation (LOURENÇON *et al*. 2019).

At the end of the reaction, the reactor was immediately depressurized and cooled down, in order to stop the hydrolysis. The reaction mixture was filtered, resulting in the hydrothermally treated solids (HTT-solids) and liquor (hydrolysate). The HTT-solids were washed with deionized water and the hydrolysate collected for soluble lignin (SL) quantification.

Two routes to extract lignin from HTT-solids were investigated, as shown in Figure 13. In *Route 1*, the lignin is immediately extracted from HTT-solids with 9:1 acetone/water (v/v) solution at room temperature, until reaching colorless filtrate. The resulted products are the acetone-extracted solids (AE-solids) and the acetone extracted-lignin, named AEL. The AE-solids were then used as substrate for enzymatic hydrolysis (EH). The AEL was collected, concentrated by a rotary evaporator, and quantified gravimetrically after drying it overnight at 40°C in a vacuum oven (LOURENÇON *et al.* 2019).

In *Route* 2, all HTT steps followed the same, the HTT-solids is first used as substrate for enzymatic hydrolysis, prior to the acetone extraction. This acetone extracted-lignin -after EH- is named EAEL. The resulted solids after EH and acetone extraction is named EH-AE-solids.

The chemical composition analysis of generated HTT-solids, AE-solids and EH-AE-solids was determined by the same protocols as those for the original biomasses.

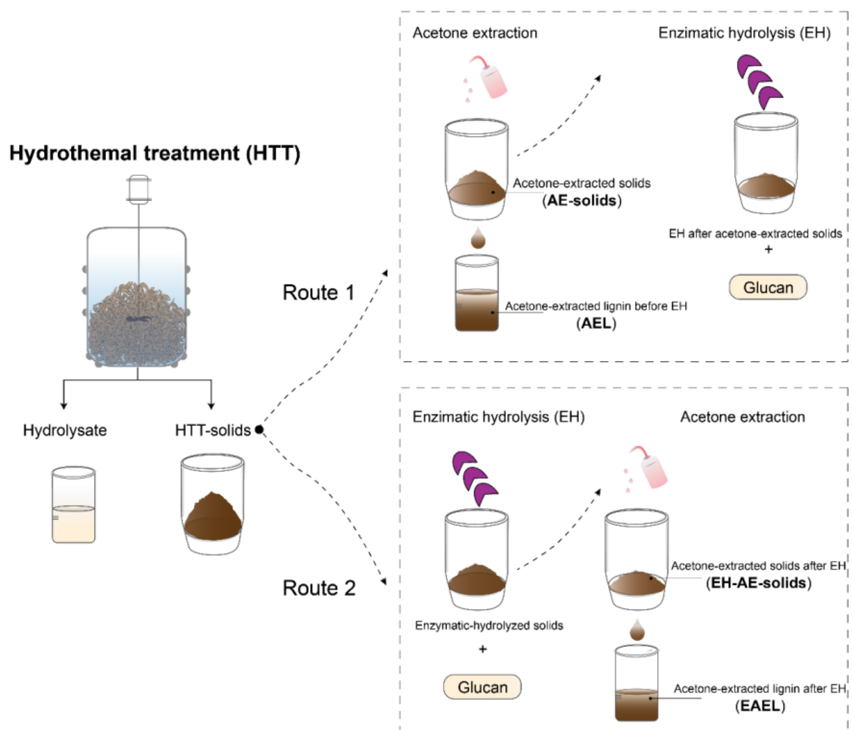

Figure 13. Scheme of the hydrothermal treatment of biomasses B1 and B2. The resulted hydrolysate and HTT-solids followed two routes. In Route 1, lignin was extracted from the HTT-solids, resulting in the acetone-extracted solids (AE-solids), followed by enzymatic hydrolysis and the acetone-

extracted lignin (AEL). In Route 2, the HTT-solids followed the EH prior to the acetone extraction, generating the acetone-extracted solids after EH (EH-AE-solids) and the acetone-extracted lignin after EH (EAEL).

2.4 Enzymatic hydrolysis

The enzymatic hydrolysis (EH) applied in Route 2, in the HTT-solids prior to acetone extraction, followed an adapted procedure adopted by Palonen (2004). A buffer composed by (Na-acetone) 100mM was used to keep the pH around 5. Commercial enzyme Cellic CTec 2, purchased from Sigma Aldrich, presenting 257 mg of protein/ml of solution, was applied at the dosage of 20 mg of protein/g of biomass dry-matter (DM). The sample dilution was 1:100 and all the samples, being performed in triplicates, were placed in an incubator for 24h, at 50˚C under subtle shaking. The samples were boiled for ten minutes in order to stop the enzymatic reaction, and the dosages and dilution values were selected after preliminary screening tests.

After the 24h of EH, the hydrolysates were centrifuged recovering supernatants. The DNS (3,5-dinitrosalicylic acid) was added to the samples and sealed in polypropylene PCR plates diluted at 1:10 and 1:20, and glucose absorbance was measured at 540 nm by Multiskan MS Microplate Reader. To subtract the glucan content present in CTec 2 solution, a blank sample was prepared by using the same dosage of enzyme however in the absence of substrate.

The high enzyme dosage (20mg/g) adopted in the experiment is due to the fact that the masses are very hydrophobic, taking into account that an adaptation was carried out including an immersion step at high temperatures to allow higher enzymatic activity.

The Shapiro & Wilk test (1965) was used to test the normality of the data. The data were also submitted to analysis of variance using the Cochran test (1950) to evaluate differences between treatments. The Tukey’s t-test was applied at a 95 % significance level when significant differences between the results were found.

3. RESULTS AND DISCUSSION

3.1. Chemical composition of the biomasses

The chemical composition of both evaluated species differs as showed in Table 13. Biomass B2 presented higher extractives and carbohydrates content than B1. On the other hand, total lignin content is similar between the biomasses, while S/G ratio is higher at biomass B2. The lignin content found for these two native Brazilian hardwood species are in the range of that found for the very popular hardwood specie used currently, *Eucalyptus* spp. (GOMIDE *et al.* 2005; MORAIS *et al.* 2017).

Regarding the carbohydrate content, the biomasses presented similar values found in the wood composition of some tropical hardwood species (SANTANA & OKINO 2007; MOKFIENSKI *et al.* 2008), but lower when compared with results (64.5 - 70.2%) found in the studies for *Eucalyptus* spp. (GOMIDE *et al.* 2005; MORAIS *et al.* 2017). The same observation can be made for contents of acetyl groups and uronic acid (GOMIDE *et al.* 2005; SANTANA & OKINO 2007).

Table 13. Chemical composition of the studied biomasses.

Biomass	Lignin (%)			Extractives (%)	Acetyl Groups	Uronic Acids	Carbohydrates			S/G
	ASL	AIL	Total				Glc	Xyl	Man	
B1	3.2 (0.02)	22.3 (0.1)	25.5 (0.1)	11.1 (0.1)	2.2	2.8	40.9 (5.5)	10.9 (1.5)	2.0 (0.2)	1.52 (0.03)
B2	3.1 (0.04)	21.4 (0.4)	24.5 (0.5)	17.6 (0.1)	3.5	2.8	54.5 (0.1)	14.8 (0.1)	1.9 (0.1)	1.81 (0.01)

Note: B1: *Joannesia princeps* Vellozo; B2: *Astronium concinnum* (Engl.) Schott; ASL: acid soluble lignin; AIL: acid insoluble lignin; S/G: syringyl/guaiacyl ratio. Data in parentheses corresponds to the standard deviation value.

Remarkably, both biomasses B1 and B2 presented higher contents of extractives, especially when compared to eucalypt wood content (up to 5%) (GOMIDE *et al*. 2005; GOMES *et al*. 2015). When the wood is used for pulping, basic density, cooking conditions and extractives content may affect and compromise the adopted treatments (GOMIDE *et al*. 2005; MORAIS *et al.* 2017; ZANUNCIO *et al.* 2017). However, if these species are used in another biorefinery process, such high contents of extractives may be seen as an advantage. As stated by Routa *et al.* 2017, the isolation of extractives prior further conversion of biomass is a valuable way of adding value to this stream as well.

Each solid generated in HTT at different severities, from biomasses were analyzed regarding its main chemical composition (Figure 14). It is possible to observe that both biomasses show difference in composition of solids when the severities of process are different.

In the lowest severity (P-800) it can be observed lower amount of glucan in the HTT solids. On the other hand, the higher contents of glucan and lignin at higher severity (P-2000) can be explained, as observed by Lourençon *et al.* (2019), due to the formation of "pseudolignin" originated from the degradation/fragmentation of polysaccharides (SIPPONEN *et al.* 2014; SHINDE *et al.* 2018) in the hydrothermal processes. It is important to mention that these lignin amount can also have some extractives amount influence.

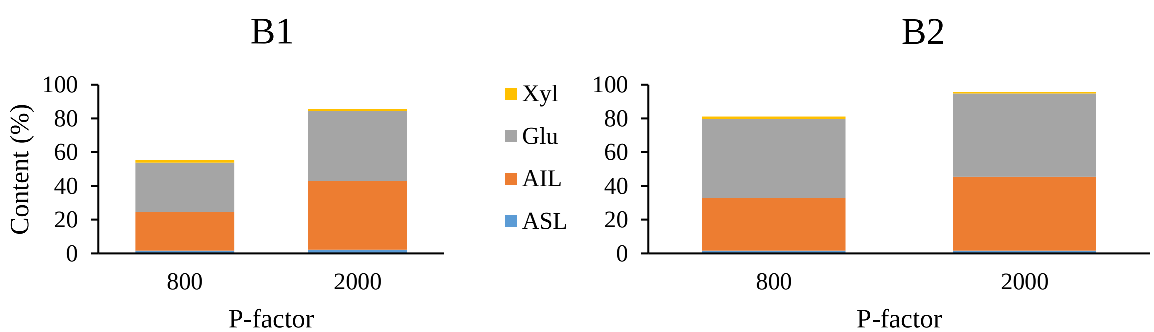

Figure 14. Residual lignin and carbohydrate contents of solids from hydrothermal treatments at different severities. Note: Xyl = xylan content; Glu = glucan content; ASL = acid soluble lignin; AIL = acid insoluble lignin. Mannose content was lower than 1% for both biomasses.

3.2. Hydrolysate from HTT

The other product obtained by HTT reaction, among the solids, is the hydrothermal treated residual liquid, also known as hydrolysate or filtrate liquor. In order to analyze the residual lignin in the HTT present in this liquor the soluble lignin analysis was realized. The Table 14 presents the residual lignin amounts presented in the filtrate liquor.

Table 14. Soluble lignin (SL) amount presented in the HTT hydrolysates in the studies severities (P-factor 800 and 2000) from B1 (*Joannesia princeps* Vellozo) and B2 (*Astronium concinnum* (Engl.) Schott).

Specie	**P-Factor**	**SL (%)**	**SL, on lignin in feedstock (%)**
B1	800	0.4	1.6
B1	2000	0.5	2.0
B2	800	1.8	7.6
B2	2000	4.0	16.4

B1 presented very low content of soluble lignin (SL) in hydrolysate. For both biomasses higher soluble lignin contents are present in hydrolysate at higher HTT severity. Moreover, B2 presents considerably higher value of SL at higher severity.

Leschinsky *et al.* (2008) studied that the wood lignin partly dissolves at HTT and precipitates in the cooling process. The partial depolymerization of lignin and breaking of lignin–hemicellulose linkages can produce part of the phenolics present in the hydrothermal processing liquors (ESTEVES *et al.* 2008; GULLÓN *et al.* 2008; RUIZ *et al.* 2013). Lourençon *et al.* (2019) also obtained lower values of soluble lignin values in the hydrolysates studying birch., however, higher values were obtained in higher severity process.

Ruiz *et al.* (2011) evaluated delignification using the sequence HTT followed by an organosolv process and concluded that the temperature and time as well as chemical structure were variables that showed a strong influence on lignin precipitation. Lourençon *et al.* (2019) studying birch found higher values of soluble lignin in hydrolysate and higher yields of AEL the severity of the hydrothermal process is increases.

The Figure 15 shows the results of the chemical composition (carbohydrates and lignin) of studied routes solids.

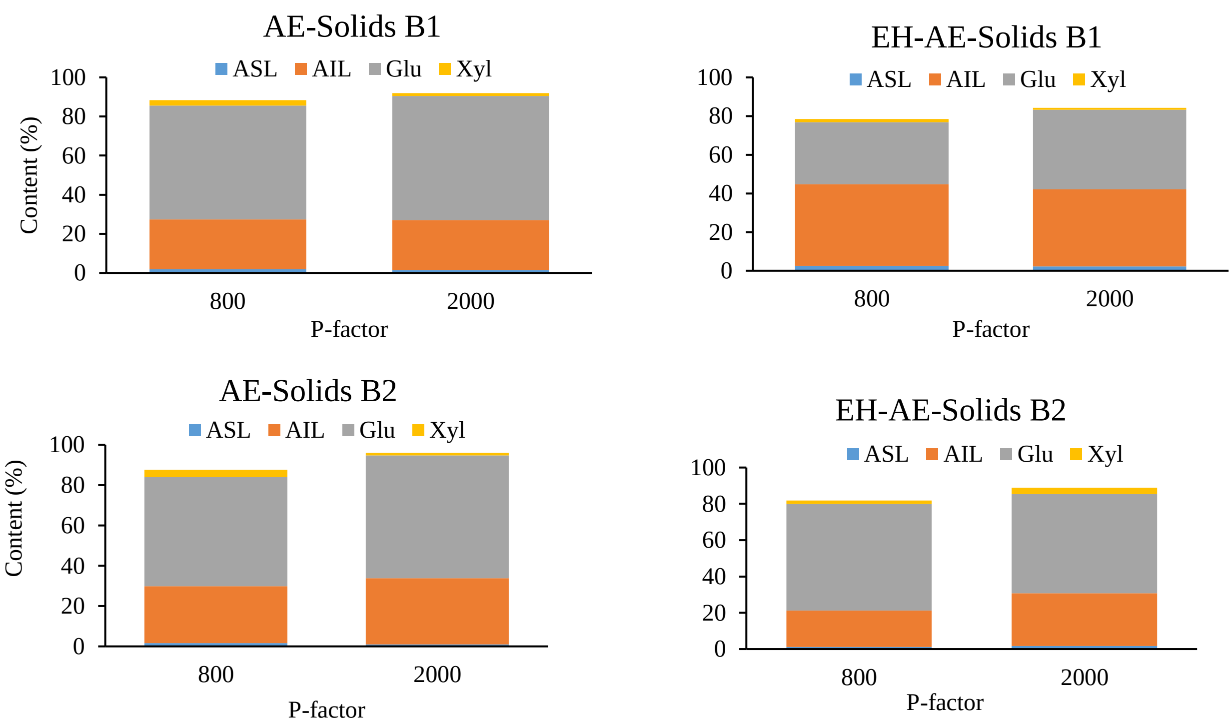

Figure 15. Chemical composition of the AE-Solids and EH-AE-Solids from biomasses 1 (B1) and 2 (B2) based on the initial biomass. Note: ASL = acid soluble lignin; AIL = acid insoluble lignin; Glu = glucan content; Xyl = xylan content.

Regarding the AE-solids in Route 1, B1 and B2 showed stability and increased AIL and Glu content in solids when the severity was high (P-2000), unlike the ASL and Xyl contents that dropped. The EH-AE solids, studied in Route 2, B1 presented an increase of 9% in the glucan content and a decrease in the values of lignin and xylan. B2 showed the opposite behavior, showing an increase of 0.8% in the value of ASL, 8.8% in AIL, 1.6% in Xylan and a drop of 3.9% in the value of Glu. The yields of acetone-lignin extraction and conversion of glucan (Glc) from extracted solids in Route 1 is shown in Figure 16.

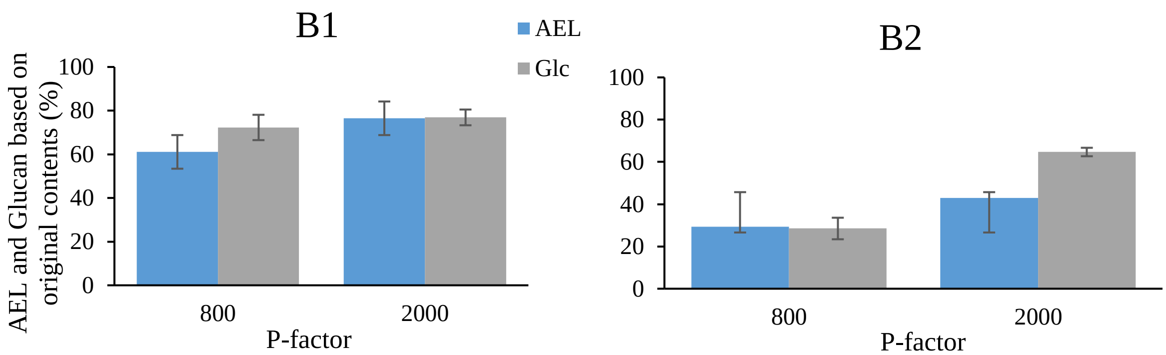

Figure 16. Yields of acetone-extracted lignin before enzymatic hydrolysis (AEL) and glucan (Glc) conversion, based on content in the original wood feedstock.

In route 1, both biomasses showed a higher acetone-extraction lignin (AEL) and glucan conversion yields, at higher severities. However, B2 presented lower yields than B1 in both severities.

In both biomasses, increasing the severity of the process, promoted a greater extraction of lignin (AEL), corroborating Lourençon *et al.* (2019) results of AEL from birch wood. When comparing the biomasses, it is possible to observe higher AEL in B1 than B2, regardless of severity. The B1 has different content of extractives compared to B2, and more sinapyl alcohols, (Table 13). Besides, the chemical differences, B1 presents lower basic density (ROLIM & PIOTTO 2019; SILVA *et al.* 2020), implying in easier reactivity during HTT. Moreover, hardwoods have syringyl units and these lignin fragments are most susceptible to degradation from hydrothermal treatments (SHIMIZU *et al.* 1989). This information is important due to the fact of higher content of coniferyl groups, increasing the probability of chemical bonds and interactions.

Although B2 presents higher Glc in feedstock composition (Table 1), the biomass showed lower results when compared to B1 conversion data. The glucan conversion was higher for B1, but statistically differences were not observed at the different severities. On the other hand, B2 presented higher conversion at higher severity (P-factor 2000) being double than that obtained in the P-factor 800.

The results of lignin extraction following Route 2 and glucan conversion (applied before acetone extraction) is shown in Figure 17.

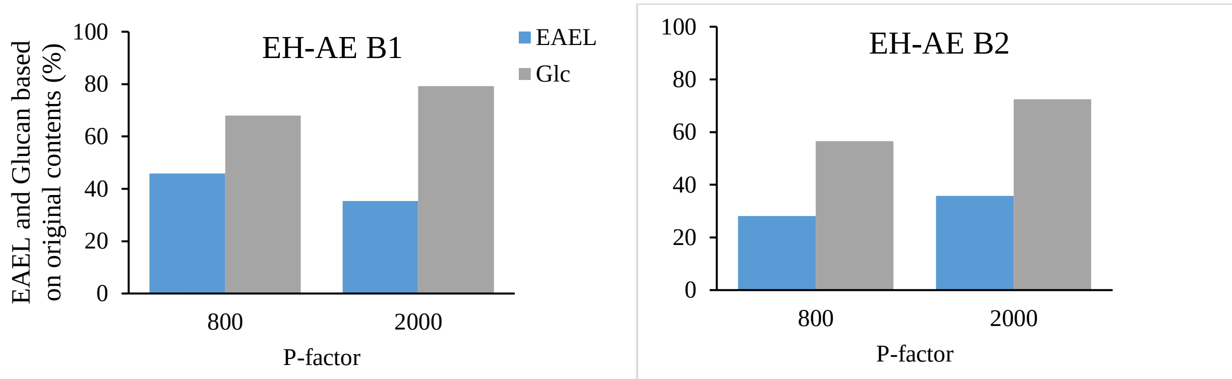

Figure 17. Yields of acetone-extracted lignin after enzymatic hydrolysis (EAEL) and glucan (Glc) from acetone-extracted solids (EH-AE-solids). Lignin and glucan yields are based on content in the original wood feedstock.

When evaluating the route 2 it is possible to observe that B1 presented sugar conversion of 68% in P-factor 800, and 80% at higher severity. These values were higher than biomass 2 comparing each P-factor. As indicated in the studies of Kumar *et al.* (2012) and Tian *et al.* (2017), the presence of the called residual lignin in steam-pretreated woody substrates can be problematic for the subsequent enzymatic hydrolysis of the cellulose, despite the use of a relatively high enzyme loading. In this study, the route 2 showed good conversion compared to route 1, mainly for B2.

The recondensation of the lignin can occur under acidic pretreatment conditions, and this can result in an increase in the molecular weight of the lignin, compromising its extractability. The enzymatic digestibility is strongly related to the lignin content, and that lignin removal greatly enhances enzymatic hydrolysis (HARMSEN *et al.* 2010).

According to Trajano *et al.* (2013) the most effective lignin removal or alteration during pretreatment leads to improved enzymatic hydrolysis. The knowledge of lignin repolymerization kinetics and the impact of lignin composition impacts the lignin removal. The pseudolignin can affect the enzymatic hydrolysis performance (SHINDE *et al.* 2018; LOURENÇON *et al.* 2019).

Typically, lignin and hemicellulose in the lignocellulosic materials need to be removed before the enzymatic hydrolysis of cellulose (PEI *et al.* 2016; ZHENG *et al.* 2018). The presence of extractives, which also negatively affect the extent of enzymatic degradation of lignocellulosic biomass also affects the enzymatic hydrolysis of holocellulose (BUZALA *et al.* 2017).

The hemicellulose removal increases porosity and improves enzymatic digestibility, with maximum enzymatic digestibility usually coinciding with complete hemicellulose removal (CHEN *et* *al.* 2007). Organosolv processes use an organic solvent or mixtures of organic solvents with water for removal of lignin before enzymatic hydrolysis of the cellulose fraction. In addition to lignin removal, hemicellulose hydrolysis occurs leading to improved enzymatic digestibility of the cellulose fraction (GHOSE *et al.* 1983; SUN & CHENG 2002; HARMSEN *et al.* 2010). The solvent itself can be an inhibitor for the enzymatic hydrolysis and fermentation step (HARMSEN *et al.* 2010). The HTT removes the majority of hemicellulose in raw material, but it is less efficient in removing lignin (LU *et al.* 2013). Previous studies have revealed that after hydrothermal and acid pretreatment, lignin is deposited as droplets on the surface of solid residues, which inhibited the enzymatic hydrolysis of cellulose in materials (SELIG *et al.* 2007; HU *et al.* 2012; LUO *et al.* 2014; JING *et al.* 2015; ZHENG *et al.* 2018).

Other researchers found that that re-localization of lignin during pretreatment improved the accessibility of enzymes to cellulose microfibrils (SUN & CHENG 2002; ISHIZAWA *et al.* 2007; LIU *et al.* 2017, ZHENG *et al.* 2018).

Analyzing the yields obtained and comparing the studied routes on feedstock content, it is possible to affirm that B1 had the higher lignin removal efficiency in lower severities (P-factor 800) and using Route 1. The B2 showed better results (AEL) using the higher severity treatment characterized by longer time reactions. The Route 2 (EAEL) lignin extraction yields were significantly lower when compared with route 1 results.

The removal of lignin by aqueous-acetone approach prior to EH (Route 1) did not improve glucan conversion, comparing to glucan conversion without prior lignin removal (Route 2); however, in Route 2 the EH prior to acetone-extraction did not result in higher yields of lignin. Therefore, Route 1 is the most suitable path to follow, if both bio-products are aimed.

4. CONCLUSIONS

The Route 1 resulted in greater efficiency in lignin removal (AEL) more pronounced in B1 (*Joannesia princeps* Vellozo). The inclusion of EH sequence after HTT did not result in higher removal efficiency of lignin (EAEL) for the two biomasses studied, but influenced the glucan conversion yield. The B1 showed a greater potential for lignin extraction when submitted to longer time reactions at 195°C, a fact related to chemical, anatomical structure and physical properties. This lignin can return to the industrial process being applied into the development of biofuels, chemicals and/or biomaterials.

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GENERAL CONCLUSIONS

The physical properties analysis indicated that the six studied species were divided into four density classes, showed also that the use of resistographic is feasible and highlights the relationship with higher density wood species. The potential use of sawmill residues with Kraft lignin (KL) as binder for densification approaches can be influenced by the wood chemical composition and purity of the used binder. The addition of 6% of KL with the pressure value of 1500 PSI promoted the better briquettes physical and mechanical properties of *Joannesia princeps* Vell., but did not influenced the heating values. *Astronium concinnum* (Engl.) Schott. presented a different behavior, being the best results promoted when using 2% of KL with 900 PSI. In general, kraft lignin improved the briquettes characteristics when used 2% KL, being a possibility to export this densified biomaterial. Analyzing the chemical routes of deconstruction of biomass aiming to promote glucan conversion and lignin extraction showed that the lignin removal (AEL) after HTT was more pronounced in *Joannesia princeps* Vellozo. The inclusion of EH sequence after HTT positively influenced the glucan conversion yield, but negatively affected the lignin extraction. A greater number of researches on native Brazilian species, from different biomes, is recommended for the generation of forestry data and technological properties aiming at their potential use in different industrial segments.