REVISTA BRASILEIRA DE ENERGIAS RENOVÁVEIS

WASTE OF THE LICURI (*Syagrus coronata*) NUT SHELLS: AN ALTERNATIVE ENERGY SOURCE[1]

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Abstract

The licuri nut shell is a potential source of biomass for energy production. The aim of this study was the physicochemical characterization of the licuri shell, focusing on the increase of its use as a fuel. The material was collected in Caldeirão Grande-BA and the characterization included a wide range of analyses such as: moisture content, bulk density, particle size distribution, ash content, volatile matter, fixed carbon, high heating value (HHV), hot water and cyclohexane/ethanol extractions, *Klason* lignin content, and thermogravimetric analysis (TGA). The obtained results were: moisture content (11,1%), HHV (4652 kcal.kg^{-1}), *Klason* lignin content (36,86%), volatile content (74,91%), and fixed carbon (21,19%). The results showed that the material can be considered suitable for the purpose of generating energy when compared with other types of biomasses. The ash content (3,9%) and the extractives content (46,75%) are in accordance with the values observed for the babassu nut shell, Brazilian nut shell, and coconut. Finally, by the TGA analysis, it was observed that the degradation peak occurred at 272°C with a loss of 65% of weight. With these results, the licuri nut shell has shown to be potentially promising for the energy production.

Keywords: Biomass; *Syagrus coronate*; Renewable energy.

RESÍDUO DA CASCA DO LICURI (*Syagrus coronata*): UMA FONTE ALTERNATIVA DE ENERGIA

Resumo

A casca do licuri é uma potencial fonte de biomassa para a produção de energia. O objetivo do trabalho foi caracterizar quimicamante e fisicamente o epicarpo desse fruto, com foco na aplicação energética. O material foi coletado no município de Caldeirão Grande – BA e as análises de caracterização incuíram a determinação do teor de umidade, densidade à granel, distribuição granulométrica, teor de cinzas, teor de materiais voláteis, teor de carbono fixo, poder calorífico superior, teor de lignina Klason e análise termogravimétrica (TGA). Os resultados obtidos foram: teor de umidade (11,1%), poder calorífico superior (4652 $kcal.kg^{-1}$), teor de lignina Klason (36,86%), teor de voláteis (74,91%) e carbono fixo (21,19%). Os valores obtidos demonstram que o material pode ser considerado viável para a finalidade energética quando comparado com demais resíduos vegetais. Os valores de cinzas (3,9%) e o conteúdo de extratuvos (46,75%) estão de acordo com os valores determinados para a castanha de babaçu, castanha do Pará, e coco. As análises termogravimétricas demonstraram que o pico máximo de degradação ocorre a 272 °C, com uma perda de massa de 65%. Esses resultados demonstram que o epicarpo do licuri apresenta um promissor potencial para a aplicação energética.

Palavras-chave: Biomassa; *Syagrus coronata*; Energia renovável.

INTRODUCTION

Most of the energy consumed in our planet comes from petroleum, natural gas, and coal, which elevate the atmospheric CO_2 concentrations, one of the gases responsible for the greenhouse effect (DIAS et al., 2012). In contrast, the use of energy from renewable sources, such as biomass, is a sustainable alternative that allows to give a more suitable use to the waste, such as in corn farming, sugarcane, and wood waste (GONÇALVES; SARTORI; LEÃO et al., 2009).

In the Brazilian ‘Caatinga’, the licuri (*Syagrus coronata*), a typical palm tree of the semiarid region, has been used as human and animal food (CREPALDI et al., 2001). The main use of licuri is the production of vegetable oil, for cosmetics, and food. The shell is considered a waste in this process.

The licuri nut shell is currently neglected and discarded, but its potential energy could contribute to the increase in income for the communities that use the licuri shell (RISSI; GALDINO, 2011).

The use of the licuri nut shell as a fuel can also contribute to reduce the pressure on shrubby species widely used for energy purposes in the Caatinga, such as *Caesalpinia pyramidalis*, reducing the impact of deforestation in the biome (FIGUEIRÔA et al., 2008, RUFINI et al., 2008).

The research related to the licuri palm is concentrated in the social and nutritional areas. Research articles that characterize the licuri nut shell are meager, especially for the energetic purposes. (CREPALDI et al., 2001; RUFINI et al., 2008). For the babassu palm there are studies reporting the use of the nuts shells for power generation, which justifies the study of the energy potential of the licuri palm tree, since they are plants of the same family and possibly possess similar energy-yielding qualities (LIMA-JÚNIOR et al., 2014; PAVLACK et al., 2007; PROTÁSIO et al., 2014). However, the shell is still seen only as a waste byproduct of the nut extraction for most producers and gatherers.

The objective of this study was to investigate the energy potential of the licuri nut shell (*Syagrus coronata*), assessing its physical and chemical characteristics.

MATERIAL AND METHODS

Two kilograms of licuri nut shells (Fig. 1) were obtained in the community of Caldeirão Grande - BA, a city with 13,260 inhabitants belonging to Jacobina microregion, located at 11° 01'12' 'S and 40° 18' 10° W (INSTITUTO BRASILEIRO DE GEOGRAFIA E ESTATÍSTICA, 2018).

Figure 1 – Licuri nut shell.

For the granulometric analysis, 200 g of the air-dried shells was used. The material was placed in the orbital sieve shaker MARCONI model MA750 for 5 minutes. To this process, sieves were used of 4.00 mm, 2.00 mm, 0.50 mm, and 0. 25 mm.

Bulk density was obtained according to the NBR 6922-81 standard (ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS, 1981), with six replicates.

The licuri nut shell was milled and manually sieved. The material that passed through the 0.50 mm sieve was separated for proximate analysis, extractives, and higher heating value (HHV).

The moisture content was obtained from the moisture content determiner MARCONI model ID 200, in triplicate. For the ash content, volatile matter, and fixed carbon, the methodology proposed in ASTM D3172-89 (AMERICAN SOCIETY TESTING AND MATERIALS, 1997) with six replicates was used. The high heating value (HHV) was obtained in a calorimeter bomb IKA model C200 from the methodology proposed by ASTM D5865-13 (AMERICAN SOCIETY TESTING AND MATERIALS, 2013) in triplicate.

The extractives content in cyclohexane/ethanol (1:1) and hot water was obtained from the methods proposed by TAPPI T204 cm-97 (TECHNICAL ASSOCIATION OF THE PULP AND PAPER INDUSTRY, 2007) and *Klason* lignin content by TAPPI T222 om-02 (TECHNICAL ASSOCIATION OF THE PULP AND PAPER INDUSTRY, 2011). Total extractives were obtained by the sum of extractives in hot water and in cyclohexane/ethanol. These chemical analyses were performed in triplicate.

For the thermogravimetric analysis (TGA) the equipment TGA Pyris1 - Perkin Elmer was used. The temperature ranged from 30ºC to 750ºC, with a heating rate of 10ºC.min^{-1} and synthetic air flow of 20 mL.min^{-1}.

RESULTS AND DISCUSSION

The results of the granulometric distribution for the licuri nut shell can be seen in Table 1.

Table 1. Granulometric distribution for the licuri nut shell.

Sieve opening (mesh)	Licuri nut shell (%)
5	99.71
20	0.13
35	0.06
60	0.07
100	0.03
<100	0

The granulometric analysis showed a homogeneity among the licuri residues. The results demonstrated that 99.7% of the sample was retained in the 4.0 mm sieve, which means that the material was mostly fed in large fragments. The sample homogeneity is a favorable factor for energy production because it facilitates the control of the burning process in boilers (FURTADO et al., 2012).

Regarding the bulk density, the material presented a mean value of 0.387 (± 0.015 g.cm^{-3}). This result was expected due to large-sized particles that were observed in the raw material, after collection. This is considered a low value and not ideal for energy generation.

The bulk density interferes in logistics, handling, and the material stocking. With greater density it will be possible to obtain a greater amount of energy stored per unit (QUIRINO et al., 2004). For industrial uses, a grinding process previously to the transport and storage is indicated, however, for domestic uses, the low bulk density has minors implications. Also, the licuri nut shells compaction can be an alternative to increase the bulk density, improving the use of this material as a solid fuel.

The results for the proximate analysis and higher heating value (HHV) can be seen in Table 2.

Table 2. Proximate analysis and higher heating value for the licuri nut shell.

Moisture Content (%)	Ash Content (%)	Volatile Matter (%)	Fixed Carbon (%)	HHV (kcal.kg^{-1})
11.1 ±1.30	3.9 ±1.42	74.91 ±5.55	21.19	4652

The result of the moisture content of the licuri nut shell was 11.1% (±1.30). According to Quirino et al. (2004), moisture content ranging from 8 to 12% is ideal for a material used for energy purposes. The obtained low moisture content can be justified by the origin of the material, which was collected in a region with hot and dry weather.

The HHV is inversely proportional to the moisture content (LIMA; ABDALA; WENZEL, 2008). The HHV for licuri nut shells was 4652 kcal.kg^{-1}. This value is slightly higher when compared to other biomass material that is already in use for energy production, such as sugarcane bagasse (4511 kcal.kg^{-1}) (PROTÁSIO et al. 2011), bamboo (4458 kcal.kg^{-1}) (BRITO; TOMAZELLO FILHO; SALGADO, 1987), and sawdust of *Eucalyptus grandis* (4229 kcal.kg^{-1}) (GONÇALVES et al. 2013).

Differences above 300 kcal.kg^{-1} in the HHV are considered significant (FURTADO et al., 2012). The licuri nut shell was significantly superior to the sawdust of *Eucalyptus grandis* when compared to the biomass mentioned above. The licuri nut shell is a promising biomass for energy production in terms of the amount of energy released in its combustion process.

The ash content is an important characteristic to define the fuel quality. It is a significant aspect for the material when considered for burning purposes. The excess of ashes can adhere in the pipes and walls of the combustion equipment, affecting the burning efficiency (HAMAGUCHI AND VAKKALAINEN, 2010).

The ash content becomes the main residue of biomass burning. Several researchers have been trying to find the best alternative for its use: sand substitution in the construction industry, fertilizer in agriculture, and as adsorbents in the treatment of industrial effluents (CACURO AND WALDMAN, 2015).

The average value found for the ash content of the licuri nut shell is similar to the values reported for coconut (3,8%) (VALE; BARROSO; QUIRINO, 2004), and higher when compared to other biomasses such as babassu endocarp (1,94%) (SILVA; BARRICHELO; BRITO, 1986), Brazilian nut shell (1,88%) (PINHEIRO; RENDEIRO; PINHO, 2005), and giant bamboo (1,09%) (MARINHO et al., 2012). Therefore, the ash content does not represent a problem when the licuri nut shell is used as a solid fuel. However, as an agroforestry residue, the ash content is expected to be variable due to the association with external residues, such as sand particles and others soil elements.

The material volatile matter was 74.91%, which was higher than reported by Pinheiro, Rendeiro e Pinho (2005) for Brazilian nut shells (71.08%) and similar to walnut shells (75.86%), but it is considered low when compared to other lignocellulosic biomasses. According to Eloy et al. (2014) the volatile substances content interferes in the fuel ignition, since its presence accelerates the combustion, thus confirming that the licuri nut shell is not a biomass capable of rapid ignition.

The fixed carbon content for the licuri nut shell was determined as 21.19 %, which is higher to the one reported for *Mimosa scabrella* (17,02%) (ELOY et al., 2014), and similar to the 21.1 % reported for coconut by Vale, Barroso and Quirino (2004). The low volatiles value along with the high fixed carbon content indicates that the material does not have a fast ignition and exhibits a slower burning.

The extractives in cyclohexane / ethanol, in hot water and total extractives, as well as the Klason lignin content are exhibited in Table 3.

Table 3. Extractives and lignin content for the licuri nut shell.

Extractives in hot water (%)	Extractives in cyclohexane/ethanol (%)	Total extractives (%)	Lignin content (%)
28.46 ±0.41	18.29 ±2.79	46.75	36.86 ±2.6

The extractives have, in their molecules, contents that are released during the combustion process, influencing the values of HHV (JARA, 1989). The licuri nut shell presented 46.75% of total extractives. In hot water it presented almost 30% of extractives, which is considered high when compared to other materials such as *Pinus oocarpa* (4,31%) (MORAIS; NASCIMENTO; MELO, 2005) and for giant bamboo (9,62%) (MARINHO et al., 2012).

The value determined for the lignin content of 36.86% is considered high in comparison to other biomasses, such as the babassu endocarp (27,9%) (SILVA; BARRICHELO; BRITO, 1986), giant bamboo (22,7%) (MARINHO et al., 2012), and the *Pinus oocarpa* wood (25,1%) (MORAIS; NASCIMENTO; MELO, 2005). The high lignin content is a good indicator that the material presents good energy potential, since lignin is the major responsible for the energy potential of the lignocellulosic biofuels. Also, due to its thermal resistance, lignin has a slower burning process, thus contributing to a better material energy efficiency (JARA, 1989).

The thermogravimetric analysis (TGA) is used to characterize the materials thermal degradation and in the quantification of chemical components, such as lignin content. It can also indicate the influence that the components exert on the combustion when associated with differential thermogravimetric analysis (DTG) (CARRIER et al., 2011; SEBIO-PUÑAL et al., 2012). In Figure 2 it is possible to observe the TGA curve for licuri nut shell in four levels (I, II, III, and IV), the same burning behavior observed for other biomasses.

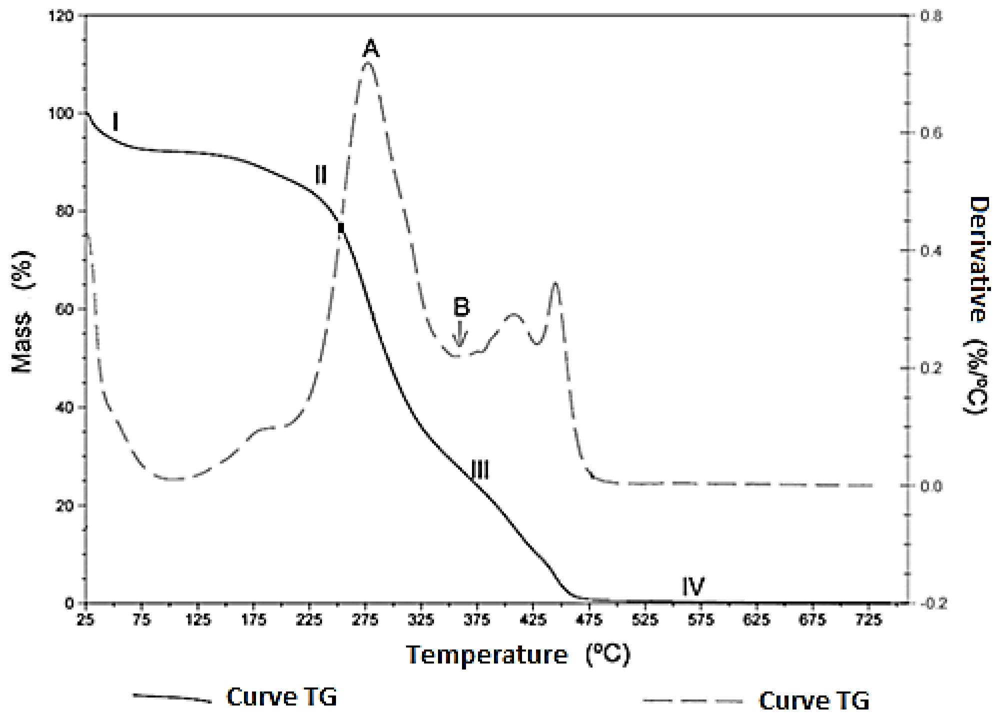

Figure 2 - TGA curve for licuri nut shell in four stages (I, II, III, IV) and curve DTG of licuri nut shell with decomposition peak (A) and cellulose decomposition shoulder (B).

Level I, up to 150°C, showed a loss of 9% of mass and represents the loss of free water present in the material, which can easily be removed by raising the temperature. This free water is located in the vessels and lumen of the cells (PINHEIRO; RENDEIRO; PINHO, 2005). The moisture content verified by TGA analysis was compatible with that verified in the moisture content balance analyzer. Level II, started at 151 ºC and ended at 300ºC, presenting a mass loss of 53.2%. It represents the loss of volatile molecules such as CO_2 and H_2, besides water attached to the cellular wall of the fibers by hydrogen bonds (LIMA; ABDALA; WENZEL, 2008).

Level III, from 301ºC to 455ºC, with 35.3% of loss in mass, represents the sample carbonization. Level II and level III represent the cellulose degradation and lignin decomposition, respectively. Since they represent the levels with greater loss, they indicate that the main material composition is cellulose and lignin. Level IV, from 456 to 750ºC, presented a residue of 2.3% of the mass, which corresponds to the inorganic matter in the sample, corresponding to the ash content of the biomass (CARRIER et al., 2011; SEBIO-PUÑAL et al., 2012). Corradini et al. (2009) presented similar values for green coconut fiber, with a loss of 4.1% in mass for level I, loss of 65.9% in mass for level II, and loss of 20% in mass for level III.

Through the DTG curve it was possible to verify that the peak of shells decomposition is at 275ºC with a loss of 35% of the mass (letter A, Figure 2). This peak (275°C) represents the beginning of the cellulose and lignin degradation, which occurs between 300 and 500°C, and the exit of volatile molecules and constituents of extractives, such as oils (CARRIER et al., 2011).

The shoulder observed at 350°C (letter B, Fig. 2) indicates the beginning of degradation of more thermally stable compounds, such as lignin, with the range of degradation represented in the temperatures between 200°C to 500°C (CARRIER et al., 2011).

CONCLUSION

The licuri nut shell has great energy-producing potential. The high values for HHV and lignin content and low values for moisture and ash content are similar to the values obtained for biomasses traditionally used for energetic purposes. The thermal degradation (TGA) of the licuri nut shell showed the same behavior as other biomasses commonly used in energy applications.

Due to these characteristics, the licuri nut shell is characterized as a suitable alternative for the families that live in Caatinga for energy production.

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