Torrefaction of Babassu: A Potential Utilization Pathway

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Because of its energy and mechanical properties, babassu shell is a promising energy crop for the future. Its production potential in Brazil is estimated at 6.8 million tons of fruits/year. The aim of this study was to evaluate the effects of torrefaction on the main energy and mechanical properties of *Orbignya speciosa* (Babassu). Three different torrefaction temperatures (220, 250, and 280°C) and two different durations (15 and 30 minutes) were employed. The influence of sample orientation was taken into account. The results showed that the energy properties of babassu are greatly improved during heat treatment. Torrefaction also led to uniform resistance to babassu shell compression. It was found that low temperature treatment was sufficient to envisage grinding and babassu use in pulverulent form.

Keywords: Babassu; Torrefaction; Energy Yield; Mechanical Properties

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INTRODUCTION

Brazil is one of the few countries in the world that offers major potential for expansion of biomass production and use. Sugarcane bagasse and eucalyptus plantations are two main sources of biomass for energy. However, there are other species that are currently unexploited. Various palms native to Amazonia and other tropical regions of Latin America have been the subject of research and development (R&D) since the late 1970s, with extremely diverse results, extending from total failure to success in the modern market (Clement *et al.* 2005). More recently, Teixeira (2008) found that babassu palm fruits are a potential source of biomass for energy. He estimated the Brazilian potential at 6.8 million tons of fruits/year (main potential in Maranhão state, 92%). Availability varies from 1.6 million tons of fruits/year on the actual baseline scenario, up to 4.1 if an improved collecting system is used. The same study indicated that at least two of the fruit components have energy-use potential, with very distinctive behaviour for the epicarp (11% of the fruit, LHV of 20,238 $kJ.kg^{-1}$) and the endocarp (59%, LHV of 21.179 $kJ.kg^{-1}$). Furthermore, its production is greatly related to the small-scale extractive sector, which is roughly equivalent to wage labour and to agriculture in its contribution to households in rural areas of tropical Brazil (Zylbersztajn *et al.* 2000).

Efficient conversion technologies may be the key to taking advantage of babassu's characteristics for various applications in the iron and steel industry or pulverized systems requiring small-sized samples. Among existing technologies to improve biomass for energy production, torrefaction is one of the most efficient means of recovering energy from biomass. Torrefaction is a thermal pretreatment process that enables energy densification of biomass and biomass homogenization. It is a mild

pyrolysis process carried out at temperatures ranging from 200 to 280°C under atmospheric pressure in the presence of limited or no oxygen (Van der Stelt *et al.* 2011). The advantages of torrefaction include removing water uptake properties, eliminating biomass decomposition, reducing grinding energy requirements (Chen *et al.* 2011), and creating a more uniform fuel for pulverized systems.

The purpose of this study was thus to increase our knowledge of babassu (*Orbignya speciosa*) torrefaction for energy production. Experiments were carried out in a laboratory scale reactor adapted for small and large samples. We investigated changes in the physical, mechanical, and chemical characteristics of babassu samples when subjected to mild pyrolysis treatment in the temperature range of 220, 250, and 280°C for 15 and 30 minutes. Weight loss was measured during the process. The torrefied babassu was further characterized in terms of its composition and calorific value. Both proximate and ultimate analyses were used to compare torrefied babassu characteristics with other solid fuels.

Extractive activities are important in the Amazon region as inputs to household reproduction, and are critical as a source of cash income. Access to a highly competitive market demands a different product – competing with a similar product demands competence of a high level (Fig. 1). Consequently, the authors of this study hope, through this technical study, to contribute to babassu utilization as a significant source of both use and exchange values.

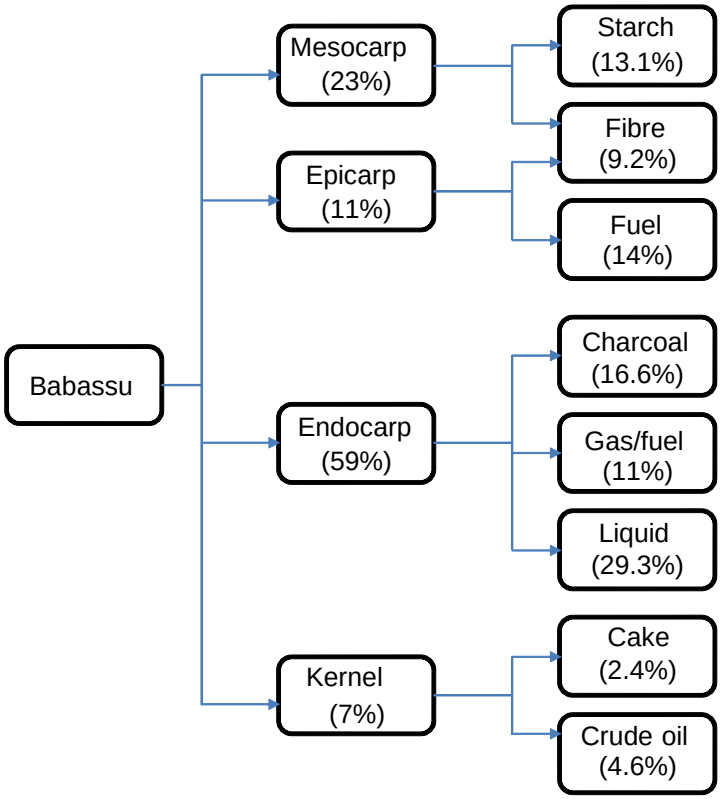

Fig. 1. Products from the industrialization of babassu nuts (Oliveira *et al.* 2009)

EXPERIMENTAL

Material Preparation

Babassu (*Orbignya speciosa*) biomass is a very abundant palm tree in the northern-central region of the country, especially in the State of Maranhão. The tree is large in size, up to 20 m, having a trunk with a crown containing a number of fruits in ellipsoidal form. Each fruit consists of a thin peel (epicarp) that has a starchy secondary layer (mesocarp), endocarp, and kernel amounting for 11, 23, 59, and 7% of the mass, respectively (Cirad and Brasileiro 2008).The fruits weigh 90 to 280 g (Fig. 2). The babassu nuts used in this study were harvested by a local cooperative in the Maranhão region. Ten fruits were tested for the study. They were cut lengthwise and widthwise. The nomenclature for each sample is given in Table 1. It can be seen that for the low temperature (220°C), only the 30 min residence time was tested. Before undergoing torrefaction, all the samples were previously dried to a constant weight at 103°C.

After torrefaction, the material was tested to evaluate its mechanical properties compared to the control. The samples were then ground and sieved to a maximum particle size of 60 mesh and stored in a desiccator at room temperature pending chemical and physical analysis.

Fig. 2. Transversal section of the babassu (http://brazilbyabrazilian.blogspot.com.br/2009/04/some-brazilian-plants.html)

Torrefaction Protocol

The thermal treatment of babassu nuts was carried out using a laboratory-scale reactor that measured simultaneously the dynamics of biomass weight loss and the temperature inside the biomass throughout the course of the experiment. A programmable PID (proportional-integral-derivative) controller was used to control the temperatures and heating rate of the reactor by way of three thermocouples: one near the electric heater, one inserted through the lid of the reactor, and the last one inside the sample to monitor its temperature, as described in Rousset *et al.* (2012). Finally, two samples were tested in each trial run, one coupled to a precision balance to monitor mass loss and the other to a thermocouple to monitor the internal temperature.

The temperature programme, consisting of an isothermal heating period, was applied to perform torrefaction. The temperature was raised from ambient temperature to the appropriate torrefaction temperature (*i.e.* 220, 250, and 280°C) with a constant heating rate (3°C min^{-1}) and held for 15 and 30 min, followed by a natural cooling period.

Thermogravimetric analyses versus biomass temperature were obtained from the recorded distribution of weight and temperature.

Chemical Analysis

Gross Calorific Value (GCV) was determined on the basis of thermal energy generated by complete combustion of the sample in a constant pressure chamber. A PARR 1261 bomb calorimeter was used in compliance with standard NBR 8633/ 84. The energy yield (η_e) was also determined. It relates the mass yield to the higher heating value (HHV) of wood and is calculated by the formula (Rodrigues and Rousset 2009), where *HHVtorr* and *HHVcont* represent respectively the higher heating value of torrefied wood and the untreated sample.

$$\eta_e = \eta_m \left(\frac{PCS_{Torr}}{PCS_{Cont}}\right) \eta_e = \eta_m \left(\frac{HHV_{Torr}}{HHV_{Cont}}\right) \quad (1)$$

Gravimetric yield (η_m) is the ratio of torrefied wood mass (M_{Torr}) to initial feedstock mass (M_{Cont}), dry at 0%.

$$\eta_m = \left(\frac{M_{Torr}}{M_{Cont}}\right) \times 100 \quad (2)$$

A proximate analysis was conducted to determine the fraction of ash (Ash) and volatile matter (VM). The fixed carbon (fC) content was obtained by difference. The values of the proximate analysis were obtained in compliance with the procedure of the Brazilian Association of Technical Standards ABNT NBR 8112/86. The ultimate analysis provided the composition of the biomass in wt.% of carbon, hydrogen, and oxygen (the major components) as well as sulphur and nitrogen. The ultimate analysis values were obtained in compliance with the European procedure XP CEN/TS 15104.

Specific Surface and Pore Size Distribution

The quality of activated carbons is evaluated in terms of their physical properties of adsorption and of superficial area, using different analytical methods for liquid and for gas phase adsorption. This property is very important for use in metal oxide reduction in an industry such as steelmaking. Of all the raw materials existing in Brazil, babassu is probably the most typical and traditional raw material for the preparation of activated biomass. Adsorption-desorption isotherms for nitrogen adsorption onto carbon were acquired using a Micromeritics ASAP 2010 instrument. The samples were previously outgassed at 200°C for 2 h. Specific surface areas were calculated by the multi-point Brunauer-Emmett-Teller (BET) method at relative pressures of P/P0 = 0.06 to 0.3. The pore size distributions were obtained from the desorption branch of the nitrogen isotherms using the Barrett-Joyner-Halenda (BJH) method. The sample weight was around 1 g.

Mechanical Analysis

Compressive static tests were conducted using a universal testing machine, Instron model 1127, and the maximum load (ML) until crushing was determined. In this test the specimen was compressed over its surface area at a speed of 0.3 mm/min. Figure 3 depicts an example of the test carried out with babassu heated to 280°C for 30 min. A

virtually linear increase in load was found up to shell breakage at around 800 kgf, corresponding to the maximum load that babassu shell can withstand.

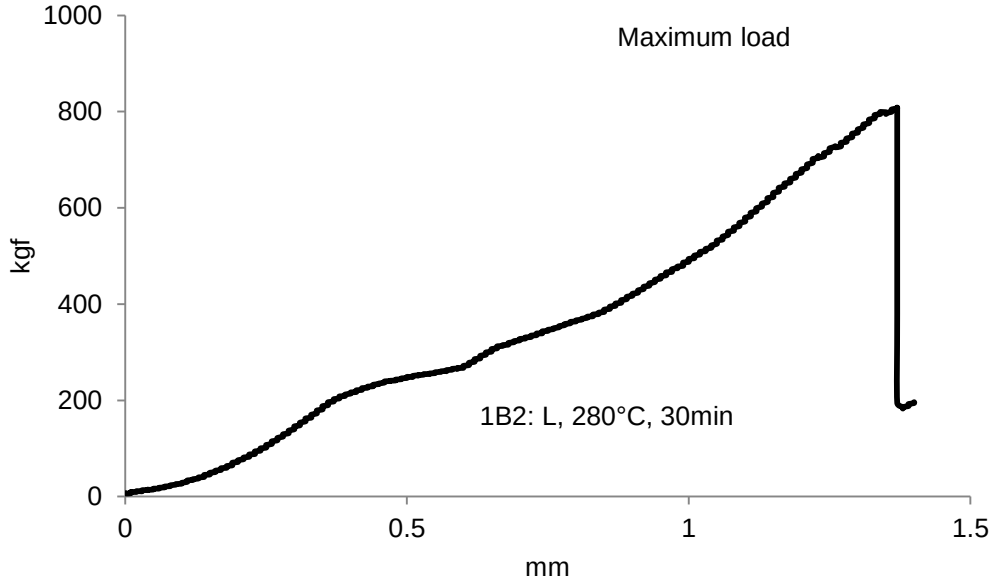

Fig. 3. Compressive static test with babassu (1B2) in the longitudinal section treated at 280°C for 30 min. Compression speed: 0.3 mm/min. 1 kgf = 9.8 N

Statistical Analysis

Statistical analyses were conducted using a specific software product, XLSTAT (addinsoft), to enhance the analytical capabilities of Excel. Eight variables in response to the experiments (temperature, time, and section) were analysed and discussed: the mass loss (Wt%), the fixed carbon content (FC%), the gross calorific value (GCV), the compression value (Cv), the carbon content (C%), the hydrogen content (H%), the nitrogen content (N%), and the oxygen content (O%).

Untreated and treated nuts were subjected to a variance analysis (ANOVA) and the Tukey test at a probability of 5%. Tukey's test is one of the main applications of an ANOVA to check whether or not the parameters for the various categories of a factor differ significantly. It is a single step multiple comparison procedure and a statistical test to find which means are significantly different from each another. The test compares the means of each treatment to the means of every other treatment, *i.e.* it applies simultaneously to the set of all pairwise comparisons and identifies where the difference between two means is greater than the standard error would be expected to allow.

RESULTS AND DISCUSSION

Overall Results

Table 1 gives the averages obtained for the eight variables studied considering two replicates per treatment; gravimetric yield (η_m), fixed carbon content (fC), gross calorific value (GCV), compression value (Cv), and ultimate analysis (C, H, and O).

Table 1. Average of Duplicate Samples for Five Response Variables Considering Two Replicates per Treatment

Samples	Dir.	*T*	*D*	η_m	fC	HHV	Cv	Ultimate analysis (%)		
		(°C)	(min)	(%)	(%)	(kcal.kg^{-1})	(Kgf)	C	H	O
Control	L	-	-		18.3e	4608f	2185bc	51.1h	5.8a	42.9b
Control	T	-	-		18.2e	4700f	8176a	50.5i	5.8a	43.4a
5A	L	220	30	91.7g	20.0e	4903e	678de	52.4g	5.8a	41.5c
5B	T	220	30	93.0h	19.5e	4656f	2608b	51.2h	5.7b	42.9b
4A	L	250	15	75.6ef	28.0cd	5205d	761cde	56.6ef	5.5c	37.7d
4B	T	250	15	71.5e	30.6c	5243d	1837bcd	56.9e	5.2e	37.7d
3A	L	250	30	63.5d	27.7d	5225d	234e	57.3d	5.5c	38.0d
3B	T	250	30	70.2f	28.2cd	5184d	1271bcde	56.5f	5.2e	36.9e
2B	L	280	15	84.1b	35.4b	5491b	643de	59.9b	5.1f	34.7g
2A	T	280	15	63.9c	35.5b	5420bc	462de	59.2c	5.0g	35.5f
1B	L	280	30	56.4b	34.4b	5381c	823cde	60.0b	5.3d	34.1h
1A	T	280	30	58.7a	38.7a	5595a	997cde	60.7a	4.9h	34.7g

Dir.:L/T: Longitudinal/Transversal section; Control = Untreated
Means followed by the same letter are not significantly different (α = 5%)

Type III sum of squares analyses were carried out to determine which parameters interfered significantly (α = 0.05) with four response variables, along with the effect on the torrefied babassu properties (Table 2). Of the parameters studied, temperature and duration were the factors with the greatest impact on the four response variables. Sample orientation (L or T) did not influence the variables.

Mass Loss

Figure 4 shows the mass loss of heat-treated babassu nuts. As expected, the mass loss increased with temperature and time of torrefaction. Exposure of wood to temperatures of >150°C during drying may cause thermal degradation of its structure, often accompanied by mass loss. Devolatilization and carbonization of hemicelluloses, deploymerisation, and devolatilization/softening of lignin and depolymerization and devolatilization of cellulose are observed. The degree of structural damage depends on the tree species as well as the process parameters, such as treatment duration, temperature, and relative humidity. All structural changes observed in the biomass due to moisture loss influence its mechanical properties, such as bulk density and grindability. The lowest gravimetric yields (η_m) were obtained at the highest temperatures or treatment times. For instance, it was found that for a treatment time of 30 minutes at 250°C, mass loss was equivalent to that obtained at 280°C for 15 minutes with 63.5 and 63.9%, respectively. These results confirm those obtained in the literature (Rousset *et al.* 2011).

Table 2. Analysis of Variance of Temperature (*T*), Duration (*D*), and Direction (*L*/*T*) along with their First Order Interactions for the Four Response Variables Analyzed *

	T (°C)	D (min)	Direction (L/T)
$\eta_{m\ (\%)}$	* *<0.0001*	* *0.004*	ns *0.826*
fC (%)	* *<0.0001*	* *0.002*	ns *0.699*
GCV (kcal.kg^{-1})	* *<0.0001*	* *<0.0001*	ns *0.811*
Cv (kgf)	* *0.0001*	* *<0.0001*	ns *0.052*

*Significant at 5%; ns = not significant at 5%; *P*-values are in italics

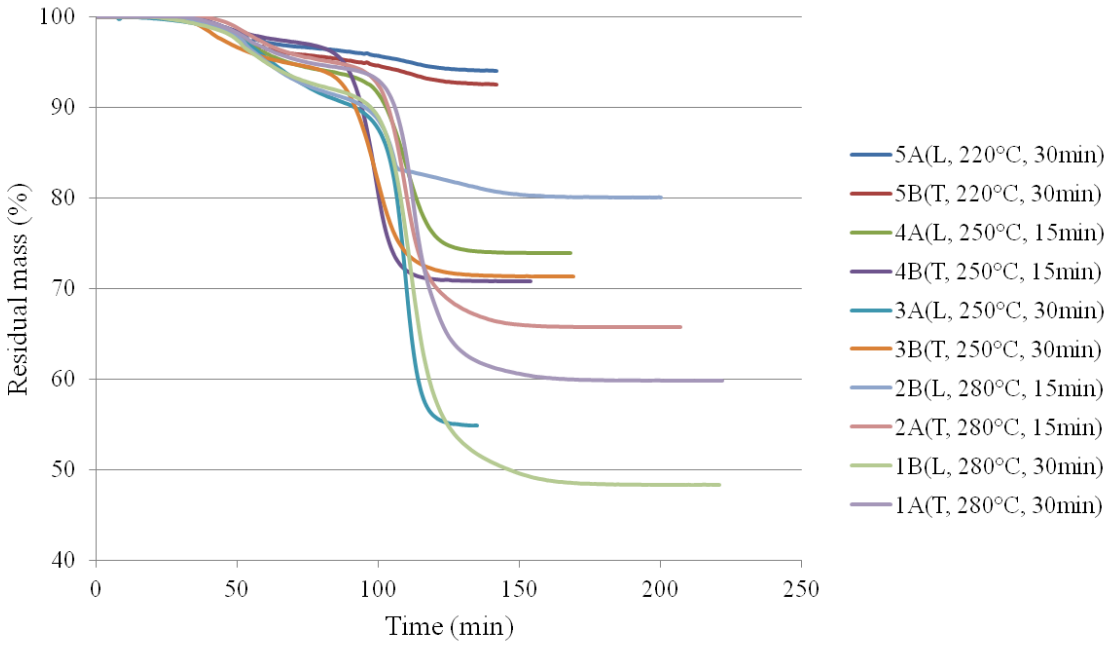

Fig. 4. Thermogravimetric analysis for each treatment

Despite some more pronounced differences for the high temperatures, up to a difference of 10%, the orientation of the sample did not have any significant impact on this variable, as shown by the variance study (Table 2). Indeed, the Direction factor (L/T) did not seem to be significant (Table 1), as the only major difference between L and T seemed to occur between 2A and 2B. This was not enough to deduce statistical significance. However, the significant difference was induced by the duration factor D (15/30 min). The figures show that when heating for 15 min, the gravimetric yield η_m values were always greater for direction L and the opposite when heating for 30 min. Figure 5 gives the changes in mass loss depending on the two parameters "duration and

direction". The explanation may come from heat transfers within the sample that were facilitated in the direction of the fibres at low temperature.

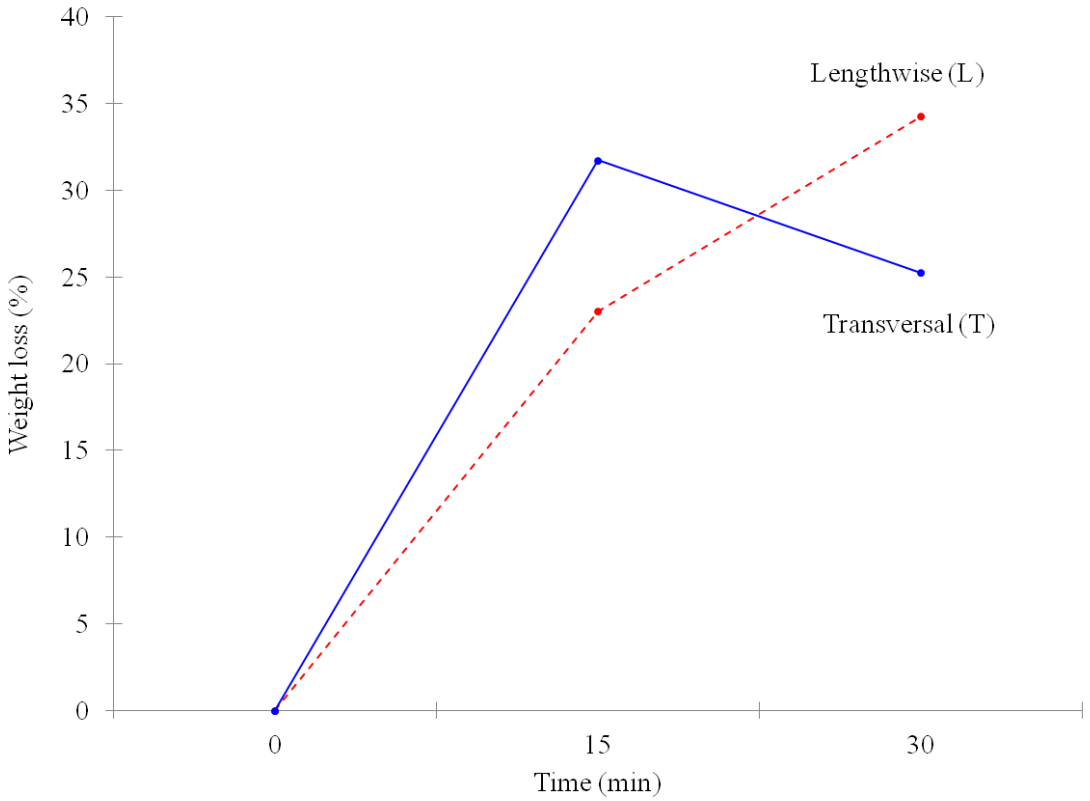

Fig. 5. Average weight loss depending on time for each of the directions, L and T

Energy Characteristics

Table 3 summarizes the descriptive statistics for four variables: ash, volatile matter, fixed carbon, and gross calorific value for the set of treatments. These variables were highly correlated to the model for the third interaction T×D×Dir with a *P*-value <0.0001 and a coefficient of determination over 0.99.

Table 3. Descriptive Statistics for the Four Variables Analysed

Variables	Minimum	Maximum	Means	Standard deviation	R^2	T×D×Dir *p-value*
Ash (%)	1.200	2.660	1.874	0.450	0.996	*<0.0001*
Volatile matter (%)	58.750	80.900	70.237	7.552	0.995	*<0.0001*
Fixed Carbon (%)	17.660	38.750	27.888	7.224	0.996	*<0.0001*
GCV ($Kcal.kg^{-1}$)	4579.960	5609.850	5134.647	331.231	0.997	*<0.0001*

T = Temperature; *D* = Duration; Dir = Orientation of samples (L/T)

Figure 6 shows the energy yield as a function of gravimetric yield. The linear regression model obtained shows that the two parameters were highly correlated with a coefficient of determination over 0.98. These figures tally with the literature (Pierre *et al.* 2011). More severe treatments will lead to a displacement of the points to the origin of the graph, up to obtaining properties similar to those of wood charcoal.

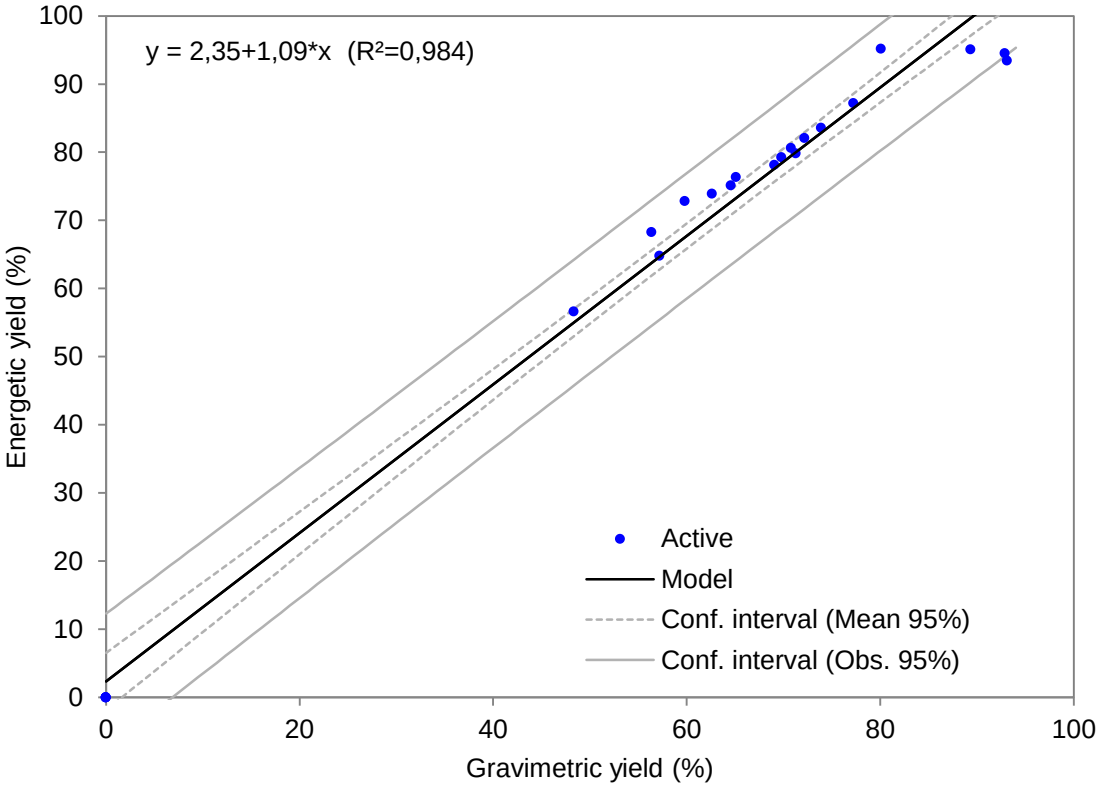

Fig. 6. Linear regression energy yield *vs.* gravimetric yield with the model

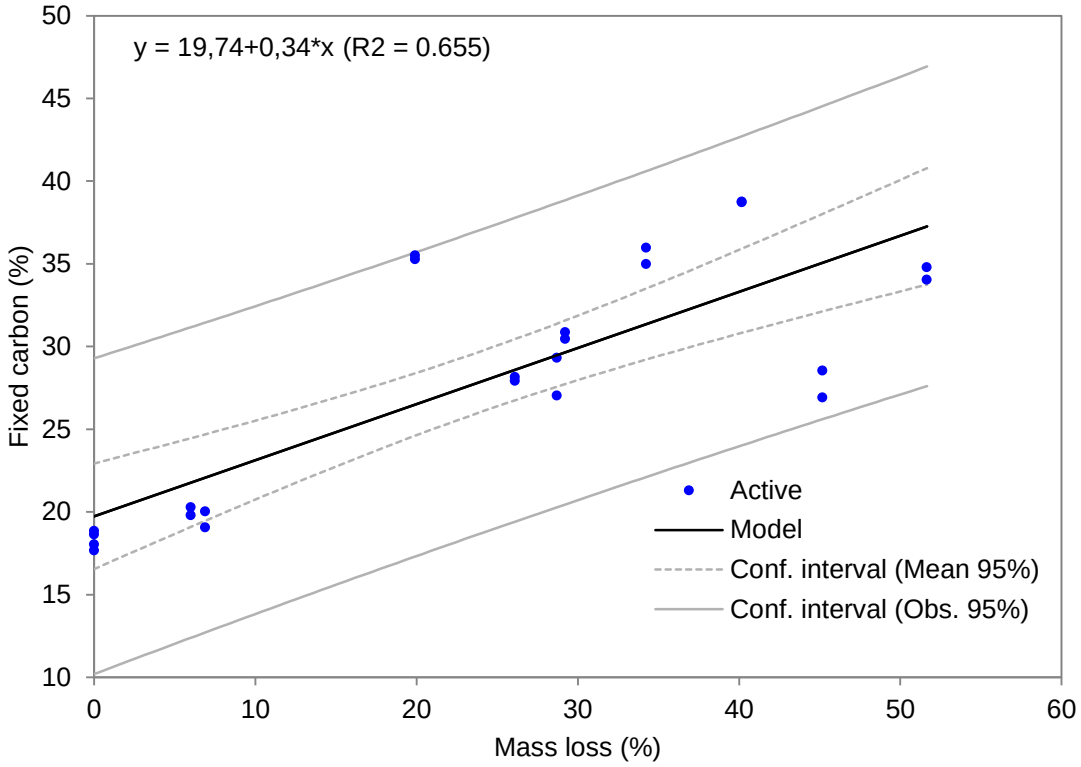

Fig. 7. Linear regression for fixed carbon *vs*. mass loss with the model

As the gross calorific value is correlated to the amount of fixed carbon present in the sample, Fig. 7 shows the changes in this parameter (fixed carbon) depending on mass loss. The trend shows that a higher mass loss leads to enrichment in fixed carbon. The linear model remained within the confidence interval at 95% but showed a weaker correlation ($R^2 = 0.66$) than that obtained on wood (Chen *et al.* 2011). Table 1 shows that the highest percentages of fixed carbon corresponded to the highest temperatures, with the FC% equal to 36.55, 27.95, and 19.75% at 280, 250, and 220°C, respectively for 30 min. The statistical analysis (Table 1) of the fixed carbon rate and of the gross calorific value showed that there were five significantly different groups for the fixed carbon rate and six for the gross calorific value. It can be seen that at 220°C for 30 min the results obtained were not significantly different from the untreated samples. This confirms the low degradation of the constituents for the low temperatures (Chen and Kuo 2010) and the different behaviour of a shell compared to wood.

Specific Surface Area and Pore Size Distribution

In Table 4, the BET surface area and the pore size distribution are represented for the untreated samples and samples heated to 220°C/30min and 280°C/30min. The results show that torrefaction had no effect on the specific surface area of babassu shells and that only activation at high temperatures (>800°C) led to an increase in BET surface area (Jaguaribe *et al*. 2005).

Table 4. BET Surface Area, VM, and Molecular Cross Section for Babassu Shells Untreated and Heated to 220 and 280°C for 30 min

Samples	BET surface area $m^2.g^{-1}$	VM $cm^3.g^{-1}$	Molecular cross section (nm^2)
Untreated	0.6503 ± 0.0045	0.149381	0.1620
220°C/30min	0.5439 ± 0.0050	0.124945	0.1620
280°C/30min	0.6602 ± 0.0054	0.151653	0.1620
Babassu activated at 900°C (Jaguaribe *et al*. 2005)	874		
Coconuts activated at 900°C (Jaguaribe *et al.* 2005)	712		
Bagasse activated at 800°C (Jaguaribe *et al.* 2005)	806		

Mechanical Analysis

Figure 8 gives the maximum load withstood by the babassu samples depending on the thermal treatment and sample orientation. The control sample displayed a very great statistically significant difference depending on its orientation (L or T). For instance, for the transversal direction, the load to be applied was four times greater than for the longitudinal direction, with 8176 and 2185 kgf, respectively. When the two directions were compared, the transversally-oriented samples always exhibited greater resistance than the longitudinally-oriented samples. Whatever the orientation, the thermal treatment greatly reduced the resistance of the nuts, as has also been found for other types of

biomass (Phanphanich and Mani 2011). This reduction was found to occur right from the low temperatures (220°C). The set of results revealed five distinct groups. It was seen that there were no significant differences in the results obtained for the high temperatures. It is interesting to note that the load obtained at 220°/30' in the longitudinal direction was statistically the same as that obtained at the highest temperatures. This finding shows that it is not necessary to treat babassu shells at very high temperatures to achieve a significant reduction in its resistance prior to subsequent grinding.

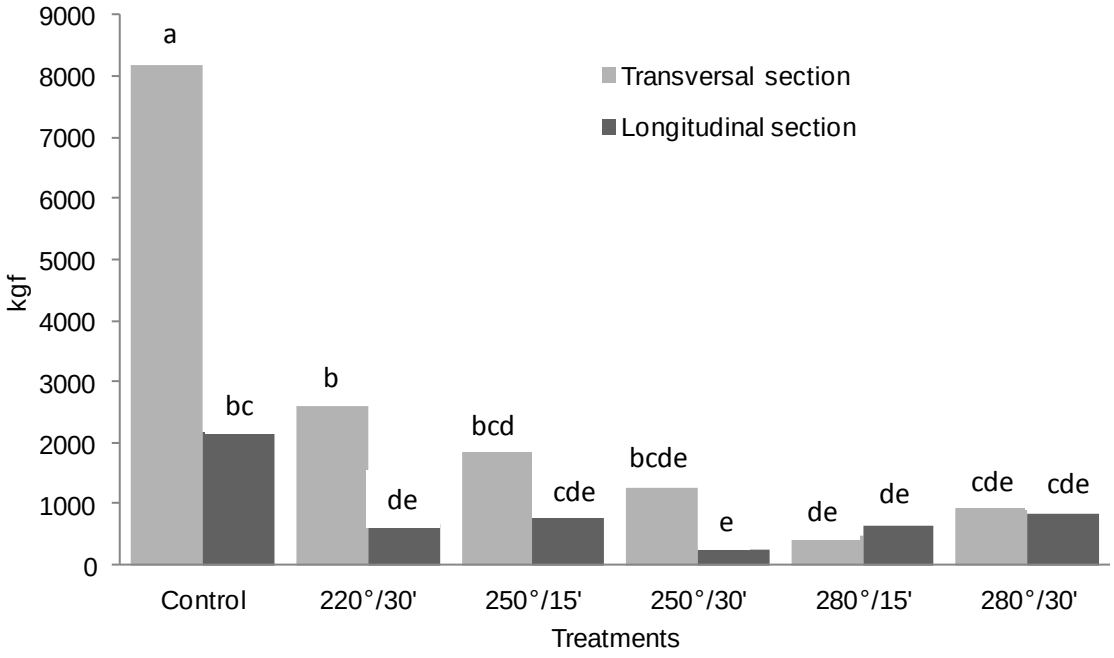

Fig. 8. Compressive test of babassu untreated and treated at different temperatures and times depending on the direction of the samples. For each group, the means with the same letter were not significantly different at 5% (α = 0.05).

CONCLUSIONS

Light and severe torrefaction of babassu were studied to identify the weight loss dynamics of the biomass and the impact of torrefaction processes on energy and mechanical properties. All the results obtained were statistically processed:

1. For the set of results obtained, the "sample orientation" parameter had little impact compared to the temperature and torrefaction time.
2. By adjusting the time/temperature combination, it was possible to change the physical and mechanical properties of babassu shells.
3. The linear regression model obtained showed that the energy yield and mass loss were highly correlated.
4. The percentage of fixed carbon showed a weaker correlation compared to the gravimetric yield.

5. Torrefaction did not increase the porosity of babassu shells; the BET surface area remained the same as the untreated samples.
6. The thermal treatment greatly reduced nut resistance, whatever the orientation of the samples.
7. Shell resistance was greatly reduced right from the low temperatures (220°C), so it is not necessary to apply severe treatments to obtain similar results.

Lastly, we hope that this study will open up new ways of using babassu shells, notably in energy systems requiring pulverized biomass with a high calorific value. Their use in torrefied form might help to revitalize this exclusively extractivist sector.

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REFERENCES CITED

Chen, W.-H., Hsu, H.-C., Lu, K.-M., Lee, W.-J., and Lin, T.-C. (2011). "Thermal pretreatment of wood (Lauan) block by torrefaction and its influence on the properties of the biomass," *Energy* 36, 3012-3021.

Chen, W.-H., and Kuo, P.-C. (2010). "A study on torrefaction of various biomass materials and its impact on lignocellulosic structure simulated by a thermogravimetry," *Energy* 35(6), 2580-2586.

Cirad (2008). *Guide Technique pour une Utilisation Energétiques des Huiles Végétales* (in french), G946, 288p, CDU(2.ed.) 662.756.3, Brasilia, Brazil.

Clement, C. R., Lleras Pérez, E., and van Leeuwen, J. (2005). "The potential of Brazilian tropical palms: successes and failures of recent decades," *Agrociencias* 9(1-2), 67-71.

http://brazilbyabrazilian.blogspot.com.br/2009/04/some-brazilian-plants.html.

Jaguaribe, E. F., Medeiros, L. L., Barreto, M. C. S., and Araujo, L. P. (2005). "The performance of activated carbons from sugarcane bagasse, babassu, and coconut shells in removing residual chlorine," *Braz. J. Chem. Eng*. 22, 41-47.

Oliveira, H., Andrade, T., and Silva, J. (2009). "O babaçu (Orbignya ssp) e seu potencial para a produção de biocombustiveis no estado do Tocantins," 2° Simposio Nacional de Biocombustiveis, Recife.

Phanphanich, M., and Mani, S. (2011). "Impact of torrefaction on the grindability and fuel characteristics of forest biomass," *Bioresource Technology* 102(2), 1246-1253.

Pierre, F., Almeida, G., Perré, P., and Brito, J. O. (2011). "Influence of torrefaction on some chemical and energy properties of maritime pine and pedunculate oak," *BioResources* 6(2), 1204-1218.

Rodrigues, T. O., and Rousset, P. (2009). "Effects of torrefaction on energy properties of *Eucalyptus grandis* wood," *Cerne, Lavras* 15(4), 446-452.

Rousset, P., Davrieux, D., Macedo, L., and Perré, P. (2011). "Characterisation of the torrefaction of beech wood using NIRS: Combined effects of temperature and duration," *Biomass Bioenergy* 35, 1219-1226

Rousset, P., Macedo, L., Commandré, J., and Moreira, A. (2012). "Biomass torrefaction under different oxygen concentrations and its effect on the composition of the solid by-product," *J. Anal. Appl. Pyrolysis* 96, 86-91.

Teixeira, M. A. (2008). "Babassu – A new approach for an ancient Brazilian biomass," *Biomass Bioenergy* 32, 857-864.

Van der Stelt, M. J. C., Gerhauser, H., Kiel, J. H. A., and Ptasinski, K. J. (2011). "Biomass upgrading by torrefaction for the production of biofuels: A review," *Biomass Bioenergy* 35(9), 3748-3762.

Zylbersztajn, D., Marque, C. A. S., Nassar, A. M., Pinheiro, C. M., Martinelli, D. P., Adeodato, A., Neto, J., Marino, M. K., and Nunes, R. (2000). "Reorganization of the agribusiness of the babaçu in the state of Maranhão," 120 pp., Grupo Pensa-USP Ed., Sao Paulo, Brazil (in Portuguese).

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