

# Banana (*Musa sp. cv. Pacovan*) Pseudostem Fibers are Composed of Varying Lignocellulosic Composition throughout the Diameter

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Agricultural residues represent a disposal problem and a biomass source for chemical production. Lignocellulosic composition varies in plants as a function of several factors such as physiological age and tissue function. Banana pseudostem is a large biomass resource that is usually wasted, in spite of the possibility that it can be used as a source of organic compounds such as cellulose and hemicelluloses. The aim of this paper is compare the lignocellulosic content and physicochemical properties of different sheaths of Pacovan banana pseudostems. The trunk was divided into four different fractions, from the outermost sheaths to the core of the structure. There was a significant difference between the lignocellulosic compositions of the fractions. The X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric analysis, and differential scanning calorimetry measurements reflected this difference in the sheaths. These results indicate that the Pacovan banana pseudostem cannot be considered to be a uniform biomass, and future approaches to its use as a biorefinery feedstock must consider a preliminary separation of the sheaths prior to chemical extraction of organic components.

*Keywords:* Agribusiness; Biorefinery; Fractionation; Agriculture wastes; Byproducts; Pulping; Cellulose

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## INTRODUCTION

Agricultural residues represent a disposal problem because they can lead to environmental pollution and biomass spoilage. Some of these residues are composed of plant waste fibers, an abundant, low cost, and readily available source of lignocellulosic biomass (Oliveira *et al.* 2007). Many agricultural crops are cultivated in Brazil because of the large area of farmland, fertile soil, and adequate climate conditions. Cotton, sugarcane bagasse, coconut, jute, pineapple, ramie, sisal, and banana are conventional fiber resources in Brazil (Satyanarayana *et al.* 2007).

Brazil produced ~7 million tons of bananas in 2011. Together with India, China, the Philippines, and Ecuador, it was one of the five largest producers of banana in 2011 (FAOStat 2014). After harvesting the fruit in bunches, around 6.6 million tons of banana biomass are produced (Satyanarayana *et al.* 2007). This biomass is usually left on the

plantation soil to avoid erosion, control the growth of weeds, and to act as an organic fertilizer.

The varieties Prata, Prata Anã, and Pacovan are responsible for approximately 60% of the harvested area of banana plants in Brazil (Embrapa 2014). The banana plant of the cultivar Pacovan, *Musa* AAB, subgroup Prata, is mostly cultivated in the Brazilian Northeast. It is also grown in India, Australia (Queensland), and the Western Pacific islands, where it is known respectively as Pachanadan or Pacha Naadan, Improved Lady's Finger, and Lady's finger (Ploetz *et al.* 2007).

The banana plant has a very juicy aerial stem, properly denoted as the pseudostem, which is a clustered, cylindrical aggregation comprised of leaf stalk bases of leaf-petiole sheaths (Mukhopadhyay *et al.* 2009). There is also a subterranean stem, known as the corm, as well as the part that supports the banana fruit, named the peduncle, stalk, or rachis. The leaves and stalk of the pseudostem are disposed of after the fruit has been harvested. Collectively, the waste of banana production is an estimated ~220 tonnes of byproduct per hectare annually (Padam *et al.* 2012).

The biorefinery concept involves the integral and diversified use of a fractionated lignocellulosic biomass to obtain a wide variety of chemicals, added value products, and bulk chemicals (Arshanitsa *et al.* 2013; Shi *et al.* 2013; Fiorentino *et al.* 2014; Prinsen *et al.* 2014; Rincón *et al.* 2014; Zamudio *et al.* 2014). Many authors who have studied the utilization of banana pseudostem as a bioresource, even using a biorefinery, usually consider the whole trunk as a uniform material (Li *et al.* 2010; Akpabio *et al.* 2012; Ho *et al.* 2013; Gabhane *et al.* 2014). However, the pseudostem can be separated into several sheaths. The physicochemical properties of each sheath may be different, because they have different physiological ages and functions. So, it could be possible to fractionate the same pseudostem in several sheaths, as a simple physical pretreatment, and each group of sheaths can be used for the most suitable application in accordance to its properties instead of using a mixture of all the fractions and performing chemical treatments to separate each organic fraction.

The objective of this paper is to determine the chemical composition and physicochemical properties of four different morphological regions of *Musa* sp. cv. Pacovan: core, inner, middle, and outer sheaths.

## EXPERIMENTAL

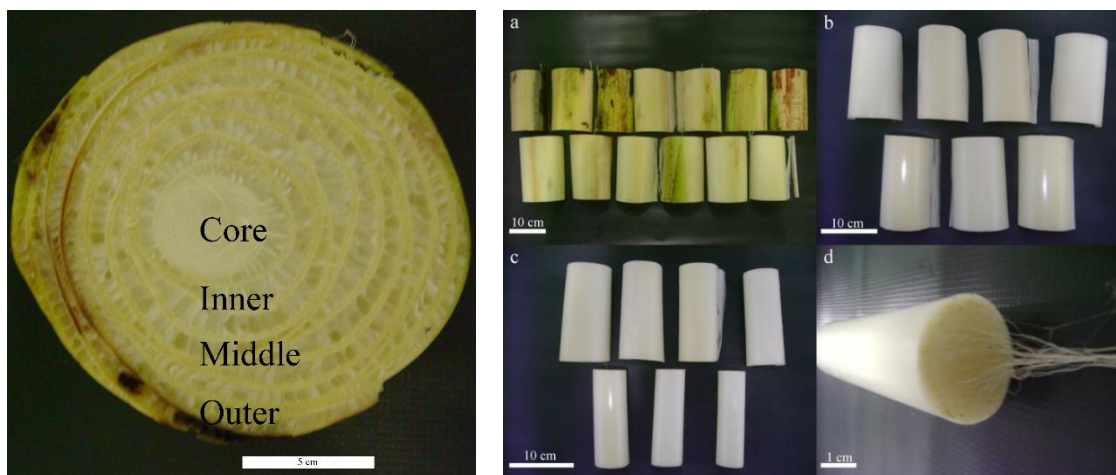
### Materials

The banana pseudostem (BPS) samples of *Musa* sp., cultivar Pacovan, were harvested in January 2011 from a banana plantation at the Experimental Field of the Embrapa Tropical Agroindustry, located in the municipal district of Paraipaba, Ceara State, Brazil. The samples were obtained from mature plants, randomly selected, after cutting the banana bunches. The material was stored at 10 °C before the separation procedure and analysis.

All reagents were of analytical grade: NaOH 97% (w/w), H<sub>2</sub>O<sub>2</sub> 30% (w/w), CH<sub>3</sub>COOH 99.7% (w/w), and H<sub>2</sub>SO<sub>4</sub> 98% (w/w) were supplied by Vetec Química Fina Ltda (Duque de Caxias, RJ, Brazil), and NaClO<sub>2</sub> 80% (w/w) was provided by Sigma-Aldrich (Saint Louis, MO, USA). The reagents were used as received, with no additional purification.

## Preparation of the Fractions

The BPS was manually fractionated into four morphological regions: core, inner, middle, and outer sheaths. The visual aspect of each fraction can be seen in Fig. 1. The regions are differently colored: the outer fraction is composed of green sheaths (Fig. 1a); the middle fraction has a light yellow-pale brown color, a little darker than the inner fraction (Figs. 1b and 1c); the core is white, has no sheath, and contains a smooth and thin fiber bundle with the appearance of a fabric (Fig 1d). Each fresh fraction was weighed to determine its contribution to the whole pseudostem. Prior to analysis, each fraction was cut into parts of about 10 cm length and 3 cm width and dried in an air-circulating oven at 60 °C for two days. The fractions were then ground in a Willey knife mill (FORTINOX, model STAR FT680; São Paulo, Brazil).



**Fig. 1.** Macrophotographs of different fractions of Pacovan banana pseudostem: (a) outer sheaths, (b) middle sheaths, (c) inner sheaths, and (d) core

## Characterization of the Fractions

### *Chemical composition*

The ash content, extractives, and moisture were determined following the respective TAPPI methods (TAPPI T413 om-93 1993; TAPPI T204 cm-97 1997; TAPPI T550 om-03 2003). The hemicellulose and  $\alpha$ -cellulose contents were determined according to the description given by Yokoyama *et al.* (2002). To obtain the Klason lignin, the TAPPI T 222 om-22 (2002) method with slight modifications was adopted (without overnight settling step).

### *X-ray fluorescence spectrometry*

The ash at 600 °C, remaining after heating in a QUIMIS Q318M24 microprocessor-controlled oven (Brazil) was analyzed by X-ray fluorescence to identify the inorganic material present. The analysis was performed on a Rigaku spectrometer, model ZSX Mini II (Brazil), with a Pd tube, operating at 40 kV and 1.2 mA.

### *Scanning electron microscopy (SEM)*

The morphology of the samples was examined using a Zeiss DSM-940A scanning electron microscope (Germany) operating at an accelerating voltage of 30 keV in a secondary electron imaging mode (SEI). The materials were mounted on brass studs and coated with gold in a K 550 Emitec sputter coater (UK).

### *X-ray diffraction (XRD)*

The analysis by X-ray powder diffraction of different dried fractions was carried out in a Panalytical diffractometer, model Xpert Pro MPD (The Netherlands) with a Co tube, operating at 40 kV and 40 mA. The crystallinity index,  $I_{cr}$ , was calculated using the following equation (Segal *et al.* 1959):

$$\%I_{Cr} = (1 - I_{am}/I_{002}) \times 100 \quad (1)$$

where  $I_{am}$  is the intensity at the minimum of the diffraction related to the amorphous material ( $21^\circ < 2\theta < 22^\circ$ ), and  $I_{002}$  is the intensity at the maximum of the crystalline peak 002 ( $25^\circ < 2\theta < 26^\circ$ ).

### *Fourier transform infrared (FTIR) spectroscopy*

The FTIR spectra were obtained on a Shimadzu FTIR-8300 spectrophotometer (Japan) in the range of 4000 to 400  $\text{cm}^{-1}$  with materials that had been dried in an oven at 90 °C for 2 h and stored under vacuum. The dried samples were mixed with KBr in a proportion of 3% (w/w) and pressed (3 tons).

### *Thermal analysis (TGA and DSC)*

Thermogravimetric analysis (TGA) of the dried fractions was conducted in a temperature interval of 25 to 700 °C under a synthetic air atmosphere with a flow rate of 60 mL/min using platinum crucibles. Masses of approximately 8.0 mg were heated at a constant rate of 10 °C/min. A Q50 Universal V20.10 thermal analyzer (TA Instruments, USA) was used for this study.

The DSC measurements were carried out on a Q20 Universal V4.7A (TA Instruments) differential scanning calorimeter. Samples of around 5.0 mg mass were heated in a temperature range of 25 to 400 °C, at a constant heating rate of 10 °C/min. The experiments were performed under a nitrogen atmosphere at a flow rate of 50 mL/min. Platinum crucibles were used.

### *Statistical analysis*

The data was analyzed for statistical significance ( $p < 0.05$ ) by the Tukey's test using Sisvar 5.3 software (Federal University of Lavras, Lavras City, Brazil).

## RESULTS AND DISCUSSION

### **Chemical Composition**

The outer sheaths corresponded to ~41% of the total mass of the BPS, the middle fraction corresponded to ~27%, the inner section to ~21%, and the core to just ~11%.

The  $\alpha$ -cellulose and hemicellulose contents decreased from the outer fraction to the core (Table 1). The same tendency for  $\alpha$ -cellulose content to radially decrease inwards has been reported in *M. acuminata*, *M. acuminata x balbisiana*, and Nendran type *Musa* sp. (Aziz *et al.* 2011; Jayaprabha *et al.* 2011). The extractives and ash contents, on the other hand, increased radially inwards. The major function of the inner sheaths and core is transport of nutrients, which would certainly contribute to the higher ash and extractives contents (Oliveira *et al.* 2007; Jayaprabha *et al.* 2011).

**Table 1.** Lignocellulosic Composition of Pacovan Banana Pseudostem Fractions on a Dry Weight Basis

Component	Content of the fractions (% w/w)			
	Outer	Middle	Inner	Core
Ashes	15.6 ± 1.0 <sup>a</sup>	16.1 ± 0.9 <sup>ab</sup>	18.2 ± 0.4 <sup>bc</sup>	18.0 ± 0.2 <sup>c</sup>
Extractives	30.8 ± 1.7 <sup>a</sup>	42.3 ± 0.2 <sup>b</sup>	61.6 ± 0.5 <sup>c</sup>	67.3 ± 0.5 <sup>d</sup>
Insoluble lignin	10.4 ± 1.9 <sup>a</sup>	8.1 ± 1.0 <sup>ab</sup>	3.6 ± 0.1 <sup>bc</sup>	5.8 ± 1.2 <sup>c</sup>
Alpha-cellulose	28.6 ± 1.2 <sup>a</sup>	22.8 ± 2.3 <sup>b</sup>	10.0 ± 0.9 <sup>c</sup>	5.6 ± 0.7 <sup>c</sup>
Hemicellulose	14.7 ± 2.3 <sup>a</sup>	10.7 ± 1.4 <sup>ab</sup>	6.6 ± 0.7 <sup>bc</sup>	3.3 ± 0.4 <sup>c</sup>

\* Means followed by the same letter in the row are not significantly different from each other at  $p < 0.05$

The core has a considerable amount of starch, sugars, and minerals (Bhaskar *et al.* 2011; Padam *et al.* 2012) and is used as a medicine in India (Saravanan and Aradhya 2011; Kumar *et al.* 2012; Surendar *et al.* 2013). The pseudostem is a source of fibers for textile, composites, paper, and adsorbent applications (Reis 2006; Sapuan *et al.* 2007; Satyanarayana *et al.* 2007; Mohapatra *et al.* 2010).

The outer sheaths are more suitable as a source of fibers and cellulose, whilst the core and inner sheaths are better used as sources of extractives and ash. The ash content was low, consisting mainly of silicon, which could be troublesome for pulping (Cordeiro *et al.* 2004). The lignin content may be considered as relatively low, because it was 13% or less (Cordeiro *et al.* 2004; Oliveira *et al.* 2007; Jayaprabha *et al.* 2011).

The main chemical elements in the BPS Pacovan fraction ashes are shown in Table 2. Potassium is the main element for all fractions, followed by chlorine. Calcium was detected only in the outer sheath, while magnesium was absent in the core. Oliveira *et al.* (2007) obtained a similar result in *M. acuminata* Colla, Cavendish variety, with potassium as main ash component, and with the presence of calcium, silicon, phosphorus, and magnesium.

**Table 2.** X-Ray Fluorescence Analysis of the Main Chemical Elements Detected in the Ash of Pseudostem Fractions of Pacovan Banana

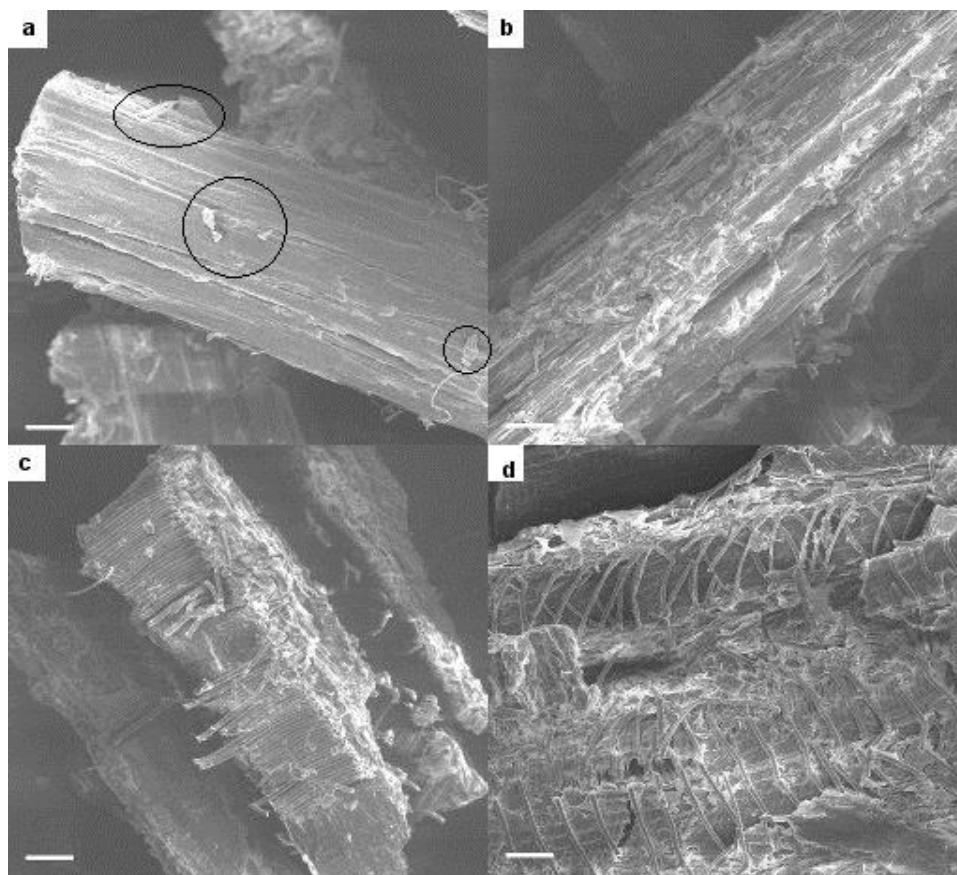
Elements	Percentage (% w/w)			
	outer	middle	Inner	core
K	62.9	66.8	58.5	62.3
Cl	20.6	25.9	32.5	31.7
Ca	10.3	—	—	—
P	3.1	1.8	2.6	1.2
Mg	1.6	2.8	5.1	—
Si	1.0	0.58	0.79	4.0
S	0.10	0.11	0.25	0.48

These results indicate that the pseudostem should not be considered as a sole material for extraction of fibers or for other materials, but a rich source of molecules for both technological pathways. This approach is in accordance to the biorefinery concept, where biomass is converted to fuels and chemicals in multi-step and multi-product approaches (Cherubini and Ulgiati 2010; FitzPatrick *et al.* 2010; Kurian *et al.* 2013).

## Scanning Electron Microscopy

The elementary fibers of the outer sheaths were arranged in a compact configuration and a preferential alignment parallel to the bundle axis (Fig. 2a). The same was observed for the inner sheaths (Fig. 2c). The presence of non-fibrous material (denoted by circles in Fig. 2a) can be noted in some regions of the outer sheaths on the SEM micrograph. In the case of the middle sheath fibers, this non-fibrous material covered the bundle (Fig. 2b). Gañán *et al.* (2004b) and Jayaprabha *et al.* (2011) reported that the non-fibrous materials encrusted on banana fibers are essentially constituted of hemicellulose, lignins and pectins.

In the inner fraction, close to the fiber bundle covered with non-cellulosic materials, tube-like structures were apparent. Two preferential orientations of fibers have been reported for banana pseudostem by Li *et al.* (2010) and Gañán *et al.* (2004b): parallel and perpendicular to the bundle axis. The authors described the perpendicular fibers as narrow fibers. In the core, elementary fibers could not be observed, and only narrow fibers in the form of pipes rather than fiber bundles were evident (Fig. 2d). This structure contributes to the transportation of water and nutrients in the core.



**Fig. 2.** SEM images of different fractions of Pacovan banana pseudostem: (a) outer sheaths, (b) middle sheaths, (c) inner sheaths, and (d) core. Scale bar equals 1:50  $\mu\text{m}$

## X-ray Diffraction

The diffractogram of fractions (Fig. 3) shows a decrease in the relative intensity of the peaks attributed to cellulose from the outer layer to the core. For the  $\text{CoK}\alpha$  radiation, the main peak for cellulose is around  $25^\circ$  to  $26^\circ$  (Bonarski and Olek 2011). The crystallinity

of the fractions was 35.3% (outer sheaths), 32.7% (middle sheaths), 12.4% (inner sheaths), and 8.8% (core), in agreement with the  $\alpha$ -cellulose percentage in each fraction (Table 1). A crystallinity of 39% was reported for banana pseudostem fibers cleaned with 5% sodium hypochlorite (Guimarães *et al.* 2009), which was not very different from the value obtained for the outer sheaths (35.3%). The XRD pattern also shows three intense peaks at  $\sim 21^\circ$  (except outer fraction),  $\sim 33^\circ$ , and  $\sim 47^\circ$ , correlated to the salts of inorganic components, as potassium, chloride, calcium, and phosphor, as observed in X-ray fluorescence. Guimarães *et al.* (2009) observed narrow peaks and correlated them to inorganic substances. The absence of the reflection at  $\sim 21^\circ$  in the outer fraction is an evidence of low concentration of an inorganic fraction, which is in a higher concentration in the other fractions. This is in accordance to the chemical composition (Table 1), with the lowest ash content in the outer sheath.

The results suggest a possible advantage of separating the outer sheaths and the core as a function of the use of each fraction. For example, the processing of the whole pseudostem for extraction of fibers would decrease the mechanical resistance of the components.

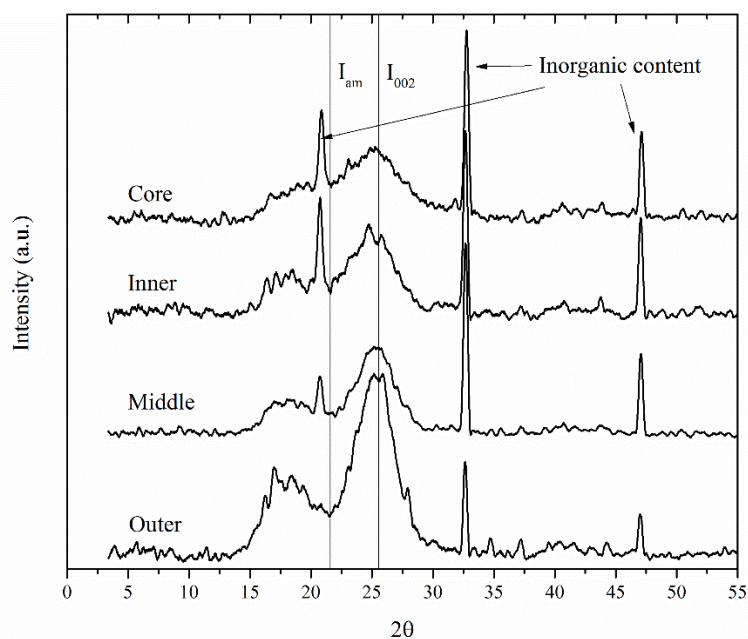
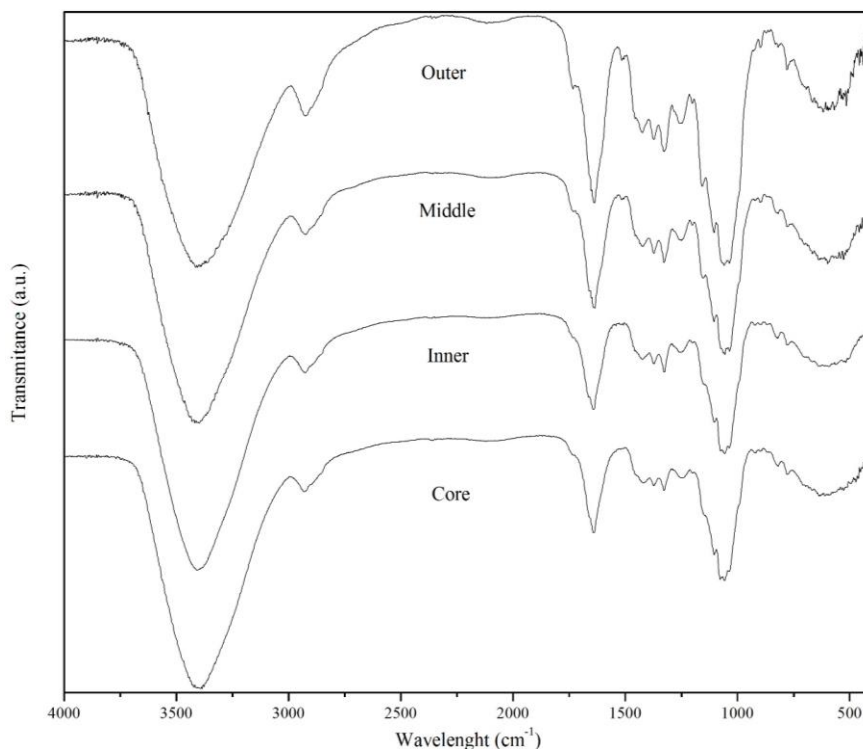


Fig. 3. Smoothed X-ray diffraction patterns of different fractions of Pacovan banana pseudostem

### Fourier Transform Infrared Spectroscopy

The main organic constituents of pseudostems ( $\alpha$ -cellulose, hemicellulose, and lignin) contain  $-\text{OH}$  groups. For comparison with the intensity of other bands and spectra, the intensity of the band at  $3400\text{ cm}^{-1}$  ( $-\text{OH}$  stretching) was considered as a standard (Fig. 4). The decrease in band intensities from  $1726\text{ cm}^{-1}$  to  $1042\text{ cm}^{-1}$  was in agreement with the decrease in the total content of organic biomacromolecule material ( $\alpha$ -cellulose, hemicellulose, and lignin) from  $\sim 54\%$  (outer sheath) to  $\sim 15\%$  (core) (Table 1). The bands at  $1515\text{ cm}^{-1}$  (aromatic ring) and  $1373\text{ cm}^{-1}$  (aromatic methoxyl), related to lignin, decreased from the outer to the core and became almost insignificant. The bands around  $1254\text{ cm}^{-1}$  to  $1042\text{ cm}^{-1}$ , related to carbohydrate functional groups, as cellulose and hemicellulose, also decreased from the outer sheath to the core, but they were not fully eliminated.



**Fig. 4.** FTIR spectra of different fractions of Pacovan banana pseudostem

**Table 3.** FTIR Analysis of the Main Chemical Elements Detected in the Ash of Pseudostem Fractions of Banana Variety Pacovan

Wave number (cm <sup>-1</sup> )	Assignment*	Origin
3400 (s)	O-H stretching	Water, Cellulose, Hemicellulose, Lignin
2920 (w)	C-H stretching	Cellulose, Hemicellulose, Lignin
1726 (sh)	C=O stretching	Aliphatic carboxylic acid and ketones of Hemicellulose
1635 (s)	OH bending/ C=C stretching and ArC=O stretching	Water/Lignin
1515 (vw)	C=C aromatic skeletal vibration	Lignin
1424 (ms)	CH <sub>2</sub> deformation	Cellulose, Hemicellulose, Lignin
1373 (ms)	CH <sub>3</sub> deformation/OH deformation	Ar-OCH <sub>3</sub> in Lignin/ Cellulose, Hemicellulose, Lignin
1324 (ms)	O-H in-plane deformation	Cellulose
1254 (w)	C-O stretching/C=C stretching	Cellulose, Hemicellulose/Lignin
1156 (sh)	C-O-C asymmetric stretching	Cellulose, Hemicellulose, Lignin
1106 (sh)	ArC-H deformation	Lignin
1056 (s), 1042 (s)	C-O stretching of COH and C-O-C symmetric stretching	Cellulose, Hemicellulose, Lignin
894 (vw)	C-H deformation/ Inorganic compounds vibrations	Cellulose, Hemicellulose/ Inorganic compounds
774 (vw)	ArC-H out of plane deformation	Lignin

\*References: Socrates 2004; Gañán *et al.* 2004a; Bilba *et al.* 2007; Guimarães *et al.* 2009; Rosa *et al.* 2010  
Band intensity: s = strong; ms = medium strong; w = weak; vw = very weak; sh = shoulder

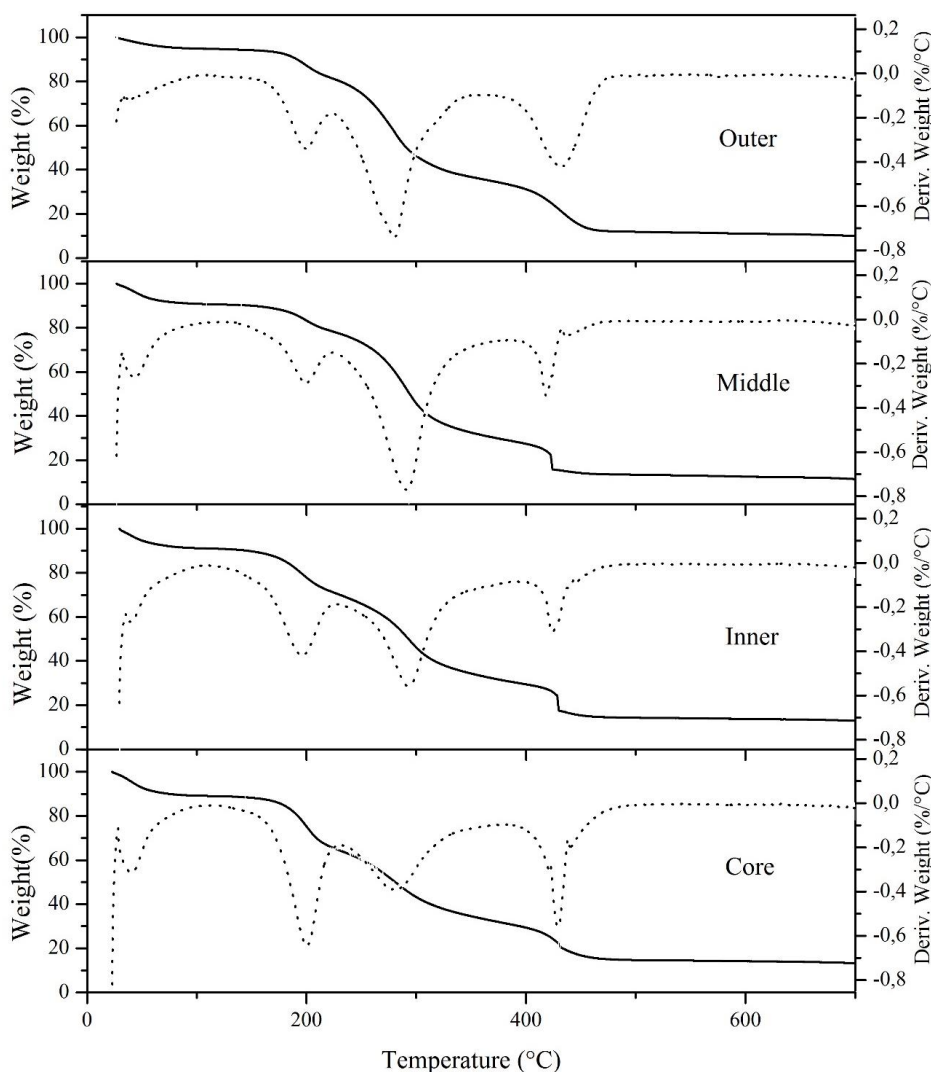


## Thermal Analyses

### TGA/dTG

Four thermal events can be clearly identified (Fig. 5 and Table 4). The first weight loss at temperatures up to 120 °C was due to moisture evaporation (water adsorbed to fiber). Hemicellulose, which has an amorphous structure, was the first substance to be thermally decomposed. Cellulose decomposes after hemicellulose, due to its crystalline structure, lack of branches, and high molecular weight. Lignins are not polysaccharides and are highly cross-linked, properties that lead to the material having a higher stability compared with the polysaccharides of fibers (Sathasivam and Haris 2012). The three events at  $T_{max}$  of 195 to 200 °C, 280 to 293 °C, and 427 to 433 °C corresponded to hemicellulose,  $\alpha$ -cellulose, and lignin thermal decomposition, respectively.

Guimarães *et al.* (2009) analyzed banana pseudostem and obtained a shoulder at around 190 °C, along with two main peaks (321 and 445 °C) in the DTG curves obtained in air. The shoulder at around 190 °C could be due to the low content of hemicellulose (0.8%). These results are in agreement with those obtained in the present study.



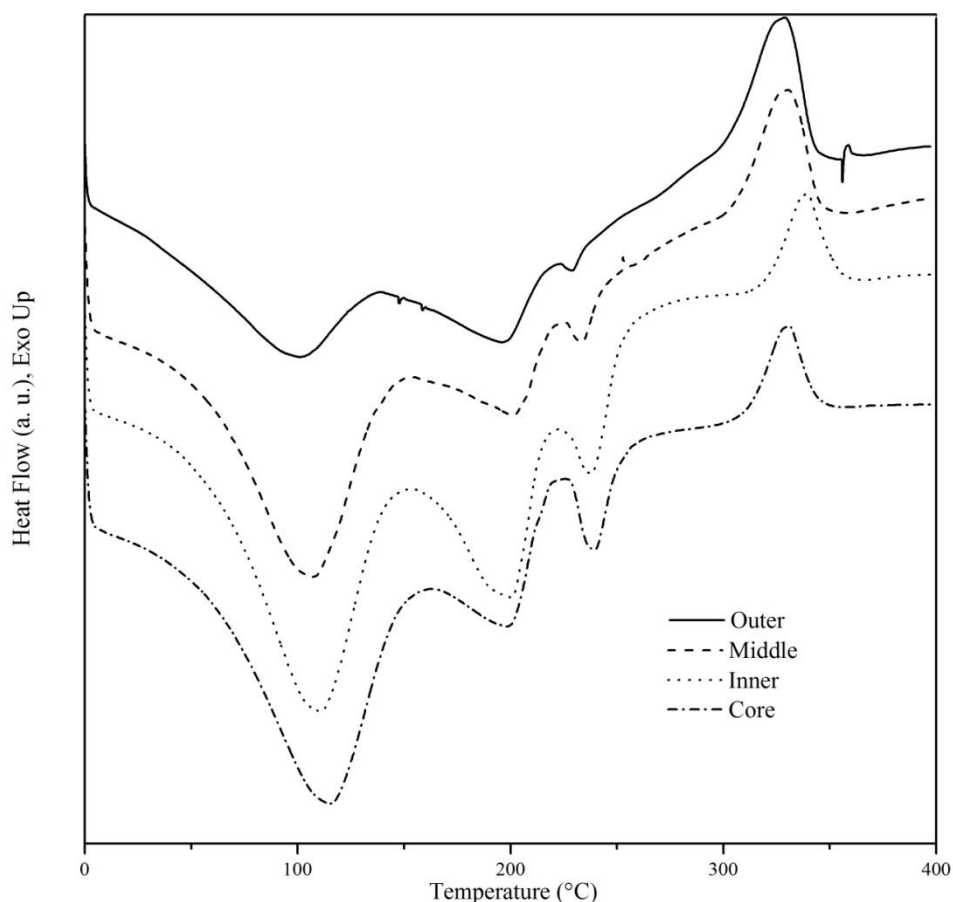
**Fig. 5.** TGA (continuous line, scale on the left) and dTG (dashed line, scale on the right) curves of pseudostem fractions of Pacovan banana cultivar in synthetic airflow

**Table 4.** TGA/DTG Curves of Pseudostem Fractions of Banana Variety Pacovan

Events	Tmax (°C)				Weight loss (%)			
	outer	middle	inner	core	outer	middle	inner	core
1	39.1	43.5	40.9	40.9	5.1	9.5	8.9	11.0
2	199	199	195	200	13.4	12.5	20.3	24.5
3	280	292	293	280	45.5	49.2	40.3	32.7
4	433	427	431	429	25.0	16.3	16.7	17.8
Residue at 700 °C					11.0	12.5	14.2	14.0

### DSC

Strong endothermic peaks at around 100 °C due to water evaporation can be seen for all fractions of the DSC thermograms for the banana pseudostem fractions (Fig. 6). The minimum temperatures increased from 102 °C (outer sheaths) to 115 °C (core), indicating an improvement in the moisture retention property, which was probably related to higher hydrophilicity in the central part of pseudostem.

**Fig. 6.** DSC thermograms for pseudostem fractions of Pacovan banana in nitrogen flow

The two endothermic peaks between 190 and 240 °C are caused by partial dehydration of the –OH primary groups and the decomposition of minor constituents in the fraction, as suggested by Khan *et al.* (2006) for jute fiber. Another possible scenario is proposed by Gangopadhyay and Ghosh (1999), who attributed these peaks to the slow pyrolytic decomposition of the sisal fiber. Probably, these minor constituents are sugars

and carbohydrates that occurs as extractives in the lignocellulosic analysis (Table 1). Paul *et al.* (2013) also found sucrose and KCl salts in banana pseudostem. Sucrose has two main endotherm events, related to the carbohydrate fusion, at ~188 °C and ~229 °C (Beckett *et al.* 2006; Eggleston *et al.* 1996; Hurtt *et al.* 2004). Mineral components can dislocate the temperatures of the thermal events in the DSC analyses, as stated by Beckett *et al.* (2006). As the extractives content is higher than the biomacromolecule contents, the extractives events may be overlapping the lignin, hemicellulose, and cellulose events, until the exothermic event at ~330 °C.

A sharp exothermic peak was present in all DSC thermograms at around 327 and 337 °C. Guimarães *et al.* (2009) found that weaker intermolecular interaction (amorphous region) in the banana pseudostem fractions promotes a reduction in the temperature of decomposition. These peaks were attributed to the decomposition of  $\alpha$ -cellulose, hemicellulose, and lignin. The decomposition of  $\alpha$ -cellulose in nitrogen gas was observed at 360 °C for the sisal fibers (Gangopadhyay and Ghosh 1999). Lignin and hemicellulose present char formation peaks at, respectively, ~350 to 450 °C and ~200 to 350 °C (Kemp 1999; Yang *et al.* 2007). Therefore, the exothermic event is a sum of the biomacromolecule exothermic peaks, caused mainly by pyrolysis reactions.

## CONCLUSIONS

1. There were significant differences ( $p < 0.05$ ) in the four analyzed lignocellulosic fractions of Pacovan banana.
2. The outer sheaths were more suitable for  $\alpha$ -cellulose extraction, while the core was more suitable for extractives extraction.
3. Macromolecule content ( $\alpha$ -cellulose and hemicellulose) increased radially from the core to the outer sheaths, and extractive and ash contents increased from the outer sheaths to the core.

## ACKNOWLEDGMENTS

The authors are grateful to Prof. José Marcos Sasaki for the X-ray analysis, INCT-INOMAT and CNPq for the financial support, and also CNPq and FUNCAP for the scholarship.

## REFERENCES CITED

- Akpabio, U. D., Udiong, D. S., and Akpakpan, A. E. (2012). "The physicochemical characteristics of plantain (*Musa paradisiaca*) and banana (*Musa sapientum*) pseudostems wastes," *Adv. Nat. Appl. Sci.* 6(2), 167-172.
- Arshanitsa, A., Ponomarenko, J., Dizhbite, T., Andersone, A., Gosselink, R. J. A., Putten, J., Lauberts, M., and Telysheva, G. (2013). "Fractionation of technical lignins as a tool for improvement of their antioxidant properties," *J. Anal. Appl. Pyrolysis* 103, 78-85. DOI: 10.1016/j.jaap.2012.12.023

- Aziz, N. A. A., Ho, L.-H., Azahari, B., Bhat, R., Cheng, L.-H., and Ibrahim, M. N. M. (2011). "Chemical and functional properties of the native banana (*Musa acuminata* x *balbisiana* Colla cv. Awak) pseudo-stem and pseudo-stem core flours," *Food Chem.* 128(3), 748-753. DOI: 10.1016/j.foodchem.2011.03.100
- Beckett, S. T., Francesconi, M. G., Geary, P. M., Mackenzie, G., and G., Maulny, A. P. E. (2006). "DSC study of sucrose melting," *Carbohydr. Res.* 341(15), 2591-2599. DOI: 10.1016/j.carres.2006.07.004
- Bhaskar, J. J., Mahadevamma, S., Chilkunda, N. D., and Salimath, P. V. (2011). "Banana (*Musa* sp. var. elakki bale) flower and pseudostem: Dietary fiber and associated antioxidant capacity," *J. Agric. Food Chem.* 60(1), 427-432. DOI: 10.1021/jf204539v
- Bilba, K., Arseno, M.-A., and Ouensanga, A. (2007). "Study of banana and coconut fibers: Botanical composition, thermal degradation and textural observations," *Bioresour. Technol.* 98(1), 58-68. DOI: 10.1016/j.biortech.2005.11.030
- Bonarski, J. T., and Olek, W. (2011). "Application of the crystalline volume fraction for characterizing the ultrastructural organization of wood," *Cellulose* 18(2), 223-235. DOI: 10.1007/s10570-010-9486-7
- Cherubini, F., and Ulgiati, S. (2010). "Crop residue as raw materials for biorefinery systems - A LCA case study," *Appl. Energy* 87(1), 47-57. DOI: 10.1016/j.apenergy.2009.08.024
- Cordeiro, N., Belgacem, M. N., Torres, I. C., and Moura, J. C. V. P. (2004). "Chemical composition and pulping of banana pseudo-stems," *Ind. Crops Prod.* 19(2), 147-154. DOI: 10.1016/j.indcrop.2003.09.001
- Eggleston, G., Trask-Morrell, B. J., and Vercellotti, J. R. (1996). "Use of differential scanning calorimetry and thermogravimetric analysis to characterize the thermal degradation of crystalline sucrose and dried sucrose-salt residues," *J. Agr. Food Chem.* 44(10), 3319-3325. DOI: 10.1021/jf950836z
- Embrapa. (2014). *Sistema de Produção da Bananeira Irrigada: Cultivares*, Embrapa Semiárido, <http://sistemasdeproducao.cnptia.embrapa.br/FontesHTML/Banana/BananeiraIrrigada/cultivares.htm>. Accessed on 02/07/2013.
- FAOStat. (2014). *FAOStat*, Food and Agriculture Organization of the United Nations, <http://faostat.fao.org/site/567/default.aspx#ancor>. Accessed on 17/08/2013.
- Fiorentino, G., Ripa, M., Mellino, S., Fahd, S., and Ulgiati S. (2014). "Life cycle assessment of *Brassica carinata* biomass conversion to bioenergy and platform chemicals," *J. Clean. Prod.* 66, 174-187. DOI: 10.1016/j.jclepro.2013.11.043
- FitzPatrick, M., Champagne, P., Cunningham, M. F., and Whitney, R. A. (2010). "A biorefinery processing perspective: Treatment of lignocellulosic materials for the production of value-added products," *Bioresour. Technol.* 101(23), 8915-8922. DOI: 10.1016/j.biortech.2010.06.125
- Gabhane, J., William, S. P. M. P., Gadhe, A., Rath, R., Vaidya, A. N., and Wate, S. (2014). "Pretreatment of banana agricultural waste for bio-ethanol production: Individual and interactive effects of acid and alkali pretreatments with autoclaving, microwave heating and ultrasonication," *Waste Manag.* 34(2), 498-503. DOI: 10.1016/j.wasman.2013.10.013
- Gañán, P., Cruz, J., Garbizu, S., Arbelaiz, A., and Mondragon, A. (2004a). "Stem and bunch banana fibers from cultivation wastes: Effect of treatments on physico-chemical behavior," *J. Appl. Polym. Sci.* 94(4), 1489-1495. DOI: 10.1002/app.21061

- Gañán, P., Zuluaga, R., Velez, J. M., and Mondragon, I. (2004b). "Biological natural retting for determining the hierarchical structuration of banana fibers," *Macromol. Biosci.* 4(10), 978-983. DOI: 10.1002/mabi.200400041
- Gangopadhyay, R., and Ghosh, P. (1999). "Uncatalyzed photografting of polyacrylamide from functionalized cellulosic materials," *J. Appl. Polym. Sci.* 74(7), 1623-1634. DOI: 10.1002/(SICI)1097-4628(19991114)74:7<1623::AID-APP3>3.0.CO;2-Z
- Guimarães, J. L., Frollini, E., Silva, C. G., Wypych, F., and Satyanarayana, K. G. (2009). "Characterization of banana, sugarcane bagasse and sponge gourd fibers of Brazil," *Ind. Crops Prod.* 30(3), 407-415. DOI: 10.1016/j.indcrop.2009.07.013
- Hurtta, M., Pitkänen, I., and Knuutinen, J. (2004). "Melting behaviour of D-sucrose, D-glucose and D-fructose," *Carbohydr. Res.* 339(13), 2267-2273. DOI: 10.1016/j.carres.2004.06.022
- Ho, L.-H., Aziz, N. A. A., and Azahari, B. (2013). "Physico-chemical characteristics and sensory evaluation of wheat bread partially substituted with banana (*Musa acuminata* X *balbisiana* cv. Awak) pseudo-stem flour," *Food Chem.* 139(1-4), 532-539. DOI: 10.1016/j.foodchem.2013.01.039
- Jayaprabha, J. S., Brahmakumar, M., and Manilal, V. B. (2011). "Banana pseudostem characterization and its fiber property evaluation on physical and bioextraction," *J. Nat. Fiber* 8(3), 149-160. DOI: 10.1080/15440478.2011.601614
- Kemp, R. B. (1999). *Handbook of Thermal Analysis and Calorimetry*, Elsevier, Amsterdam.
- Khan, F., Ahmad, S. R., and Kronfil, E. (2006). "γ-Radiation induced changes in the physical and chemical properties of lignocelluloses," *Biomacromol.* 7(8), 2303-2309. DOI: 10.1021/bm060168y
- Kumar, K. P. S., Bhowmik, D., Duraivel, S., and Umadevi, M. (2012). "Traditional and medicinal uses of banana," *J. Pharmacog. Phytochem.* 1(3), 51-63.
- Kurian, J. K., Nair, G. R., Hussain, A., and Raghavan, G. S. V. (2013). "Feedstocks, logistics and pre-treatment processes for sustainable lignocellulosic biorefineries: A comprehensive review," *Renew. Sustain. Energy Rev.* 25, 205-219. DOI: 10.1016/j.rser.2013.04.019
- Li, K., Fu, S., Zhan, H., Zhan, Y., and Lucia, L. A. (2010). "Analysis of the chemical composition and morphological structure of banana pseudo-stem," *BioResources* 5(2), 576-585. DOI: 10.15376/biores.5.2.576-585
- Mohapatra, D., Mishra, S., and Sutar, N. (2010). "Banana and its by-product utilization: An overview," *J. Sci. Ind. Res.* 69(5), 323-329.
- Mukhopadhyay, S., Figueiro, R., and Shivankar, V. (2009). "Variability of tensile properties of fibers from pseudostem of banana plant," *Text. Res. J.* 79(5), 387-393. DOI: 10.1177/0040517508090479
- Oliveira, L., Cordeiro, N., Evtuguin, D. V., Torres, I. C., and Silvestre, A. J. D. (2007). "Chemical composition of different morphological parts from 'Dwarf Cavendish' banana plant and their potential as a non-wood renewable source of natural products," *Ind. Crops Prod.* 26(2), 163-172. DOI: 10.1016/j.indcrop.2007.03.002
- Padam, B. S., Tin, H. S., Chye, F. Y., and Abdullah, M. I. (2012). "Banana by-products: An under-utilized renewable food biomass with great potential," *J. Food Sci. Tech.* 49(5), 1-19. DOI: 10.1007/s13197-012-0861-2
- Paul, V., Kanny, K., and Redhi, G. G. (2013). "Formulation of a novel bio-resin from banana sap," *Ind. Crops Prod.* 43, 496-505. DOI: 10.1016/j.indcrop.2012.07.064

- Prinsen, P., Gutiérrez, A., Faulds, C. B., and Río, J. C. (2014). "Comprehensive study of valuable lipophilic phytochemicals in wheat bran," *J. Agric. Food Chem.* 62(7), 1664-1673. DOI: 10.1021/jf404772b
- Ploetz, R. C., Kepler, A. K., Daniels, J., and Nelson, S. C. (2007). *Banana and Plantain-An Overview with Emphasis of Pacific Island*, Permanent Agriculture Resources, Hōlualoa.
- Reis, J. M. L. (2006). "Fracture and flexural characterization of natural fiber-reinforced polymer concrete," *Constr. Build. Mater.* 20(9), 673-678. DOI: 10.1016/j.conbuildmat.2005.02.008
- Rincón, L. E., Moncada, J., and Cardona, C. A. (2014). "Analysis of potential technological schemes for the development of oil palm industry in Colombia: A biorefinery point of view," *Ind. Crops Prod.* 52, 457-465. DOI: 10.1016/j.indcrop.2013.11.004
- Rosa, M. F., Medeiros, E. S., Malmonge, J. A., Gregorski, K. S., Wood, D. F., Mattoso, L. H. C., Glenn, G., Orts, W. J., and Iman, S. H. (2010). "Cellulose nanowhiskers from coconut husk fibers: Effect of preparation conditions on their thermal and morphological behavior," *Carbohydr. Polym.* 81(1), 83-92. DOI: 10.1016/j.carbpol.2010.01.059
- Sapuan, S. M., Harun, N., and Abbas, K. A. (2007). "Design and fabrication of a multipurpose table using a composite of epoxy and banana pseudostem fibres," *J. Trop. Agric.* 45(1-2), 66-68.
- Saravanan, K., and Aradhya, S. M. (2011). "Polyphenols and pseudostem of different banana cultivars and their antioxidant activities," *J. Agric. Food Chem.* 59(8), 3613-3623. DOI: 10.1021/jf103835z
- Sathasivam, K., and Haris, M. R. H. M. (2012). "Thermal properties of modified banana trunk fibers," *J. Therm. Anal. Calorim.* 108(1), 9-17. DOI: 10.1007/s10973-011-1793-1
- Satyanarayana, K. G., Guimarães, J. L., and Wypych, F. (2007). "Studies on lignocellulosic fibers of Brazil. Part I: Source, production, morphology, properties and applications," *Compos. Part A: Appl. Sci. Manuf.* 38(7), 1694-1709. DOI: 10.1016/j.compositesa.2007.02.006
- Segal, L., Creely, J. J., Marting, A. E., and Conrad, C. M. (1959). "An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer," *Text. Res. J.* 29(10), 786-794. DOI: 10.1177/004051755902901003
- Shi, Z.-J., Xiao, L.-P., Deng, J., Yang, H.-Y., Song, X.-L., and Sun, R.-C. (2013). "Isolation and structural exploration of hemicelluloses from the largest bamboo species: *Dendrocalamus sinicus*," *BioRes.* 8(4), 5036-5050. DOI: 10.15376/biores.8.4.5036-5050
- Socrates, G. (2004). *Infrared and Raman Characteristics Group Frequencies*, John Wiley & Sons, West Sussex.
- Surendar, K. K., Devi, D. D., Ravi, I., Krishnakumar, S., Kumar, S. R., and Velayudham, K. (2013). "Water stress in banana - A review," *Bull. Environ. Pharmacol. Life Sci.* 2(6), 1-18.
- TAPPI T204 cm-97. (1997). "Solvent extractives of wood and pulp," *TAPPI Press*, Atlanta, GA.
- TAPPI T222 om-02. (2002). "Acid-insoluble lignin in wood and pulp," *TAPPI Press*, Atlanta, GA.

TAPPI T413 om-93. (1993). "Ash in wood, pulp, paper and paperboard: Combustion at 900 °C," *TAPPI Press*, Atlanta, GA.

TAPPI T550 om-03. (2003). "Determination of equilibrium moisture in pulp, paper and paperboard for chemical analysis," *TAPPI Press*, Atlanta, GA.

Yang, H., Yan, R., Chen, H., Lee, D. H., and Zheng, C. (2007). "Characteristics of hemicellulose, cellulose and lignin pyrolysis," *Fuel* 86(12-13), 1781-1788. DOI: 10.1016/j.fuel.2006.12.013

Yokoyama, T., Kadla, J. F., and Chang, H. M. (2002). "Microanalytical method for the characterization of fiber components and morphology of woody plants," *J. Agric. Food Chem.* 50(5), 1040-1044. DOI: 10.1021/jf011173q

Zamudio, M. A. M., Alfaro, A., de Alva, H. E., García, J. C., García-Morales, M., and López, F. (2014). "Biorefinery of paulownia by autohydrolysis and soda-anthraquinone delignification process. Characterization and application of lignin," *J. Chem. Technol. Biotechnol.* Online version prior to publication. DOI: 10.1002/jctb.4345

Article submitted: March 28, 2014; Peer review completed: September 14, 2014; Revised version received and accepted: October 21, 2014; Published: October 31, 2014,