

Mass and energy balance of the carbonization of babassu nutshell as affected by temperature

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Abstract – The objective of this work was to evaluate the carbonization yield of babassu nutshell as affected by final temperature, as well as the energy losses involved in the process. Three layers constituting the babassu nut, that is, the epicarp, mesocarp and endocarp, were used together. The material was carbonized, considering the following final temperatures: 450, 550, 650, 750, and 850°C. The following were evaluated: energy and charcoal yields, pyroigneous liquid, non-condensable gases, and fixed carbon. The use of babassu nutshell can be highly feasible for charcoal production. The yield of charcoal from babassu nutshell carbonization was higher than that reported in the literature for *Eucalyptus* wood carbonization, considering the final temperature of 450°C. Charcoal and energy yields decreased more sharply at lower temperatures, with a tendency to stabilize at higher temperatures. The energy yields obtained can be considered satisfactory, with losses between 45 and 52% (based on higher heating value) and between 43 and 49% (based on lower heating value) at temperatures ranging from 450 to 850°C, respectively. Yields in fixed carbon and pyroigneous liquid are not affected by the final carbonization temperature.

Index terms: alternative biomass, charcoal, iron industry, renewable energy.

Balanço de massa e energia da carbonização da casca do coco babaçu em função da temperatura

Resumo – O objetivo deste trabalho foi avaliar os rendimentos da carbonização da casca do coco babaçu em função da temperatura final, bem como as perdas energéticas envolvidas nesse processo. Foram utilizadas conjuntamente as três camadas constituintes do coco babaçu, ou seja, o epicarpo, o mesocarpo e o endocarpo. O material foi carbonizado tendo-se considerado as seguintes temperaturas finais: 450, 550, 650, 750 e 850°C. Foram avaliados: rendimentos em carvão vegetal e energético, líquido pirolenhoso, gases não condensáveis e carbono fixo. O uso da casca do babaçu pode ser altamente viável para a produção de carvão vegetal. O rendimento em carvão vegetal da carbonização da casca do coco babaçu foi maior que o relatado na literatura para a carbonização da madeira de *Eucalyptus*, ao se considerar temperatura final de 450°C. Os rendimentos em carvão e energético diminuíram de forma mais acentuada em temperaturas mais baixas, com tendência de estabilização em temperaturas mais elevadas. Os rendimentos energéticos obtidos podem ser considerados satisfatórios, com perdas entre 45 e 52% (com base no poder calorífico superior) e entre 43 e 49% (com base no poder calorífico inferior) para as temperaturas de 450 a 850°C, respectivamente. Os rendimentos em carbono fixo e líquido pirolenhoso não são afetados pela temperatura final de carbonização.

Termos para indexação: biomassa alternativa, carvão vegetal, siderurgia, energia renovável.

Introduction

Brazil stands out as the largest producer in the world of pig iron from charcoal (Associação Brasileira de Produtores de Florestas Plantadas, 2012), and *Eucalyptus* plantations are the main responsible for the supply of this bio-reducer. In 2011, 4,127,781 tons of charcoal were produced (Instituto Brasileiro de

Geografia e Estatística, 2013), of which approximately 65% were from planted forest (Associação Brasileira de Produtores de Florestas Plantadas, 2012).

However, forest plantations are not able to meet the demand for charcoal from iron industries on a sustainable basis. Furthermore, industries that use charcoal will have to increase the use of this fuel, which comes from sustainable sources, until 2020 (Plano de

ação para prevenção e controle do desmatamento e das queimadas, 2010). Therefore, researches related to the evaluation of alternative lignocellulosic materials that may be used for charcoal production in iron industries, such as the babassu nutshell, are necessary.

Babassu is considered the largest native oil resource worldwide, with 14,563,000 ha, and occurs naturally in Brazil, mainly in the North and Northeast regions (Babaçu, 1984). It refers to three distinct genera of the *Arecaceae* family: *Scheelea*, *Attalea*, and *Orbignya*, and the species *Orbignya phalerata* Mart. is the most common and widespread (Teixeira, 2008).

The residue from the babassu nut (or shell) comprises all three constituent layers of the fruit: epicarp, mesocarp, and endocarp. These layers correspond to approximately 93% of the total fruit (Babaçu, 1984; Emmerich & Luengo, 1996; Dias et al., 2012). Therefore, for each ton of babassu nut, there are 930 kg of residues.

Currently, there are 1,409,016 tons of residues from the babassu nut in Brazil (Dias et al., 2012), which can be used in charcoal production; however, according to estimates by Teixeira (2008), this value may exceed 6 million tons, and the state of Maranhão has the highest potential (92%).

The babassu nut charcoal is likely to be used in the iron industry as a direct substitute for metallurgical coke (Silva et al., 1986; Emmerich & Luengo, 1996), because it solves two factors constraining the use of wood charcoal: low density and low compressive strength (Emmerich & Luengo, 1996).

However, despite the considerable supply of babassu nut and the demand for charcoal from iron industries in the North and Northeast of Brazil, there are few studies related to the feasibility in the use of this raw material for that purpose. It is known that *Eucalyptus* plantations are mostly deployed in the South and Southeast of the country (Associação Brasileira de Produtores de Florestas Plantadas, 2012), but the North and Northeast also have iron industries that could use babassu nut charcoal, mitigating the exploitation of native forests and contributing to the increase in the income of extractive communities in the region.

The objective of this work was to evaluate the carbonization yield of babassu nutshell as affected by final temperature, as well as the energy losses involved in this process.

Materials and Methods

The babassu nut was collected in the rural area of the municipality of Sítio Novo do Tocantins, in the state of Tocantins, Brazil (5°36'9"S, 47°38'23"W), and comes from the extractive exploitation by local communities. The three layers constituting the babassu nut, that is, the epicarp, mesocarp, and endocarp, were used together.

Carbonizations were carried out in an electric oven (muffle) with a water-cooled condenser and a collection vessel for vapors (pyroligneous liquid). About 500 g of babassu nutshell were used in each assay. The samples were previously oven-dried at 103±2°C. The initial temperature of the assay was 100°C, and the final temperatures were: 450, 550, 650, 750, and 850°C, considering a heating rate of 1.67°C min⁻¹ (100°C h⁻¹). The electric oven was stabilized at the final temperatures for 30 min. The total carbonization time was four, five, six, seven, and eight hours at the temperatures of 450, 550, 650, 750, and 850°C, respectively.

Four replicates were performed for each final temperature. The procedure used in laboratory carbonizations is similar to that described for wood in the literature (Neves et al., 2011; Protásio et al., 2011, 2013b; Assis et al., 2012; Pereira et al., 2012).

After carbonization, the gravimetric yield in charcoal was calculated by dividing the dry mass of charcoal by the dry mass of babassu nutshell multiplied by 100, with the following equation: $GYC = (MC/MB)100$, in which GYC is the gravimetric yield in charcoal (%); MC is the dry mass of charcoal (g); and MB is the dry mass of the babassu nutshell (g).

The yield in pyroligneous liquid was calculated by dividing the mass of liquid by the dry mass of the babassu nutshell multiplied by 100, as in the equation: $YPL = (ML/MB)100$, in which YPL is the yield in pyroligneous liquid (%); ML is the mass of the liquid (g); and MB is the dry mass of the babassu nutshell (g).

The yield in non-condensable gases was obtained by difference, using the following equation: $YNCG = 100 - GYC - YPL$, in which YNCG is the yield in non-condensable gases (%); GYC is the gravimetric yield in charcoal (%); and YPL is the yield in pyroligneous liquid (%).

The proximate analysis was performed in the charcoal samples, in order to determine moisture, volatile matter, ash, and fixed carbon by difference, according to the American Society for Testing

Materials (ASTM), standard D1762-84 (American Society for Testing Materials, 2007). Therefore, it was possible to obtain the yield in fixed carbon by the product of the gravimetric yield in charcoal and the fixed carbon content of the charcoal, using the equation: $YFC = (GYC \times FC)/100$, in which YFC is the yield in fixed carbon (%); GYC is the gravimetric yield in charcoal (%); and FC is the fixed carbon content of the charcoal (%).

To calculate the energy yields, it was necessary to determine the higher heating value of charcoal and fresh biomass, according to ASTM E711-87 (American Society for Testing Materials, 2004) in the calorimeter, IKA C-200 (LabControl Instrumentos Científicos Ltda., São Paulo, SP, Brazil). The lower heating value was calculated based on the following equation: $LHV = [HHV - (600 \times 9H)/100]$, in which LHV is the lower heating value (kcal kg^{-1}); HHV is the higher heating value (kcal kg^{-1}); and H is the hydrogen content (%).

The hydrogen content was obtained through an elemental vario micro cube universal analyzer (Biovera, Rio de Janeiro, RJ, Brazil) in duplicate. The samples were crushed and sieved, and the fraction that passed through the 200 mesh sieve and that was retained on the 270 mesh sieve was used. Subsequently, the samples were dried in an oven at $103 \pm 2^\circ\text{C}$, and approximately 2 mg were placed in tin capsules and brought to the equipment. The analyzer uses helium and oxygen as carrier and ignition gases, respectively.

The hydrogen contents found, on a dry weight basis, were 3.4, 2.8, 2.2, 1.8, and 1.6% for charcoals produced in the final temperatures of 450, 550, 650, 750, and 850°C , respectively.

Therefore, the energy yields (EY_1 and EY_2) were obtained based on the HHV and LHV equations: $EY_1 = GYC(HHV_{\text{charcoal}} / HHV_{\text{fresh}})$ and $EY_2 = GYC(LHV_{\text{charcoal}} / LHV_{\text{fresh}})$, in which GYC is the gravimetric yield in charcoal (%); HHV_{charcoal} and LHV_{charcoal} are the higher and lower heating values of charcoal (kcal kg^{-1}), respectively; and HHV_{fresh} and LHV_{fresh} are the higher and lower heating values of fresh biomass (kcal kg^{-1}).

Univariate variance analyses were performed, as well as adjustments of linear regression models, using a completely randomized design with four replicates for all calculated yields and considering the effect

of the final carbonization temperature as a variation factor.

A test for homogeneity of variances was conducted (Bartlett's test, at 5% probability) preliminary to analysis of variance. In addition, it was possible to determine the normality of residues by the Shapiro-Wilk test, at 5% probability. For all the parameters evaluated, deviations from these analysis' assumptions were not observed.

Principal component analysis was also performed in order to group similar temperatures, based on the carbonization yields of babassu nutshell. The relationship between the variables (multicollinearity) is not a problem in this analysis. Therefore, only standardized means (with unit variance) of all yields were considered. This procedure allows higher accuracy in the analysis.

All statistical analysis was performed using the R software, version 3.0.1 (R Development Core Team, 2013) through the packages ExpDes (Ferreira et al., 2013) and Stats (R Development Core Team, 2013).

Results and Discussion

The yield in fixed carbon, which expresses the amount of carbon present in fresh biomass and retained in charcoal, was not influenced by the final carbonization temperature (Table 1). The experimental coefficient of variation found for this parameter was 1.20%.

This yield is obtained by the product of the fixed carbon content and the gravimetric yield in charcoal, and these two variables have a negative correlation (Protásio et al., 2011; Reis et al., 2012). Therefore, for yield calculation in fixed carbon, proportionality was kept, in which the yield in charcoal tends to decrease and the fixed carbon content tends to increase with the final carbonization temperature (Trugilho & Silva, 2001; Demirbas, 2004; Titiladunayo et al., 2012; Vieira et al., 2013).

The average yield in fixed carbon found for babassu nutshell was 25.8%, that is, the carbonization of 100 kg of absolutely dry shell provides 25.8 kg of fixed carbon. This value is similar to that obtained for the carbonization of wood from *Eucalyptus* clones at 34, 42, and 68 months, of 25.8, 25.2, and 25.2%, respectively (Neves et al., 2011; Assis et al., 2012; Protásio et al., 2013b), and shows the potential of

fixed carbon production through the slow pyrolysis of babassu nut residues.

The yield in pyroligneous liquid, which consists of a complex mixture of pyroligneous acid and insoluble tar, also showed no significant differences for the final carbonization temperatures considered, and a low experimental coefficient of variation was observed (4.50%) (Table 1). The average yield in pyroligneous liquid found for babassu nutshell was 45.7%. This result can be explained by the chemical constitution of the babassu nut (Protásio et al., 2014) and by the differential resistance of cell wall components to thermal degradation.

Cellulose and hemicelluloses (holocellulose) are the main constituents of biomass, responsible for gas production during pyrolysis, since they have a low resistance to thermal degradation (Yang et al., 2007) and make up the largest cell wall fraction (Protásio et al., 2013a, 2014). Hemicelluloses are degraded at temperatures between 220 and 315°C, and cellulose, between 315 and 400°C (Yang et al., 2007), that is, at temperatures below those used in the carbonization of babassu nutshell. Protásio et al. (2014) verified a maximum rate of thermal decomposition for babassu nutshell at 303°C, validating the discussion held.

However, despite losing mass at lower temperatures, between 150 and 900°C (Yang et al., 2007), lignin has a much lower loss rate when compared to other chemical constituents of plant biomass (Pereira et al., 2012; Burhenne et al., 2013).

The average yield in pyroligneous liquid obtained for the carbonization of babassu nutshell is similar to that found in the literature for *Eucalyptus* clones at 34 and 42 months, of 43.0 and 41.4%, respectively (Assis et al., 2012; Protásio et al., 2013b). This was possibly due to the similarity in the holocellulose content of *Eucalyptus* wood and babassu nutshell.

The babassu nutshell analyzed in the present study shows total lignin and holocellulose levels of 31 and 62%, respectively (Protásio et al., 2014). For

commercial clones of *Eucalyptus* spp., Neves et al. (2011) reported average total lignin and holocellulose contents of 30 and 66%, respectively. The same authors found an average yield in pyroligneous liquid of 45.4% for these clones, i.e., similar to that obtained in the present study for the carbonization of babassu nutshell in the final temperature of 450°C (45.7%). This result can be attributed to the chemical similarity between the studied biomass and the wood from *Eucalyptus* spp. clones, as well as to the similarity in the process used in pyrolysis.

A significant effect of the final carbonization temperature on gravimetric yields was observed in charcoal, non-condensable gases, and energy yields based on HHV and LHV. The experimental coefficients of variation found for these variables were: 0.92, 8.91, 1.38, and 1.36%, respectively. Therefore, the final carbonization temperatures can be analyzed to maximize the productivity of high-quality charcoal for use in blast furnaces and with the lowest energy losses involved in this process.

The gravimetric yield in charcoal presented a marked decrease, with an increase in the final carbonization temperature. In the temperatures of 750 and 850°C, a tendency for stabilization of the gravimetric yield in charcoal was observed (Figure 1), which can be credited to a severe thermal degradation of holocellulose at temperatures below 400°C. At temperatures above 600°C, the main volatilization phase of H₂, which has a low molecular weight, occurs (Yang et al., 2007; Amutio et al., 2012), justifying the tendency for the yield in charcoal to stabilize.

The quadratic model better described the effect of the final carbonization temperature on charcoal yield; moreover, it was statistically significant and showed all significant coefficients. By obtaining the first derivative of this quadratic function and equating the result to zero, it is possible to determine the curve inflection point at 830°C, which, in this case, is a minimum point,

Table 1. Yield in fixed carbon (YFC) and in pyroligneous liquid (YPL) as affected by the final carbonization temperature of the babassu nutshell.

Yield	450°C	550°C	650°C	750°C	850°C	General mean	F-value	p-value
YFC (%)	25.5 (0.52) ⁽¹⁾	26.1 (0.21)	26.1 (0.33)	25.7 (0.18)	25.8 (0.14)	25.8	2.790 ^{ns}	0.0648
YPL (%)	44.9 (0.69)	46.1 (1.26)	45.8 (1.77)	45.6 (3.12)	46.0 (2.50)	45.7	0.249 ^{ns}	0.9058

⁽¹⁾Standard deviation in parentheses. ^{ns}Nonsignificant by the F test, at 5% probability.

since the second derivative shows that the function is positive definite.

For the final temperature of 450°C and rate of 100°C h⁻¹, the gravimetric yield in charcoal for *Eucalyptus* clones at 34, 42, and 68 months is, on average, 32% (Neves et al., 2011; Assis et al., 2012; Protásio et al., 2013b), that is, approximately 9% lower than that observed for babassu nutshell (GYC=35%). This result can be explained by the qualitative differences of the lignin found in the babassu nut, compared to *Eucalyptus* wood, and shows the feasibility of charcoal production from this lignocellulosic material.

The lignin found in hardwoods (eudicotyledonous angiosperms) has higher amounts of syringyl precursor units (trans-sinapyl alcohol) than guaiacyl (trans-coniferyl alcohol) in varying proportions (Nunes et al., 2010; Castro et al., 2013; Pereira et al., 2013). However, the lignin found in monocotyledonous angiosperms, such as babassu, is composed of syringyl, guaiacyl, and coumaryl units (trans-p-coumaric alcohol), and syringyl is present in smaller amounts (Nowakowski et al., 2010).

As reported by Pereira et al. (2013) and Protásio et al. (2014), the basic difference between the types of lignin is the amount of methoxyl groups and the amount of C-C bonds on the aromatic ring. The absence of methoxyl groups in the structure of coumaryl lignin enables a higher lignin condensation, due to an increase in C-C bonds with another coumaryl unit (Protásio et al., 2014). Therefore, the more coumaryl units in the lignin

macromolecule, the greater will be the condensation of the molecule, i.e., the greater the number of bonds between the aromatic rings and the greater the energy required to break these chemical bonds. Consequently, biomass will be thermally more stable and the yield in charcoal will be higher. Based on this discussion, it can be stated that the highest gravimetric charcoal yield observed for babassu nutshell can be attributed to a higher condensation and thermal stability of the lignin molecule.

The simple linear model best described the influence of the final carbonization temperature on yield in non-condensable gases (Figure 2). These results are an indicative that, for each 1°C increase in temperature, an increase of approximately 0.012% occurs in yield in non-condensable gases. The quadratic model was not significant by the F test (p-value=0.3160), at 5% probability, proving the validity of the fit of the simple linear regression model.

As temperature rises, the organic constituents of biomass are degraded, volatilized, and produce by-products; a gas fraction is condensed and a smaller quantity is released to the atmosphere. The main components of these non-condensable gases are CO, CO₂, CH₄, H₂, and low molecular mass hydrocarbons (Yang et al., 2007; Amutio et al., 2012).

The lower the yield in non-condensable gases, the lower will be the emission of fuel gases, as well as of gases causing the greenhouse effect in the atmosphere. In this context, in order to mitigate the effects of these emissions, it is possible to choose the

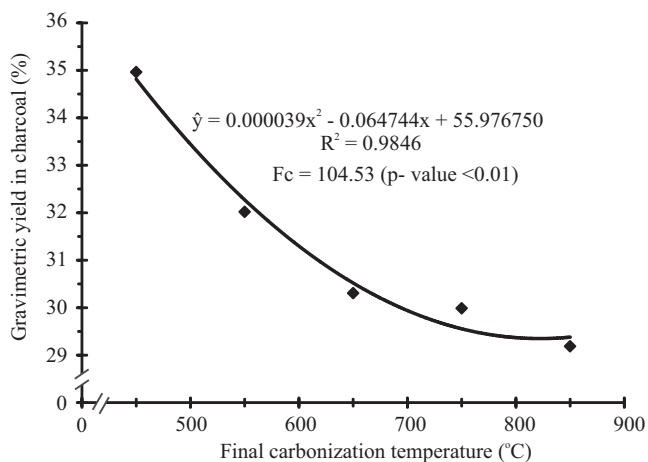


Figure 1. Gravimetric yield in charcoal of the babassu nutshell residues as affected by the final carbonization temperature.

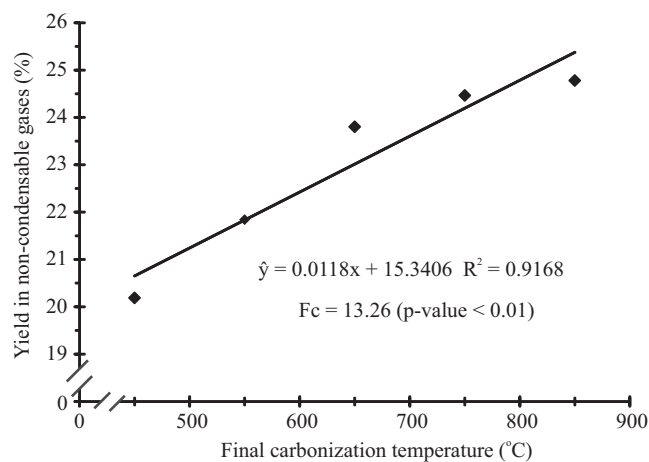


Figure 2. Yield in non-condensable gases of the carbonization of babassu nutshell residues.

complete combustion of gases from carbonization and to emit only CO₂ and H₂O, given that the plants can absorb carbon dioxide and turn it into biomass by the photosynthetic process during their growth. The use of babassu nut charcoal could contribute to the preservation of native forests and reduce CO₂ emissions, since the palm tree is not cut, in contrast to what happens in the conventional production of wood charcoal (Emmerich & Luengo, 1996).

For the temperatures of 500, 600, 700, 800, and 900°C, Vieira et al. (2013) reported yield in gases of 23, 29, 22, 24, and 29%, respectively, for the carbonization of *E. microcorys* wood. The obtained yield is higher than that found for the charcoal from babassu nutshell, of 20, 22, 24, 24, and 25% (Figure 2) for the temperatures of 450, 550, 650, 750, and 850°C, respectively.

Protásio et al. (2013b) observed an average yield in gases of 27% for *Eucalyptus* sp. clones at 42 months of age, given the final carbonization temperature of 450°C. For the same final carbonization temperature, Neves et al. (2011) found an average yield in gases of 26% for *Eucalyptus* sp. clones at 68 months. It is worth mentioning that these authors used the same experimental procedure as the one adopted in the present study. These results can be considered advantageous and reinforce the potential of the studied residual biomass for charcoal production with less environmental impact, as discussed earlier.

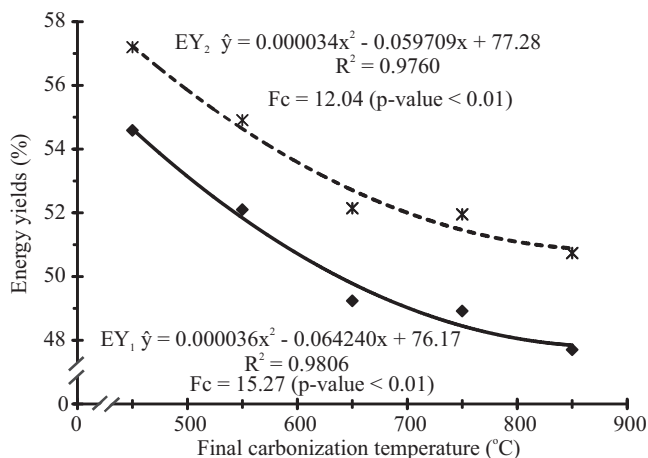


Figure 3. Energy yields as affected by the final carbonization temperature of the babassu nutshell residues.

Quadratic regression models best described the effect of the final carbonization temperature on energy yields and were significant by the F test (Figure 3). All model coefficients were also significant by the t test. The tendency was similar to that found for the gravimetric yield in charcoal, since charcoal productivity is considered in the calculations of these energy efficiencies.

The calculated energy yield based on LHV was higher than that based on HHV (Table 2). This may be due to the volatilization of the hydrogen present in biomass during pyrolysis and to a higher carbon concentration in the charcoal. Protásio et al. (2013a) observed a hydrogen content of 6.3% in the wood from *Eucalyptus* clones, and, when the same wood was carbonized, considering the final temperature of 450°C, the authors reported a hydrogen content of 3.1% in the charcoal.

Therefore, HHV and LHV in charcoal tend to be similar, and the ratio between LHV in charcoal and fresh biomass is higher than the ratio between HHV in these fuels (Protásio et al., 2013a, 2013b). LHV is calculated on a dry basis and does not consider the amount of energy required to evaporate the water formed by the hydrogen contained in the material.

The energy yields obtained can be considered satisfactory, with losses between 45 and 52% (based on HHV) and between 43 and 49% (based on LHV) at temperatures ranging from 450 to 850°C, respectively. However, fuel gases derived from carbonization can be reused in power generation and contribute decisively to increase the efficiency of converting biomass into charcoal.

The lower temperatures (450 and 550°C) showed higher yields in charcoal with the lowest energy losses, and the opposite situation was found for the

Table 2. Higher heating value (HHV) and lower heating value (LHV) of fresh biomass and charcoals of the babassu nutshell residues.

Biofuels	HHV (MJ kg ⁻¹)	LHV (MJ kg ⁻¹)	HHV _{charcoal} / HHV _{fresh}	LHV _{charcoal} / LHV _{fresh}
Fresh biomass	18.47 (0.10) ⁽¹⁾	17.16 (0.09)	-	-
Charcoal 450°C	28.84 (0.21)	28.07 (0.17)	1.56	1.64
Charcoal 550°C	30.06 (0.39)	29.43 (0.39)	1.63	1.71
Charcoal 650°C	29.93 (0.22)	29.44 (0.23)	1.62	1.72
Charcoal 750°C	30.14 (0.27)	29.73 (0.27)	1.63	1.73
Charcoal 850°C	30.19 (0.60)	29.83 (0.58)	1.63	1.74

⁽¹⁾Standard deviation in parentheses.

temperatures of 750 and 850°C (Figure 4). The last two carbonization temperatures can be considered similar and produced the highest amount of gases. This result can be attributed primarily to yields in gas, in charcoal, and in energy, because these original variables have the most significant eigenvectors for the first principal component.

The three main components obtained explained 99.9% of the total variance in the dataset. Therefore, the most relevant information of the original sample data is contained in these three components (Figure 4). The first principal component showed the largest eigenvalue and, consequently, the highest proportion of explained variance (79%), and can be considered as a performance index of carbonization. It was observed that the eigenvectors associated with the variables GYC, EY_1 , EY_2 , and YNGC were 0.4573, 0.4467, 0.4461, and -0.4383, respectively. For this reason, the higher the scores of this latent variable, the higher will be the energy and productive carbonization performances.

Therefore, in order to obtain higher yields in charcoal and to decrease the carbonization-related energy expenditure, the final temperature of 750°C can

be used instead of 850°C. The temperature of 650°C can be considered intermediate in relation to the others.

Conclusions

1. The use of babassu nutshell can be highly feasible for charcoal production.
2. Charcoal and energy yields are lower at low temperatures, with a tendency to stabilize at higher temperatures.
3. Yields in fixed carbon and pyrolygneous liquid are not affected by the final carbonization temperature.
4. The temperatures of 750 and 850°C produce charcoal with similar yields, and the temperature of 650°C produces charcoal with intermediate yields.

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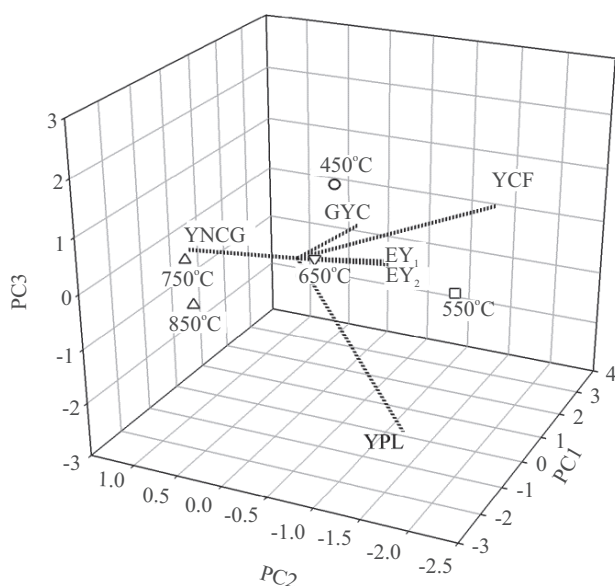


Figure 4. Scores and eigenvectors of principal components one (PC1), two (PC2), and three (PC3). GYC, gravimetric yield in charcoal; EY_1 and EY_2 , energy yields 1 and 2, respectively; YPL, yield in pyrolygneous liquid; YNGC, yield in non condensable gases; YFC, yield in fixed carbon.

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