MINISTÉRIO DA EDUCAÇÃO UNIVERSIDADE FEDERAL RURAL DA AMAZÔNIA-UFRA PROGRAMA DE PÓS-GRADUAÇÃO EM CIÊNCIAS FLORESTAIS

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BIOENERGETIC PROPERTIES AND A PRACTICAL OPENING TECHNOLOGY OF THE BRAZIL NUTSHELL

BÉLEM-PA

2023

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Dissertation presented to the Universidade Federal Rural da Amazônia as part of the requirements of the Post Graduate Program in Forest Sciences, to obtain the title of Masters.
Area: Forest Engineering and Resources
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Date of Approval: March 31st, 2023.

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ABSTRACT

Brazil Nut is one of the main non-timber exports from the Amazon, with 85% of the fruit consisting of residues from its harvest and debarking yearly available. The Amazon communities that harvest the nuts could benefit from its sustainable use. This work comprises three aims and stages: (i) to review current research and technologies for the sustainable potential of Brazil Nut residues, (ii) to evaluate the energy potential of biomass and charcoal from both fresh and degraded Brazil Nutshell (BNS) mesocarp and (iii) to design and produce a device capable of removing the Brazil Nuts from the fruit easily. Brazil Nut residues are suitable for conversion into many bioproducts and biofuels. However, carbonization is applied nowadays, where the current applied method leaves a lot of residues partially carbonized, which decreases BNS market value. This undesired result is mainly because the shape of residues harms carbonization. Since BNS has remarkable physical properties and strength, cutting them into a suitable shape for traditional carbonization is difficult. Therefore, a device has been designed for a quick, safe, and efficient cutting of the BNS for later carbonization without harming the edible nuts. The device is basically a modification of the Miter Saw Vonder Sev857 to hold and cut open Brazil nuts. The device was able to cut the shells into equal halves. Fresh BNS mesocarp samples presented a net calorific value of 4,797 kcal/kg and basic density of 1 g/cm^3, while degraded BNS mesocarp samples showed a net calorific value of 4,600 kcal/kg and basic density of 0.84 g/cm^3. Thermogravimetric analysis indicated that fresh and degraded BNS mesocarp samples are suitable for carbonization and have energy potential, but their thermal behavior differed. The charcoal produced at T = 400 °C from degraded BNS showed 43.2% of volatile matter, 3.5% of ash, and 53.3% of fixed carbon, while fresh samples showed 18.63% of volatile matter, 1.23% of ash, and 80.14% of fixed carbon. It was concluded that degradation in the forest floor decreases the bioenergy potential of Brazil nut shells, especially by altering their chemistry.

Keywords: Higher Calorific Value, Bioenergy, Lignocellulose, Pyrolysis, Mechanics, Kinetics

RESUMO

A Castanha do Brasil é uma das principais exportações não madeireiras da Amazônia, com 85% da fruta composta por resíduos de sua colheita e descascamento disponíveis anualmente. As comunidades amazônicas que colhem as castanhas podem se beneficiar de seu uso sustentável. Este trabalho compreende três objetivos e etapas: (i) revisar as pesquisas e tecnologias atuais para o potencial sustentável dos resíduos da Castanha do Brasil, (ii) investigar o potencial energético da biomassa e do carvão vegetal do mesocarpo fresco e degradado da casca da castanha do Brasil (CCB) e (iii) projetar e produzir um dispositivo capaz de retirar a Castanha do Brasil do fruto com facilidade. Os resíduos da Castanha do Brasil são adequados para conversão em muitos bioprodutos e biocombustíveis. No entanto, a carbonização é aplicada hoje em dia. O método atual de carbonização de resíduos de CCB deixa grande parte do resíduo parcialmente carbonizado, o que diminui o valor de mercado. Esse resultado indesejado ocorre principalmente porque a forma dos resíduos prejudica a carbonização. Como a Casca da Castanha do Brasil possui notáveis propriedades físicas e resistência, é difícil cortá-la em um formato adequado para a carbonização tradicional. Portanto, foi desenvolvido um dispositivo para o corte rápido, seguro e eficiente da CCB para posterior carbonização sem prejudicar as castanhas comestíveis. O dispositivo em si é basicamente uma modificação para o Mitre Saw Vonder Sev857 para segurar e abrir castanhas-do-Pará. O dispositivo foi capaz de cortar as conchas em tamanhos iguais. Amostras frescas de mesocarpo CCB apresentaram poder calorífico líquido de 4.797 kcal/kg e densidade básica de 1 g/cm3, enquanto amostras degradadas de mesocarpo CCB apresentaram poder calorífico líquido de 4.600 kcal/kg e densidade básica de 0,84 g/cm3. A análise termogravimétrica indicou que as amostras de mesocarpo de CCB frescas e degradadas são adequadas para carbonização e possuem potencial energético, mas seu comportamento térmico diferiu. O carvão produzido a T = 400°C a partir de CCB degradado apresentou 43,2% de matéria volátil, 3,5% de cinzas e 53,3% de carbono fixo, enquanto as amostras frescas apresentaram 18,63% de matéria volátil, 1,23% de cinzas e 80,14% de carbono fixo. Concluiu-se que a degradação do solo da floresta diminui o potencial bioenergético das cascas da Castanha-do-Brasil, principalmente por alterar sua composição química.

Palavras-chave: Poder Calorífico Superior, Bioenergia, Lignocelulósicos, Pirólise, Propriedades Mecânicas, Cinética

1. CONTEXTUALIZATION

Biomass gathers all the living matter on Earth (GARG; DATTA, 1998). The term refers to a collective name for substances derived from developing plants or animal waste. Agricultural wastes and their byproducts, municipal solid waste, animal waste, food processing waste, aquatic plants, and algae are all included in this category. One of humanity's first energy sources was biomass. Humans have used it as an energy source for thousands of years, primarily in the form of wood. Biomass is a promising renewable energy source for both rich and developing countries. Traditionally, it has been utilized through direct combustion worldwide. Using biomass from forest residues as an input in energy production has been arousing interest globally because of its renewable potential and job opportunities in both forests and energy production sectors. Sustainable use of forestry residues creates new markets for forest waste residues (SANTIAGO, 2013).

The Brazil nut tree (*Bertholletia excelsa* H. B. K.) occurs in vast forests from the Amazon Basin, mainly in Brazil, Venezuela, Colombia, Bolivia, and Peru. The Brazil nut's edible seed is greatly appreciated for its nutritional value. It has always been an important resource for local populations and is the only globally traded seed crop collected from natural forests (SHEPARD; RAMIREZ, 2011). Several attempts have been made to develop Brazil nut cultivation methods that would allow large-scale plantations; however, the productivity of cultivated trees remains low. As a result, few plantings of Brazil nut exist, and most have forest restoration as their primary objective (HOMMA et al., 2014). The exploitation of Brazil nuts thus relies on harvesting from trees of natural forests (WILLEM et al., 2019). Its harvesting does not require logging; hence, it has a low environmental impact on the rainforest (WADT et al., 2008). The extraction has become a source of income for the local communities that see deforestation as a direct threat to the viability of Brazil nut tree populations (KALLIOLA; FLORES, 2011). Therefore, locals readily contribute to the conservation of the Amazon Forest while protecting Brazil nut trees (GUARIGUATA et al., 2017). However, the extraction of Brazil nuts generates a lot of lignin, hemicelluloses, and cellulose-rich agroforestry wastes (TORRES et al., 2019). Currently, locals use shells as biomass for rudimentary energy generation in rural areas.

Blue Timber is a forest management company in the global forest sector which operates on sustainability principles while having an impact on both the social and environmental aspects of the relative forest areas and communities. It has the FSC® certification (FSC-C149775), meaning that the forest is managed responsibly, following socio-environmental principles, criteria, and normative legal precepts. The company carries out certified forest management in the Paru State Forest, in the municipality of Monte Alegre, located in northern Pará state, Brazil. The harvested tropical hardwoods are destined for sawing and veneering. The companies provide training for the local community for later employment in forest exploration activities. Between tree harvests, there is a latent period (December – March) during which the workers and other people of the community harvest Brazil nutshells to sell and have additional income. The community reported many accidents and physical efforts for the nutshell manual cutting. Besides, the shells are left in the field. Such wasted biomass could be converted into bioproducts and bioenergy, providing one more alternative income for the local populations.

1.1 Objective

1.1.1 General Objective

To characterize the bioenergy properties of Brazil Nutshells available fresh and degrading in the forest and to develop a practical technology that helps the workers to open shells and improves primary biomass for further carbonization.

1.1.2 Specific Objectives

- To review the sustainable potential of residues from Brazil Nut fruits in different applications, focusing the carbonization;
- To compare the chemical, physical and energetic properties of fresh and degraded Brazil Nutshell mesocarp;
- To compare the chemical, physical and energetic properties of fresh and degraded Brazil Nutshell charcoal;
- To develop a simple device to open the Brazil nutshell that concurrently protects the edible nuts (the target commercialization product) is safe for the workers and results in homogeneous pieces of shells for future carbonization.

1.2 References

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2. REVIEW OF CURRENT AND EMERGING TECHNOLOGIES FOR CONVERTING BRAZIL NUT WASTES INTO BIOPRODUCTS AND BIOENERGY

Abstract

One of the main non-timber Amazonian products traded in the international market is the Brazil Nut. Its harvest and production generate much lignocellulosic waste, corresponding to almost 90% of the fruit. Therefore, many investigations were carried out to find suitable applications of the wastes, such as the husk and seed shells, for a variety of industrial applications, including water treatment and the production of activated carbon, eco-plastic composites, composting, biochar, and construction materials. Here, we reviewed the academic literature exploring the properties of Brazil nut-waste materials and their applications in multiple industries besides the current technology used for carbonization of the Brazil nut wastes.

Keywords: Amazon, Bioenergy, Bioproducts, Sustainability

2.1 INTRODUCTION

The Brazil Nut (*Bertholletia excelsa* H. B. K.) is a tree from South America, mainly occurring in the Brazilian Pará state, Venezuela, Guianas, eastern Colombia, Peru, and Bolivia. Its fruit, also called Brazil Nut, is edible and commercially harvested (de SOUZA et al., 2019). The Brazil Nuts have an excellent nutritional value and are the only globally traded seeds collected from naturally occurring trees (Figure 1, SHEPARD; RAMIREZ, 2011). It is not possible to grow many trees of this species in a single area; hence, large-scale plantations are not viable. Still, the fruit collected in the natural forests is an important resource for the local populations. Furthermore, Brazil Nut extraction does not require logging; hence it provides income for the local communities while conservating the Amazon Forest by protecting the Brazil Nut trees (GUARIGUATA et al., 2017).

Brazil Nut trees have an average height of 30 m and an average diameter of 2 m, with some reaching up to 60 m in height and 5 m in diameter (PIRES, 1984; VILLACHICA et al., 1996). These colossal trees can date back to 270 years, and some individuals with a ≈ 5 m diameter may even be 1000 years old (PIRES, 1984). Brazil Nut trees have intermittent distribution throughout the Amazonian Forest, coupled with advanced tree ages. Based on this combination, Adolpho

Ducke (1946) hypothesized that ancient homocentric activities were responsible for these trees' landscape in the rainforest. Research in ecology, genetics, linguistics, and archeological data reinforces this hypothesis (SHEPARD; RAMIREZ, 2011).

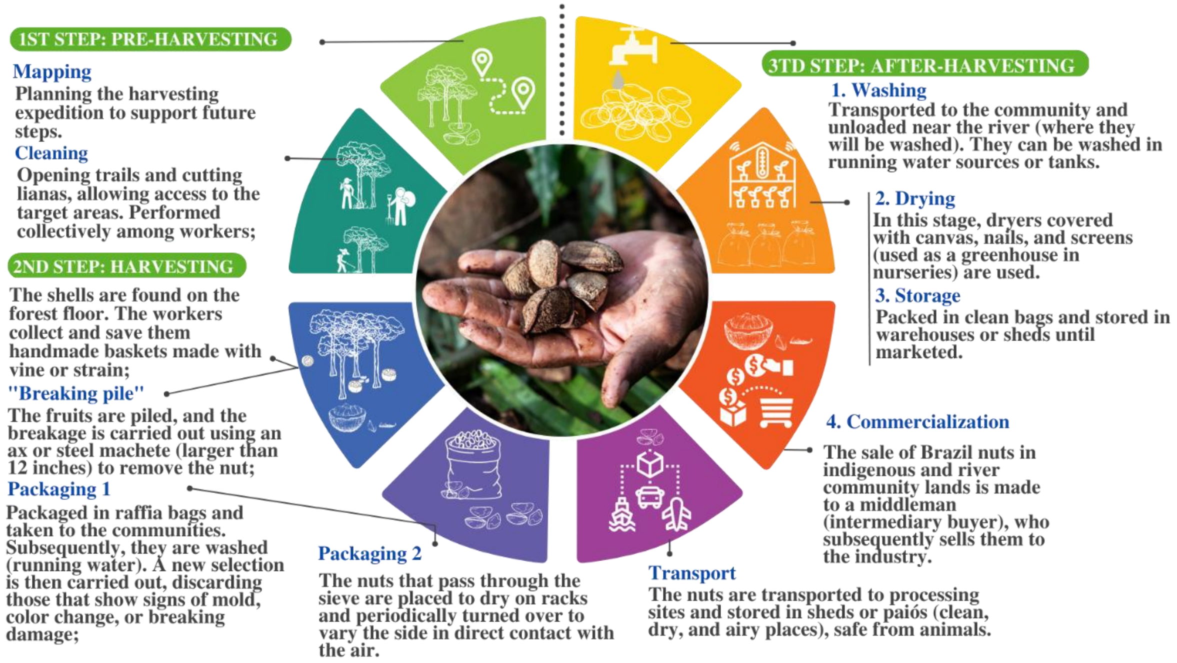
Figure 1. Brazil Nut trees in their natural environment.

The fruit of the Brazil Nut tree, also called Brazil Nut, is a large woody sphere containing around 12 to 24 seeds, each with a surrounding shell. These seeds are extracted, shelled, and exported, while the remaining waste constitutes around 85% of the fruit. Considering the large amount of waste generated from the harvest of Brazil nuts each year (approx. 19,600 tons), many research categories were carried out to find a practical use for this biomass (INAMURA et al., 2013).

Converting any biowaste into bioproducts or bioenergy requires considering their chemical and physical structure, energy properties, and thermal and kinetic parameters. Researchers have discussed various potential uses of the wastes derived from Brazil nut ranging from charcoal production, bio-absorbents, and even application in impact-resistant materials, considering the high strength of the mesocarp comprised of a complex arrangement of fibers in its lignocellulosic structure. This study aims to examine the literature on converting Brazil's nut wastes into sustainable bioproducts and bioenergy based on their chemical, morphological, structural, and kinetic properties, besides the current process for their carbonization.

The production chain of the Brazil nut is summarized in Figure 2.

Figure 2. Summary of the production chain of the Brazil nut.



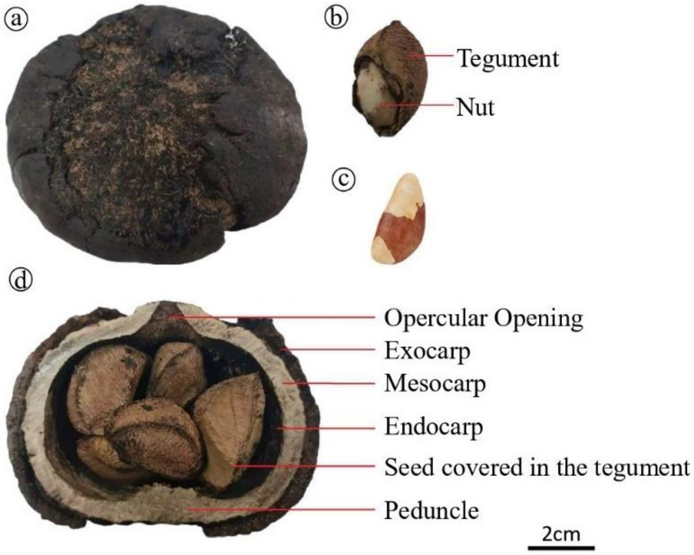
2.2 MATERIAL AND METHODS

A literature review was conducted to retrieve academic documents evaluating the multiple applications of Brazil nut wastes. For this purpose, the Scopus () and Google Scholar () databases were consulted by applying the keywords "*B*razil nut" or "*Bertholletia excelsa*" in conjunction with "*waste*" or "*shell*" or "*residue*" or "*fiber*" or "*biowaste*" or "*sustainable*" or "*mesocarp*" or "*lignocellulosic material*." Relevant literature published from 1993 to 2022 was selected and categorized based on Brazil Nut wastes' chemical, physical, structural, mechanical, morphological, kinetic, and thermodynamic properties.

2.3 BRAZIL NUT CHARACTERISTICS

The seed endosperm is the edible part of Brazil nuts. Each seed is protected by a hard shell (tegument). In addition, all the seeds are encased by a very hard, dry, woody globular pericarp consisting of three layers (PETRECHEN et al., 2019): the exocarp (outer layer), mesocarp (intermediate layer), and endocarp (inner layer), the outer shell (Figure 3).

Figure 3. Brazil nut: (a) fruit, (b) seed, and (c) debarked seed (d) vertical cross-section of Brazil Nut fruit.



Brazil Nuts rely mainly on the mesocarp and seed tegument for protection (SONEGO et al., 2019). Only the edible part (seeds) is commercialized in the international market. The seed shell and the pericarp are considered waste making up 85% of the Brazil nut fruit's total weight (SONEGO et al., 2019). Inamura et al. (2016) characterized the pericarp and seed shell waste. They found that the pericarp and the tegument have a cellulose content of 53.3% (wt.) and 38.2% (wt.), respectively. The lignin content was 35.8% for the pericarp and 54.1% for the tegument. Leandro et al. (2019) and Inamura et al. (2016) calculated the proximate composition of Brazil nut wastes, as shown in Table 1.

Table 1. Chemical composition of the Brazil nut wastes

Property content (%)	Waste composition		
	Nutshell[1]	Tegument (seed shell)[1]	Nutshell + tegument[2]
Lignin	54.1 ± 1.10	35.8 ± 0.80	55.8 ± 6.6
Cellulose	38.2 ± 1.00	53.3 ± 1.10	37.1 ± 0.1
Extractives	3.9 ± 0.20	7.5 ± 0.20	4.5 ± 0.3
Moisture	14.7 ± 0.09	10.3 ± 0.03	10.6 ± 0.1
Volatile matter	-	-	65.7 ± 0.3
Ashes	-	-	2.1 ± 0.1
Fixed carbon	-	-	21.6 ± 0.3

Sources : [1]Inamura et al. (2016); [2]Leandro et al. (2019)

These chemical characteristics make Brazil nut wastes suitable for developing high-quality activated carbon (APAYDINVAROL; ERÜLKEN, 2015). In addition, a higher lignin content will alter the ash content and elemental composition (BONELLI; CUKIERMAN, 2015) and promote a denser and less porous structure, which results in higher tensile strength, Young's modulus and toughness, as previously observed in coconut shells (GLUDOVATZ et al., 2017).

Concerning anatomy and morphology, the mesocarp is a rigid, impermeable, and fibrous structure composed of sclereids and fibers (another sclerenchyma tissue) in a composite-like arrangement and a vascular system (SONEGO et al., 2019). Sclereid cells are $\sim 30\ \mu$m in diameter and have a thick lignified cell wall and an isometric shape. In comparison, fibers are $\sim 20\ \mu$m in diameter, elongated, and organized in bundles (SONEGO et al., 2020).

Nanoindentation to the cross and longitudinal sections of the fiber and sclereid cells in the mesocarp revealed the reduced modulus (Er) and hardness (H) of the fiber cross and longitudinal sections were 13.02 and 0.30 GPa, respectively. Furthermore, the Er was significantly higher than in the tegument of the Brazil nut, reaching up to 5.4 GPa (KAUPP; NAIMI-JAMAL, 2011) and higher than those of most nutshells (LUCAS et al., 2012). Based on such mechanical properties, Brazil nut waste offers excellent potential for a wide range of bio-product-inspired applications.

2.4 SUSTAINABLE APPLICATIONS BASED ON MECHANICAL AND STRUCTURAL PROPERTIES

2.4.1 Impact-Resistant Materials

Brazil nut is famous for its outer shell's toughness, attributed to its mesocarp's structure. Sonego et al. (2019) investigated how the Brazil Nutshell mesocarp's mechanical properties could help develop bioinspired impact and puncture-resistant materials. They used chemical extraction techniques to find the chemical composition, besides microscopy and microtomography (microCT) analyses, to study the microstructure of the mesocarp. The authors found that the mesocarp of Brazil Nutshell has more lignin (56%) than other nutshells and is comprised of a complex structure of intertwined sclereids and fiber cells rather than arranged in separate layers, as commonly found in nature. The structure had an internal and external layer with fibers oriented from the peduncle to the opercula opening and a middle layer where entangled fibers are latitudinally oriented. This complex arrangement of fibers is the reason for the increased toughness of the mesocarp. Sonego et al. (2019) performed a compression test to find the force needed to open the mesocarp shell, which required 10,079 ± 1,460 N (parallel to the latitudinal section) and 14,785 ± 4,050 N (perpendicular to the latitudinal section. These values were much higher than the forces needed to open most nutshells like hazelnut or walnut shells (SONEGO et al., 2019). Mechanical properties at different scaling lengths were measured using shore D hardness testing and nanoindentation. The data were analyzed with the TriboScan software (HysitronInc.) according to the method described by Oliver and Pharr (1992). The authors found that, although the modulus of the cell walls of the fibers was lower than that of the sclereids, both had similar hardness. They concluded that Brazil Nutshell has excellent potential for developing bioinspired impact-resistant products.

2.4.2 Gelatine/Brazil nut fiber composites

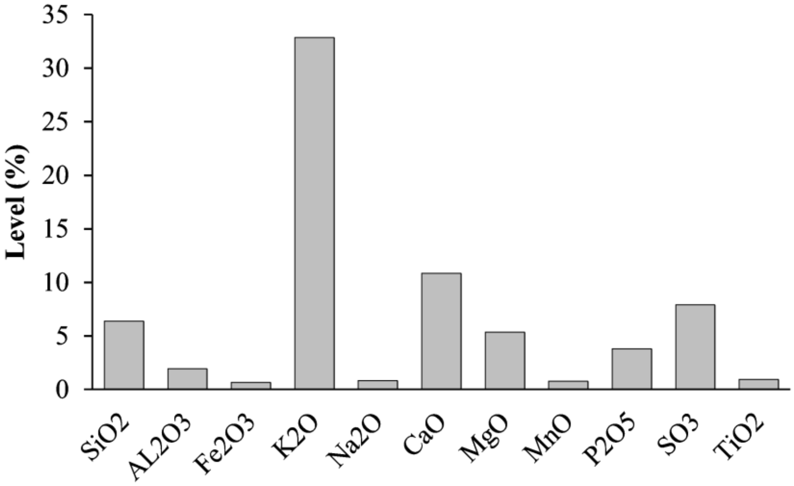
Cellulose, hemicelluloses, and lignin are the primary components of all lignocellulosic wastes, and they can reinforce and enhance the mechanical properties of polymers. Inamura et al. (2010) investigated the mechanical properties of a specimen prepared with Brazil nutshell fibers, gelatin, glycerine, and acrylamide. The specimen was further treated with electron beam radiation to facilitate the polymer's crosslinking for improving the mechanical properties by increasing the elastic and flexural moduli by 2.85% and 18.75%, respectively. The researchers concluded that an irradiated gelatin/Brazil nutshell fiber composite showed favorable characteristics and was a promising substitute for elastomers.

2.4.3 Construction Materials

Porous and lightweight ceramic materials have recently gained significant importance because of good porosity-related thermal insulation, the desired characteristic for constructing bricks. Different raw materials are used to produce bricks, and various pore-forming materials are added to the clay to achieve the desired porosity. Escalera et al. (2015) used diatomite as the pore-forming material for making lightweight bricks. Sintering is one of the essential steps in producing lightweight bricks with high strength; however, it is important to have a low sintering temperature to avoid extra energy costs. Thus, the researchers added Brazil nut ash as a flux material to help with the sintering process and the material to achieve the required strength.

Escalera et al. (2015) calculated the chemical composition in oxide form (wt%) of Brazil nutshells (Figure 4) and verified a loss of ignition of 27.5%.

Figure 4. Chemical oxide composition of Brazil nut outer shell.



Source: Escalera et al. (2015)

Escalera et al. (2015) observed that Brazil nut ash is rich in alkaline elements and can potentially lower the sintering temperature, thus being an attractive and lower-cost alternative to traditional fluxing materials. Also, adding Brazil nut ash as a flux increased the strength of the bricks three times (from 7.5 to 24 MPa) compared to bricks produced without it.

2.5 SUSTAINABLE APPLICATIONS BASED ON CHEMICAL AND MORPHOLOGICAL PROPERTIES

2.5.1 Activated carbons from Brazil Nutshells and Açaí seeds

Souza (2019) studied the potential of activated carbons from Açaí seeds and Brazil Nut for the adsorption of Color Index (C.I.) basic blue 26 (BB26) from aqueous solutions. Desirable characteristics of activated carbon are suitable chemical surface, porosity, adsorption capacity, high specific surface area, and proper regeneration once used. Brazil Nut and Açaí wastes have high availability and low cost, favorable attributes of solid wastes for producing activated charcoals. The authors prepared the activated charcoals using chemical activation with H_3PO_4 and studied the physicochemical and textural properties of the resulting product. They added the samples to a dyed aqueous solution and obtained the initial equilibrium and kinetic adsorption data. The thermodynamic parameters indicated a spontaneous and exothermic in-nature adsorption process. Thus, chemically activated charcoals produced with H_3PO_4 from Açaí, and Brazil Nut wastes were promising toward removing BB26 from aqueous solutions. Such research contributed to an environmentally friendly solution to removing dyes from the aqueous medium using activated carbons from low-cost solid materials, besides adding value to solid wastes.

2.5.2 Water treatment using activated carbons from Brazil Nut waste

Lima (2019) studied the production of activated charcoal from Brazil Nut wastes by 1:1 and 1:1.5 (solution: biomass mass) $ZnCl_2$ activation and formed samples with two compositions, named BNS1.0 and BNS1.5, respectively. The authors studied the adsorption mechanism of acetaminophen (paracetamol) and the treatment of synthetic hospital effluents using both samples. The results revealed a spontaneous, exothermic, and energetically favorable in-nature thermodynamic assessment of the adsorption. The magnitude of the enthalpy for the adsorption was compatible with physisorption. The higher surface area of the activated carbons formed from the Brazil Nut wastes made it a suitable raw material. The authors observed the high efficiency of the adsorption (up to 98.9%), while 74% of the adsorbent was regenerated and reusable for up to four cycles of the adsorption process. The authors concluded that Brazil Nut waste is a perfect raw material for producing activated carbons with $ZnCl_2$ activation for treating aqueous waste from hospitals.

2.6 SUSTAINABLE APPLICATIONS BASED ON KINETIC AND THERMAL PROPERTIES

2.6.1 Thermochemical conversions of Brazil Nutshells

One of the practical ways to deal with residual biomass is pyrolysis, as it yields valuable products and is less harmful to the environment than traditional waste accumulation or open-field burning. Pyrolysis thermally decomposes biomass without oxygen to produce biochar, bio-oil, and biogas. The yield of each fraction depends on the parameters used to carry out the process (DILKS et al., 2016). Slow pyrolysis can transform solid biomass wastes into charcoal with high carbon yields. This charcoal can be directly burned as a biofuel or further treated to produce activated carbons.

Lignocellulosic materials have a complex structure consisting of varying amounts of cellulose, hemicelluloses, and lignin, depending on the source from which they came (BONELLI et al., 2001). This complex structure of lignocellulosic materials makes the pyrolysis complex because each component has different reactivities at different temperatures (ANTAL; VARHEGYI, 1995). The number of lignocellulosic components varying among the many wastes hinders the creation of a general model for kinetic properties (DELLA ROCCA et al., 1999; CUKIERMAN et al., 1996). For Brazil Nutshells, it is essential to study their chemical, textural, and morphological properties during pyrolysis and thermal degradation behavior by thermogravimetric analysis. Bonelli et al. (2001) performed a non-isothermal thermogravimetric analysis for Brazil Nutshells and analyzed the decrease in the volatile matter and increase in fixed carbon and ash contents with increasing temperatures during pyrolysis. They observed significant changes in the sample structures at relatively higher temperatures (>350 °C). They also noticed changes in the residual cellular structure and increased sample surface porosity with increasing temperatures, besides larger pores formed at 600 °C. At 850 °C, the micropores became strongly predominant.

Thermogravimetric analysis (TG) provides us with the ratio of mass loss of the biomass as a function of temperature during the pyrolysis process (HU et al., 2021), while its association with mass spectrometry provides a triangular relationship between mass loss, temperature, and gas emission assessment (DONG et al., 2015). Colpani et al. (2022) studied in detail the kinetics of pyrolysis of the Brazil Nut wastes, including the shell and seed husk. They used an inert atmosphere to conduct the thermogravimetric analysis and determined the kinetic and thermodynamic parameters. The mean activation energy for both residues was 137.05 kJ/mol for the shells and 152.93 kJ/mol for the seed husks. These differences might be due to the difference in chemical composition between the shell and husk. The pyrolysis of Brazil Nut wastes was observed to be a non-spontaneous endothermic process with a little external energy required to generate products. Colpani et al. (2022) concluded that Brazil Nut residues have a good potential for renewable energy based on the high heating values of the samples, 13.6 MJ/kg for the shells and 14.6 MJ/kg for the seed husk. In addition to the kinetic and thermodynamic analysis, they also studied Ion fragments (*m/z*) of possible gaseous emissions from Brazil nut residue biomass (Table 2).

Table 2. Ion fragments (*m/z*) of possible gaseous emissions from Brazil nut residue biomass.

Mass/Charge (*m/z*)	**Potential Fragment/Molecule**
12	C
15	CH_3^+
16	CH_3^+
17	NH_3, OH^-
18	H_2O
26	C_2H_2, CN
28	C_2H_4, CO
30	C_2H_6, HCHO, CH_3NH, NO
44	C_3H_8, CO_2
46	NO_2, HCOOH
53	$C_7H_6O^{++}$
55	$C_3H_3O^-$, $C_4H_7^+$
57	C_4H_9
60	COS, CH_4CO_2
74	$C_4H_{10}O$, $C_3H_6O_2$
81	$C_5H_5O^-$
84	C_6H_{12}, $C_4H_4O_2$

Source: Colpani et al. (2022).

According to the author, these emissions are much less harmful to the environment than traditional fossil fuel emissions. Oliveira and Lobo (2002) calculated a higher heating value (HHV) of Brazil Nutshells of 19.77 MJ/kg, indicating their great potential for energy purposes. The HHV of biomass depends on elemental, macromolecular, immediate chemical composition, and moisture content (VALE et al., 2011). Carmona et al. (2017) studied three sample compositions: waste from the shells alone, waste from the seed husks alone, and a mixture of equal amounts of the shell and the seed husk. They observed that the ash from all three samples was close to the average ash proportion found for charcoals derived from other biomass wastes (BARROS, 2006). Therefore, they suggested using Brazil Nut wastes for producing pellets would be efficient considering their properties. Furthermore, they analyzed the gravimetric yield of charcoal from both waste compositions indicating their potential for carbonization.

With increasing concerns about environmental pollution and keeping up with the high demand for fuels worldwide, the need for alternative fuel sources is increasing. One of the alternatives for traditional fossil fuels is the pyrolysis of biomass. Waste with suitable energy properties and kinetic parameters are valuable biofuel resources. Noszczyk et al. (2021) discussed how nutshells are an underrated source for producing biofuels. They characterized various raw nutshells based on HHV and moisture content properties. After applying thermal treatments, the authors noted a significant increase in the HHV, activation energy, and heating rates. They also stated that thermal processing via pyrolysis and torrefaction significantly improved the residue for energy generation, biopolymer production, and fertilizer production. They concluded that higher temperatures improved the thermal properties of the biomass by increasing the HHV, decreasing the moisture content, and improving the hydrophobicity of the resulting biochar.

2.6.2 Thermal and morphological analysis of brazil nut flour for feeding purposes

Brazil Nuts have a high nutritional value consisting mainly of proteins and lipids (COUTINHO AND COZZOLINO, 1998; CARDARELLI AND OLIVEIRA, 2000; GONZAGA, 2002), so new applications in the food industry are constantly researched. Santos et al. (2010) suggested processing the nuts into flour with no change in its energy content. The final product had a high energy value of 431.48 kcal, protein content of 45.92g, and fiber content of 17.14% per 100 g (about 3.53 oz). They further stated that adding other protein components, such as soy protein isolate, does not affect the reactivity or thermal properties. The morphological properties of Brazil Nut flour indicated many similarities with the structure of globular proteins (NELSON; COX, 2002). Lluch et al. (2001) studied the structural models of different proteins. They observed that even though each protein features a unique pattern, there are similarities that may lead to the development of databases that allow for comparing different protein structures. Santos et al. (2010) concluded that the flour obtained by the processing of Brazil Nut maintains its thermal reactivity and nutritional value, thus making it suitable for use in the food industry.

2.7 SUMMARY

Table 3 summarizes the research regarding the potential sustainable uses of lignocellulosic wastes, mainly from Brazil Nut.

Table 3. Summary of the emerging research on technological applications of Brazil Nut.

Focus	**Objectives**	**Findings and Conclusions**	**References**
Brazil Nutshells	*To measure the effect of pyrolysis temperature on the composition, surface properties, and thermal degradation rates of Brazil Nutshells.*	*Significant changes in chemical, textural-morphological, and surface properties were observed with the development of pores at higher pyrolysis temperatures.*	Bonelli et al. (2001)
Brazil Nut Wastes	*To measure the energy potential of biomass and charcoal obtained from Brazil Nut wastes.*	*Both the nutshell and the seed shells have the potential to generate energy, but due to lower HCV, charcoal conversion is preferred.*	Carmona et al. (2017)
Brazil Nut Wastes	*To analyze the bioenergy potential of brazil nut reside pyrolysis by studying kinetics, thermodynamic parameters, and gas emissions.*	*Pyrolysis of Brazil Nut wastes is a viable way of converting biomass into energy. The emission of gases detected during burning had a less harmful environmental profile.*	Colpani et al. (2022)
Brazil Nut Flour	*To conduct the characterization, thermal and morphological analysis of processed Brazil Nut flour.*	*Brazil Nut is nutritionally viable with no changes in thermal properties with the addition of foreign proteins, and morphological analysis showed a protein-like granular structure. The flour maintained its high energy content and resistance to high temperatures even after processing.*	Santos et al. (2010)
Ligno-cellulosic Biomass	*To observe the pyrolysis kinetics of lignocellulosic materials*	*Each lignocellulosic material reached maximum weight loss at different final temperatures during pyrolysis due to degradation differences of the various components of the solid reactant.*	Balci et al. (1993)
Nutshells	*To study the kinetic parameters for pyrolysis of different nutshell wastes.*	*Raw nutshells have remarkable energy potential with a significant increase in HHV after initial thermal treatment. Still, thermal treatment requires basic knowledge of kinetic parameters to facilitate the design of bioreactors and optimize the conditions for obtaining specific properties of the processed waste.*	Noszczyk et al. (2021)
Brazil Nut Mesocarp	*To study the mechanics of the mesocarp of Brazil Nutshell to apply the properties in impact-resistant materials.*	*Brazil Nut mesocarp has great potential for developing bioinspired impact and puncture-resistant structures, but due to irregular hardness gradient throughout the mesocarp, further studies are required for implementation.*	Sonego et al. (2019)
Gelatin and Brazil Nutshell fibers	*To study the mechanical properties of irradiated gelatin/Brazil nutshell fiber composite*	*Irradiated Gelatin/Brazil nutshell fiber composite showed favorable mechanical properties to substitute elastomers.*	Inamura et al. (2010)
Diatomite and Brazil Nutshell ash	*To produce porous brick material using Diatomite and Brazil Nutshell ash as raw materials to increase strength and porosity.*	*Diatomite bricks showed increased thermal insulation, and adding Brazil Nutshell ash as a flux increased the strength of brick three folds.*	Escalera et al. (2015)
Acai residue and Brazil Nutshells	*To study the removal of basic blue 26 dye from aqueous solutions by adsorption using* H_3PO_4*-activated carbons produced from açai stones and Brazil nutshells.*	*The activated carbons produced in this work had high porosity and adequate adsorption characteristics. They effectively removed BB26 from aqueous solutions.*	de Souza et al. (2019)

Brazil Nutshells	*To study Brazil Nutshells as a biosorbent for methylene blue and indigo carmine from aqueous solutions.*	*Brazil nut shells were useful low-cost biosorbents for removing acid and basic dyes from aqueous solutions.*	de Oliveira et al. (2009)
Brazil Nutshells	*To study the effectiveness of activated carbons from Brazil nut shells for removing acetaminophen from water and hospital effluents.*	*Using activated carbons from Brazil nut shells for treating simulated hospital wastewater containing several pharmaceuticals, organics, and inorganic salts, presented up to 98.83% of total removal.*	Lima et al. (2019)

2.8 CURRENT TECHNOLOGY FOR THE CARBONIZATION PROCESS OF BRAZIL NUT WASTES

2.8.1 Technique

Nogueira (2011) studied the carbonization of Brazil Nut wastes. Carbonization was performed in cylindrical metallic drums with a volume of 0.2 m³, reusing the lubricating oil containers. Carbonization was guaranteed by completely removing the cover in one end and partially removing it in the other, maintaining a supporting edge. Air control was necessary to use the drum as a reactor. Thus, the part removed from the bottom was used as a lid and supported on the top of the reactor to ensure the system's sealing. Carbonization starts after weighing and supplying the wastes corresponding to a reactor with a mass of approximately 80% of the total height of the reactor.

It was necessary to control the entry of the oxidizer into the reactor to carry out the carbonization process. Thus, in this technique, the oxygen of the atmospheric air (oxidizing agent) enters the reactor through openings at the base of the drum, made by digging two channels, in the form of a cross, with an average height of 10 cm, in the soil immediately below the drum. The air inlets were also used to start the carbonization process. Carbonization was started with a blowtorch connected to a 13 kg cylinder of domestic gas at the base of the reactor so that the shells located at the base of the drum were combusted to provide sufficient heat for the pyrolysis process.

The production of charcoal was tested by air intakes in the ground and by installing a raised base with a perforated bottom to increase the free area for air admission. After the carbonization started, which was determined by the movement of the heat front to the average height of the shell mass, the air inlets at the base of the reactor were sealed to guarantee the reduced environment necessary for carbonization. The complete sealing of the reactor was carried out by installing the metal lid and sealing the upper part with a mass formed by mud to reduce heat loss and oxygen entry. The reactor sealing moment was determined by the presence of flames in the upper part to ensure sufficient temperature for carbonization throughout the reactor. After the reactor was sealed, pyrolysis occurred, and the carbonized mass cooled. As the reactor has no thermal insulation, the cooling occurs by natural convection by the air on the lateral surface of the furnace. After the pyrolysis and cooling were completed, the carbonized biomass was removed.

2.8.2 Charcoal quality

Since the Brazil nutshell is not a massive structure, Nogueira (2011) observed that the charcoal produced had a thinner wall than wood charcoal, thus facilitating the breakage and generation of a large volume of materials with small dimensions. The partially carbonized material could return to the reactor in the upper part to be used as a heat source for the pyrolysis process. Time was a decisive factor for the high content of non-carbonized material in the nutshell mass. The duration for complete carbonization of the residue was insufficient before the reactor started to cool down. Since the reactor had no thermal insulation, the cooling started before the complete carbonization of the residues.

2.8.3 Future Improvements

The drum method is adapted to produce charcoal from the shells of Brazil nuts; however, the thermal insulation of the reactor could be improved in future works. Modifying the shape of the residual mesocarp from the Brazil Nut is another possible advancement for its carbonization. If the sample to be carbonized has a greater surface area, it will greatly reduce the chances of partial carbonization (NOGUEIRA, 2011). The author stated that charcoal's gravimetric yield was low compared to other carbonization methods, possibly due to the lack of thermal insulation. Besides, the carbonization time in the reactor was considerably shorter than those obtained for carbonization in a laboratory muffle of similar products.

The problems of this carbonization system by Nogueira (2011) are:

- There is no temperature control.
- The energy source is internal (part of the biomass needs to be burned to provide energy for the endothermic reactions of pyrolysis).

- There is no control of the gases.
- The carbonization time in the reactor was considerably shorter than those obtained after carbonization in a laboratory muffle of similar products.
- The charcoal produced by the drum method showed chemical, physical, and thermal characteristics comparable to charcoal from other wood and non-wood species.
- There is a need to deepen the studies of raw materials.

The final charcoal produced by the drum method showed chemical, physical, and thermal characteristics comparable to charcoal from other wood and non-wood species. The tested method was simple, presented suitable production conditions for the local harvesting communities, and could be transferred to the production site.

2.9 CONCLUSIONS

Brazil nut wastes are very promising for their potential for biofuels and bioproducts because of the residue's interesting mechanical and kinetic properties. The mechanical properties and structural composition of the Brazil nutshell residues show the potential of this material to be used for impact-resistant purposes and the strengthening of polymers and construction bricks due to the high lignin content. Brazil Nutshell residues also show potential for carbonization and can be used as biofuel for both pellets and charcoal. The current carbonization method available is suitable for the context of local Amazonian communities. The drawbacks, such as partial carbonization, can be overcome with better process control and preparation of the collected wastes.

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3. BIOENERGY PROPERTIES OF FRESH AND DEGRADED BRAZIL NUT SHELLS AND DERIVED CHARCOALS

Abstract: The Brazil Nut is one of the main non-timber exports from the Amazon, but a lot of waste (85% of the fruit) is generated each year from its collection and harvest. This work aims to consider the potential of Brazil nutshell (BNS) biomass degrading in the forest to produce bioenergy. Fresh BNS mesocarp samples showed 67.23% of volatile matter, 28.75% of fixed carbon and 4.02% of ash, and a higher calorific value of 4,797 kcal/kg; Degraded BNS mesocarp samples showed 75.7% of volatile matter, 3.3% of ash, 20.9% of fixed carbon, and a higher calorific value of 4,600 kcal/kg. The average basic density was slightly lower for degraded BNS (0.84 ± 0.16 g/cm³) than for the fresh ones (1.00 ± 0.21 g/cm³). Thermogravimetric analysis indicated that fresh and degraded BNS mesocarp samples are suitable for carbonization, but their thermal behavior differed. The charcoal produced at T = 400°C in a hot-tail furnace from degraded BNS showed 43.2% of volatile matter, 3.5% of ash, and 53.3% of fixed carbon, while 18.63% of volatile matter, 1.23% of ash, and 80.14% of fixed carbon for fresh samples. It was concluded that degradation in the forest floor decreases the bioenergy potential of Brazil nut shells, especially by altering their chemistry.

Keywords: Amazon, Carbonization, Bioenergy, Lignocellulosic biomass, Pyrolysis

3.1 INTRODUCTION

The use of forest biomass as an energy input, in different forms, has been arousing interest in several countries due to its renewable potential, in addition to emerging as a generation of job opportunities and creating new markets for forestry wastes (SANTIAGO, 2013). Brazil is one of the largest producers of wood and agricultural products due to its remarkable biodiversity, area of cultivation, and tropical climate that favors crops largely (PAULA, 2010). However, this profile also results in large amounts of agroforestry wastes with great potential for various uses. Consequently, research is being carried out to find an appropriate use of these residues as an alternative source for energy production.

The Brazil Nut (*Bertholletia excelsa* H. B. K.) is a tree from South America, found in the Brazilian Amazon states, Venezuela, Guianas, eastern Colombia, Peru, and Bolivia. Its fruit, also called Brazil Nut, is edible and commercially harvested (SOUZA et al., 2019). The trees have an average height of 30 m and an average diameter of 2 m, with some reaching up to 60 m in height and 5 m in diameter (PIRES 1984; VILLACHICA et al.1996). The fruit is a large woody sphere containing 12 to 24 seeds, each with a surrounding shell. Many local communities in the Amazon rainforest practice extraction by collecting Brazil Nut fruits that fall from the trees once matured.

Collection of Brazil Nut fruits is one of the most economically important activities in the region. However, as this practice is seasonal, income is only generated during the harvest season; therefore, an alternative activity would remunerate the communities during the off-season (NOGUEIRA, 2011). Furthermore, these seeds are extracted, shelled, and exported, while the remaining waste constitutes around 85% of the fruit and is left on the forest floor degrading (LIMA et al., 2019).

Considering the large amount of waste generated from the harvest of Brazil nuts each year (approx. 19,600 tons), many research categories were carried out to find a practical use for this biomass (INAMURA et al., 2013). For the rational and adequate use of any biomass residues, it is necessary to study their energetic properties (PROTÁSIO et al., 2011). Therefore, knowledge of biomass characteristics – such as elemental chemical composition (carbon, hydrogen, oxygen) and macromolecular (cellulose, lignin, hemicelluloses, extractives), density, moisture content, immediate chemical composition (volatile materials, fixed carbon, and ash) – are essential for its best use as an energy source, as all these properties influence the calorific value (VALE et al. 2011). Therefore, this work aimed to compare the chemical, physical and energetic properties of fresh and degraded Brazil Nutshell mesocarps and derived charcoals.

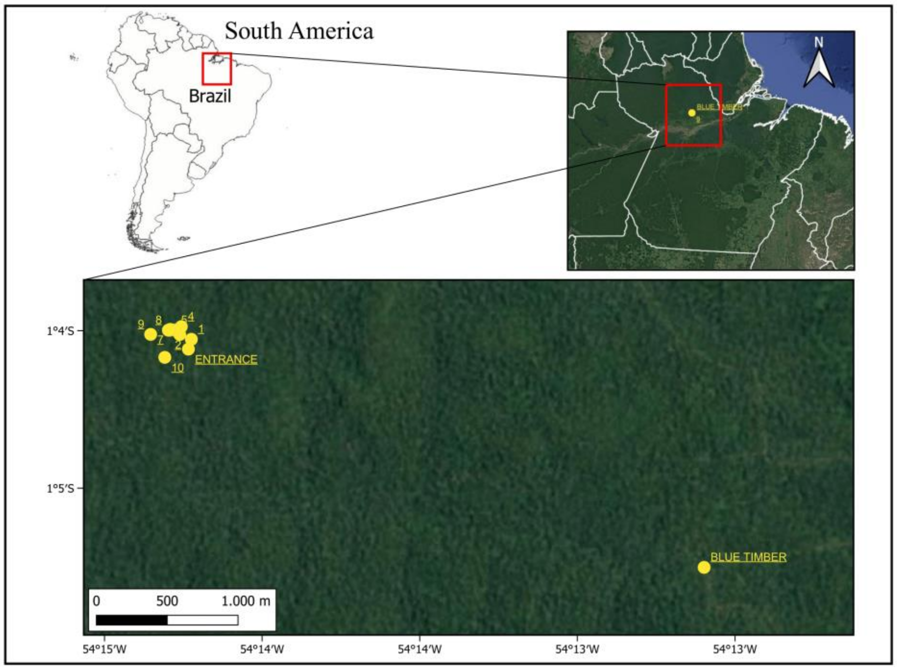
3.2 MATERIALS AND METHODS

3.2.1 Samples collection and preparation

Fresh and degraded samples of Brazil Nuts were collected from the Amazon Forest surrounding the Blue Timber field station in Estrada Vicinal da Serra Azul, S/N – Lote IV Flota Paru, Serra Azul, Monte Alegre – Pará. Samples of both types were collected from a cluster of Brazil Nut trees (Figure 1) at different sites. The map (Figure 2) was made using Quantum GIS (QGIS 3.28 Frienze), WGS-84 datum, and Mercator map projection.

Figure 1. Brazil Nut trees (*Bertholletia excelsa*) in the collection sites

Figure 2. Collection sites for Brazil Nut samples (*made by author*)



A total of 70 samples were collected, of which 40 were from the fresh harvest, and the rest were degraded samples from previous harvests (about one year on the forest floor, according to the workers). After collection, the samples were washed and dried under natural sunlight for 48 hours before being transferred to the lab for analysis (Figure 3).

Figure 3. Fresh and degraded Brazil Nut samples

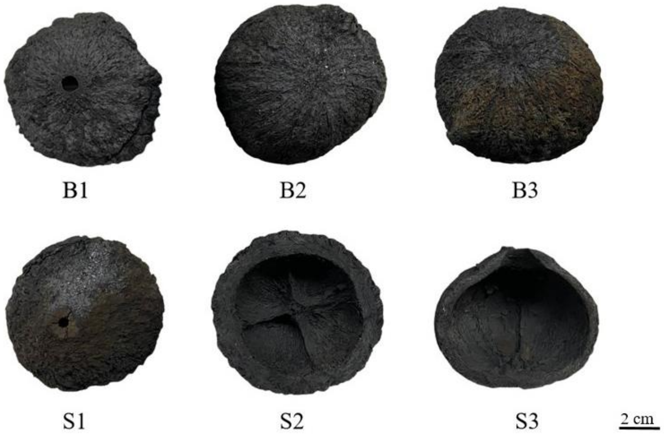
When the samples arrived in the lab, they were dried in an oven at 100°C for 24 hours to allow storage without the risk of rotting. Deionized water was used throughout the analyses. The samples selected for characterization were first grounded, milled, and sieved. For proximate analysis, samples between 40 and 60 mesh size were used, while samples with particle diameter size of (ϕ < 270 μm) were used for thermogravimetric analysis and calorific value calculation.

3.2.2 Carbonization

For carbonization, the samples were placed in a cylindrical oven of a local carbonization facility with an external combustion chamber (Figure 4). The samples were encased in a tin container to avoid contamination from the woody materials in the oven. Carbonization occurred at 350~400ºC, and the samples were kept in the oven for 96 h. The resulting carbonized samples are shown (Figure 5).

Figure 4. The oven used for the carbonization.

Figure 5. Carbonized Brazil nutshell samples (at T= 400°C) used for density analysis are S1, S2, and S3 from fresh BNS, and B1, B2, and B3 from degraded BNS.



3.2.3 Characterization of the shells and charcoals

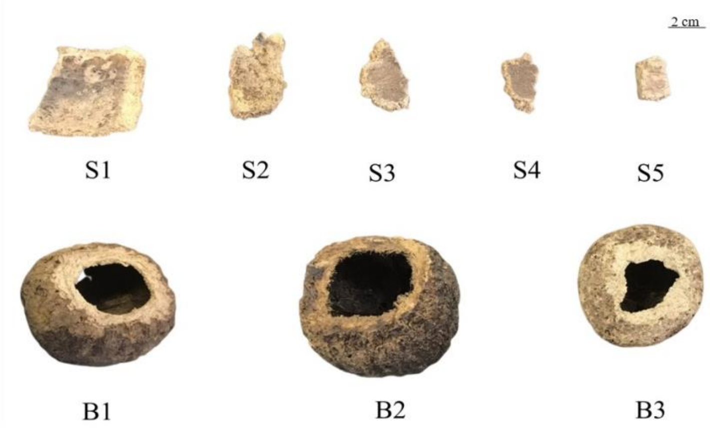
3.2.2.1 Chemical and proximate analyses

The NBR 14577 (ABNT, 2010b) standard was used to determine water-soluble extractives. Proximate analyses of the shell biomass and charcoals were performed following the American Society for Testing and Materials ASTM D1762/84 standard (ASTM, 2013). Samples were prepared for triplicate determinations for each value.

3.2.2.2 Basic Density

Eight Brazil Nutshell samples of various sizes were prepared for density analysis (Figure 4).

Figure 4. Brazil nutshell samples used for density analysis: S1, S2, S3, S4, and S5 are the fresh BNS, and B1, B2, and B3 are the degraded BNS.



The biomass and charcoal samples were saturated in deionized water until volume stabilization. Approximately 500 mL of water was added to a beaker and placed on a scale (accuracy of 0.001 g). Subsequently, the volume was obtained by fully immersing the sample, held by a rod, in the water in the flask, taking care that the sample did not touch either the bottom or the side of the container. The displaced volume of water was recorded, corresponding to the sample volume, considering the water density equal to 1 g cm^{-3}. After determining the volume, the samples were dried in the open air for 24h and then stored in an oven at 103 ± 2º C until they reached a dry mass. The same method was used to calculate the density of charcoal samples obtained at T=400°C for fresh and degraded BNS mesocarp.

3.2.2.3 Mechanics

The exocarp was removed from all the samples before testing, and the effects of the endocarp and the stored seeds were ignored. Compression tests were conducted using a Universal Testing Machine (Artoec WDW-100E, China) with a maximum force of 50 kN. Force was measured by a load cell with a maximum force of 50 kN. The crosshead displacement rate was set to 5 mm min^{-1}. The specimens were loaded to a maximum force of 0.05 N with a force rate of 0.05 N min^{-1} to hold the spherical specimen in the correct orientation before starting the actual compression test. All tests were performed in ambient air at room temperature. Compression forces were applied both parallel and perpendicular to the latitudinal specimen section.

Figure 5. Compression testing of Brazil Nut

3.2.2.4 Higher Calorific Value and Energy Density

The Higher Calorific Value (HCV) was determined in the mesocarp samples, following the recommendations of the EN ISO 18125 (2017) Standard, in a calorimetric bomb (C-200, IKA). To determine the basic density (Db), procedures recommended by ABNT MB 1269 (2003) were adopted. The energy density (De) was obtained according to Equation 1:

$$De = Db * \text{HCV} \qquad \text{(Equation 1)}$$

Where: □□ = energy density (MJ m^{-3}); □□ = basic density (kg m^{-3}); HCV= higher calorific value (MJ kg-1).

The average density was obtained from the arithmetic mean of the density of all the samples.

For the HHV estimation of carbonized samples for both fresh and degraded samples, the correlation (Equation 2) developed by Cordero (2001) was used.

$$\text{HHV} = 3545.3\text{FC} + 170.8\text{VM} \qquad \text{(Equation 2)}$$

where HHV is the higher heating value (kJ/kg); FC is the fixed carbon content (%); and VM is the volatile matter content (%).

3.2.2.5 Thermogravimetric analysis (TGA)

Samples from both fresh and degraded Brazil Nutshells were used for thermogravimetric analysis. The prepared material (5 g per sample) was inserted into the thermogravimetric analyzer SDT 2960 TGA/DSC (TA Instruments, Inc. - New Castle, DE, USA). The crucible with the sample material was introduced into the reactor integrated with the laboratory scale using calibration standards Alumel (154.2 °C), Nickel (354.4 °C), Perkalloy (596.0 °C), and Iron (780.0 °C) to control the change of its mass as a function of time and process temperature. Nitrogen gas was introduced to the chamber to maintain pyrolysis conditions at a rate of 100mL min^{-1}.TGA was carried out from 50°C to 600°C, and a heating rate of 20°C min^{-1} was applied.

3.3 RESULTS AND DISCUSSION

3.3.1. Shell characterization

The fresh samples depicted lower contents of extractives, volatile matter, and more fixed carbon, besides slightly more ashes than the degraded samples (Table 1). The increasing volatile matter indicates an ongoing degradation of the more stable chemical compounds of the shells.

Table 1: Proximate chemical analysis of Brazil Nutshells

Properties	Brazil Nutshell	
	Fresh	**Degraded**
Extractives[a] (%)	3.17 ± 0.10	4.43 ± 0.69
Volatile matter[a] (%)	67.23 ± 1.65	75.67 ± 0.72
Fixed Carbon[a] (%)	28.75 ± 1.36	20.97 ± 0.58
Ash[a] (%)	04.02 ± 0.23	03.36 ± 0.46

[a]Dry basis
[b]Dry and extractive-free basis

Sonego et al. (2019) found an extractive content of 2.5%, while Bonelli et al. (2001) found 3.4% for the Brazil nutshells. Those values are closer to that found for the fresh samples of this work, indicating that the degradations increase the level of leachable components as more primary components are degraded to secondary over time. Both fresh and degraded samples presented a low ash content which is a desirable characteristic for any biomass to be used for energy purposes (ZHAO et al., 2017). Moisture in biomass generally decreases its heating value. Ash and extractive content are two important parameters directly affecting the heating value. A low ash content of a BNS mesocarp makes it less desirable as fuel, whereas high extractive content adds to its desirability. Higher lignin and extractives make biomass sources more suitable for combustion (DEMİRBAŞ, 2003), characteristics which can be found in BNS mesocarp samples.

The degradation slightly decreased the basic density of the nutshells but considerably affected the calorific value (Table 2). Therefore, the main alteration caused by degradation is on the chemical composition, harming the energy properties of the nutshells; as we can see, the degraded samples presented significantly lesser energy density than fresh samples.

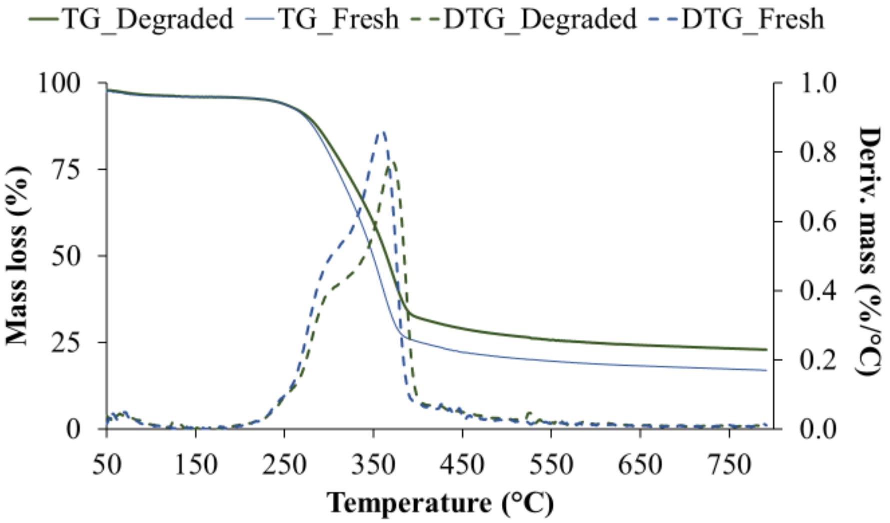
Table 2: Comparision of the density of fresh and degraded BNS mesocarp

Sample	Basic density (g/cm^3)	Calorific value (cal/g)	Energy Density (kJ/m^3)
Fresh	1.00 ± 0.21	4,797 ± 25	20.084
Degraded	0.84 ± 0.16	4,600 ± 49	16.177

Generally, biomass sources have low energy density (ZHAO et al., 2017). Here we observe fresh samples to have greater basic density than degraded samples in turn affecting the energy density. With higher basic densities, more mass per volume is added in the combustion process enhancing yields thus making fresh samples more suitable for carbonization.

The TGA of the fresh and degraded samples showed the typical pyrolysis stages of water loss, initial irreversible degradation up to stabilization after around 550°C. However, the DTG revealed the prominent degradation peak's left displacement and the hemicelluloses' shoulder's weakening (Figure 6).

Figure 6: Thermogravimetric Analysis of BNS mesocarp



Biomass is a mixture of several components; thus, the TGA curve displays the sum of the decompositions of each substance (KACZOR et al., 2020). The hemicelluloses decompose in an approximate temperature range of 220–315 °C, while the cellulose degrades from 315 to 400 °C (YANG et al. 2007). Table 3 shows the greatest mass loss to occur between the temperature range of 300– 400°C for both fresh and degraded samples of BNS mesocarp, being slightly greater for fresher samples indicating better carbonization results. We observe lesser mass loss (%) for both fresh and degraded samples as the temperature becomes greater than 400 °C. The slight mass decrease reflects the lignin pyrolysis, the most thermally resistant component of biomass (Hu et al. 2016).

Table 3: Comparision of mass loss at different temperature ranges for fresh and degraded BNS mesocarp

Temperature Range	Mass loss (% wt)	
	Degraded BNS mesocarp	Fresh BNS mesocarp
Until 100°C	1.62	1.64
100–200°C	0.79	0.47
200–300°C	13.18	16.09
300–400°C	50.52	54.1
400–500°C	5.07	4.86
500–600°C	2.24	1.88

Figures 9 and 10 show the load-deformation curve for fresh and degraded Brazil Nutshell mesocarp samples during compression testing in a universal testing machine. Thirty samples, fifteen fresh and fifteen degraded, were subjected to longitudinal and latitudinal compression. Both fresh and degraded samples showed an increase in strength during longitudinal compression. Brazil Nutshells have significant strength values as it was observed that for the strongest of all the samples tested, the fracture force was 24.96 kN and 23.02 kN for fresh and degraded samples, respectively, during latitudinal compression. For longitudinal compression, the fracture force was measured to be 32.36 kN and 32.29 kN for fresh and degraded samples. The shape and structure of Brazil nutshell caused increased resistance to longitudinal compression for fresh and degraded samples.

Figure 9: Latitudinal compression test results for (a) Degraded BNS mesocarp; (b) Fresh BNS mesocarp

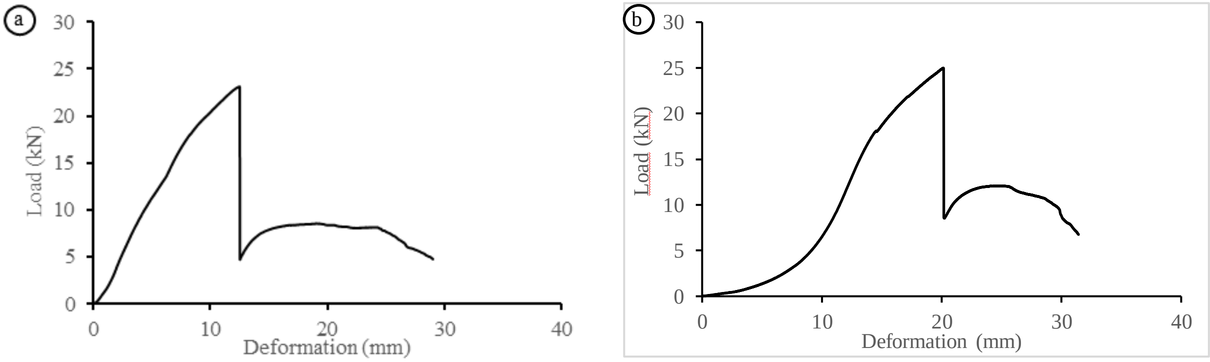
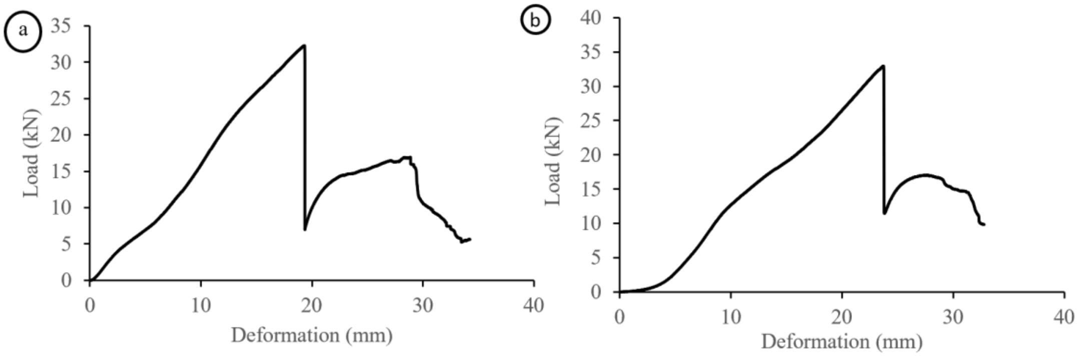


Figure 10: Longitudinal compression test results for (a) Degraded BNS mesocarp; (b) Fresh BNS mesocarp



These results show a pattern similar to the work Sonego (2019), in which he stated the higher content of lignin in Brazil nut mesocarp may be one of the reasons for increased compression resistance. Fresh samples showed a higher resistance to compression forces than degraded samples for both orientations of testing which might be a result of their increased density making them more suitable for charcoal production.

3.3.2. Charcoal characterization

The proximate composition of the charcoal derived from the fresh and degraded samples is shown (Table 3).

Table 3: Proximate chemical analysis (dry basis) of Brazil Nutshell charcoal at T=400°C

Properties	**Fresh**	**Degraded**
Volatile matter (%)	20.03 ± 0.9	18.63 ± 0.51
Fixed Carbon (%)	79.14 ± 0.95	80.14 ± 0.22
Ash (%)	0.82 ± 0.34	1.23 ± 0.57
Basic density (g/cm^3)	1.74	1.62
Calorific value[1] (cal/g)	84,529	68,661
Energy Density[2] (kJ/m^3)	615.79	465.70

[1] estimated value based on the correlation (equation 2) developed by Cordero (2001).
[2] Calculated by equation 1

Although the results of Table 3 show charcoal from degraded samples to have a slightly higher fixed carbon content compared to that of charcoal from fresh samples, Table 4 shows charcoal from fresh samples to have a higher energy density compared to degraded samples due to increased density, indicating fresher residues produce better quality charcoal compared to degraded, both being suitable for good quality charcoal production.

These results show that charcoal from Brazil nutshell mesocarp have high density, high fixed carbon content and low volatile matter and ash content, and greater higher heating value which are all characteristics of remarkable high-quality charcoals (do ROSÁRIO et al., 2018).

3.4 CONCLUSION

It can be inferred that fresh and degraded shells are suitable for charcoal production, but the degradation considerably harms the chemical composition and, consequently, the calorific value of the samples. The degradation affects less the physical and mechanical performance of the Nutshells, being both remarkably high and advantageous for charcoal quality if proper carbonization is achieved.

3.5 ACKNOWLEDGEMENTS

The authors are grateful for the Mai/Dai CNPq program for the scholarship, Blue Timber for funding, and Post Graduation Program in Chemistry of UERJ for the TG analyses and Instituto Federal de Educação, Ciência e Tecnologia do Pará (IFPA) for compression testing.

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4. BRAZIL NUTSHELL MECHANICS AND NUT EXTRACTION DEVICE

Abstract

Brazil nuts are a nutritious food source and one of the main non-timber exports from the Amazon. Still, their thick and hard shell (Mesocarp) makes them difficult to open, leading to low processing efficiency and increased labor costs. In this research, we studied the mechanics of Brazil nutshell mesocarp. We proposed a device for efficiently cutting open Brazil nuts, which combines mechanical and electronic mechanisms to achieve high processing efficiency and accuracy. A compression test evaluated the force needed to open the mesocarp shell, the results of which indicated cutting the mesocarp as a better alternative for nut extraction. The device comprises the electronic saw tool from Miter Saw Vonder Sev857, with custom-made attachments to hold the Brazil nut fruit. The device was able to cut the shells into two halves.

Key-words: Compression, stress, strain, strength

4.1 Introduction

Brazil is one of the largest producers of wood and agricultural products due to its remarkable biodiversity, area of cultivation, and tropical climate that favors crops largely (PAULA, 2010). However, this profile also results in large amounts of agroforestry wastes with great potential for various uses. Consequently, research is being carried out to find an appropriate use of these residues as an alternative source for energy production.

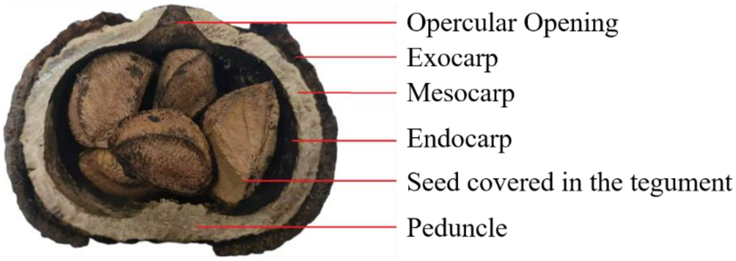
Brazil nut is one of the main non-timber exports from the Amazon, and the collection of its fruits is one of the most economically important activities in the region. These seeds are extracted, shelled, and exported, while the remaining waste constitutes around 85% of the fruit. Approximately 19,600 tons of waste is generated annually from the shelling and collecting of Brazil nuts (INAMURA et al., 2013). The nutshells, which are typically discarded as waste after the nuts are harvested, have the potential to be used in making a variety of products that have practical and industrial applications (FERNANDO et al., 2021). Currently, the local forest communities use waste to make rudimentary charcoal generation.

Brazil Nut is the globular, dry, and woody fruit of the Brazil nut tree (*Bertholletia excelsa*), a relatively big tree with a diameter of 10 to 12 cm and heights reaching up to 50 m

(MORI; PRANCE, 2016). These fruits have an outstanding impact resilience since they survive a free fall from very high trees, and one fruit can weigh up to 1 kg. Brazil nuts display outstanding mechanical qualities and astonishing fracture resistance.

The shell of the Brazil Nut contains three layers, as shown in Figure 1: the exocarp, which is made up of matured dead cells that decompose and are expelled; the mesocarp, which is made up of a thin, glabrous, slightly fibrous, and septate layer; and the endocarp (SANTOS et al., 2006; BALBAA et al., 1952). Since the exocarp is already rotten when the fruits fall to the ground and the endocarp is so thin, it can be safely assumed that these layers play a negligible role in the mechanical properties of the Brazil nut fruit; however, the mesocarp, the thickest and most robust layer, is responsible for the mechanical resistance of the fruit (Figure 1). As a result, the mesocarp was the focus of our study.

Figure 1: Cross-section of a Brazil Nut fruit with all three outer shell layers



One alternative for avoiding wastage of the nutshell is producing domestic charcoals for cooking. However, traditional cutting results in two pieces with very different sizes and shapes that can lead to poor or different carbonization efficiencies. Cutting the shell into two similar halves would significantly improve their carbonization. However, this achievement must also consider the safety of the workers and keeping the integrity of the edible nuts. This work aimed to study the mechanical strength of the Brazil nutshell and to propose a device for efficiently cutting open Brazil nuts, which combines mechanical and electronic mechanisms to achieve high processing efficiency and accuracy.

4.2 Material and Methods

4.2.1 Sample Collection

Brazil Nut fruits were collected from the Amazon Forest surrounding the Blue Timber field station in Estrada Vicinal da Serra Azul, S/N – Lote IV Flota Paru, Serra Azul, Monte Alegre – Pará.

4.2.2 Mechanics

The exocarp was removed from all the samples before testing, and the effects of the endocarp and the stored seeds were ignored. Compression tests were carried out using a Universal Testing Machine (Artoec WDW-100E, China) with a maximum force of 50 kN. Force was measured by a load cell with a maximum force of 50 kN. The crosshead displacement rate was set to 5 mm min^{-1}. The specimens were loaded to a maximum force of 0.05 N with a force rate of 0.05 N min^{-1} to hold the spherical specimen in the correct orientation before starting the actual compression test. All tests were performed in ambient air at room temperature. Compression forces were applied both parallel and perpendicular to the latitudinal specimen section.

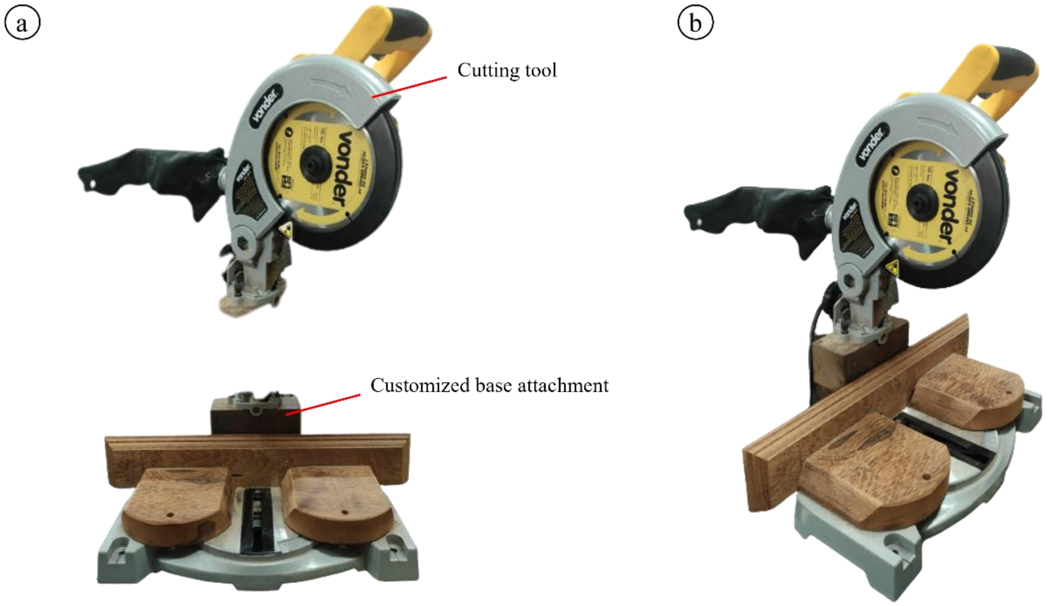
4.2.3 Device design

The cutting device had three primary design criteria (Table 1). Device components include custom-designed wooden parts (to hold the fruit in place), standard fasteners, and an electronic cutting tool from Miter Saw Vonder Sev857 (Fig. 2). The wooden parts were designed according to the size of the samples collected. The cutting tool is covered with a protective lid for safety.

Table 1: Device design criteria and corresponding design features

Design Criteria	Design Features
1) Precise cutting	Movable electronic saw tool able to cut with accuracy
2) Safety	Protective lid that covers the blade
3) Fast and economical to produce	Wooden parts for a customized base, standard fasteners, and bolts

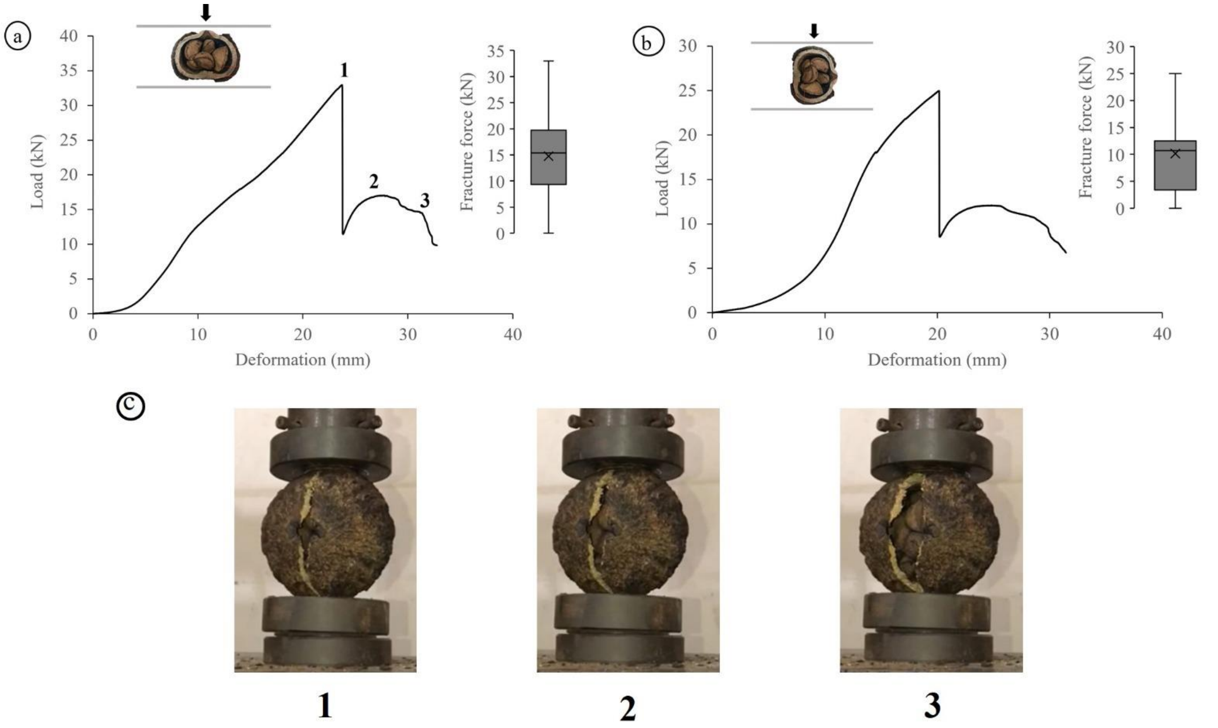
Figure 2: Device components and assembly. (a) The device has two major components, one electronic cutting tool and a customized base attachment. (b) A protective lid covers the cutting tool when assembled, and the base holds the Brazil Nut in place.



4.3 Results and Discussion

The load-deformation curve for Brazil Nutshell mesocarp samples during compression testing is shown (Figure 3). Thirty samples were subjected to both longitudinal and latitudinal compression and showed increased strength during longitudinal compression. Brazil Nut mesocarp has significant strength values as it was observed that for the strongest of all the samples tested, the fracture force was 24.96kN during latitudinal compression. For longitudinal compression, the fracture force was measured to be 32.29kN.

Figure 3: Typical behavior of Brazil nutshell mesocarp in a compression test: (a) force applied perpendicular to the latitudinal section, (b) force parallel to the latitudinal section, (c) images during phases (1-3) of the specimen during test (b).



In phase 1, the regions in contact with the compression plates are deformed, and small cracks nucleate there. This first phase is shown (Fig. 3c). The main crack (2) causes a sudden decrease in force. This main crack and the related force drop were observed in all specimens of both loading directions. The main crack (2) nearly always went through the peduncle, as shown in (Fig. 3c), suggesting that the peduncle is a weak region in the structure. After the sudden force drop, the force increases again even though the main crack grows further (Fig. 3c—phase 2).

Interestingly, the force increases to almost half its maximum, even for substantial crack lengths. Finally, in phase 3, the force slowly decreases with the formation and propagation of additional cracks (Fig. 3c — phase 3) until the total collapse of the mesocarp. These results indicated cutting as a much better alternative to breaking the mesocarp open as it would require unreasonable force. Figure 4a shows the device loaded with the fruit, and Figure 4b shows the device and fruit after the operation.

Figure 4: Device (a) before and (b) after the operation.

The device can cut Brazil Nut mesocarp in half with minimal kernel damage. During testing, the device shows 85% efficiency, with only 15% of kernels having minimal damage after each test. Figure 5 shows the Brazil Nut cut using the device.

Figure 5. Brazil Nut opened using the device.

The device's efficacy was evaluated through trials involving different sizes of Brazil nuts. The results showed that the device efficiently cuts open nuts of different sizes with high precision and minimal damage to the kernels. Furthermore, the device was easy to operate, maintain, and clean, making it suitable for use in commercial settings.

4.4 Conclusion

In conclusion, the proposed device provides a practical and effective solution for efficiently processing Brazil nuts, potentially reducing labor costs and increasing productivity in the nut processing industry. Furthermore, the residues obtained from this device are much more suitable for carbonization than those obtained from traditional methods due to the greater surface area of the residues for carbonization. Future research can focus on optimizing the device's design and operation parameters to improve further safety, performance, and adaptability to different nut sizes and varieties.

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GENERAL CONCLUSION

The potential of Brazil nut wastes for biofuels and bioproducts is promising due to their interesting chemical, physical, structural, mechanical, morphological, kinetic, and thermodynamic properties. The residues from Brazil nutshells can be utilized for carbonization to produce biofuels such as pellets and charcoal, especially in the context of local Amazonian communities. Although there are some drawbacks, such as partial carbonization, these can be addressed through improved process control and preparation of the collected wastes.

The degradation of these residues has been studied, and it has been found that both fresh and degraded Brazil nutshell residues can be used for charcoal production. However, degradation significantly affects the chemical composition and calorific value of the samples, which may impact the overall quality of the charcoal. Nevertheless, the physical and mechanical performance of the nutshells are less affected by degradation, and they still exhibit high performance, making them advantageous for charcoal quality when properly carbonized.

The traditional extraction of Brazil nuts results in irregularly shaped residues, which can pose challenges for proper carbonization. To address this issue, a device has been designed to safely extract the nuts and generate more homogeneous shaped residues that are more suitable for carbonization. This proposed device offers a practical and effective solution for processing Brazil nuts, potentially reducing labor costs and increasing productivity in the nut processing industry. Additionally, the residues obtained from this device have a larger surface area, making them more suitable for carbonization.

Future research can focus on optimizing the design and operation parameters of the device to further improve safety, performance, and adaptability to different nut sizes and varieties. This can lead to more efficient and effective processing of Brazil nut wastes for the production of biofuels and bioproducts, contributing to sustainable utilization of this valuable resource and addressing waste management challenges in Brazil nut processing industries.